

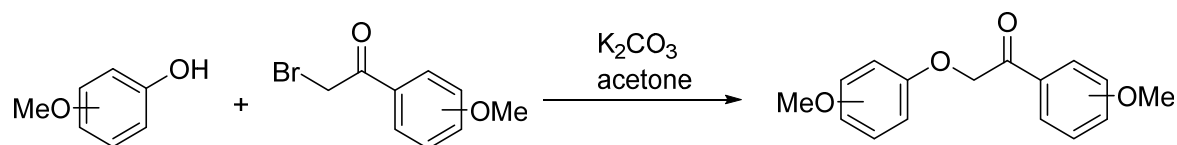
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## General experimental

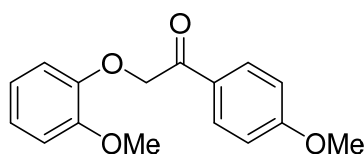
Commercially available reagents were used throughout without purification unless otherwise stated. Anhydrous solvents were used as supplied. All reactions were routinely carried out in oven-dried glassware under a nitrogen atmosphere unless otherwise stated. Analytical thin layer chromatography was performed using silica plates and compounds were visualized at 254 and/or 360 nm ultraviolet irradiation followed by staining with either alkaline permanganate or ethanolic vanillin solution. Infrared spectra were obtained using a Perkin Elmer spectrum One Fourier Transform Infrared spectrometer as thin films between sodium chloride plates. Absorption maxima are expressed in wavenumbers ( $\text{cm}^{-1}$ ). Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. NMR spectra were recorded as indicated on an NMR spectrometer operating at 500, 400 and 300 MHz for  $^1\text{H}$  nuclei and 125, 100 and 75 MHz for  $^{13}\text{C}$  nuclei. Chemical shifts are reported in parts per million (ppm) relative to the tetramethylsilane peak recorded as  $\delta 0.00$  ppm in  $\text{CDCl}_3/\text{TMS}$  solvent, or the residual DMSO ( $\delta 2.50$  ppm) peak. The  $^{13}\text{C}$  NMR values were referenced to the residual acetone ( $\delta 29.9$  ppm) chloroform ( $\delta 77.1$  ppm), DMSO ( $\delta 39.5$  ppm) peak.  $^{13}\text{C}$  NMR values are reported as chemical shift  $\delta$  and assignment.  $^1\text{H}$  NMR shift values are reported as chemical shift  $\delta$ , relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant ( $J$  in Hz) and assignment. Assignments are made with the aid of DEPT 90, DEPT 135, COSY, NOESY and HSQC experiments. All experiments were conducted at 298 K. Conventional NMR tubes (5 mm diameter, Norell) using a sample volume of 500  $\mu\text{L}$  were used. High resolution mass spectra were obtained by electrospray ionization in positive ion mode at a nominal accelerating voltage of 70 eV on a microTOF mass spectrometer. GPC was carried out with a refractive index detector, triple columns (TSKgel G3000HXL, G2000HXL, and G1000HXL) having the exclusion limit at 60000 Da (PS), and THF as the mobile phase. GC-MS analyses were performed on a PerkinElmer Cluauus SQ8 with capillary column TC-1701 (GL Sciences, length 60 m, i.d. 0.25 mm, and film thickness 0.25  $\mu\text{m}$ ). Typical sample size was 0.1  $\mu\text{L}$  of a solution of 6mg or 2 mg of sample dissolved in 0.2 mL of THF.

### **General Procedure A: Synthesis of phenoxyacetophenone $\beta$ -O-4 models**



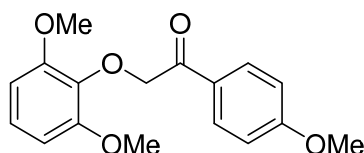
A solution of the appropriate  $\alpha$ -bromoacetophenone (2.3-15.70 mmol), the appropriate phenol (4.00-19.40 mmol) and  $K_2CO_3$  (8.70-161.10 mmol) in acetone (8-39 mL) were stirred at room temperature for the time stated. The reaction mixture was filtered, and the filtrate concentrated under reduced pressure. Recrystallisation of the crude solid from ethanol gave the desired  $\beta$ -O-4 model.

#### **2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (6)**



According to General Procedure A, stirring 2-bromo-4'-methoxyacetophenone (1.4 g, 9.40 mmol), guaiacol (2.0 g, 16.10 mmol) and  $K_2CO_3$  (4.4 g, 161.10 mmol) in acetone (26 mL) for 24 h gave the *title compound* (2.1 g, 7.76 mmol, 83%) as an beige solid; M.p. 89- 90 °C (78 – 80 °C)<sup>1</sup>;  $\delta_H$  (400 MHz,  $CDCl_3$ ) 8.00-8.01 (2 H, m, 2 x CH), 6.97-6.92 (4 H, m, 4 x CH), 6.85-6.84 (2 H, m, 2 x CH), 5.28 (2 H, s,  $CH_2$ ), 3.89 (3 H, s, Me), 3.88 (3 H, s, Me). NMR data is consistent with the literature<sup>1</sup>.

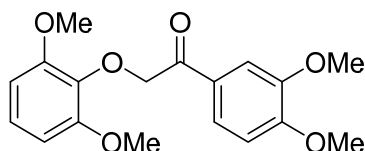
#### **2-(2,6-Dimethoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (20)**



According to General Procedure A, stirring 2,6-dimethoxyphenol (3.0 g, 19.40 mmol), 2-bromo-4'-methoxyacetophenone (3.6 g, 15.70 mmol) and  $K_2CO_3$  (6.6 g, 47.80 mmol) in acetone (39 mL) at rt for 2 d gave the *title compound* (3.7 g, 12.40 mmol, 79%) as a beige solid; M.p. 97-99 °C (82-84 °C)<sup>2</sup>;  $\delta_H$  (400 MHz,  $CDCl_3$ ) 8.08 (2 H, d,  $J$  9.1, 2 x CH), 7.00 (1 H, t,  $J$

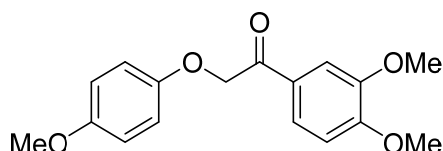
8.2, CH), 6.94 (2 H, d,  $J$  9.1, 2 x CH), 6.58 (2 H, d,  $J$  8.2, 2 x CH), 5.13 (2 H, s, CH<sub>2</sub>), 3.87 (3 H, s, Me), 3.80 (6 H, s, 2 x Me). NMR data is consistent with the literature<sup>3</sup>.

### 2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethan-1-one (21)



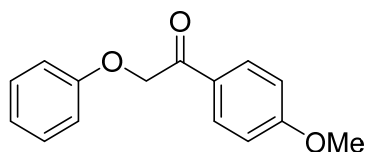
According to General Procedure A, stirring 2,6-dimethoxyphenol (500 mg, 3.24 mmol), 2-bromo-1-(3,4-dimethoxyphenyl)ethanone (600 mg, 2.31 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.5 g, 10.87 mmol) in acetone (8 mL) at 65 °C for 24 h gave the *title compound* (422 mg, 1.27 mmol, 40%) as a colorless solid. M.p. 106-110 °C (100-103 °C)<sup>9</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.74 (1 H, dd,  $J$  8.2, 1.6, CH), 7.65 (1 H, d,  $J$  1.6, CH), 7.01 (1 H, t,  $J$  8.2, CH), 6.89 (1 H, d,  $J$  8.2, CH), 6.58 (2 H, d,  $J$  8.2, 2 x CH), 5.15 (2 H, s, CH<sub>2</sub>), 3.950 (3 H, s, Me), 3.945 (3 H, s, Me), 3.82 (6 H, s, 2 x Me). NMR data is consistent with the literature<sup>10</sup>.

### 1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(4-methoxyphenoxy)propan-1-one (22)



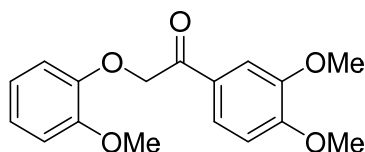
According to General Procedure A, stirring 2-bromo-1-(3,4-dimethoxyphenyl)ethanone (600 mg, 2.30 mmol), 4-methoxyphenol (500 mg, 4.03 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.2 g, 8.70 mmol) in acetone (8 mL for 5 h gave the *title compound* (693 mg, 2.30 mmol, 100%) as a beige solid. M.p. 85-91 °C (104 °C)<sup>5</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.65 (1 H, dd,  $J$  8.3, 2.1, CH), 7.57 (1 H, d,  $J$  2.1, CH), 6.91-6.88 (3 H, m, 3 x CH), 6.83-6.81 (2 H, m, 2 x CH), 5.17 (2 H, s, CH<sub>2</sub>), 3.96 (3 H, s, Me), 3.94 (3 H, s, Me), 3.76 (3 H, s, Me). NMR data is consistent with the literature<sup>5</sup>.

### 1-(4-Methoxyphenyl)-2-phenoxyethan-1-one (23)



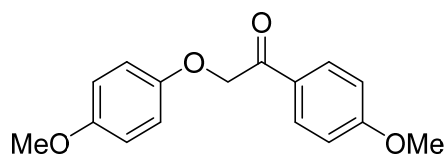
According to General Procedure A, stirring 2-bromo-4'-methoxyacetophenone (1.2 g, 5.30 mmol), phenol (1.0 g, 10.60 mmol) and  $K_2CO_3$  (2.4 g, 17.39 mmol) in acetone (16 mL) for 1.5 h gave the *title compound* (537 mg, 2.13 mmol, 41%) as a colorless solid. M.p. 68-71 °C (66-67 °C)<sup>6</sup>;  $\delta_H$  (400 MHz,  $CDCl_3$ ) 8.01-7.98 (2 H, m, 2 x CH), 6.97-6.95 (2 h, m, 2 x CH), 6.90-6.88 (2 H, m, 2 x CH), 6.83-6.81 (2 H, m, 2 x CH), 5.16 (2 H, s,  $CH_2$ ), 3.88 (3 H, s, Me), 3.76 (3 H, s, Me). NMR data is consistent with the literature<sup>3</sup>.

### 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (24)



According to General Procedure A, stirring 2-bromo-1-(3,4-dimethoxyphenyl)ethanone (600 mg, 2.32 mmol), guaiacol (500 mg, 4.03 mmol) and  $K_2CO_3$  (1.2 g, 8.70 mmol) in acetone (8 mL) for 3 d gave the *title compound* (540 mg, 1.79 mmol, 72%) as a beige solid. M.p. 97-100 °C (95-96 °C)<sup>7</sup>;  $\delta_H$  (400 MHz,  $CDCl_3$ ) 7.08 (1 H, d,  $J$  8.1, CH), 7.60 (1 H, s, CH), 6.97-6.85 (5 H, m, 5 x CH), 5.29 (2 H, s,  $CH_2$ ), 3.96 (3 H, s, Me), 3.94 (3 H, s, Me), 3.89 (3 H, s, Me). NMR data is consistent with the literature<sup>8</sup>.

### 2-(4-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (25)



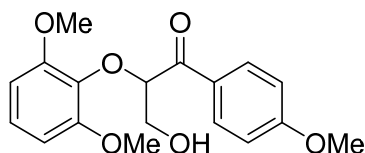
According to General Procedure A, stirring 2-bromo-4'-methoxyacetophenone (1.2 g, 5.3 mmol), 4-methoxyphenol (1.0 g, 8.06 mmol) and  $K_2CO_3$  (2.4 g, 17.39 mmol) in acetone (16

mL) for 24 h gave the *title compound* (487 mg, 1.79 mmol, 34%) as a colorless solid. M.p. 80-81 °C (76-77 °C)<sup>2</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 8.01-7.98 (2 H, m, 2 x CH), 6.97-6.95 (2 h, m, 2 x CH), 6.90-6.88 (2 H, m, 2 x CH), 6.83-6.81 (2 H, m, 2 x CH), 5.16 (2 H, s, CH<sub>2</sub>), 3.88 (3 H, s, Me), 3.76 (3 H, s, Me). NMR data is consistent with the literature<sup>4</sup>.

### **General Procedure B: Synthesis of hydroxymethyl $\beta$ -O-4 ketone models**

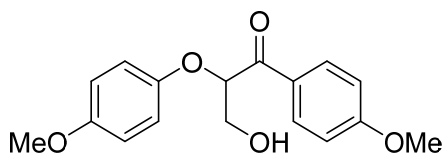
The appropriate phenoxyacetophenone model (0.90 - 5.75 mmol) was dissolved in ethanol:acetone (1:1). K<sub>2</sub>CO<sub>3</sub> (4.7 – 10.86 mmol) and formaldehyde (37% aq. sol.) were added, and the mixture stirred at rt for 1.5 - 24 h. The mixture was then concentrated under reduced pressure, dissolved in ethyl acetate and washed with water. The organic extract was then dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. The crude oil was purified by flash chromatography on silica gel to give the desired hydroxymethyl model.

#### **2-(2,6-Dimethoxyphenoxy)-3-hydroxy-1-(4-methoxyphenyl)propan-1-one (33)**



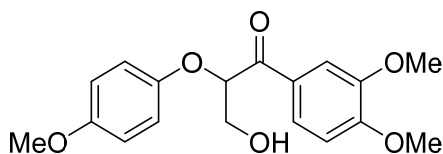
According to General Procedure B; using 2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**20**, 1.735 g, 5.75 mmol), ethanol:acetone (1:1, 120 mL), K<sub>2</sub>CO<sub>3</sub> (1.58 g, 11.44 mmol) and formaldehyde (37 %, aq. sol., 1.5 mL) for 24 h. The crude oil was purified by flash chromatography on silica gel eluting with ethyl acetate:petroleum ether (1:2) to give the *title compound* (1076 mg, 3.24 mmol, 57%) as a colorless solid. M.p. 75.8-78.3 °C; HRMS [ESI, (M + H)<sup>+</sup>] found 333.1333 [C<sub>18</sub>H<sub>20</sub>O<sub>6</sub> + H]<sup>+</sup> requires 333.1333;  $\nu_{\text{max}}$ /cm<sup>-1</sup> (neat): 3552, 2938, 9965, 1680, 1478;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 8.09 (2 H, d, *J* 9.1, 2 x CH), 7.01 (1 H, t, *J* 8.5, CH), 6.94 (2 H, d, *J* 9.1, 2 x CH), 6.57 (2 H, d, *J* 8.5, 2 x CH), 5.05 (1 H, dd, *J* 7.7, 3.0, CH), 4.04-3.99 (1 H, m, CH<sub>2</sub>), 3.87 (3 H, s, Me), 3.86-3.84 (1 H, m, CH<sub>2</sub>), 3.72 (6 H, s, 2 x Me), 1 x OH not observed;  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 195.1 (C), 163.6 (C), 152.7 (2 x C), 136.8 (C), 131.2 (2 x CH), 128.6 (C), 124.3 (CH), 113.8 (2 x CH), 105.3 (2 x CH), 88.1 (CH), 63.6 (CH<sub>2</sub>), 55.9 (2 x Me), 55.5 (Me).

### 3-Hydroxy-2-(4-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (34)



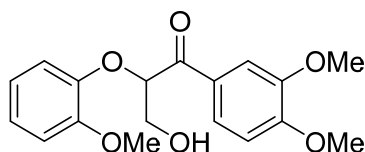
According to General Procedure B; using 2-(4-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**25**, 300 mg, 1.1 mmol), ethanol:acetone (1:1, 18 mL), K<sub>2</sub>CO<sub>3</sub> (1.5 g, 10.86 mmol) and formaldehyde (37 %, aq. sol., 0.3 mL) for 4 h. The crude oil was purified by flash chromatography on silica gel eluting with ethyl acetate:petroleum ether (3:2) to give the *title compound* (208 mg, 0.69 mmol, 63%) as a colorless solid. M.p. 93.2-96.5 °C; HRMS [ESI, (M + H)<sup>+</sup>] found 303.1218 [C<sub>17</sub>H<sub>18</sub>O<sub>5</sub> + H]<sup>+</sup> requires 303.1227;  $\nu_{\text{max}}/\text{cm}^{-1}$  (neat):3418, 2998, 2833, 1676, 1600;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 8.06-8.03 (2 H, m, 2 x CH), 6.96-6.92 (2 H, m, 2 x CH), 6.87-6.83 (2 H, m, 2 x CH), 6.80-6.76 (2 H, m, 2 x CH), 5.39 (1 H, dd, *J* 6.3, 4.3, CH), 4.14-4.05 (2 H, m, CH<sub>2</sub>), 3.87 (3 H, s, Me), 3.74 (3 H, s, Me), 1 x OH not observed;  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 195.4 (C), 164.2 (C), 154.7 (C), 131.3 (2 x CH), 127.8 (C), 117.6 (C), 116.6 (2 x CH), 114.8 (2 x CH), 114.1 (2 x CH), 82.1 (C), 63.4 (CH<sub>2</sub>), 55.7 (Me), 55.6 (Me).

### 1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(4-methoxyphenoxy)propan-1-one (35)



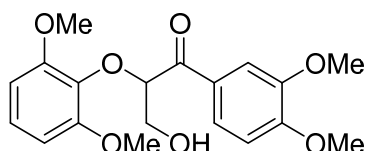
According to General Procedure B; using 1-(3,4-dimethoxyphenyl)-2-(4-methoxyphenoxy)ethan-1-one (**22**, 300 mg, 1.0 mmol), ethanol:acetone (1:1, 18 mL), K<sub>2</sub>CO<sub>3</sub> (1.5 mg, 10.8 mmol) and formaldehyde (37% aq. sol., 0.5 mL) for 4 h. The crude oil was purified by flash chromatography on silica gel eluting with ethyl acetate:petroleum ether (2:3) to give the *title compound* (208 mg, 0.63 mmol, 63%) as a yellow oil.  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.75 (1 H, dd, *J* 8.7, 1.8, CH), 7.57 (1 H, d, *J* 1.8, CH), 6.90-6.84 (3 H, m, 3 x CH), 6.80-6.77 (3 H, m, 3 x CH), 5.42 (1 H, dd, *J* 6.4, 4.2, CH), 4.14-4.08 (2 H, m, CH<sub>2</sub>), 3.95 (3 H, s, Me), 3.90 (3 H, s, Me), 3.74 (3 H, s, Me). 1 x OH not observed. NMR data is consistent with the literature<sup>11</sup>.

### 1-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one (36)



According to General Procedure B; using 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (**24**, 300 mg, 1.00 mmol), ethanol:acetone (1:1, 18 mL), K<sub>2</sub>CO<sub>3</sub> (2.5 g, 18.11 mmol) and formaldehyde (37% aq. sol., 0.4 mL) for 2 h. The crude oil was purified by flash chromatography on silica gel eluting with ethyl acetate:petroleum ether (2:3) to give the *title compound* (284 mg, 0.86 mmol, 86%) as a colorless solid. M.p. 115.9-120.1 °C (117.5-118.0 °C)<sup>12</sup>;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.76 (1 H, dd, *J* 8.1, 2.5, CH), 7.62 (1 H, d, *J* 1.8, CH), 7.02-6.98 (1 H, m, CH), 6.92-6.88 (3 H, m, 3 x CH), 6.85-6.80 (1 H, m, CH), 5.39 (1 H, t, *J* 5.0, CH), 4.07 (2 H, t, *J* 5.8, CH<sub>2</sub>), 3.95 (3 H, s, Me), 3.92 (3 H, s, Me), 3.86 (3 H, s, Me). NMR data is consistent with the literature<sup>13</sup>.

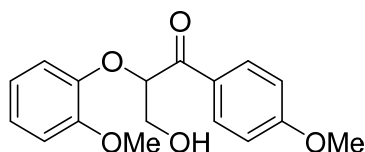
### 2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-3-hydroxypropan-1-one (37)



According to General Procedure B; using 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethan-1-one (**21**, 300 mg, 0.9 mmol), acetone:ethanol (1:1, 18 mL), K<sub>2</sub>CO<sub>3</sub> (1.5 g, 10.86 mmol) and formaldehyde (37% aq. sol., 0.3 mL) for 4 h. The crude oil was purified by flash chromatography on silica gel eluting with ethyl acetate:petroleum ether (1:1) to give the *title compound* (218 mg, 0.60 mmol, 67%) as a colorless oil.  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.73 (1 H, dd, *J* 8.3, 1.6, CH), 7.67 (1 H, d, *J* 1.6, CH), 7.02 (1 H, t, *J* 8.6, CH), 6.88 (1 H, d, *J* 8.3, CH), 6.58 (2 H, d, *J* 8.6, 2 x CH), 5.09 (1 H, dd, *J* 7.8, 3.3, CH), 4.03-3.97 (1 H, m, CH<sub>2</sub>), 3.95 (3 H, s, Me), 3.94 (3 H, s, Me), 3.86-3.82 (1 H, m, CH), 3.73 (6 H, s, 2 x Me). NMR data is consistent with the literature<sup>14</sup>.



### 3-Hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (38)

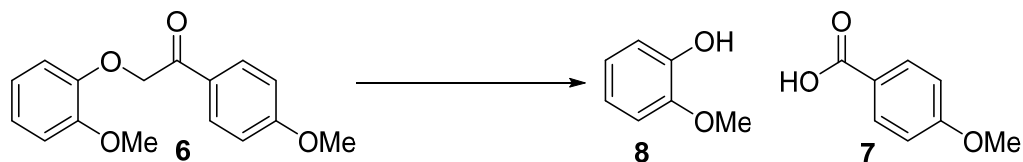


According to General Procedure B; using 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**6**, 1 g, 3.68 mmol), ethanol:acetone (1:1, 50 mL), K<sub>2</sub>CO<sub>3</sub> (650 mg, 4.70 mmol) and formaldehyde (37% aq. sol., 0.6 mL) for 1.5 h. The crude oil was purified by flash chromatography on silica gel eluting with ethyl acetate:petroleum ether (2:1) to give the *title compound* (906 mg, 3.00 mmol, 82 %) as a brown oil.  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 8.07 (2 H, d, *J* 8.6, 2 x CH), 7.02-6.98 (1 H, m, CH), 6.96-6.82 (4 H, m, 4 x CH), 6.84-6.80 (1 H, m, CH), 5.37 (1 H, t, *J* 5.5, CH), 4.05 (2 H, d, *J* 5.5, CH<sub>2</sub>), 3.87 (3 H, s, Me), 3.85 (3 H, s, Me). 1 x OH not observed. NMR data is consistent with the literature<sup>15</sup>.

