Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Investigating Homogeneous $Co/Br^{-}/H_2O_2$ Catalysed Oxidation of Lignin Model Compounds in Acetic Acid

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Model Compound Synthesis

3,4-Dimethoxybenzyl bromide (A1a)

This synthesis was adapted from the method described by Wu and Huang.[1] 3,4-Dimethoxybenzyl alcohol (7.2 mL, 50 mmol) was dissolved in dichloromethane (150 mL) and cooled to 0 °C under nitrogen. Phosphorus tribromide (5.2 mL, 55 mmol) was added slowly through a syringe, and the reaction warmed to room temperature and stirred for 3.5 h. The reaction mixture was then poured onto ice water (200 mL) and extracted with dichloromethane (3 × 50 mL). The organic layers were combined and washed with saturated aqueous sodium carbonate solution (200 mL), water (200 mL) and brine (100 mL), then dried over sodium sulfate. Filtration and evaporation under reduced pressure gave the crude 3,4-dimethoxybenzyl bromide (**A1a**) as a yellow oil which solidified on standing (11.6 g). The crude product was used without further purification in the following step. **MS (*m/z*, %) EI+:** 232 ([M(^{81}Br)]$^{+\cdot}$, 6%), 230 ([M(^{79}Br)]$^{+\cdot}$, 6%), 151 (([M-Br)]$^{+\cdot}$, 100%).

Benzyl Phenyl Ether (A1)

This synthesis was adapted from the method described by Wu and Huang.[1] Benzyl bromide (6.0 mL, 50 mmol), phenol (5.7 g, 61 mmol) and anhydrous potassium carbonate (8.3 g, 60 mmol) in acetone (AR grade, 100 mL) were heated at reflux under nitrogen overnight. The reaction mixture was then cooled, filtered, and the filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane (150 mL) and washed with 5% *w/v* potassium hydroxide solution (100 mL), water (100 mL), brine (50 mL), and dried over sodium sulfate. Filtration and solvent evaporation afforded 9.8 g of crude product. The crude product was purified by recrystallization from hexanes to yield a white solid (3.58 g, 39% yield). **m.p.** 40–45 °C (*lit.* 39–40 °C)[2]; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.776−6.921 (m, 10 H, Ar-H), 5.070 (s, 2 H, $ArCH_2$) ppm.

3,4-Dimethoxybenzyl phenyl ether (A2)

This synthesis was adapted from the method described by Wu and Huang.[1] Crude 3,4-dimethoxybenzyl bromide (**A1a**) (10.9 g, *ca* 47 mmol), phenol (5.9 g, 61 mmol) and anhydrous potassium carbonate (8.3 g, 60 mmol) in acetone (AR grade, 100 mL) were heated at reflux under nitrogen overnight. The reaction mixture was then cooled, filtered, and the filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane (150 mL) and washed with 5% *w/v* potassium hydroxide solution (100 mL), water (100 mL), brine (50 mL), and dried over sodium sulfate. Filtration and solvent evaporation afforded 11.1 g of crude product. The crude product was purified by recrystallisation from hexanes/ethyl acetate to yield an off-white solid (7.36 g, 66% yield). **m.p.** 80–84 °C (*lit.* 77.5–78.5 °C)[3]; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.317–7.260 (m, 3 H, Ar-H), 6.992–6.859 (m, 5 H, Ar-H), 4.992 (s, 2 H, $ArCH_2$), 3.891 (s, 6 H, 2 × OCH_3) ppm.

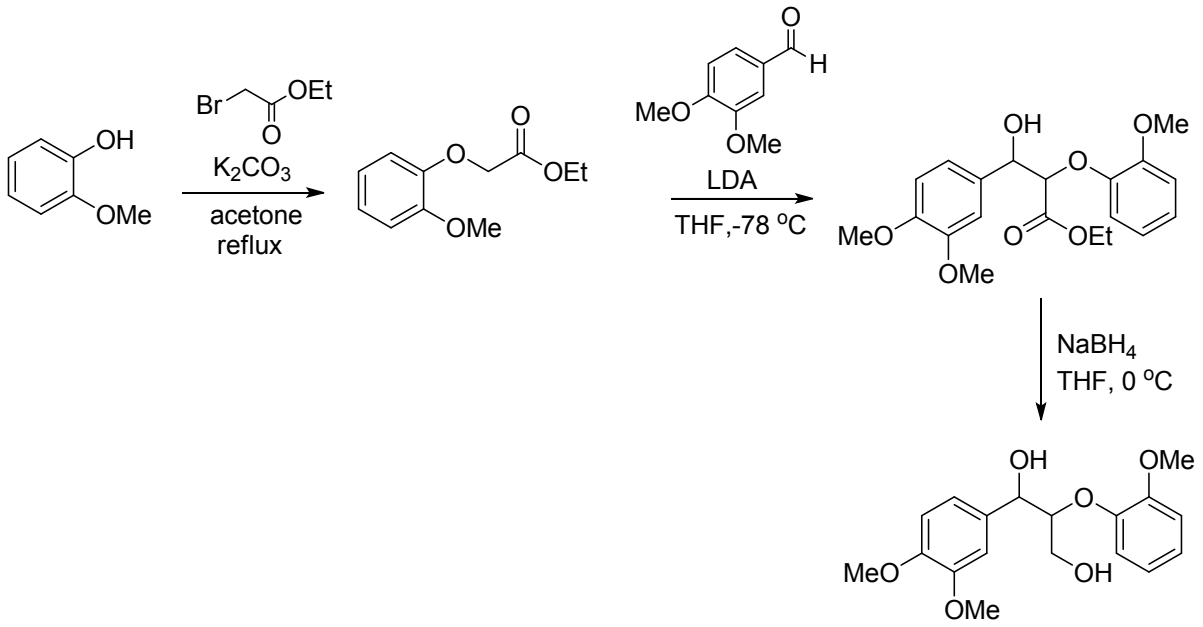
3,4-Dimethoxybenzyl-2-methoxyphenyl ether (A3)