### General Procedure C: Cleavage of phenoxyacetophenone $\beta$ -O-4 ketone models

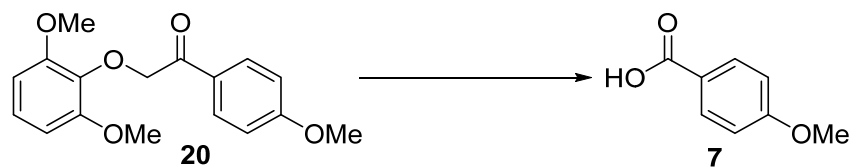
Model ketone (0.33 mmol), oxalic acid dihydrate (1.0 g) and water (0.5 mL) were stirred at 100 °C for the appropriate time. The reaction was then cooled to rt, and the resulting solid washed with ethyl acetate and the washings concentrated under reduced pressure. The crude solid was purified by flash chromatography on silica gel eluting with ethyl acetate-petroleum ether to give the corresponding phenol and carboxylic acid.

### Cleavage of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**6**)



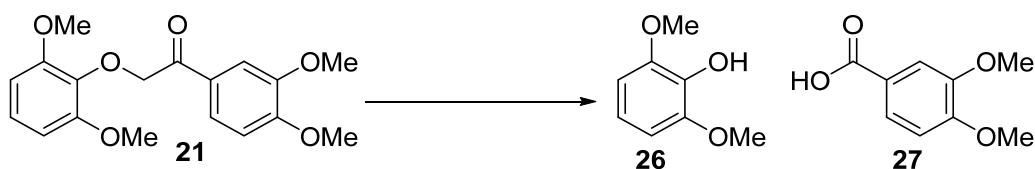
According to General Procedure C; using 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**6**, 100 mg, 0.38 mmol) for 24 h gave *p*-anisic acid **7** (40 mg, 0.28 mmol, 73 %) and guaiacol (**8**, 21 mg, 0.18 mmol, 47%).

### Cleavage of 2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**20**)



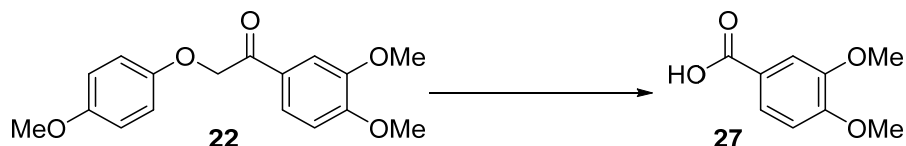
According to General Procedure C; using 2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**20**, 100 mg, 0.33 mmol) for 30 h gave *p*-anisic acid (**7**, 33 mg, 0.23 mmol, 67 %).

### Cleavage of 2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethan-1-one (**21**)



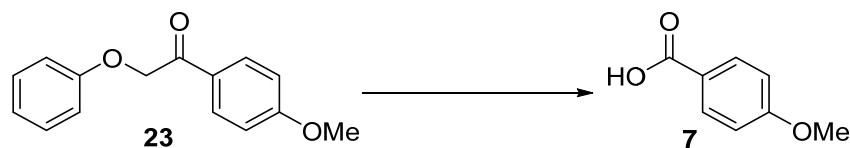
According to General Procedure C; using 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethan-1-one (**21**, 110 mg, 0.33 mmol) for 30 h gave veratric acid (**27**, 20 mg, 0.11 mmol, 37 %) and 2,6-dimethoxyphenol (**26**, 10 mg, 0.07 mmol, 22 %).

### Cleavage of 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(4-methoxyphenoxy)propan-1-one (**22**)



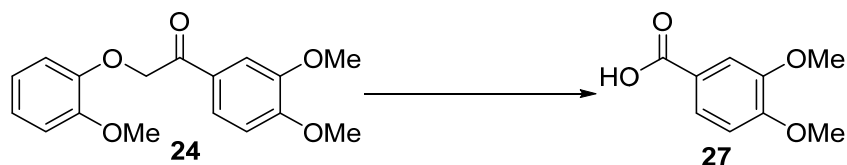
According to General Procedure C; using 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(4-methoxyphenoxy)propan-1-one (**22**, 100 mg, 0.33 mmol) for 30 h gave veratric acid (**27**, 51 mg, 0.28 mmol, 85 %).

### Cleavage of 1-(4-methoxyphenyl)-2-phenoxyethan-1-one (**23**)



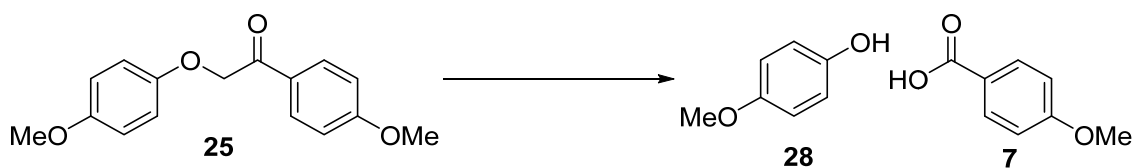
According to General Procedure C; using 1-(4-methoxyphenyl)-2-phenoxyethan-1-one (**23**, 81 mg, 0.33 mmol) for 24 h gave *p*-anisic acid **7** (13 mg, 0.09 mmol, 27 %).

### Cleavage of 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (**24**)



According to General Procedure C; using 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (**24**, 100 mg, 0.33 mmol) for 24 h gave veratric acid (**27**, 34 mg, 0.19 mmol, 57 %).

### Cleavage of 2-(4-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**25**)

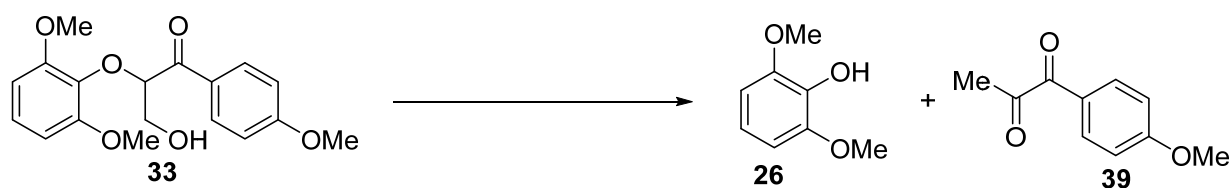


According to General Procedure C; using 2-(4-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**25**, 89 mg, 0.33 mmol) for 30 h gave *p*-anisic acid (**7**, 30 mg, 0.20 mmol, 60 %) and 4-methoxyphenol (**28**, 4 mg, 0.033 mmol, 10 %).

### **General Procedure D: Cleavage of Hydroxymethyl $\beta$ -O-4 Models**

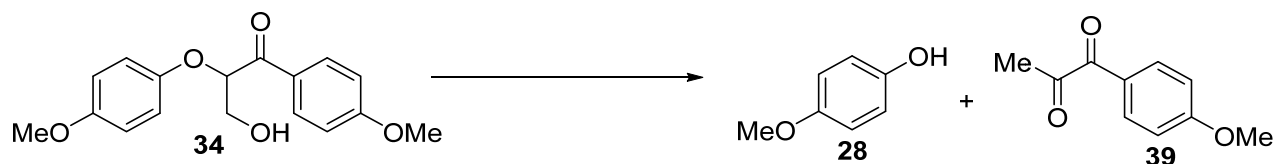
Hydroxymethyl model (0.30 mmol), oxalic acid (1 g) and water (0.5 mL) were stirred at 100 °C for 17 h. The reaction was then cooled to rt, and the resulting solid washed with ethyl acetate. The organic extract was concentrated under reduced pressure. The crude solid was purified on flash chromatography to give the corresponding phenol and diketone.

#### **Cleavage of 2-(2,6-dimethoxyphenoxy)-3-hydroxy-1-(4-methoxyphenyl)propan-1-one (33)**



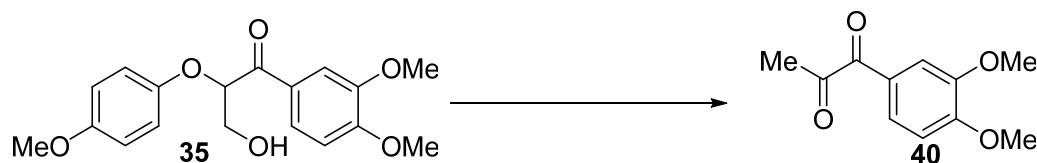
According to General Procedure D; using 2-(2,6-dimethoxyphenoxy)-3-hydroxy-1-(4-methoxyphenyl)propan-1-one (**33**, 100 mg, 0.30 mmol) gave 2,6-dimethoxyphenol (**26**, 41 mg, 0.30 mmol, 100 %) and 1-(4-methoxyphenyl)propane-1,2-dione (**39**, 48 mg, 0.27 mmol, 91 %).

#### **Cleavage of 3-hydroxy-2-(4-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (34)**



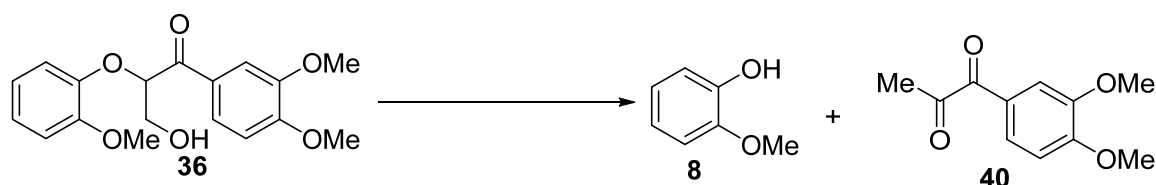
According to General Procedure D; using 3-hydroxy-2-(4-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (**34**, 91 mg, 0.30 mmol) gave 4-methoxyphenol (**28**, 10 mg, 0.08 mmol, 27 %) and 1-(4-methoxyphenyl)propane-1,2-dione (**39**, 52 mg, 0.29 mmol, 98 %).

**Cleavage of 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(4-methoxyphenoxy)propan-1-one (35)**



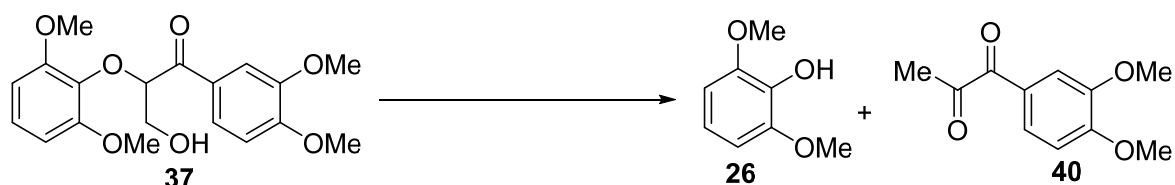
According to General Procedure D; using 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(4-methoxyphenoxy)propan-1-one (35, 100 mg, 0.30 mmol) gave 1-(3,4-dimethoxyphenyl)propane-1,2-dione (40, 53 mg, 0.25 mmol, 86 %).

**Cleavage of 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one (36)**



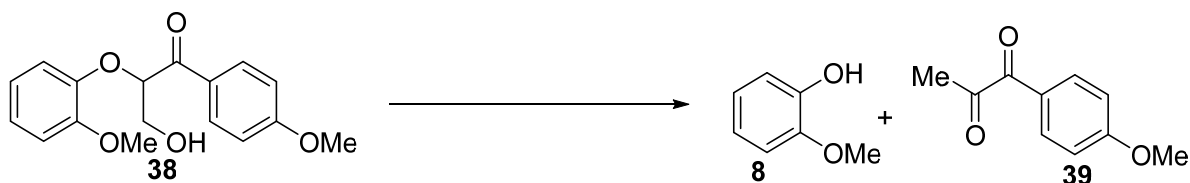
According to General Procedure D; using 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one (36, 100 mg, 0.30 mmol) gave guaiacol (8, 8 mg, 0.06 mmol, 22 %) and 1-(3,4-dimethoxyphenyl)propane-1,2-dione (40, 33 mg, 0.16 mmol, 33 %).

**Cleavage of 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-3-hydroxypropan-1-one (37)**



According to General Procedure D; using 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-3-hydroxypropan-1-one (37, 108 mg, 0.30 mmol) gave 2,6-dimethoxyphenol (26, 18 mg, 0.12 mmol, 39 %) and 1-(3,4-dimethoxyphenyl)propane-1,2-dione (40, 34 mg, 0.16 mmol, 54 %).

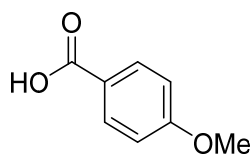
### Cleavage of 3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (**38**)



According to General Procedure D; using 3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (**38**, 91 mg, 0.30 mmol) gave guaiacol (**8**, 26 mg, 0.21 mmol, 70 %) and 1-(4-methoxyphenyl)propane-1,2-dione (**39**, 53 mg, 0.30 mmol, 100 %).

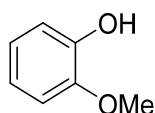
### Characterisation Data for Products from the Cleavage of $\beta$ -O-4 Model Compounds

#### *p*-Anisic acid (**7**)



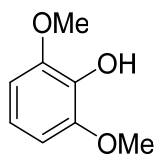
Colourless solid. M.p. 184-186 °C (186-188 °C)<sup>16</sup>; HRMS [ESI, (M - H)<sup>-</sup>] found 151.0395 [C<sub>8</sub>H<sub>7</sub>O<sub>3</sub> - Na]<sup>-</sup> requires 151.0401;  $\nu_{\text{max}}/\text{cm}^{-1}$  (neat): 3389, 2973, 2163, 1604, 1095;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 8.07 (2 H, m, 2 x CH), 6.95 (2 H, m, 2 x CH), 3.88 (3 H, s, Me), 1 x OH not observed;  $\delta_{\text{C}}$  (100 MHz, CHCl<sub>3</sub>) 171.0 (C), 164.0 (C), 132.4 (2 x CH), 121.7 (C), 113.8 (2 x CH), 55.5 (Me); NMR data is consistent with the literature.<sup>17</sup>

#### Guaiacol (**8**)



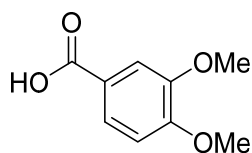
Colourless oil.  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 6.94-6.85 (4 H, m, 4 x CH), 5.60 (1 H, s, OH), 3.89 (3 H, s, Me); NMR data is consistent with the literature.<sup>18</sup>

### 2,6-Dimethoxyphenol (26)



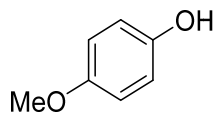
Orange solid, M.p. 56-61 °C (56-57 °C lit.)<sup>21</sup>; HRMS [ESI, (M + Na)<sup>+</sup>] found 177.0518 [C<sub>8</sub>H<sub>10</sub>O<sub>3</sub> + Na]<sup>+</sup> requires 177.0522;  $\nu_{\text{max}}/\text{cm}^{-1}$  (neat): 3484, 3445, 2964, 1598, 1478;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 6.80 (1 H, t, *J* 8.2, CH), 6.58 (2 H, d, *J* 8.2, 2 x CH), 5.53 (1 H, br s, OH), 3.89 (6 H, s, Me);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 147.3 (2 x C), 134.9 (C), 119.1 (CH), 105.0 (2 x CH), 56.3 (2 x Me); NMR data is consistent with the literature.<sup>22</sup>

### Veratric acid (27)



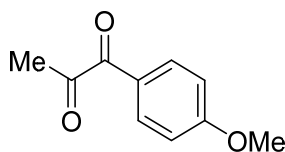
Colourless solid. M.p. 162-172 °C (176-178 °C)<sup>20</sup>; HRMS [ESI, (M + Na)<sup>+</sup>] found 205.0466 [C<sub>9</sub>H<sub>10</sub>O<sub>4</sub> + Na]<sup>+</sup> requires 205.0471;  $\nu_{\text{max}}/\text{cm}^{-1}$  (neat): 3405, 2938, 2525, 2163, 1665;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.78 (1 H, dd, *J* 8.4, 1.9, CH), 7.60 (1 H, d, *J* 1.9, CH), 6.92 (1 H, d, *J* 8.4, CH), 3.96 (3 H, s, Me), 3.95 (3 H, s, Me), 1 x OH not observed;  $\delta_{\text{C}}$  (100 MHz, CHCl<sub>3</sub>) 171.7 (C), 153.8 (C), 148.7 (C), 124.6 (CH), 121.7 (C), 112.4 (CH), 110.4 (CH), 56.1 (Me), 56.0 (Me); NMR data is consistent with the literature.<sup>20</sup>

### 4-Methoxyphenol (28)



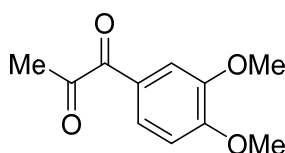
Colourless oil.  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 6.81-6.75 (4 H, m, 4 x CH), 4.74 (1 H, br s, OH), 3.76 (3 H, s, Me); NMR data is consistent with the literature.<sup>19</sup>

### 1-(4-Methoxyphenyl)propane-1,2-dione (39)



Yellow Solid. M.p. 50.5-52.7 ° C (48 °C lit.)<sup>1</sup>;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 8.01 (2 H, d,  $J$  9.0, 2 x CH), 6.96 (2 H, d,  $J$  9.0, 2 x CH), 3.89 (3 H, s, Me), 2.50 (3 H, s, Me). NMR is consistent with the literature<sup>23</sup>.

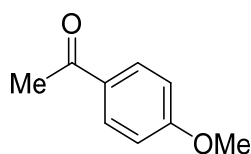
### 1-(3,4-dimethoxyphenyl)propane-1,2-dione (40)



Yellow solid. M.p. 58.6-62.8 °C (66-67 °C lit.)<sup>24</sup>;  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.65 (1 H, dd,  $J$  8.6, 2.0, CH), 7.56 (1 H, d,  $J$  2.0, CH), 6.90 (1 H, d,  $J$  8.6, CH), 3.96 (3 H, s, Me), 3.93 (3 H, s, Me), 2.50 (3 H, s, Me). NMR data is consistent with the literature<sup>24</sup>.