This synthesis was adapted from the method described by Wu and Huang.[1] Crude 3,4-dimethoxybenzyl bromide (**A1a**) (11.6 g, *ca* 50 mmol), guaiacol (6.6 mL, 60 mmol) and anhydrous potassium carbonate (8.3 g, 60 mmol) in acetone (AR grade, 100 mL) were heated at reflux under nitrogen overnight. The reaction mixture was then cooled, filtered, and the filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane (150 mL) and washed with 5% *w/v* potassium hydroxide solution (100 mL), water (100 mL), brine (100 mL), and dried over sodium sulfate. Filtration and solvent evaporation afforded 12.76 g of crude product. Approximately 6.2 g of the crude product was purified by flash chromatography (20% hexanes in dichloromethane), yielding a white solid (5.35 g); the remaining *ca* 6.5 g of crude product was purified by recrystallization from hexanes/ethyl acetate to yield pale yellow crystals (4.29 g), for a combined yield of 70%. **m.p.** 82 °C (*lit.* 78–79 °C)[4]; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.005–6.833 (m, 7 H, Ar-H), 5.083 (s, 2 H, $ArCH_2$), 3.882 (s, 9 H, 3 × OCH_3) ppm.

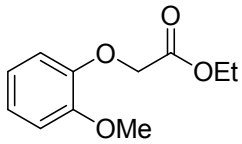
2-Phenylethyl Phenyl Ether (B1)

This synthesis was adapted from the method described by Wu and Huang.[1] 2-Phenylethyl bromide (3.8 mL, 29 mmol), phenol (3.2 g, 34 mmol) and anhydrous potassium carbonate (4.7 g, 34 mmol) in acetone (AR grade, 60 mL) were heated at reflux under nitrogen overnight. The reaction mixture was then cooled, filtered, and the filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane (150 mL) and washed with 5% *w/v* potassium hydroxide solution (100 mL), water (100 mL), brine (100 mL), and dried over sodium sulfate. Filtration and solvent evaporation afforded 6.0 g of crude product. The crude product was purified by flash chromatography (5% dichloromethane in hexanes), yielding a colourless oil (1.07 g, 19 % yield). **MS (*m/z*, %) EI+:** 198 ($[M]^{+\cdot}$, 16%), 105 ($[MPhO]^{+\cdot}$, 100%), 77 (($[M\text{-}CH_2CH_2OPh]^{+\cdot}$, 27%); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.291−6.882 (m, 10 H, Ar-H), 4.17 (t, J = 6.6 Hz, 2 H, $ArCH_2$), 3.096 (t, J = 6.6 Hz, 2 H, $ArOCH_2$) ppm.

2-Phenylethyl Phenyl Ether (B2)