### Mechanistic studies on the cleavage of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (6)

#### 4-Methoxyacetophenone (9)

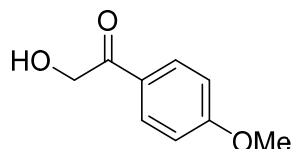


2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**6**, 100 mg, 0.38 mmol), oxalic acid dihydrate (1 g) and Rose Bengal (4 mol %, 12 mg, 0.015 mmol) were combined, and water (0.5 mL, purged with  $\text{O}_2$  for 30 min) was added. A reflux condenser was attached and the reaction vessel sealed under a blanket of  $\text{O}_2$ . The reaction was then stirred for the appropriate time at 100 °C and monitored by TLC. Upon completion of the reaction, water (10 mL) was added, and the mixture extracted with ethyl acetate (3 x 10 mL). The organic extracts were combined, dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated under reduced pressure. The crude solid was



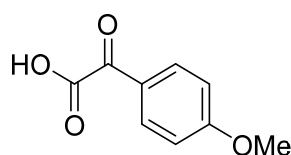
purified by flash chromatography eluting with petroleum ether-ethyl acetate (3:1) to give **7**, **8**, and the *title compound* (**9**, 5 mg, 0.033 mmol, 9%) as an orange oil.  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.94 (2 H, d,  $J$  9.0, 2 x CH), 6.94 (2 H, d,  $J$  9.0, 2 x CH), 3.87 (3 H, s, Me), 2.56 (3 H, s, Me); NMR data is consistent with the literature.<sup>25</sup>

### 2-Hydroxy-1-(4-methoxyphenyl)ethan-1-one (**12**)



A solution of 2-bromo-4'-methoxyacetophenone (200 mg, 0.88 mmol) in DMSO (5 mL) and water (0.5 mL) was stirred for 2 d at rt. Ethyl acetate (20 mL) was added, and the mixture washed with brine (3 x 20 mL). The organic extract was dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated under reduced pressure. Purification of the crude solid by flash chromatography on silica gel eluting with acetone-petroleum ether (1:3) gave the *title compound* (66 mg, 0.39 mmol, 46 %) as a colourless solid. M.p. 105-110 °C (105-107 °C lit.<sup>26</sup>)  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.91 (2 H, d,  $J$  9.0, 2 x CH), 6.98 (2 H, d,  $J$  9.0, 2 x CH), 4.82 (2 H, d,  $J$  4.5,  $\text{CH}_2$ ), 3.89 (3 H, s Me), 3.55 (1 H, t,  $J$  4.5, OH). NMR data is consistent with the literature.<sup>15</sup>

### 2-(4-Methoxyphenyl)-2-oxoacetic acid (**13**)

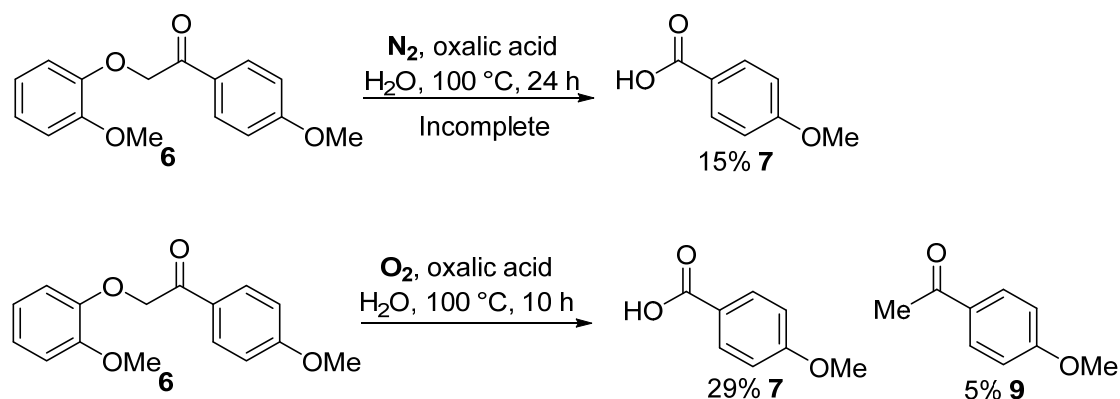


To a solution of acetanisole (**9**, 500 mg, 3.33 mmol) in water (5 mL) was added KOH (50 mg, 0.90 mmol) and  $\text{KMnO}_4$  (542.5 mg, 3.43 mmol), and the reaction mixture stirred for 16 h at rt.  $\text{Na}_2\text{S}_2\text{O}_3$  (sat sol. 20 mL) was added, the mixture filtered and the filtrate extracted with ethyl acetate (3 x 20 mL). The aqueous extract was then acidified with HCl (1 M, 20 mL) and extracted with ethyl acetate (3 x 20 mL). The organic extracts were combined, dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated under reduced pressure to give the *title compound* (267 mg, 1.48 mmol, 45%) as a yellow solid; M.p. 80-83 °C (90-91 °C lit.<sup>27</sup>);  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 9.67 (1 H, br s, OH),

8.27 (2 H, d, *J* 8.8, 2 x CH), 6.96 (2 H, d, *J* 8.8, 2 x CH), 3.89 (3 H, s, Me); NMR data is consistent with the literature.<sup>27</sup>

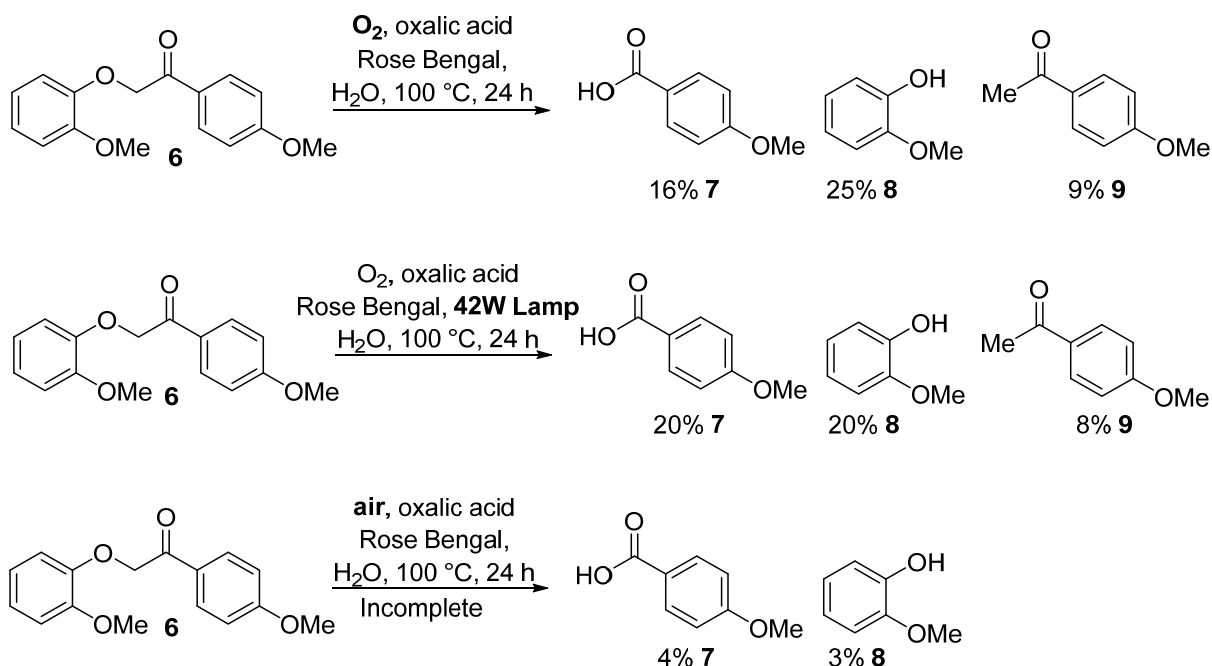
## **Mechanistic studies**

### **Atmosphere Screening**



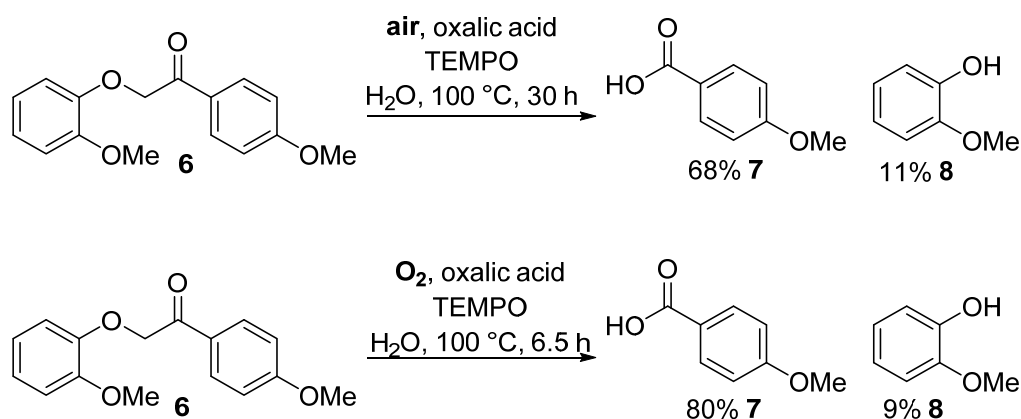
2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**6**, 100 mg, 0.38 mmol) and oxalic acid dihydrate (1 g) were combined and water (0.5 mL, purged with N<sub>2</sub> for 30 min, or purged with O<sub>2</sub> for 30 min) was added. A reflux condenser was attached and the reaction vessel sealed under a blanket of N<sub>2</sub> or O<sub>2</sub>. The reaction was then stirred for the appropriate time at 100 °C and monitored by TLC. Upon completion of the reaction, water (10 mL) was added, and the mixture extracted with ethyl acetate (3 x 10 mL). The organic extracts were combined, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. The crude solid was purified by flash chromatography eluting with petroleum ether-ethyl acetate (3:1) to give the observed cleavage products.

## Singlet Oxygen Investigation



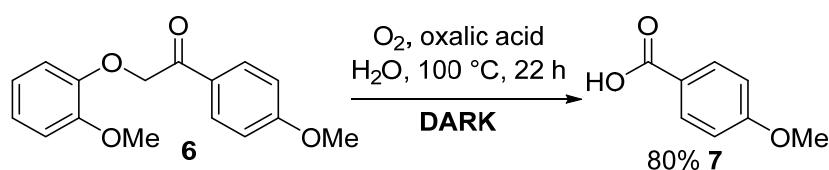
2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**6**, 100 mg, 0.38 mmol), oxalic acid dihydrate (1 g) and Rose Bengal (4 mol %, 12 mg, 0.015 mmol) were combined and water (0.5 mL, purged with O<sub>2</sub> or air for 30 min) was added. A reflux condenser was attached and the reaction vessel sealed under a blanket of O<sub>2</sub> or air. The reaction was either irradiated with light or left under ambient light conditions, and stirred for the appropriate time at 100 °C and monitored by TLC. Upon completion of the reaction, water (10 mL) was added, and the mixture extracted with ethyl acetate (3 x 10 mL). The organic extracts were combined, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. The crude solid was purified by flash chromatography eluting with petroleum ether-ethyl acetate (3:1) to give the observed cleavage products.

## Radical Quenching Studies



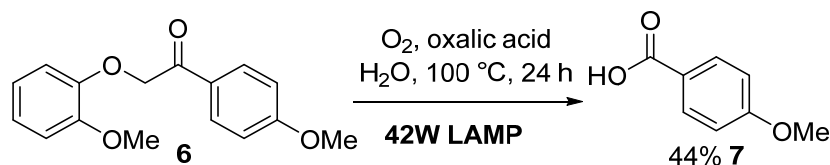
2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**6**, 100 mg, 0.38 mmol), oxalic acid dihydrate (1 g) and 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) (57 mg, 0.38 mmol) were combined and water (0.5 mL, gassed with O<sub>2</sub> or air for 30 min) was added. A reflux condenser was attached and the reaction vessel sealed under a blanket of O<sub>2</sub> or air. The reaction was then stirred for the appropriate time at 100 °C and monitored by TLC. Upon completion of the reaction, water (10 mL) was added, and the mixture extracted with ethyl acetate (3 x 10 mL). The organic extracts were combined, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated under reduced pressure. The crude solid was purified by flash chromatography eluting with petroleum ether-ethyl acetate (3:1) to give the observed cleavage products.

## Oxalic Acid Degradation Studies



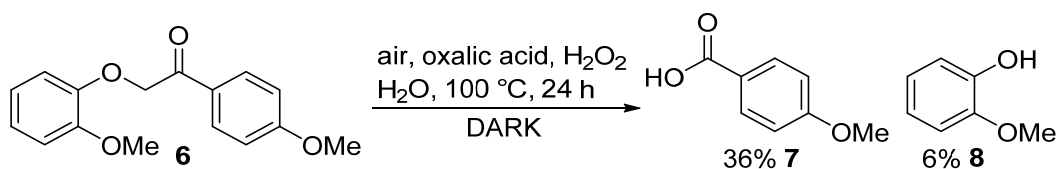
2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**6**, 100 mg, 0.38 mmol) and oxalic acid dihydrate (1 g) were combined. Then water (0.5 mL, gassed with O<sub>2</sub> for 30 min) was added. A reflux condenser was attached and the reaction vessel sealed under a blanket of O<sub>2</sub>. The entire apparatus was wrapped in tin foil, and the reaction was then stirred for 22 h at 100 °C and monitored by TLC. Upon completion of the reaction, water (10 mL) was added, and the mixture extracted with ethyl acetate (3 x 10 mL). The organic extracts were combined, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. The crude solid was purified by flash

chromatography eluting with petroleum ether:ethyl acetate (3:1) to give *p*-anisic acid (44 mg, 0.30 mmol, 80%).



2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**6**, 100 mg, 0.38 mmol) and oxalic acid dihydrate (1 g) were combined. Then water (0.5 mL, gassed with O<sub>2</sub> for 30 min) was added. A reflux condenser was attached and the reaction vessel sealed under a blanket of O<sub>2</sub>. The reaction was then irradiated with a desk lamp (42 W), and stirred for 24 h at 100 °C and monitored by TLC. Upon completion of the reaction, water (10 mL) was added, and the mixture extracted with ethyl acetate (3 x 10 mL). The organic extracts were combined, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. The crude solid was purified by flash chromatography eluting with petroleum ether-ethyl acetate (3:1) to give *p*-anisic acid (24 mg, 0.16 mmol, 44%).

### Hydrogen Peroxide Mediated Degradation Studies



To a solution of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**6**, 100 mg, 0.38 mmol) and oxalic acid dihydrate (1 g) in water (0.5 mL) was added hydrogen peroxide (35%, 0.04 mL). A reflux condenser was attached and the reaction vessel opened to the air. The entire apparatus was wrapped in tin foil, and the reaction was then stirred for 24 h at 100 °C and monitored by TLC. Upon completion of the reaction, water (10 mL) was added, and the mixture extracted with ethyl acetate (3 x 10 mL). The organic extracts were combined, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated under reduced pressure. The crude solid was purified by flash chromatography eluting with petroleum ether-ethyl acetate (3:1) to give *p*-anisic acid (20 mg, 0.14 mmol, 36%) and guaiacol (3 mg, 0.02 mmol, 6%).

## Oxalic Acid Recycling

2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**6**, 300 mg, 1.14 mmol) and oxalic acid dihydrate (3 g) were combined. Then, water (1.5 mL) was added and the reaction stirred at 100 °C for 30 h. Upon completion, the reaction was cooled to rt and the resulting crystals washed with ethyl acetate (50 mL). The filtrate was concentrated under reduced pressure to give **7** and **8**. The remaining oxalic crystals were dried for reuse. This procedure was repeated 3 times reusing the oxalic acid on 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (**6**, 100 mg, 0.38 mmol) with oxalic acid dihydrate (1 g) and water (0.5 mL). Occasionally, small quantities of used oxalic acid were added to top up the oxalic acid to the required weight.

The yield for the cleavage after repeating the above procedure three times was 60%.

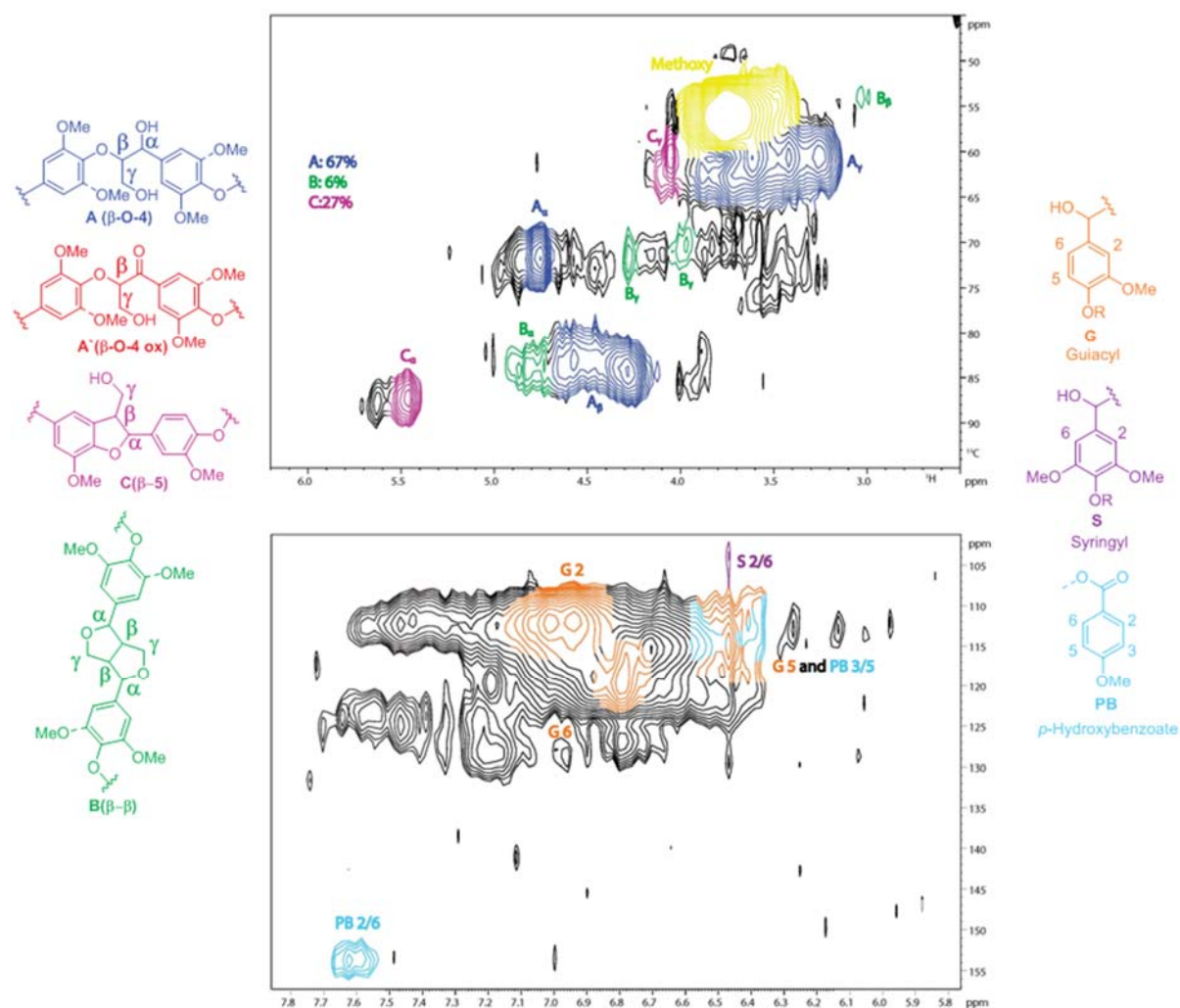
## ***Pinus radiata* MWL: Isolation, oxidation and depolymerisation**

**Lignin isolation:** *Pinus radiata* milled wood lignin was provided by New Zealand Forest Research Institute, trading as Scion according to the Björkman method:

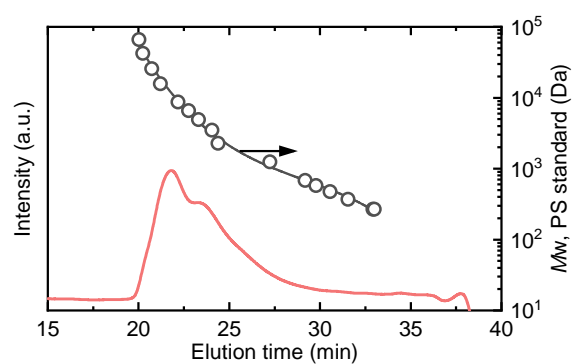
Pine samples were ground to pass 60 mesh on a Wiley mill. This product was then successively extracted with dichloromethane, water and 95% ethanol to remove extractives. In accordance with the Björkman method<sup>28</sup>, the extractive free wood (50 g) was ball milled for 4 days, followed by extraction of the resultant wood meal with 9:1 dioxane-water for 4 days. After filtration through GF filter paper, the product was concentrated under reduced pressure. The residual lignin was dissolved in acetic acid-water (80:3 mL), then precipitated into water (1400 mL). After centrifugation, the residual solid was dissolved in 210 mL of 2:1 dichloromethane-EtOH, which was precipitated into diethylether (400 mL). This precipitate was centrifuged and washed with Et<sub>2</sub>O (3 x 300 mL), then 40:60 petroleum ether was added, the material thoroughly stirred and concentrated, under reduced pressure, to yield *P.radiata* milled wood lignin (MWL) (**S1**).

Finally, before use, the *P.radiata* MWL was washed with ethyl acetate to remove smaller soluble lignin polymers, oligomers and pre-liberated aromatics. The molecular weight distribution of the washed lignin was determined by gel permeation chromatography (GPC), following acetylation of free hydroxyl groups. GPC was carried out with refractive index detector, triple columns (TSKgel G3000HXL, G2000HXL, and G1000HXL) having the exclusion limit at 60000 Da (PS), and THF as the mobile phase. Lignin acetylation was conducted using acetic anhydride (0.5 mL) and pyridine (0.5 mL) for 5 mg of *P.radiata* MWL at 40 °C for 24 h. After removing acetic anhydride and pyridine under reduced pressure in a

vacuum oven at 40 °C for 24 h, the acetylated lignin was dissolved to THF and then subjected to GPC (S2). The average molecular weight ( $M_w$ ) of the *P.radiata* MWL was 12000 Da.



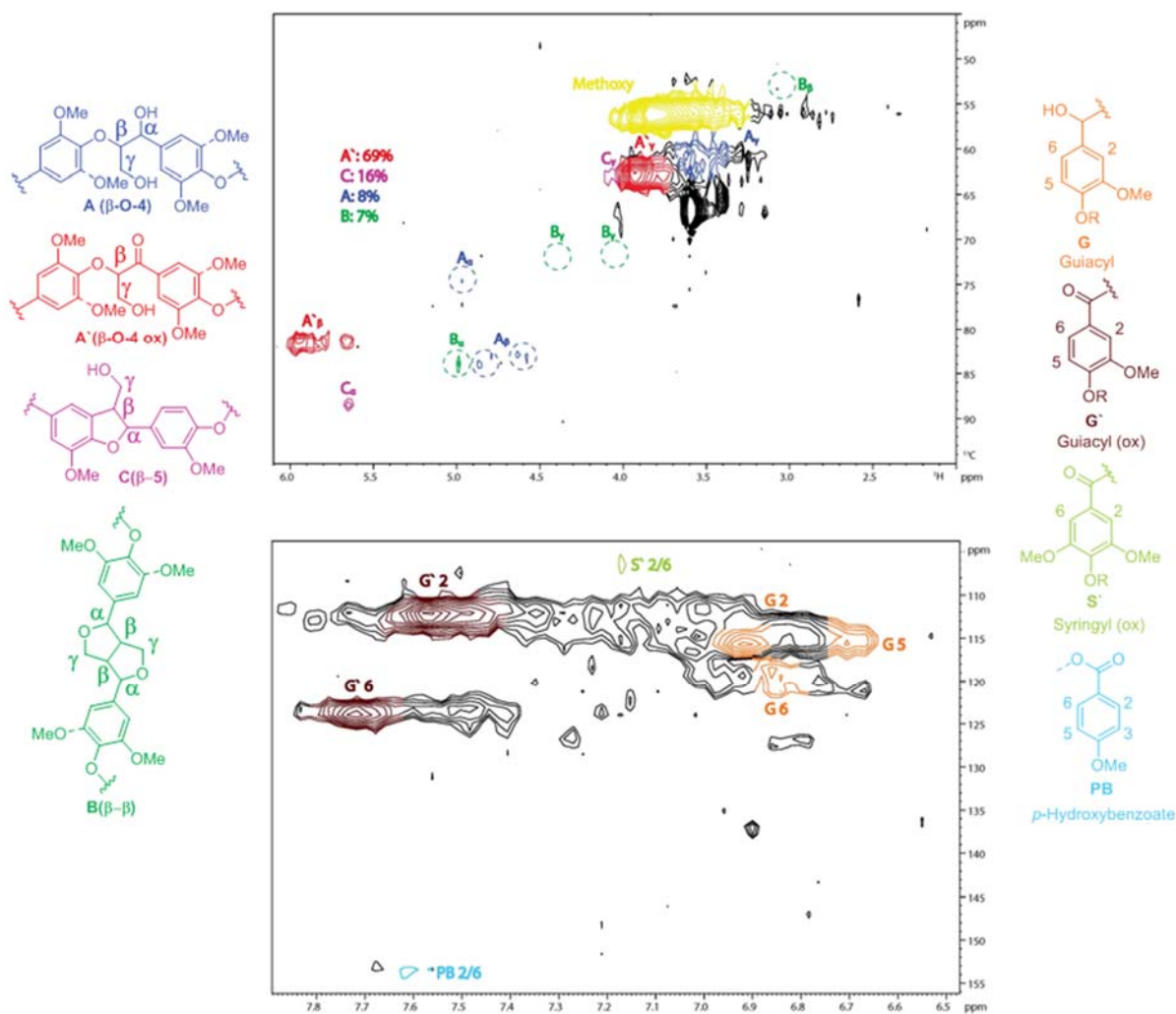
S1: 2D HSQC NMR (in DMSO- $d_6$ ) of isolated *P.radiata* MWL.



S2: GPC analysis of *P.radiata* MWL

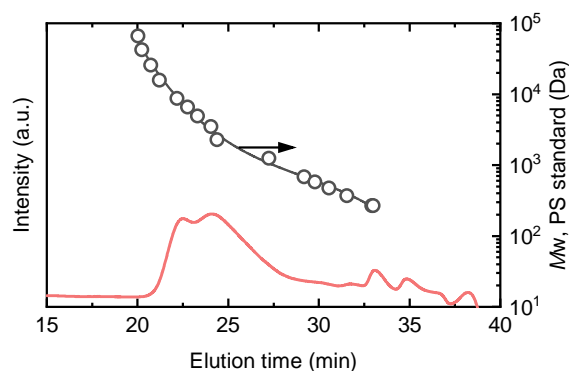
**Lignin oxidation:** To washed *P.radiata* MWL (100 mg) in dioxane (2.5 mL) was added DDQ (100 mg). The mixture was stirred at 80 °C for 3.5 h. The reaction was then cooled, filtered and the residual solid washed with dioxane (10 mL). The filtrate was then added dropwise to diethyl ether (50 mL) which resulted in precipitation. The precipitate was filtered, collected and dried under reduced pressure to give 47 mg oxidised *P.radiata* MWL which was characterised (S3), and subjected to the depolymerisation conditions.

The molecular weight distribution of the oxidised lignin was determined by GPC, following acetylation of free hydroxyl groups. The average molecular weight ( $M_w$ ) of the oxidised *P.radiata* MWL was 4000 Da (S4).



**S3:** 2D HSQC NMR (in DMSO- $d_6$ ) of oxidised *P.radiata* MWL.





**S4:** GPC analysis of oxidised *P.radiata* MWL.

***P.radiata* MWL depolymerisation:** *P.radiata* MWL (50 mg) was stirred with oxalic acid (500 mg) and water (0.25 mL) at 130 °C for 4 h. Upon completion, the mixture was allowed to cool to rt. The resultant solid was then washed with ethyl acetate (20 mL). The filtrate was collected and concentrated under reduced pressure. In order to prepare the filtrate for NMR and GC/MS analysis, the residue was suspended in ethyl acetate and washed with water until the aqueous layer was pH neutral. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure to give ethyl acetate soluble aromatics (3 mg, 6 wt%). The ethyl acetate insoluble material was washed with water until the wash was pH neutral to remove the remaining oxalic acid. This gave an insoluble black residue (16 mg, 32 wt %) which was analysed by GPC. A sample of this material (4.5 mg) was treated with acetic anhydride (0.5 mL) and pyridine (0.5 mL) at 40 °C for 24 h in order to acetylate any remaining free hydroxyl groups. The solvent was then evaporated in a vacuum oven at 40 °C for 24 h. However, acetylation did not improve the solubility of the material, and a sufficient GPC trace could not be obtained, leading to the postulation that this insoluble material possesses a char-like structure.

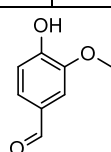
#### **Oxidised *P.radiata* MWL depolymerisation:**

Oxidised *P.radiata* MWL (36 mg) was stirred with oxalic acid (360 mg) and water (0.2 mL) at 130 °C for 4 h. Upon completion, the mixture was allowed to cool to rt. The resultant solid was then washed with ethyl acetate (20 mL). The filtrate was collected and concentrated under reduced pressure. In order to prepare the filtrate for NMR and GC/MS analysis, the residue was suspended in ethyl acetate and washed with water till the aqueous layer was pH neutral. The

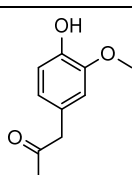
organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure to give ethyl acetate soluble aromatics (5 mg, 14 wt%). The ethyl acetate insoluble material was washed with water until pH neutral to remove the remaining oxalic acid. This gave an insoluble black char-like residue (30 mg, 83 wt%), which was analysed by GPC. A sample of this material (5.1 mg) was treated with acetic anhydride (0.5 mL) and pyridine (0.5 mL) at 40 °C for 24 h in order to acetylate any remaining free hydroxyl groups. The solvent was then evaporated in a vacuum oven at 40 °C for 24 h. However, acetylation did not improve the solubility of the material, and a sufficient GPC trace could not be obtained, leading to the postulation that this insoluble material possesses a char-like structure.

The ethyl acetate soluble fractions were analysed by <sup>1</sup>H NMR and GC/MS. A comparison of results are shown in S5 and S6.

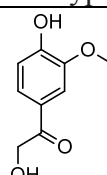
#	Time (min)	Peak Area	Probability (%)	Compound
1	43.1	8.2.E+07	50	Vanillin
2	45.5	1.1.E+07	50	Acetovanillone
3	48.5	2.5.E+08	28	2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethan-1-one



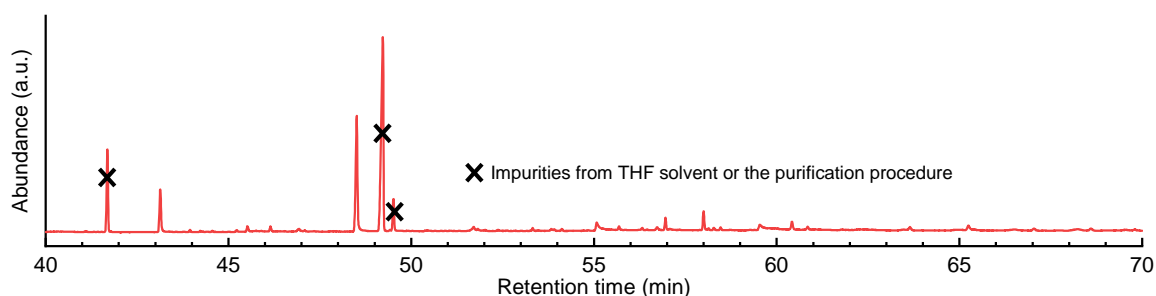
vanillin



acetovanillone

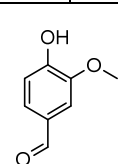


2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethan-1-one

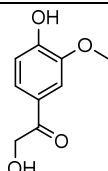


**S5:** GC/MS analysis of the ethyl acetate soluble aromatics from the depolymerisation of *P.radiata* MWL

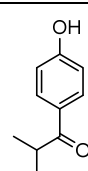
#	Time (min)	Peak Area	Probability (%)	Compounds
1	43.1	6.6.E+07	69.5	Vanillin
2	48.5	7.9.E+08	23.4	2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethan-1-one
3	51.7	3.5.E+07	21	1-(4-hydroxyphenyl)-2-methylpropan-1-one



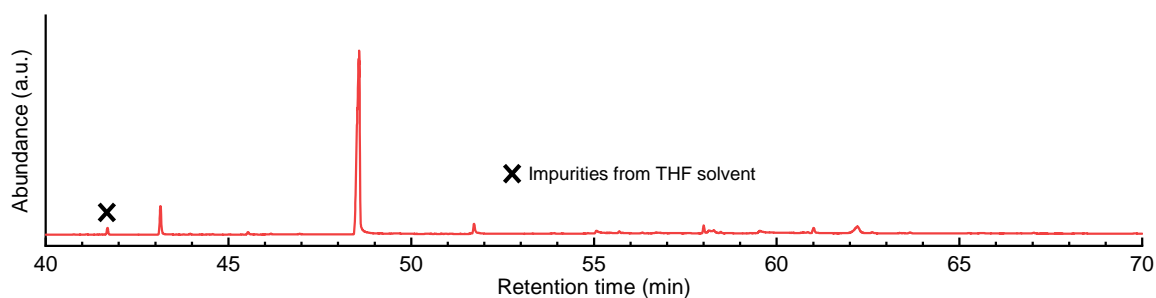
vanillin



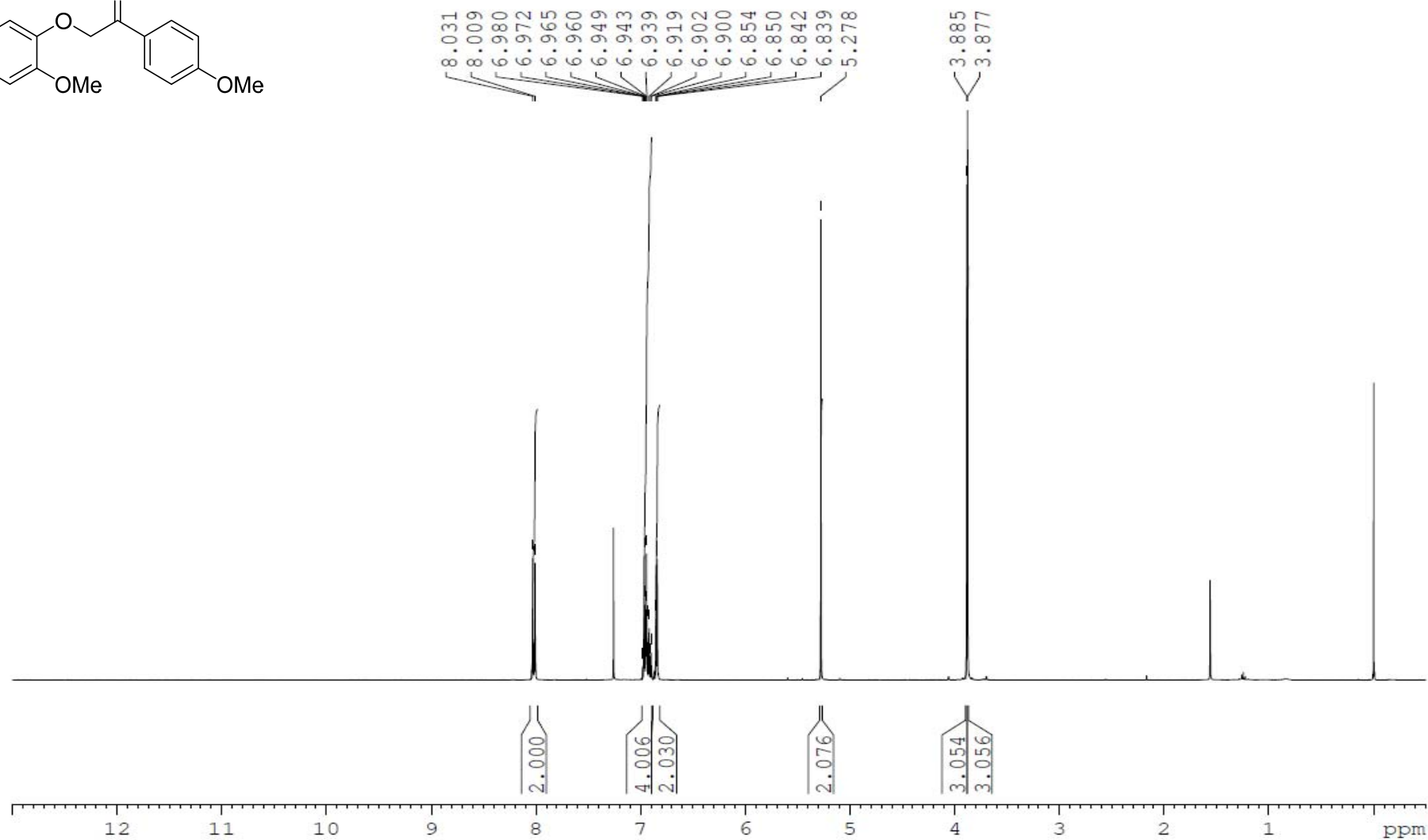
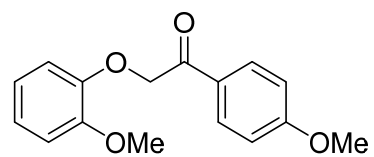
2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethan-1-one



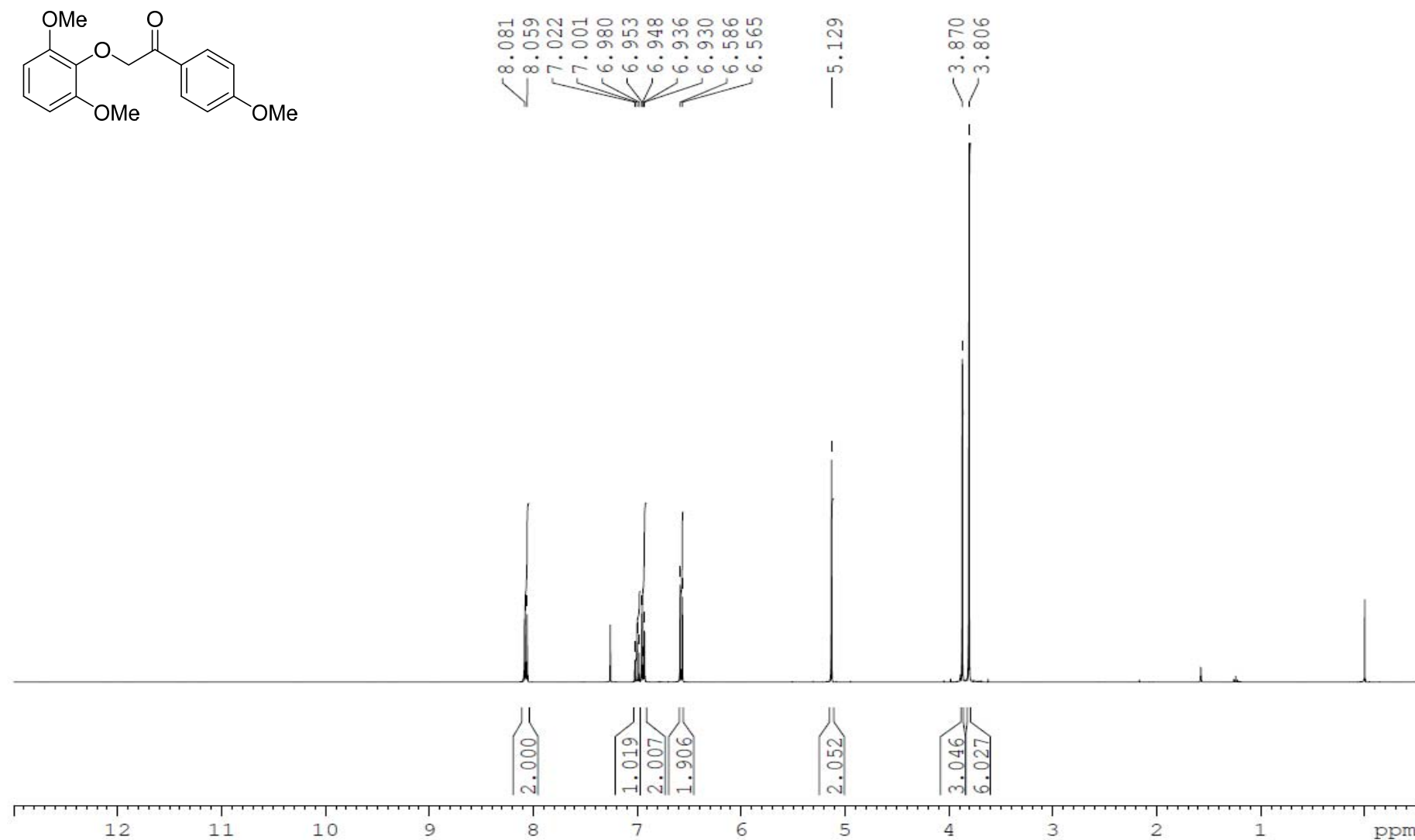
1-(4-hydroxyphenyl)-2-methylpropan-1-one



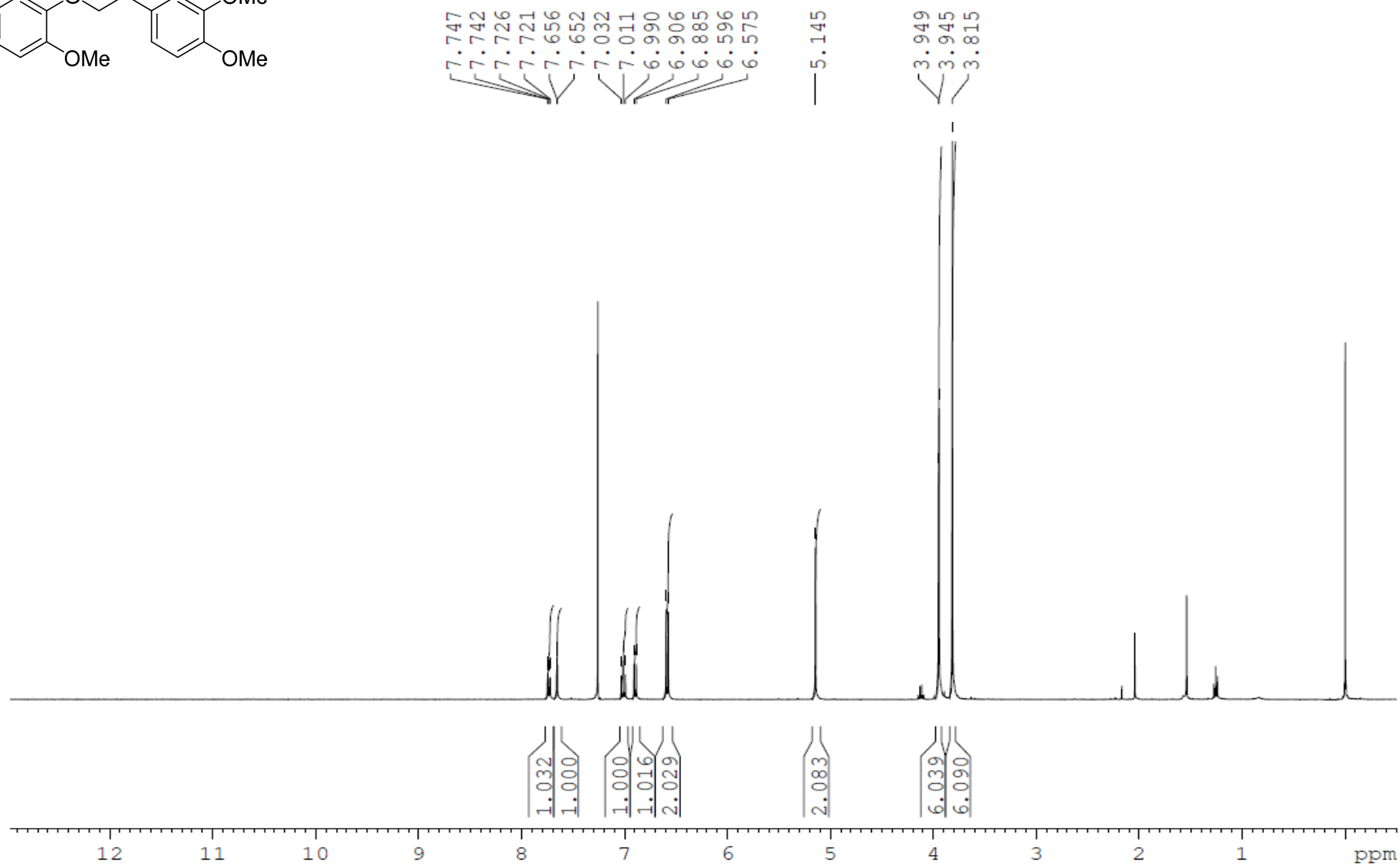
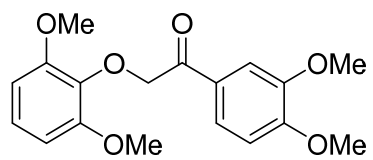
**S6:** GC/MS analysis of the ethyl acetate soluble aromatics from the depolymerisation of oxidised *P.radiata* MWL