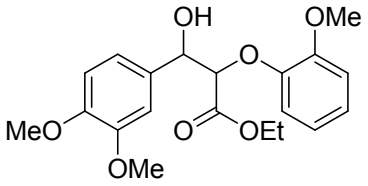


Ethyl (2-methoxyphenoxy)acetate



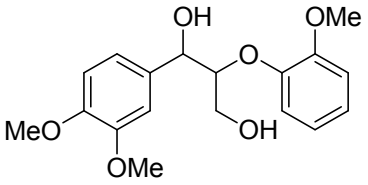
Ethyl bromoacetate (11.1 mL, 100 mmol, 1.0 eq) was added dropwise to a mixture of guaiacol (10.9 mL, 100 mmol, 1.0 eq) and potassium carbonate (13.8 g, 100 mmol, 1.0 eq) in acetone (300 mL). The resulting mixture was heated to reflux and stirred overnight. The reaction mixture was then cooled to room temperature and filtered through a pad of celite, washing with acetone (150 mL). The solvent was removed under reduced pressure and the residue diluted with Et_2O (200 mL). The organic layer was washed with 5% NaOH (2 × 50 mL), water (50 mL) and brine (50 mL). The organic layer was then dried over Na_2SO_4, filtered and concentrated in vacuo to give the title compound as a yellow oil (20.2 g, 96%), which was used in the subsequent step without further purification. $\boldsymbol{\nu_{max}}$/cm^{-1} (neat): 2980, 1755, 1732, 1593, 1503, 1457, 1249, 1174, 1127, 1023; **^{1}H NMR** (300 MHz, $CDCl_3$): 7.00–6.83 (4 H, m, Ar-H), 4.68 (2 H, s, ArOCH_2), 4.26 (2 H, q, *J* = 7.2 Hz, OCH_2CH$_3$), 3.88 (3 H, s, OCH_3), 1.28 (3 H, q, *J* = 7.2 Hz, OCH_2CH$_3$); **HRMS (ESI)**: Calculated for $C_{16=1}H_{18}O_4Na^+$ 233.0784, found 233.0787. Spectral data agrees with that previously reported.[5]

Ethyl-3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxybenzyl)propanoate



A solution of ethy(2-methoxyphenoxy)acetate (10.5 g 50 mmol, 1.0 eq) in THF (100 mL) was added to a 1 M solution of LDA in THF (60 mL, 60 mmol, 1.2 eq) at -78 °C over 1 h. The resulting solution was stirred for a further 10 min, followed by the dropwise addition of a solution of veratraldehyde (8.0 g, 53 mmol, 1.05 eq) in THF (100 mL) over 30 min. Stirring was continued for 2 h, then the reaction was quenched with solid CO_2. The reaction mixture was allowed to warm to room temp and EtOAc (100 mL) was added. The resulting mixture was washed with 1 M HCl (50 mL) and brine (50 mL). The organic layer was then dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude residue as an orange oil. The crude residue was recrystallised from Et_2O to give a white solid (11.2 g, 60%) which was found to be as a 9:1 mixture of diastereomers (erythro:threo). **m.p.** 97–98 °C, (*lit.* 99–101 °C)[6] $\boldsymbol{\nu}_{max}$/cm^{-1} (neat): 3503, 2944, 2837, 1743, 1712, 1593, 1503, 1455, 1256, 1158, 1127, 1024; **^{1}H NMR** (500 MHz, $CDCl_3$): 7.06 (1 H, d, *J* = 1.8 Hz, Ar-H), 7.02 (1 H, app dt, *J* = 7.5, 1.8 Hz, Ar-H), 6.99 (1 H, dd, *J* = 8.3, 1.8 Hz, Ar-H), 6.91 (2 H, app dt, *J* = 8.0, 1.4 Hz, Ar-H), 6.85 (1 H, dd, *J* = 7.5, 1.6 Hz, Ar-H), 6.84 (1 H, d, *J* = 8.2 Hz, Ar-H), 5.15 (1 H, d, *J* = 4.9 Hz, CHOH), 4.74 (1 H, d, *J* = 4.9 Hz, ArOCH), 4.14 (2 H, q, *J* = 7.0 Hz, OCH_2CH_3), 3.88 (3 H, s, OCH_3), 3.87 (3 H, s, OCH_3), 3.86 (3 H, s, OCH_3), 1.15 (3 H, t, *J* = 7.0 Hz, OCH_2CH_3); **^{13}C NMR** (125 MHz, $CDCl_3$): 169.5 (C), 150.8 (C), 149.0 (C), 148.9 (C), 147.4 (C), 131.9 (C), 124.1 (CH), 121.3 (CH), 119.5 (CH), 119.2 (CH), 112.5 (CH), 110.9 (CH), 110.4 (CH), 84.1 (CH), 74.0 (CH), 61.4 (CH_2), 56.1 (CH_3), 56.0 (CH_3), 55.9 (CH_3), 14.2 (CH_3); **HRMS (ESI)**: Calculated for $C_{20}H_{24}O_7Na^+$ 399.1414, found 399.1414. Spectral data agrees with that previously reported.[7]

1-(3,4-dimethoxyphenyl)-2-(2-methoxybenzyl)propane-1,3-diol (kb5061)



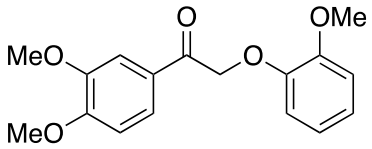
A solution of the aldol product (6.1 g, 16 mmol 1.0 eq) in THF (100 mL) at 0 °C was treated with lithium borohydride (700 mg, 32 mmol, 2.0 eq). The resulting mixture was warmed slowly to room temp and stirred overnight. The reaction was quenched with water (50 mL) and acidified with 2M HCl. The aqueous layer was extracted with Et_2O (3 × 30 mL) and the organic phase washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography (hexane:EtOAc, 1:1 to 1:3) to give the title compound as a colourless syrup (4.8 g, 91%). $\boldsymbol{\nu}_{max}$/cm^{-1} (neat): 3457, 2938, 2837, 1592, 1501, 1456, 1253, 1139, 1024; **^{1}H NMR** (500 MHz, $CDCl_3$): 7.04 (1 H, app dt, *J* = 6.9, 1.6 Hz, Ar-H), 6.96–6.85 (5 H, m, Ar-H), 6.82 (1 H, d, *J* = 8.0 Hz, Ar-H), 4.97 (1 H, d, *J* = 4.5, ArCHOH), 4.16 (1 H, dt, *J* = 5.2, 3.5 Hz, ArOCH), 3.90 (1H, dd, *J* = 12.3, 5.9 Hz, one of CH_2O),3.86 (9 H, s, 3 x OCH_3), 3.66 (1H, dd, *J* = 12.3, 3.4 Hz, one of CH_2O), 3.0 (2 H, bs, 2 × OH);

^{13}C NMR (125 MHz, $CDCl_3$): 151.7 (C), 149.2 (C), 148.6 (C), 147.1 (C), 132.7 (C), 124.3 (CH), 121.8 (CH), 121.1 (CH), 118.6 (CH), 112.4 (CH), 11.2 (CH), 109.4 (CH), 87.5 (CH), 72.9 (CH), 60.9 (CH_2), 56.1 (CH_3), 56.1 (CH_3), 56.0 (CH_3); **HRMS (ESI)**: Calculated for $C_{18}H_{22}O_6Na^+$ 357.1309, found 357.1311. Spectral data agrees with that previously reported.[7]

Synthesis of 3,4-dimethoxybromoacetophenone

Prepared according to the procedure outlined by Kwi-wan Jeong et al.[8] In brief: To a solution 3,4-dimethoxyacetophenone (5.00 g, 27.7 mmol) in ethyl acetate (100 mL) was added anhydrous copper(II) bromide (6.80 g, 30.4 mmol). The resulting suspension was heated to reflux under nitrogen until the reaction was judged complete (TLC). The reaction was filtered through diatomaceous earth, washing with ethyl acetate. The combined filtrate was concentrated under reduced pressure and washed with diethyl ether to afford the title product which was used immediately in the following procedure.

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone



Adapted from the method decscribed by Galkin & Samec:

Freshly distilled guaiacol (945 µL, 8.48 mmol) was added to a flask containing anhydrous potassium carbonate (2.67 g, 19.3 mmol) in dry acetonitrile (40 mL). The reaction was stirred under nitrogen at room temperature and a purple solution of 3,4-dimethoxybromoacetophenone (2.00 g, 7.72 mmol) in acetonitrile (20 mL) was added dropwise *via* a pressure-equalising dropping funnel over 15 min. The resulting yellow suspension was refluxed overnight to 80 °C, becoming orange with a white precipitate. The mixture was allowed to cool, filtered and the filtrate concentrated under reduced pressure. The resulting orange oil was resuspended in acetone (40 mL), filtered and concentrated and the process repeated with dichloromethane (40 mL). Decolourisation with charcoal in ethanol resulted in a transparent yellow solution from which the title product crystallised (1.80 g, 77%). ; **^{1}H NMR** (200 MHz, $CDCl_3$): 7.68 (1 H, dd, *J* = 8.4, 1.8 Hz, Ar-H), 7.60 (1 H, d, *J* = 2.0 Hz, Ar-H), 7.01–6.84 (5 H, m, Ar-H + guaiacylHs), 5.28 (2 H, s, CH_2), 3.95 (3 H, s, OMe), 3.93 (3 H, s, OMe), 3.88 (3 H, s, OMe); Spectral data agrees with that previously reported.[9]

Synthesis of 3,4-Dimethoxybenzyl Acetate

This method was adapted from the method described by Mojtahedi and Samadian.[10] 3,4-Dimethoxybenzyl alcohol (0.68 g, 4.1 mmol), acetic anhydride (1.0 mL, 10.6 mmol) and sodium acetate (0.03 g, 0.04 mmol) were stirred at room temperature overnight. The mixture was then dissolved in ethyl acetate (20 mL) and washed with water (20 mL), saturated aqueous sodium hydrogen carbonate solution (20 mL) and brine (10 mL), then dried over sodium sulfate. Filtration and solvent evaporation afforded the product as a pale yellow oil (0.77 g, 89% yield).