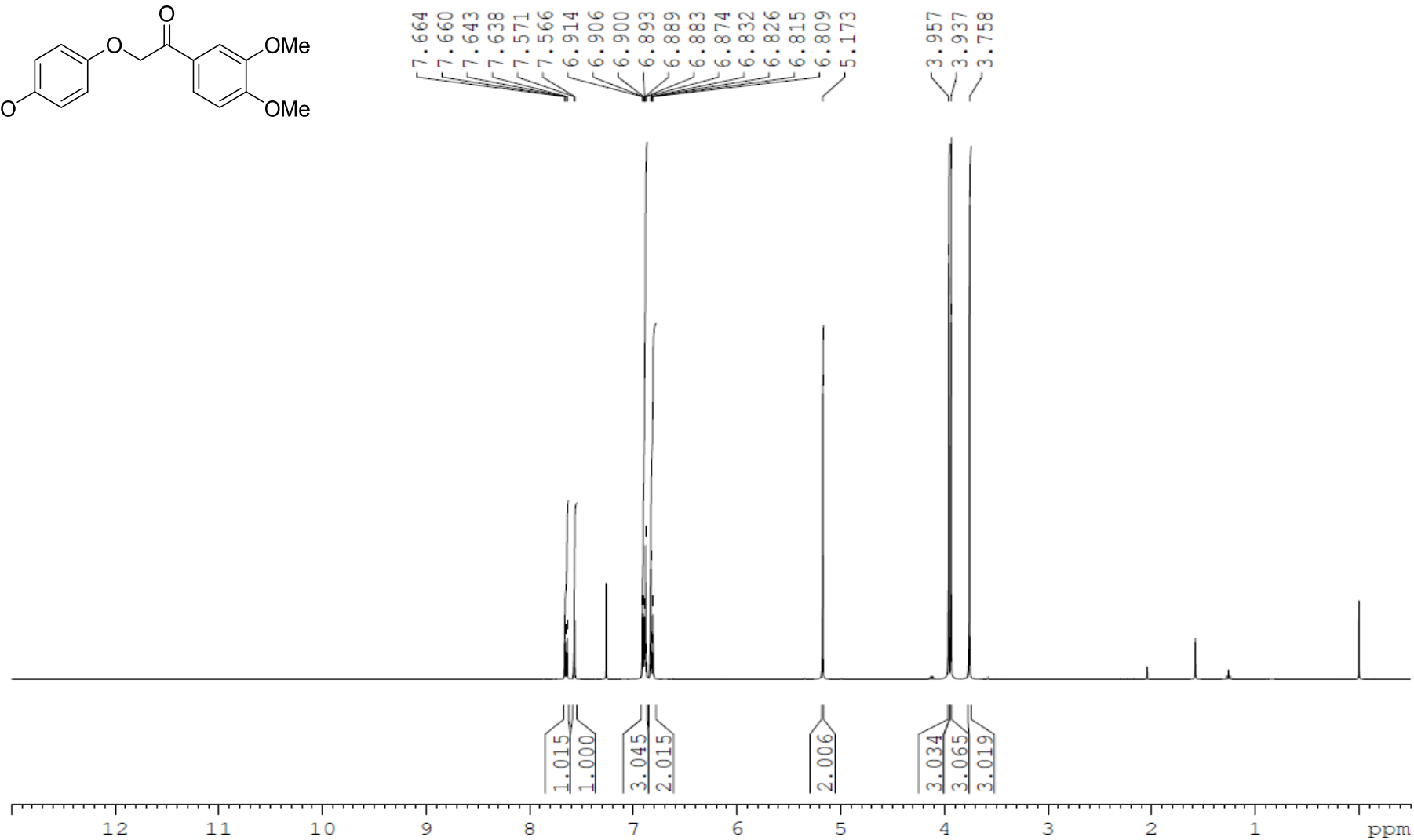
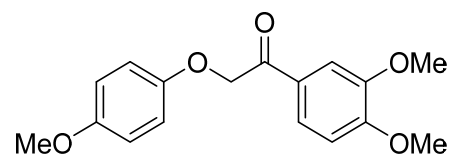
<sup>1</sup>H NMR 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (6)



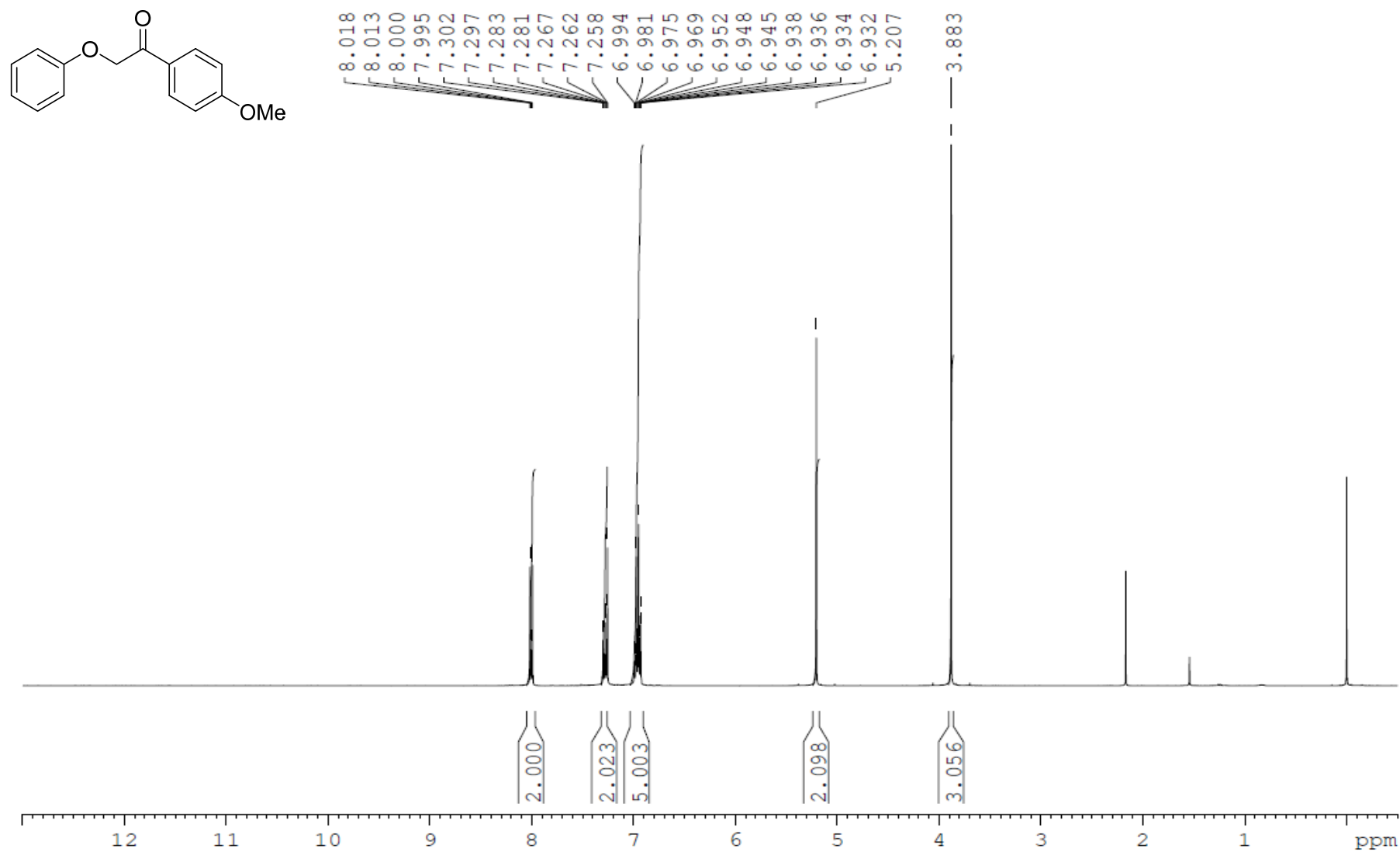
**<sup>1</sup>H NMR (2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (20)**



**<sup>1</sup>H NMR 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethan-1-one (21)**

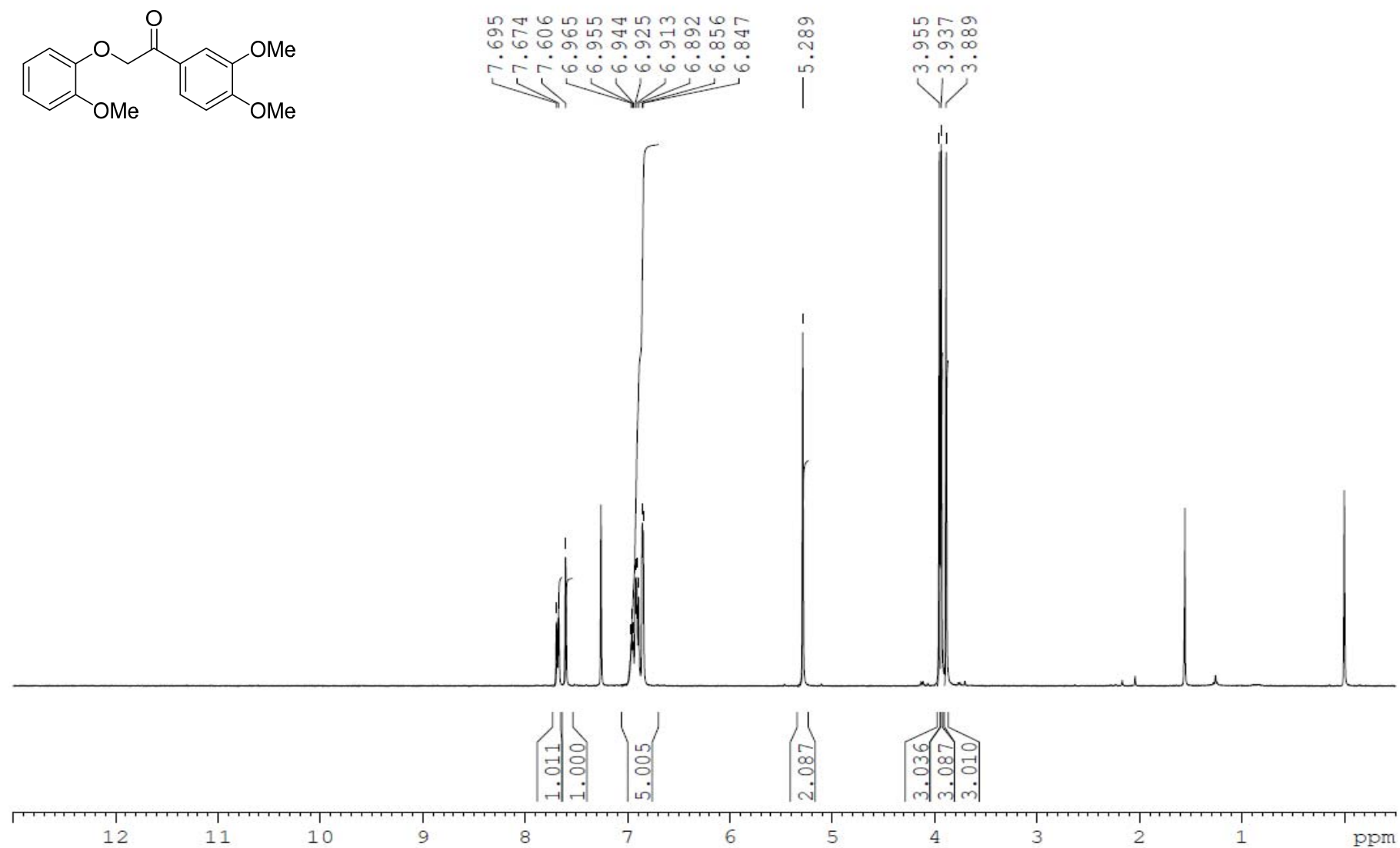


$^1\text{H}$  NMR 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(4-methoxyphenoxy)propan-1-one (22)

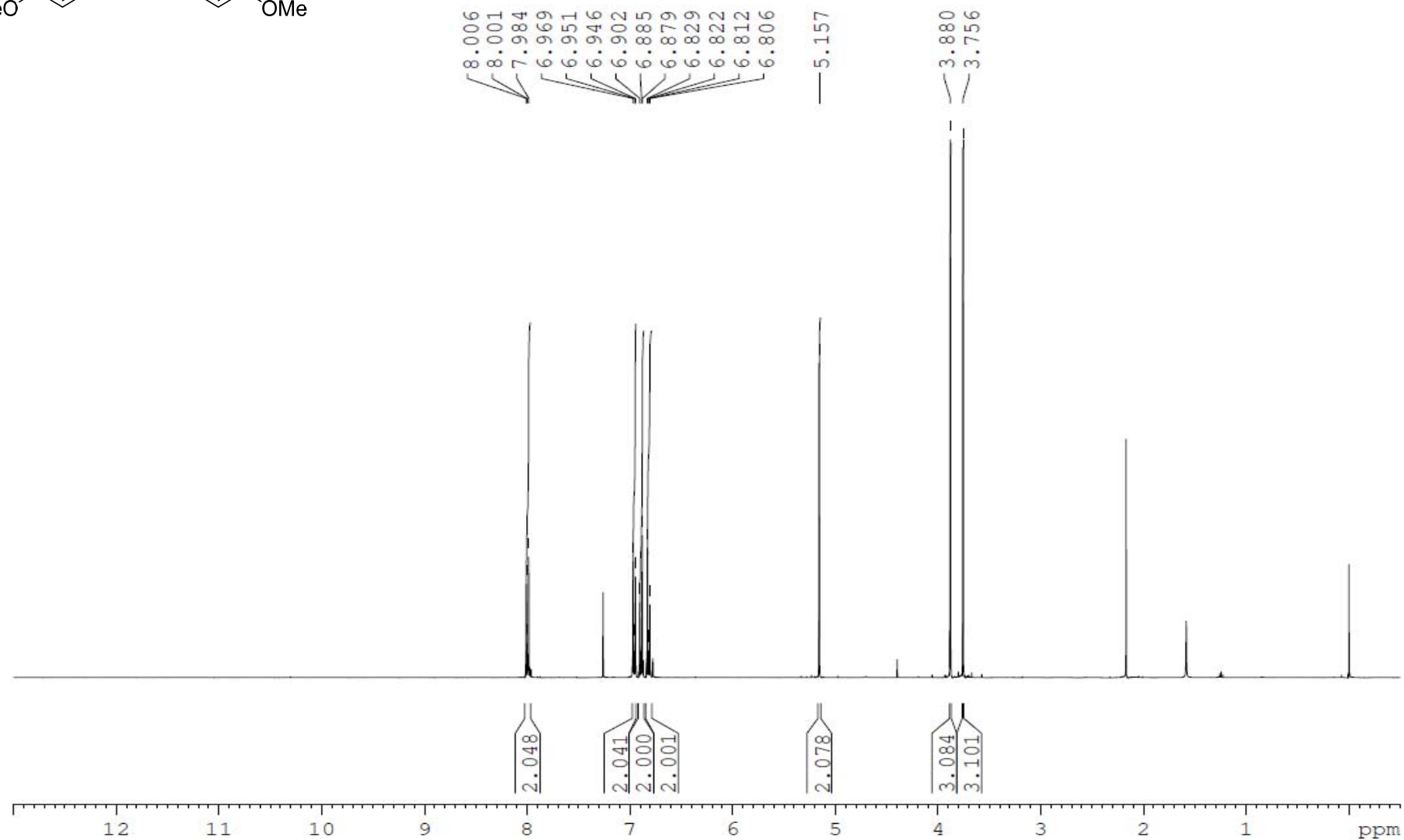
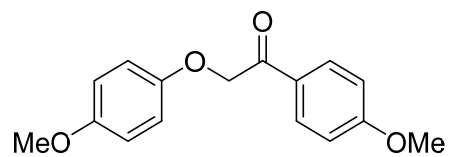


<sup>1</sup>H NMR 1-(4-methoxyphenyl)-2-phenoxyethan-1-one (23)

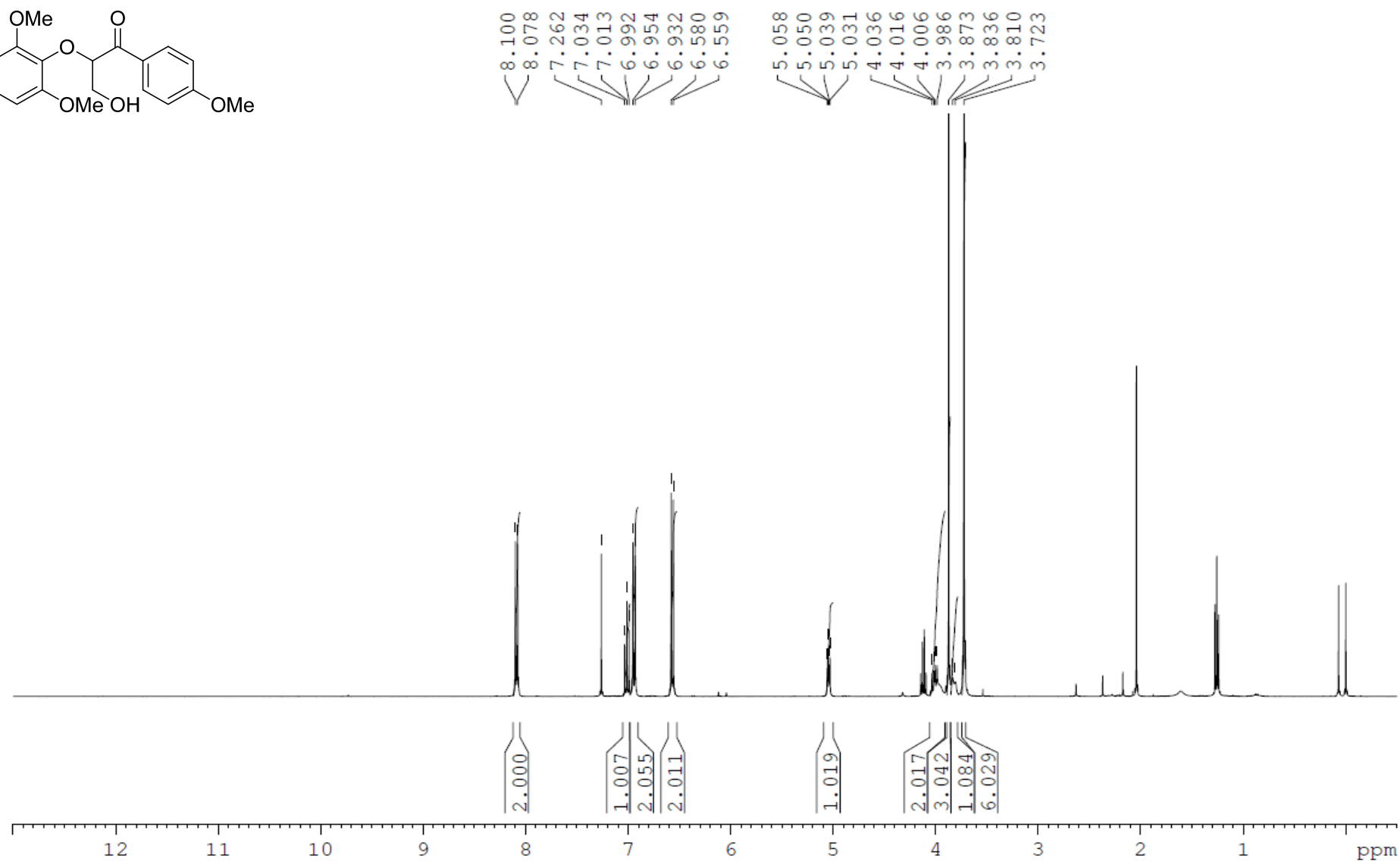
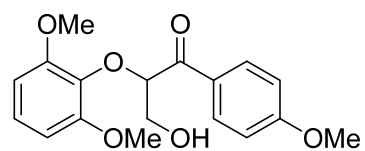




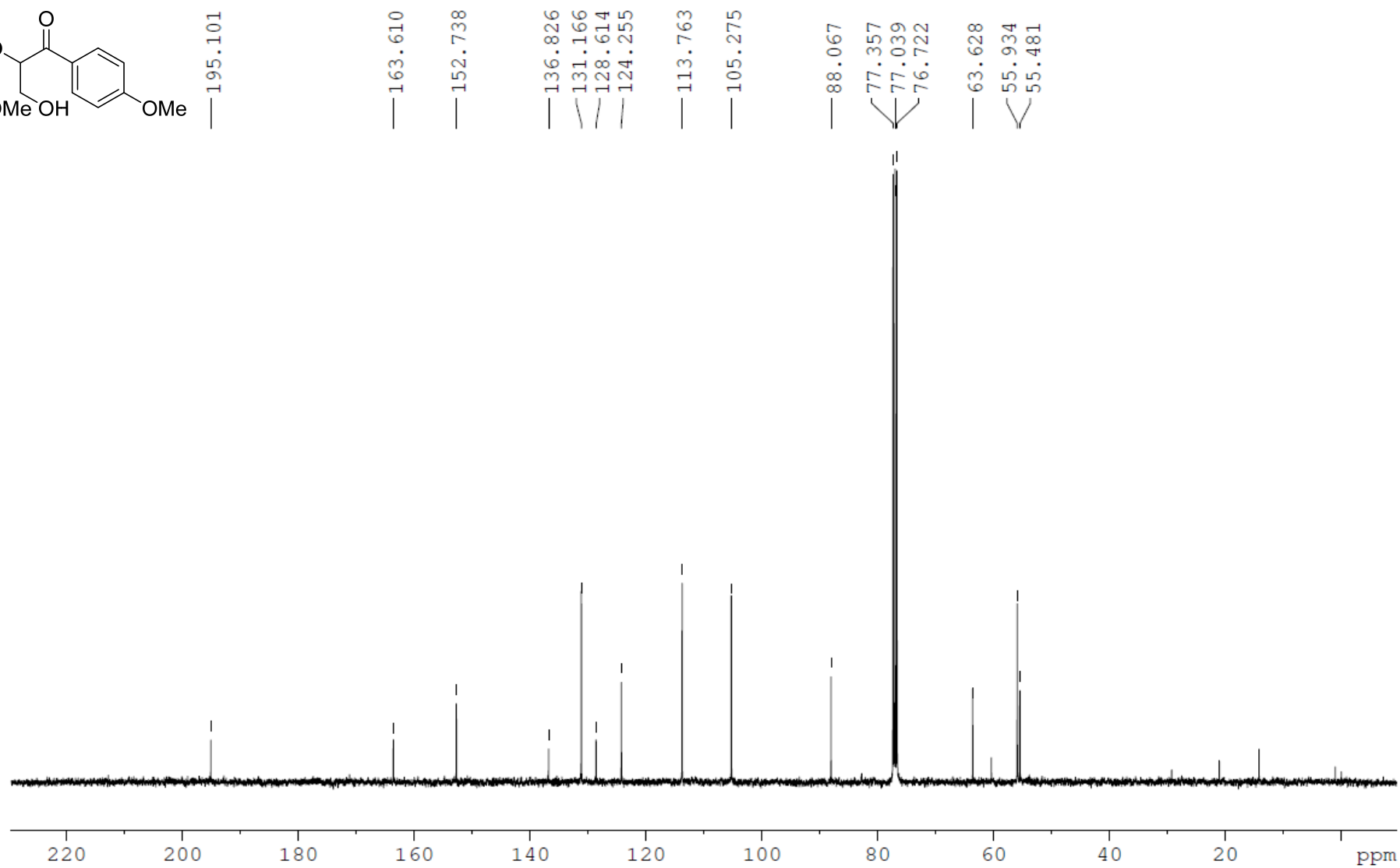
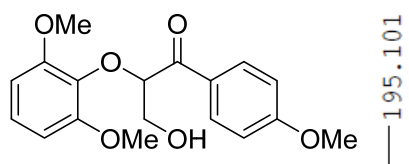
**<sup>1</sup>H NMR 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (24)**