MS (*m/z*, %) EI+: 210 ([M]+˙, 55%), 151 ([M-OAc]+˙, 100%).
^{1}H NMR (300 MHz, CDCl3): δ 6.949–6.837 (m, 3 H, Ar-H), 5.043 (s, 2 H, ArCH2), 3.894 (s, 6 H, 2 × OCH_3), 2.092 (s, 3 H, CH_3) ppm.

Synthesis of 4-Br-2,6-Dimethoxyphenol

The following procedure was from Bhattarai *et al.*[11] Under nitrogen, 2,6-dimethoxyphenol was dissolved in $CHCl_3$ (50 mL). Ethanol (400 µL) and NaH (60 %, 15 mg, 0.63 mmol) were then added to the solution. The mixture was then cooled in an acetone and dry ice bath. *N*-bromosuccinimide (5.77 g, 32.4 mmol) was then added and the mixture stirred for 1 h at this temperature. The reaction was slowly warmed to room temperature and stirred for 30 min followed by stirring at 65 °C for 5 min. The mixture was cooled and the solvent was removed in *vacuo*. The yellow residue was then dissolved in an equivalent volume of diethyl ether and filtered.

The diethyl ether was removed and the yellow residue was stirred in heptane (60 mL) at 85 °C for 15 min. The solution was then filtered and cooled allowing the product to recrystallise as white crystals (2.74 g, 36%). The crystals were washed with heptane (20 mL) and water (20 mL) and dried under vacuum.

m.p. 100 °C
MS (*m/z*, %) EI-: (100) = 231 (89 [^{79}BrAr–H]$^-$), 233(100 [^{81}BrAr–H]$^-$).
^{1}H NMR (200 MHz; $CDCl_3$): δ 6.72 (s, 2H), 3.87 (s, 6H) ppm.

Modelling the Catalytic Oxidation of Syringol

From Ulrich Neuenschwander and Ive Hermans[12],

The radical initiation occurs via a thermal step

$$ROOH + RH \xrightarrow{k_2} RO^{\cdot} + H_2O + R^{\cdot}$$

And a catalytic step

$$ROOH + Co^{II} \xrightarrow{k_{cat}} Co^{III} - OH + RO^{\cdot}$$

The radical termination is given by

$$ROO^{\cdot} + ROO^{\cdot} \xrightarrow{k_t} ROH + Q = O + O_2$$

The propagation reaction is

$$ROO^{\cdot} + RH \xrightarrow{k_p} ROOH + R^{\cdot}$$

At steady state, the rate of termination equals the rate of initiation, and so

$$k_2[ROOH][RH] + k_{cat}[ROOH][Co^{II}] = k_t[ROO^{\cdot}]^2$$

So

$$[ROO^{\cdot}]^2 = \frac{[ROOH]\left(k_2[RH] + k_{cat}[Co^{II}]\right)}{k_t}$$

If the rate of propagation, r_p, is given by

$$\frac{d[RH]}{dt} = r_p = k_p[ROO^{\cdot}][RH]$$

Then, substituting for [ROO•]

$$r_p = k_p[RH]\sqrt{\frac{k_2[ROOH][RH] + k_{cat}[ROOH][Co^{II}]}{k_t}}$$

$$\frac{d[RH]}{dt} = k_p[RH]\sqrt{\frac{k_2[ROOH][RH] + k_{cat}[ROOH][Co^{II}]}{k_t}}$$

Integral derivation, CRC Handbook 97th Edition 2016 Appendix A, p 271 integral # 133

$$\int_0^t dt = \int_{x_0}^{x} \frac{dx}{x\sqrt{bx+a}} = \frac{1}{\sqrt{a}} ln\left(\frac{\sqrt{bx+a}\ -\sqrt{a}}{\sqrt{bx+a}+\ \sqrt{a}}\right) \quad a > 0$$

Then

$$t = \frac{1}{\sqrt{a}} ln\left(\frac{\sqrt{bx_0+a}\ -\sqrt{a}}{\sqrt{bx_0+a}+\ \sqrt{a}}\right) - \frac{1}{\sqrt{a}} ln\left(\frac{\sqrt{bx+a}\ -\sqrt{a}}{\sqrt{bx+a}+\ \sqrt{a}}\right)$$

$$t\sqrt{a} = ln\left(\frac{\sqrt{bx_0+a}\ -\sqrt{a}}{\sqrt{bx_0+a}+\ \sqrt{a}}\right) - ln\left(\frac{\sqrt{bx+a}\ -\sqrt{a}}{\sqrt{bx+a}+\ \sqrt{a}}\right)$$

$$t\sqrt{a} = ln\left(\frac{(\sqrt{bx_0+a}\ -\sqrt{a})\,(\sqrt{bx+a}+\ \sqrt{a})}{(\sqrt{bx_0+a}+\ \sqrt{a})\,(\sqrt{bx+a}\ -\sqrt{a})}\right)$$

$$e^{t\sqrt{a}} = \left(\frac{(\sqrt{bx_0+a}\ -\sqrt{a})\,(\sqrt{bx+a}+\ \sqrt{a})}{(\sqrt{bx_0+a}+\ \sqrt{a})\,(\sqrt{bx+a}\ -\sqrt{a})}\right)$$

$$\left(e^{t\sqrt{a}}\right)\frac{(\sqrt{bx_0+a}+\ \sqrt{a})}{(\sqrt{bx_0+a}\ -\sqrt{a})} = \left(\frac{(\sqrt{bx+a}+\ \sqrt{a})}{(\sqrt{bx+a}\ -\sqrt{a})}\right)$$

If

$$\left(e^{t\sqrt{a}}\right)\frac{(\sqrt{bx_0+a}+\ \sqrt{a})}{(\sqrt{bx_0+a}\ -\sqrt{a})} = M$$

Then

$$M = \left(\frac{(\sqrt{bx+a}+\ \sqrt{a})}{(\sqrt{bx+a}\ -\sqrt{a})}\right)$$

So,

$$M\sqrt{bx+a} - M\sqrt{a} = \sqrt{bx+a} + \sqrt{a}$$

$$\sqrt{bx+a}\,(M-1) = \sqrt{a}(M+1)$$

$$\sqrt{bx+a} = \frac{\sqrt{a}\,(M+1)}{(M-1)}$$

$$bx+a = a\frac{(M+1)^2}{(M-1)^2}$$

$$bx = a\frac{(M+1)^2}{(M-1)^2} - a$$

$$bx = a(\frac{(M+1)^2}{(M-1)^2} - 1)$$

$$x = \left(\frac{a}{b}\right)\left(\frac{(M+1)^2 - (M-1)^2}{(M-1)^2}\right)$$

$$x = \left(\frac{a}{b}\right)\left(\frac{M^2 + 2M + 1 - M^2 + 2M - 1}{(M-1)^2}\right)$$

$$x = \left(\frac{a}{b}\right)\left(\frac{4M}{(M-1)^2}\right)$$

$$x = \left(\frac{4a}{b}\right)\left(\frac{M}{(M-1)^2}\right)$$

Where

$$\left(e^{t\sqrt{a}}\right)\frac{(\sqrt{bx_0 + a} + \sqrt{a})}{(\sqrt{bx_0 + a} - \sqrt{a})} = M$$

With the rate equation

$$r_p = k_p[RH]\sqrt{\frac{k_2[ROOH][RH] + k_{cat}[ROOH][Co^{II}]}{k_t}}$$

$$\frac{d[RH]}{dt} = k_p[RH]\sqrt{\frac{k_2[ROOH][RH] + k_{cat}[ROOH][Co^{II}]}{k_t}}$$

And so

$$b = \left(\frac{k_2}{k_t}{k_p}^2\right)[ROOH]$$

And

$$a = \left(\frac{k_{cat}}{k_t}{k_p}^2\right)[ROOH][Co^{II}]$$

So

$$\frac{a}{b} = \frac{k_{cat}}{k_2}[Co^{II}]$$

Assuming [ROOH] and [Co^{II}] are constant.

Using Maple 16, the equation,

$$x = \left(\frac{4a}{b}\right)\left(\frac{M}{(M-1)^2}\right)$$

Where

$$\left(e^{t\sqrt{a}}\right)\frac{\left(\sqrt{bx_0 + a} + \sqrt{a}\right)}{\left(\sqrt{bx_0 + a} - \sqrt{a}\right)} = M$$

Was simplified, so that

$$x = \left(\frac{4a}{b}\right)\left(\frac{\left(e^{t\sqrt{a}}\right)\left(\sqrt{bx_0 + a} + \sqrt{a}\right)}{\left(\sqrt{bx_0 + a} - \sqrt{a}\right)\left(\frac{\left(e^{t\sqrt{a}}\right)\left(\sqrt{bx_0 + a} + \sqrt{a}\right)}{\left(\sqrt{bx_0 + a} - \sqrt{a}\right)} - 1\right)^2}\right)$$

The above equation was fitted to the data points for the catalytic oxidation of syringol for 2.5 h of peroxide addition using least-squares (ordinary) fit, where 'a' and 'b' denote free variables. No weightings were used. Strict convergence criteria was demanded. The values of 'a' and 'b' obtained from the fitting were 4.209×10^{-4} and 6.043×10^{-4}. The standard error of 'a' and 'b' were 1.292×10^{-4} and 3.96×10^{-4}. The R^2 value was 0.9922.