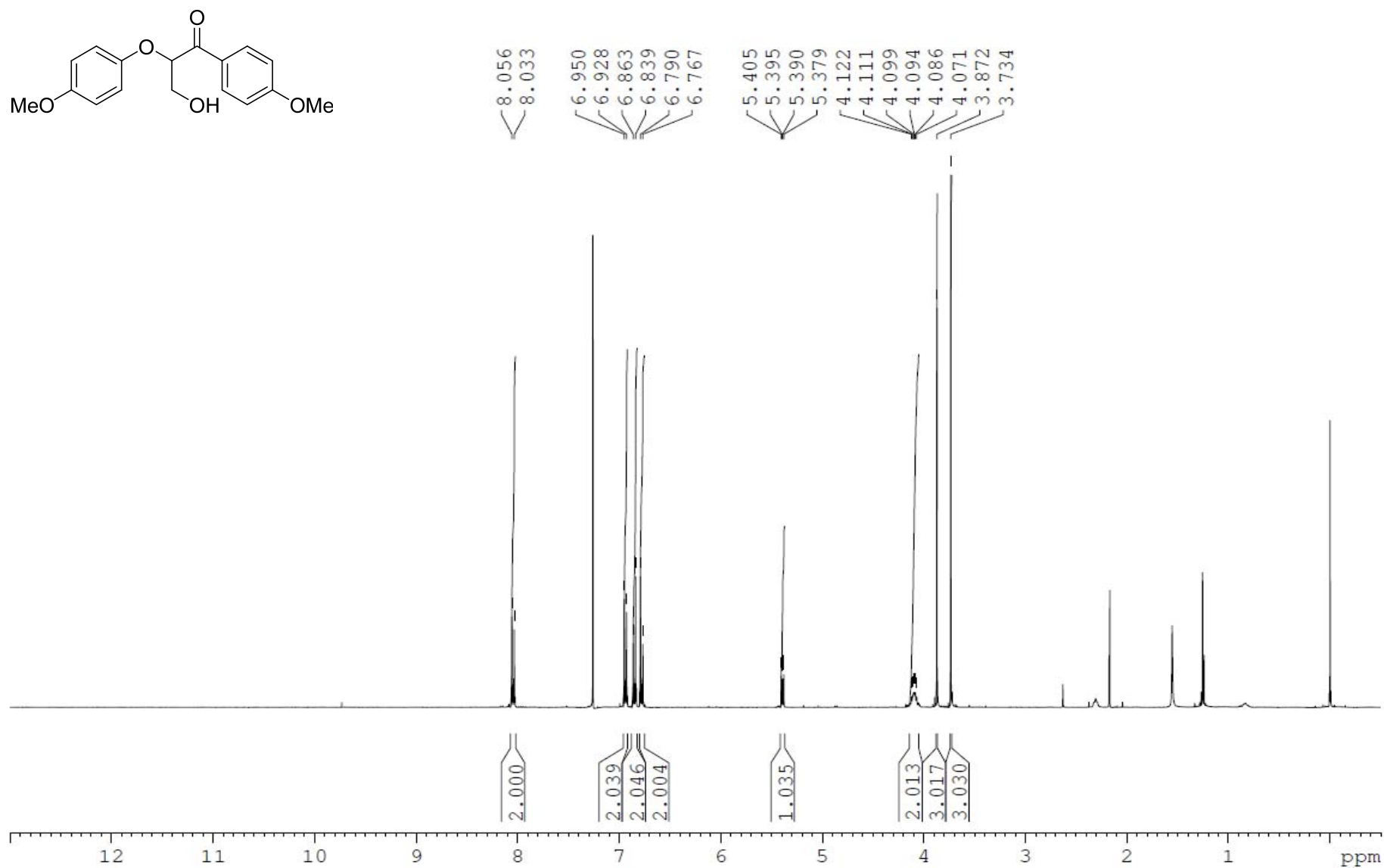
<sup>1</sup>H NMR 2-(4-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (25)



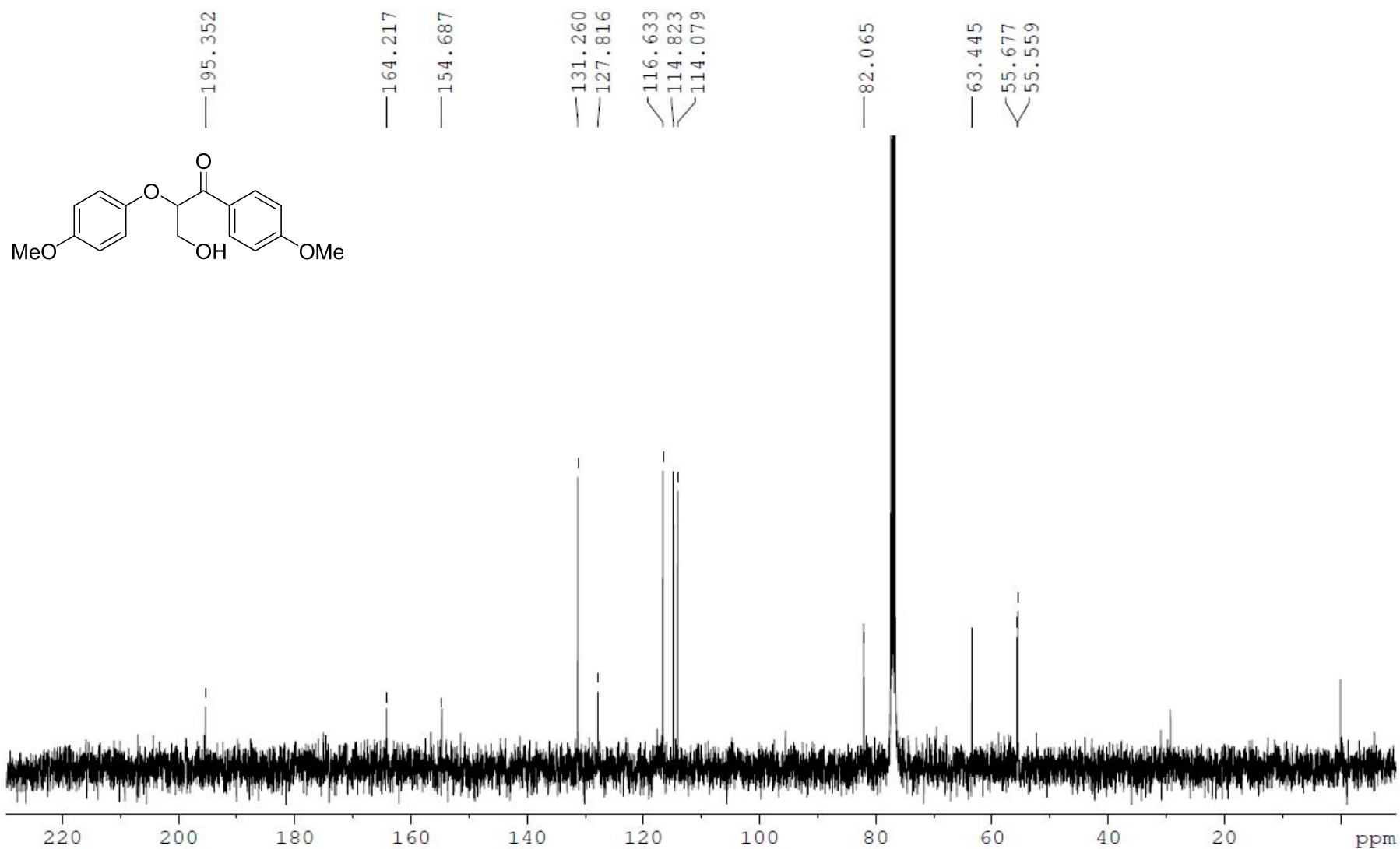
<sup>1</sup>H NMR 2-(2,6-dimethoxyphenoxy)-3-hydroxy-1-(4-methoxyphenyl)propan-1-one (33)



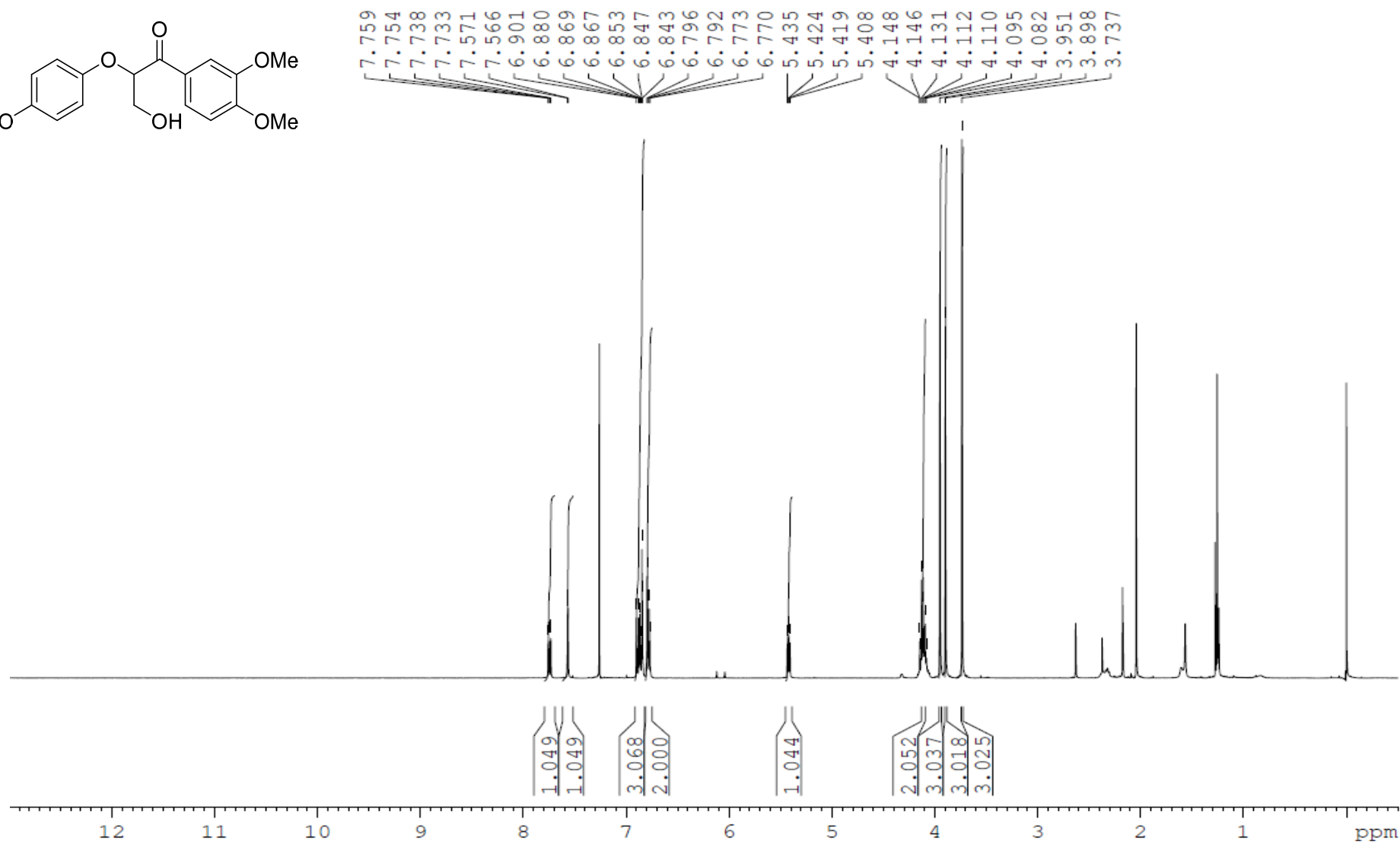
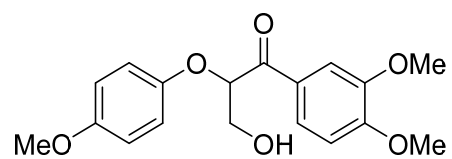
<sup>13</sup>C NMR 2-(2,6-dimethoxyphenoxy)-3-hydroxy-1-(4-methoxyphenyl)propan-1-one (33)



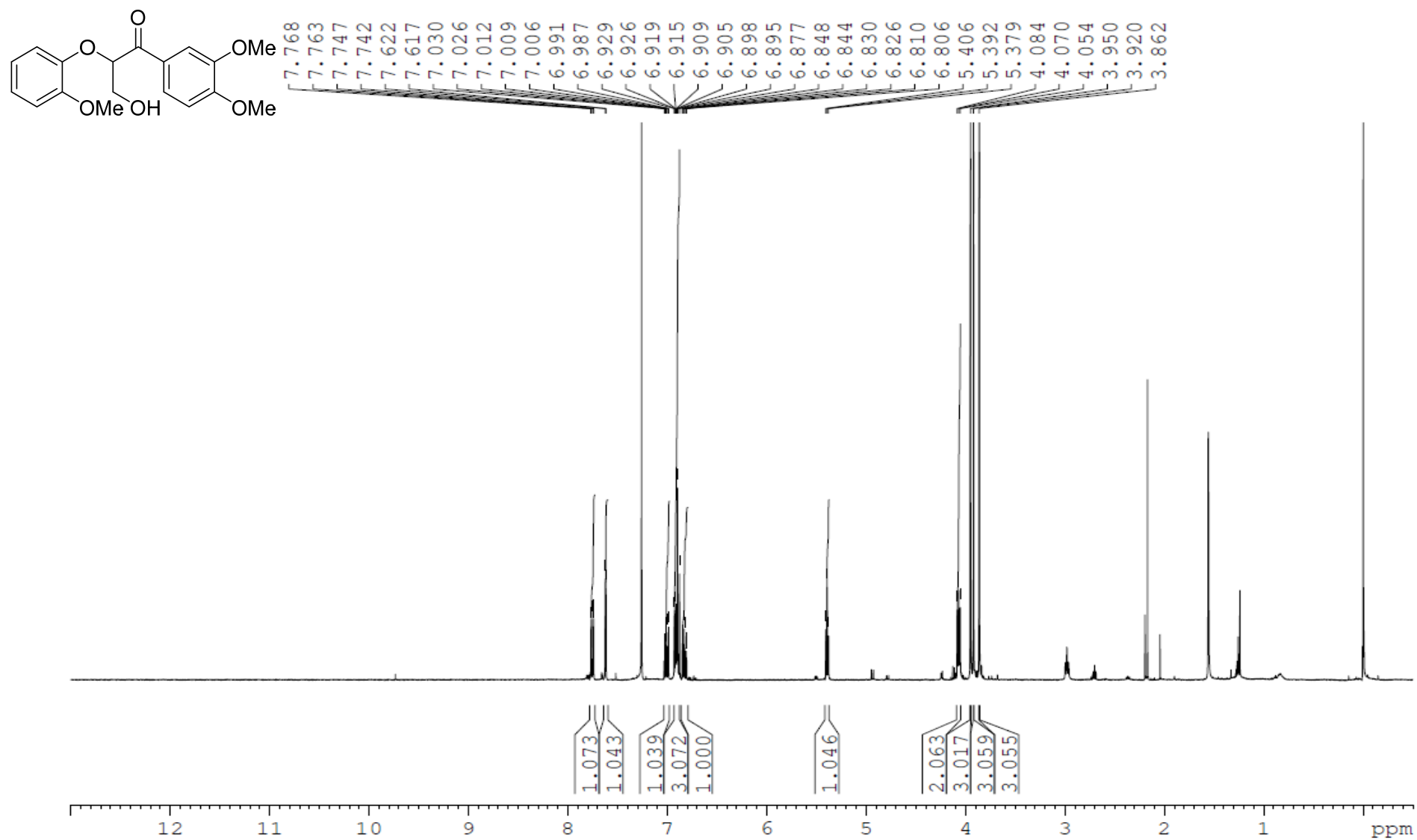
<sup>1</sup>H NMR 3-hydroxy-2-(4-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (34)



<sup>13</sup>C NMR 3-hydroxy-2-(4-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (34)

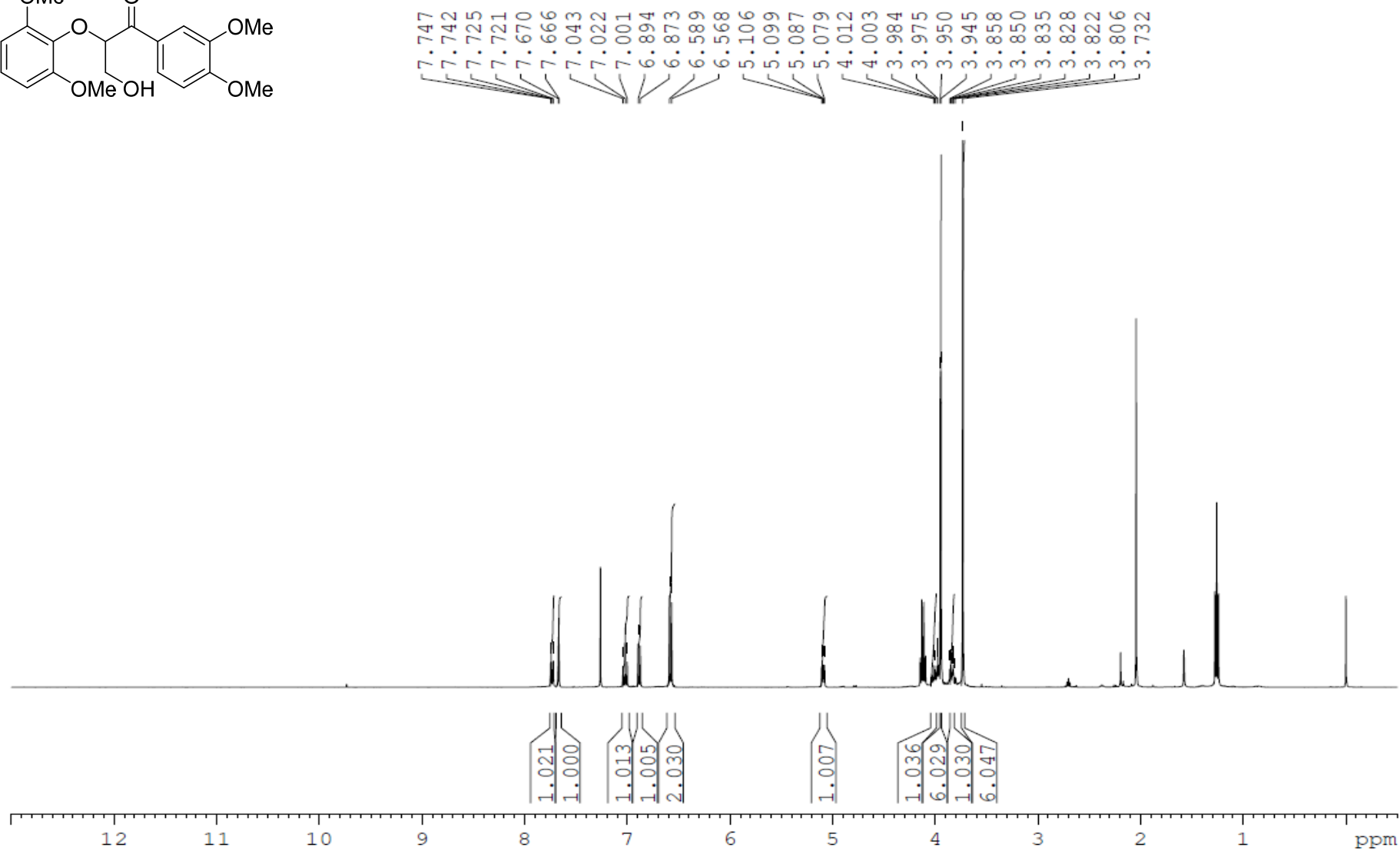
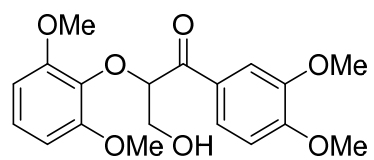


<sup>1</sup>H NMR 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(4-methoxyphenoxy)propan-1-one (35)

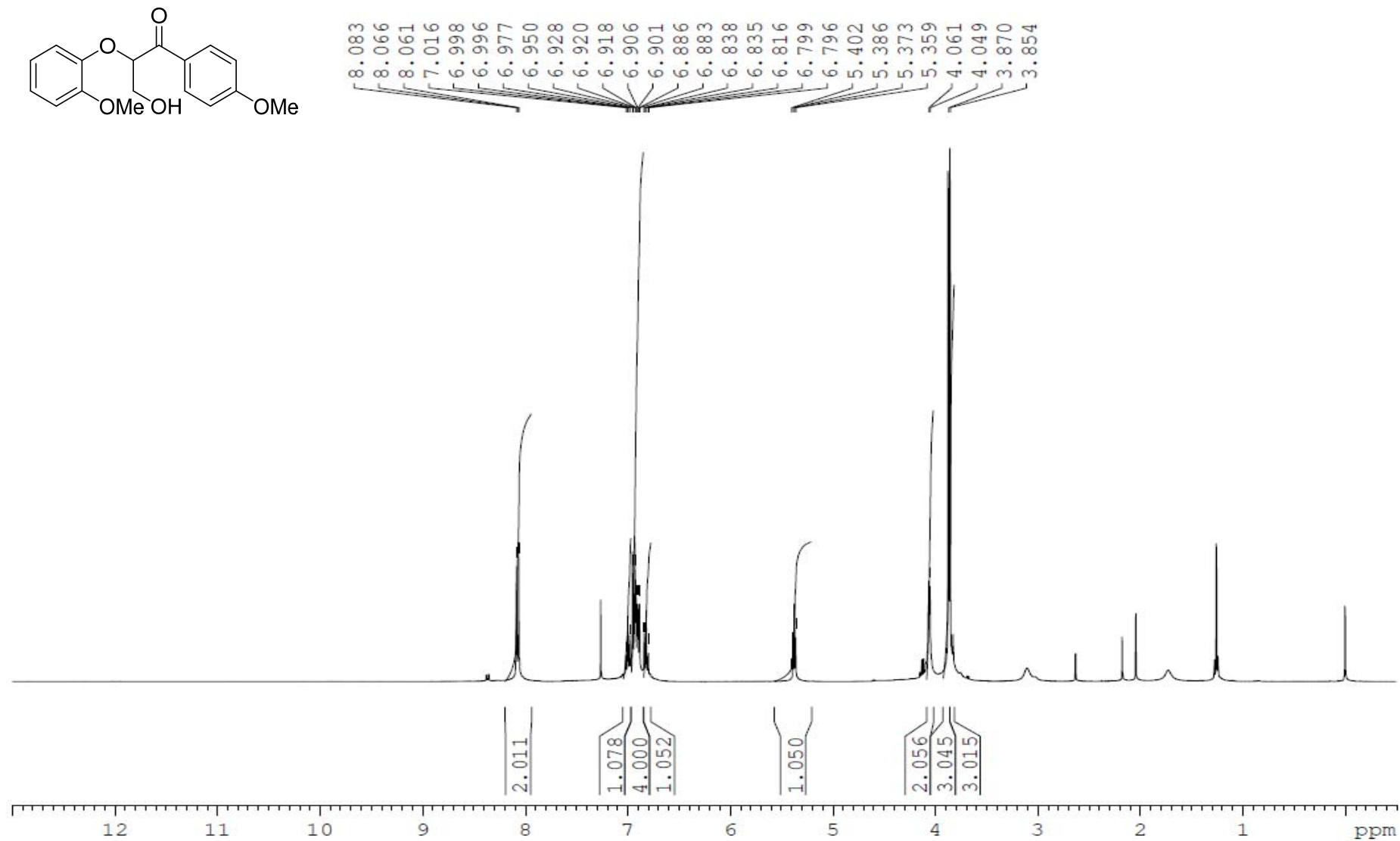


<sup>1</sup>H NMR 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one (36)

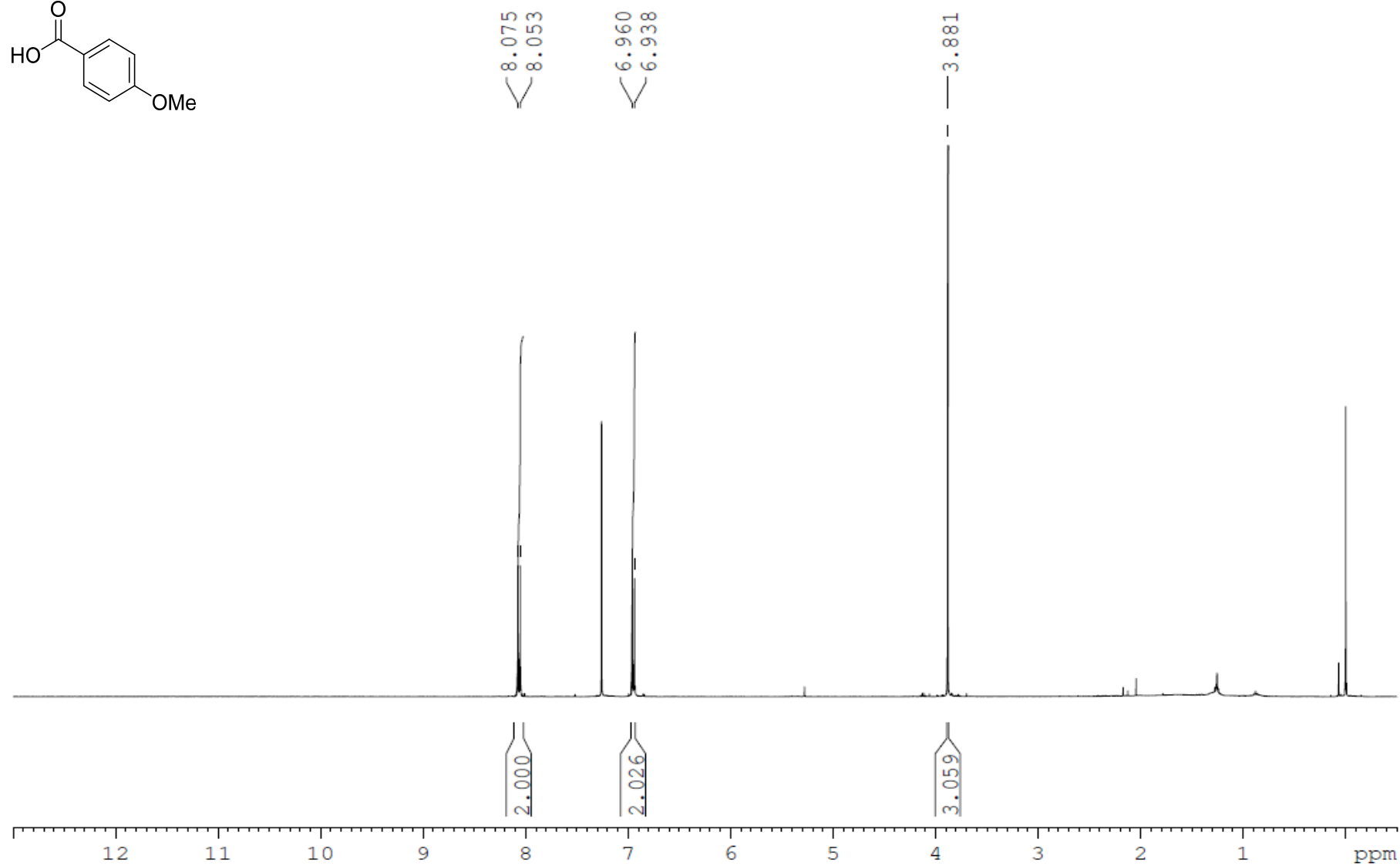
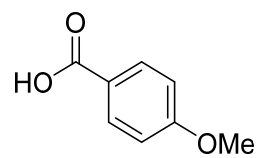




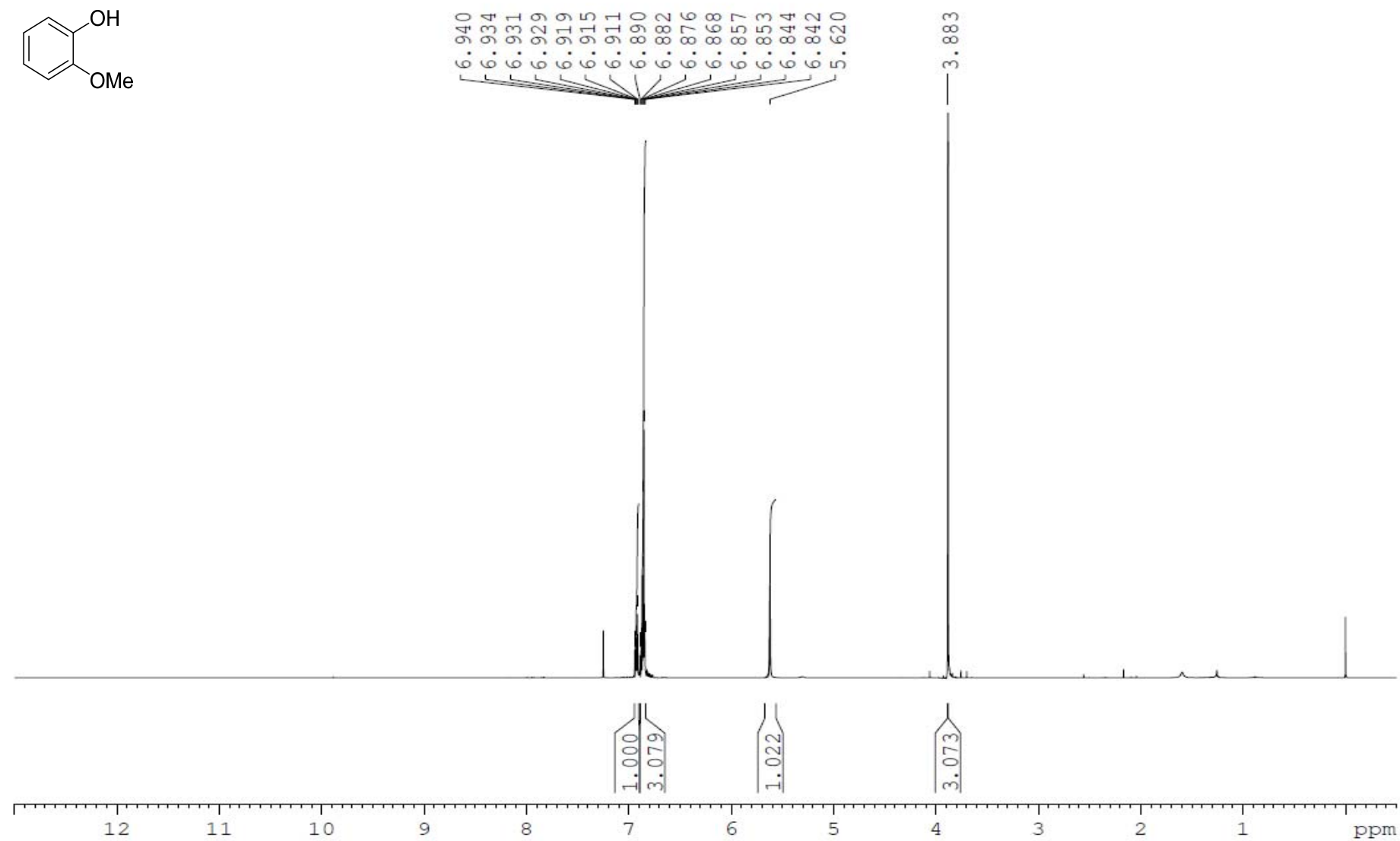
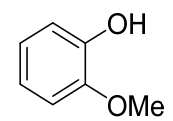
<sup>1</sup>H NMR 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-3-hydroxypropan-1-one (37)



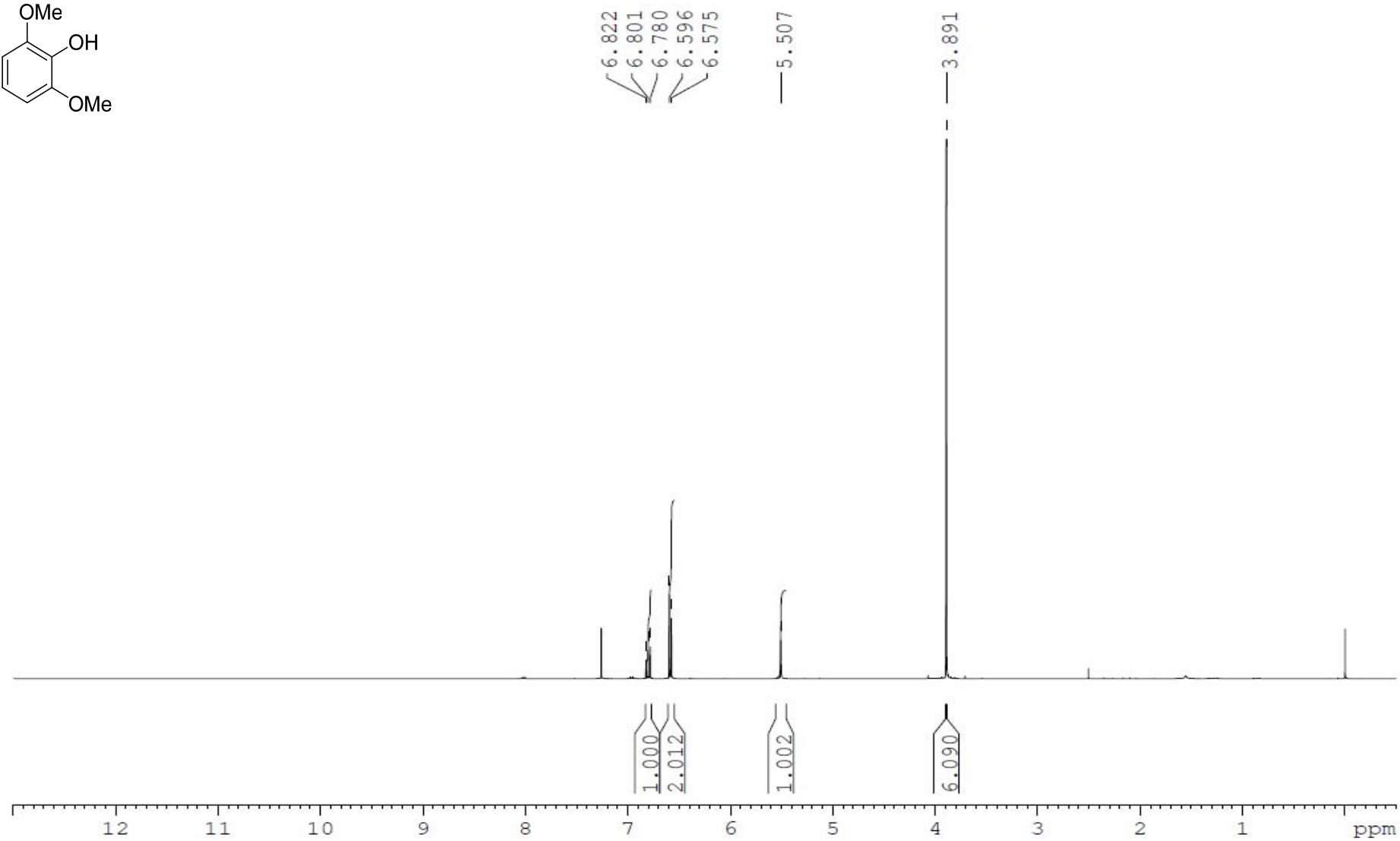
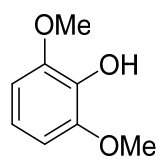
<sup>1</sup>H NMR 3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (38)



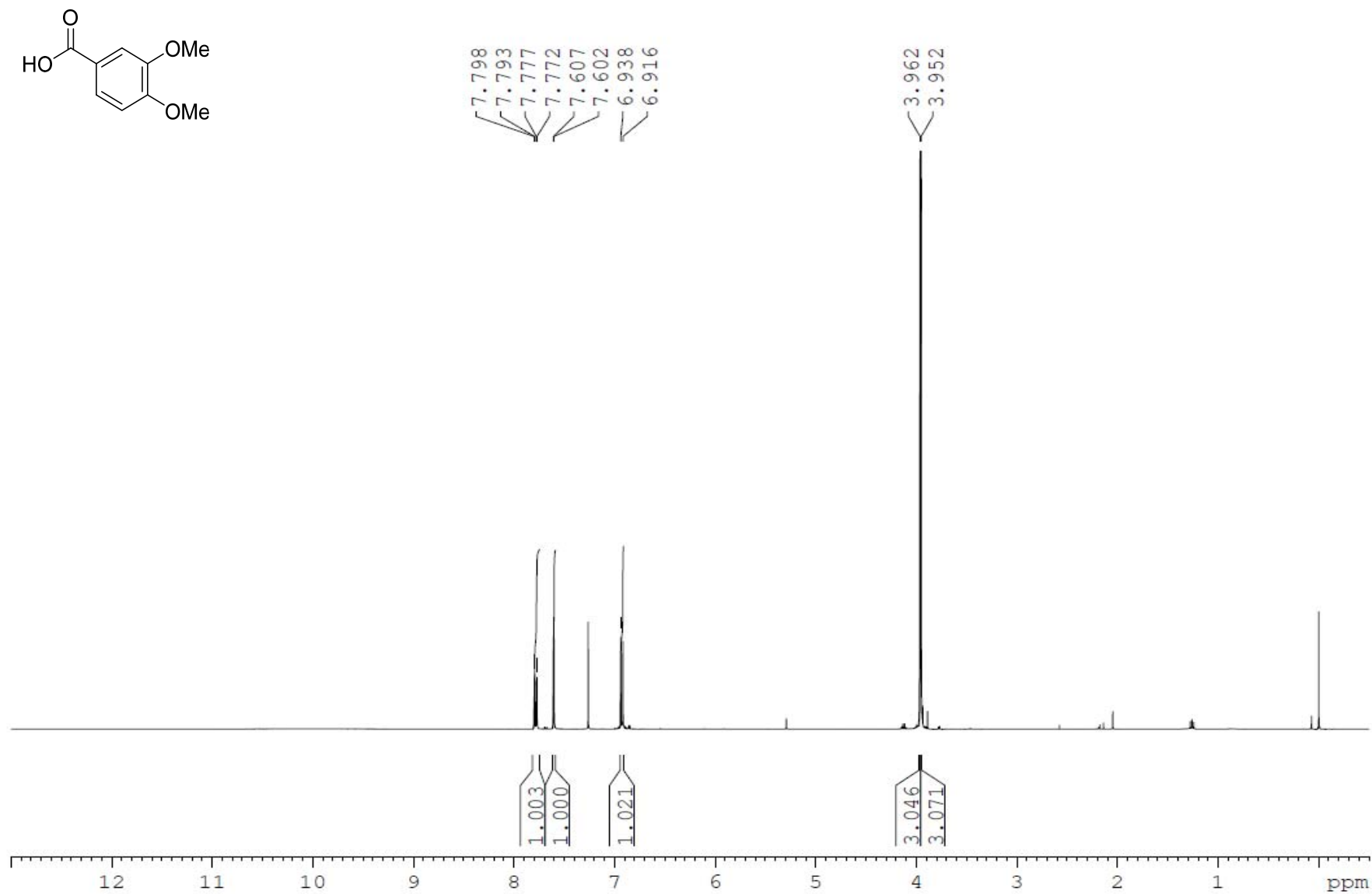
<sup>1</sup>H NMR *p*-anisic acid (7)



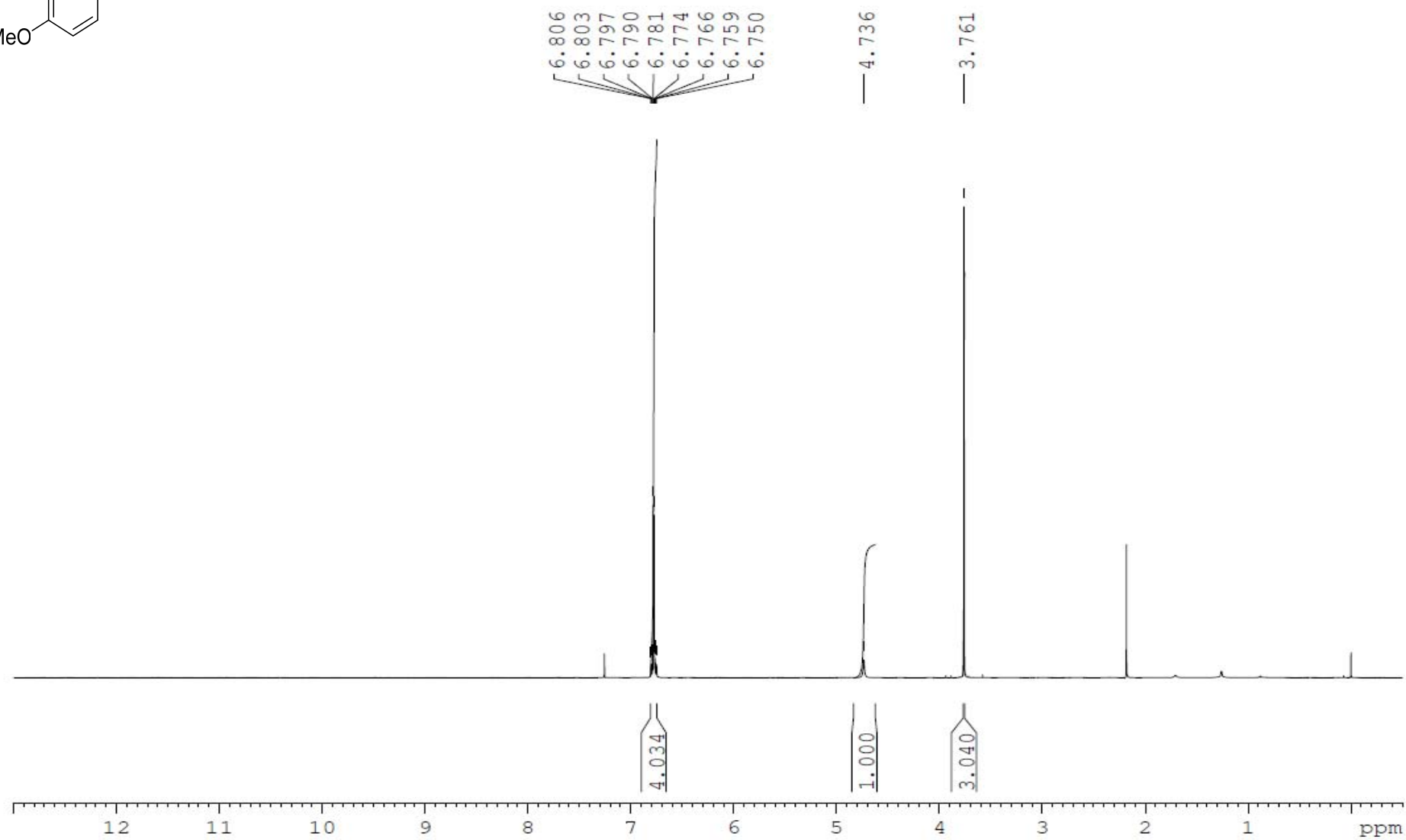
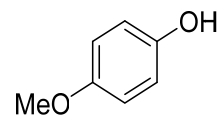
<sup>1</sup>H NMR guaiacol (8)