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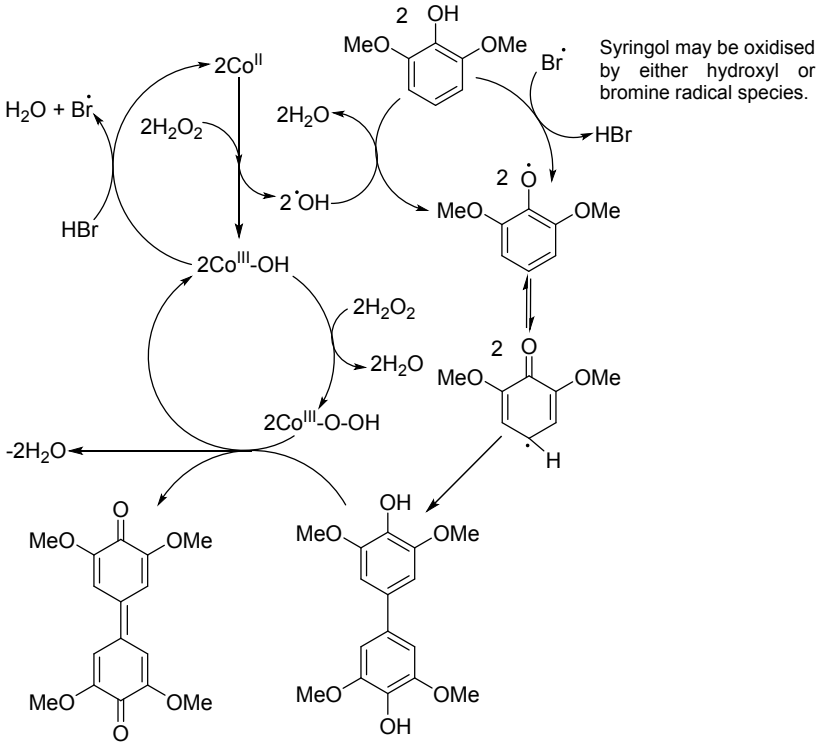
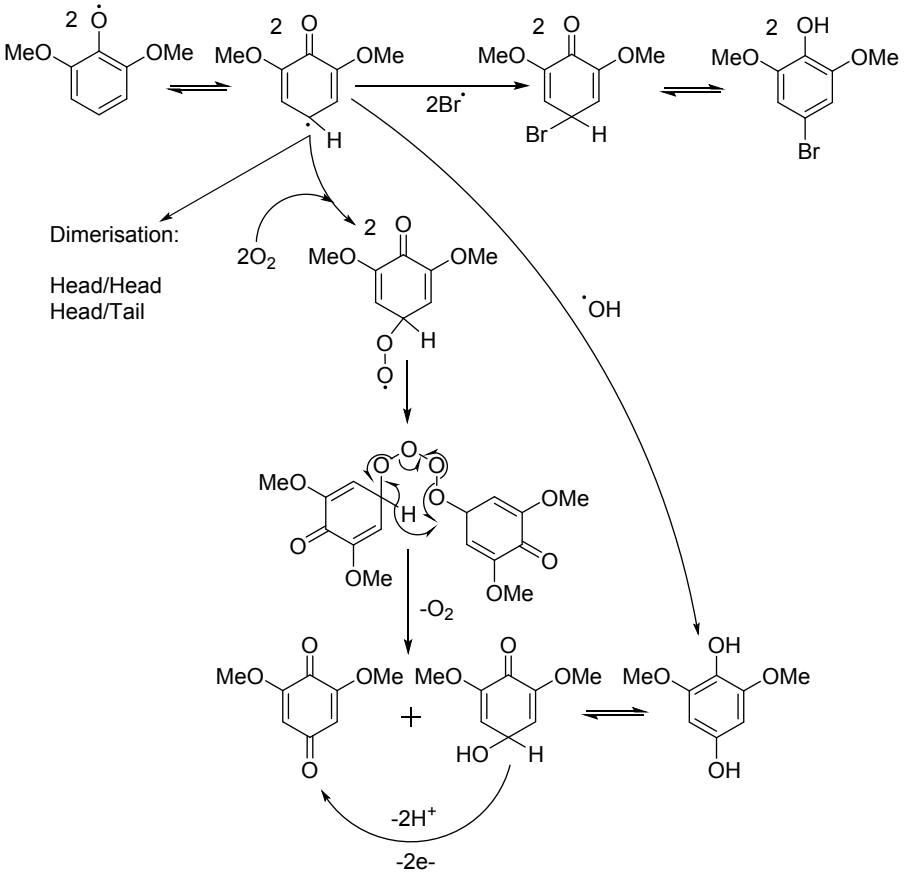


Scheme S1. Proposed mechanism to illustrate the possible reaction pathways during the oxidation of syringol to coerulignone.



Scheme S2. Proposed mechanism to illustrate the possible reaction pathways during the oxidation of syringol to 4Br2,6DMP and 2,6DMBZQ.