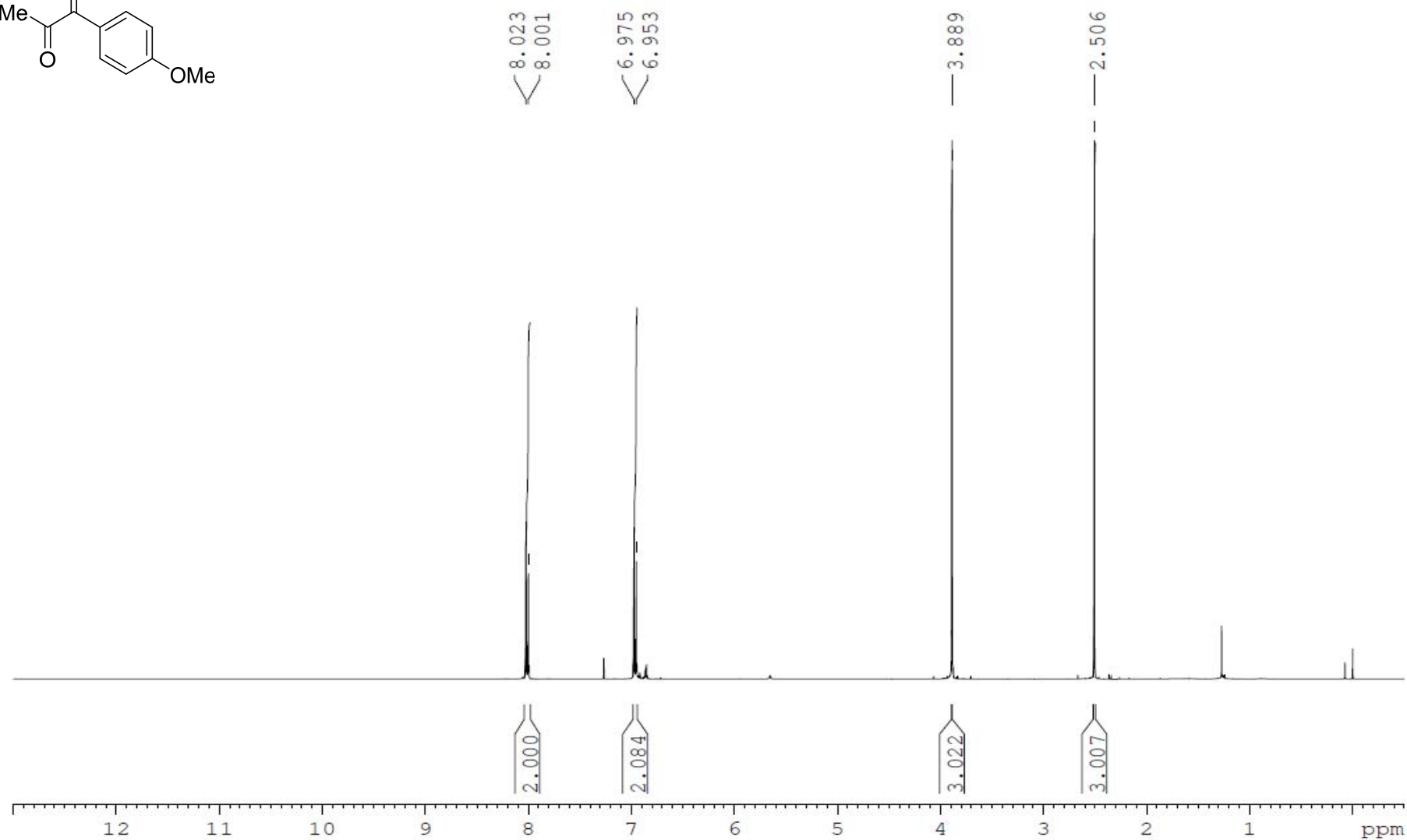
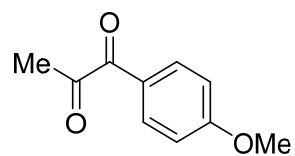
<sup>1</sup>H NMR 2,6-dimethoxyphenol (26)



**<sup>1</sup>H NMR veratric acid (27)**

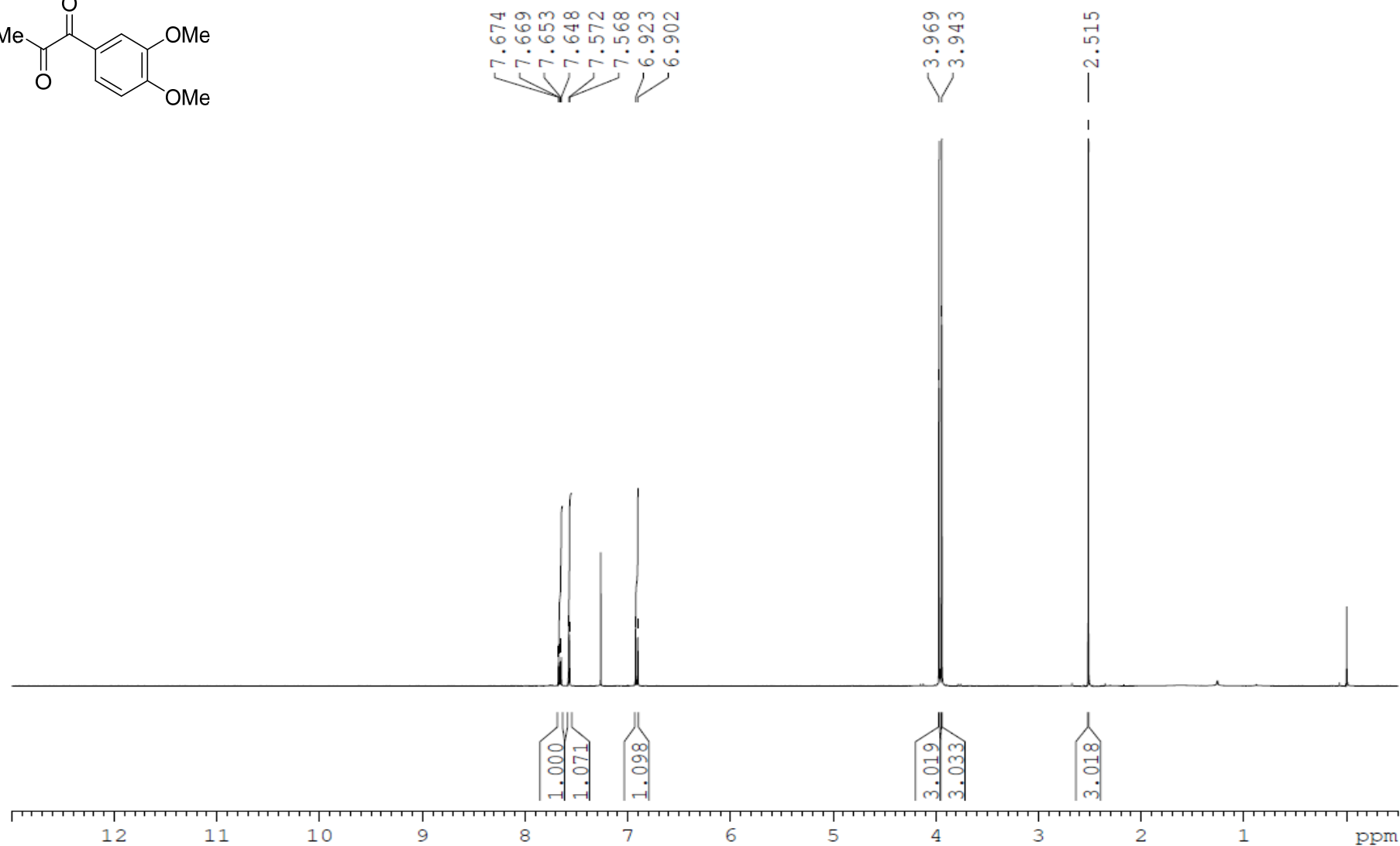
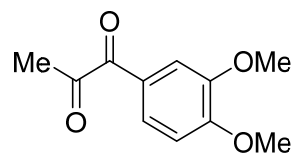


<sup>1</sup>H NMR 4-methoxyphenol (28)

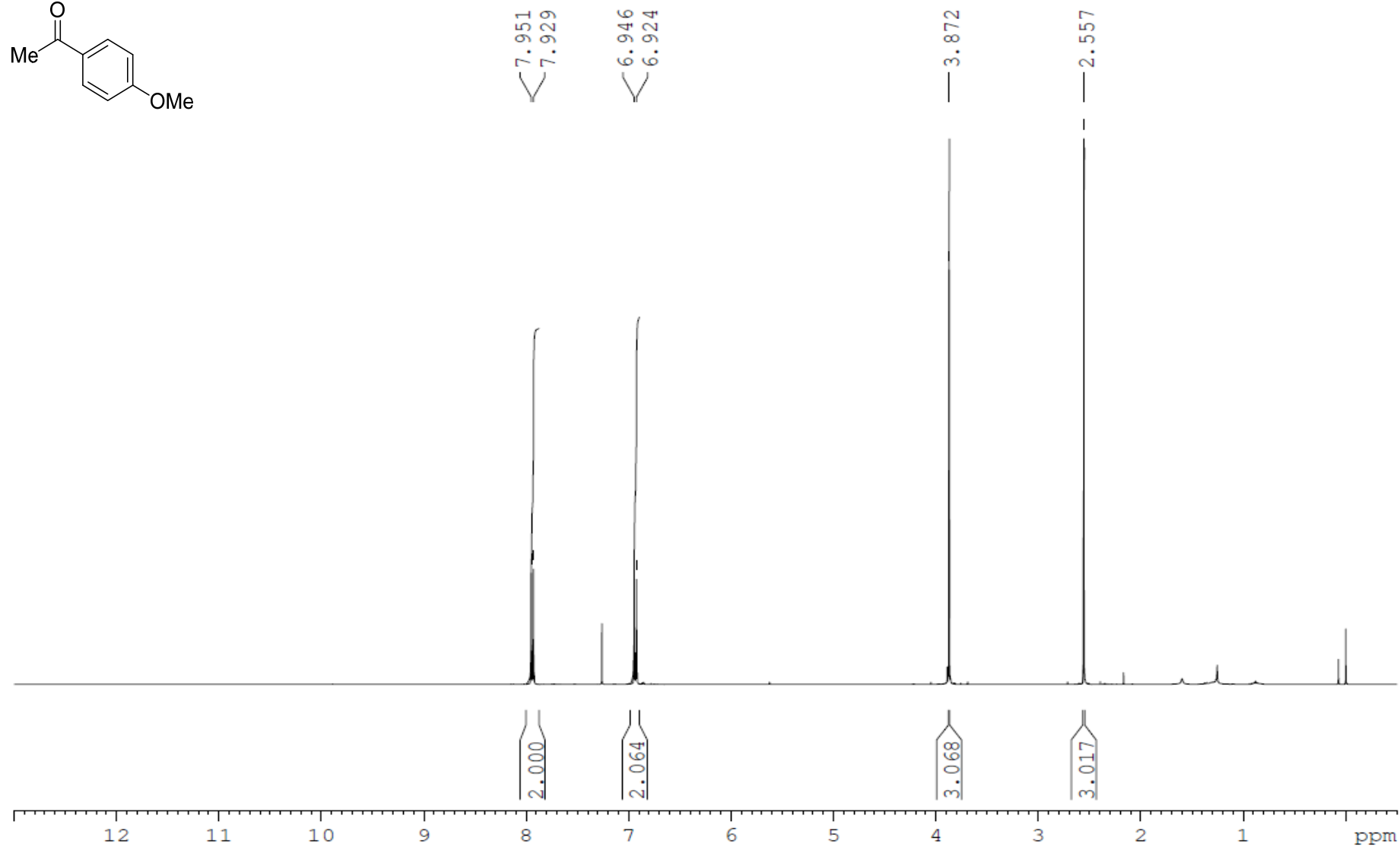
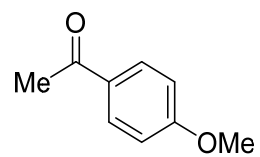


**<sup>1</sup>H NMR 1-(4-methoxyphenyl)propane-1,2-dione (39)**

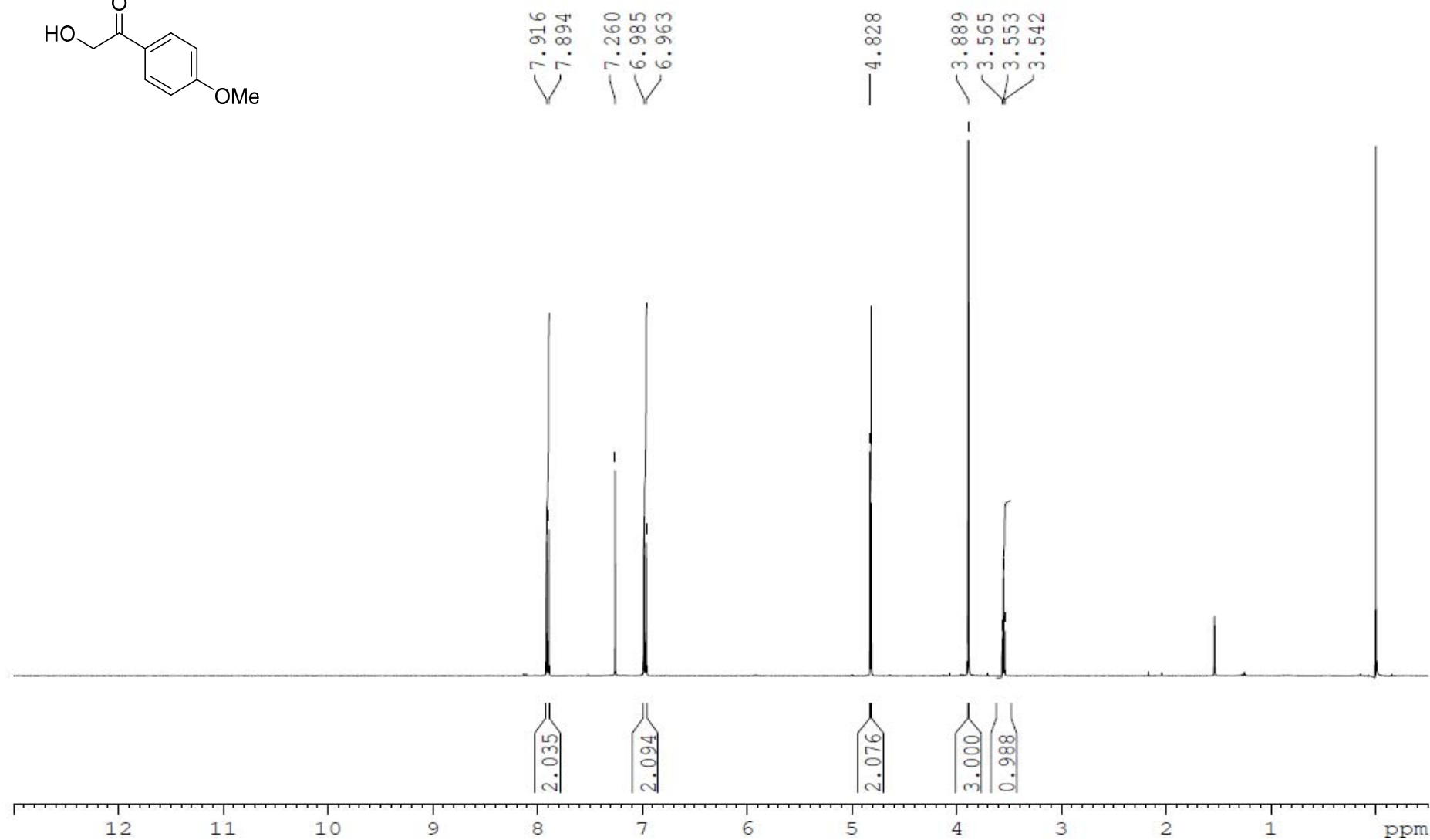
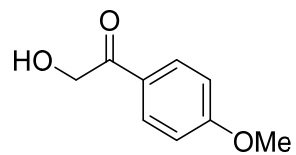




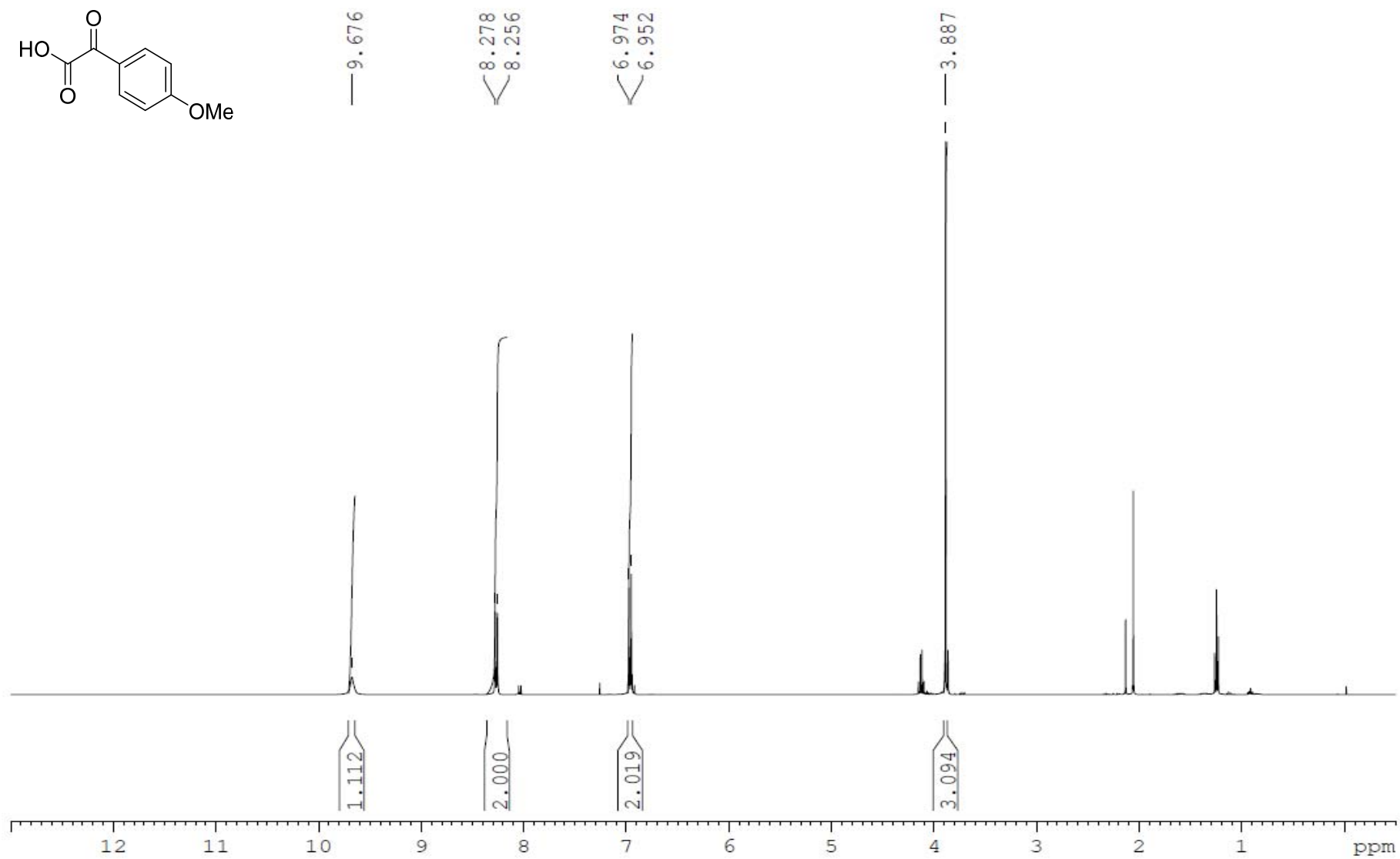
<sup>1</sup>H NMR 1-(3,4-dimethoxyphenyl)propane-1,2-dione (40)



**<sup>1</sup>H NMR 4-methoxyacetophenone (9)**



**<sup>1</sup>H NMR 2-hydroxy-1-(4-methoxyphenyl)ethan-1-one (12)**



**<sup>1</sup>H NMR 2-(4-methoxyphenyl)-2-oxoacetic acid (13)**

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