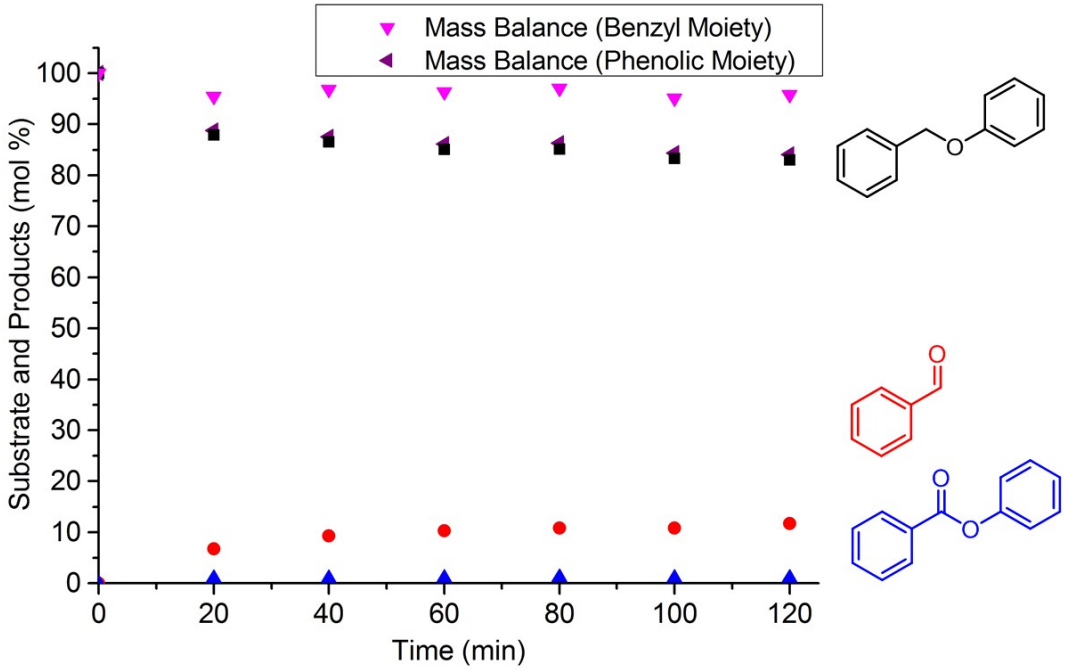


Figure S1. Time-course profile of the catalytic oxidation of A1.

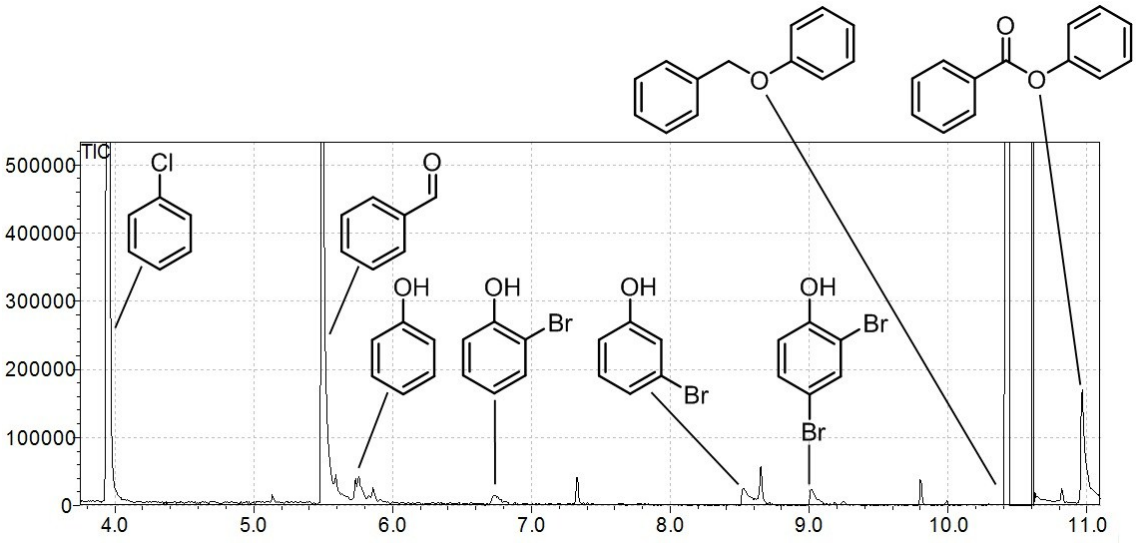


Figure S2. GC-MS chromatogram of the sample taken at 120 minutes of the catalytic oxidation of A1. Unlabelled peaks correspond to species attributed to either the solvent or the silica column. The concentration of the peak corresponding to the substrate was high to saturate the detector at approx. 10.4–10.6 min.

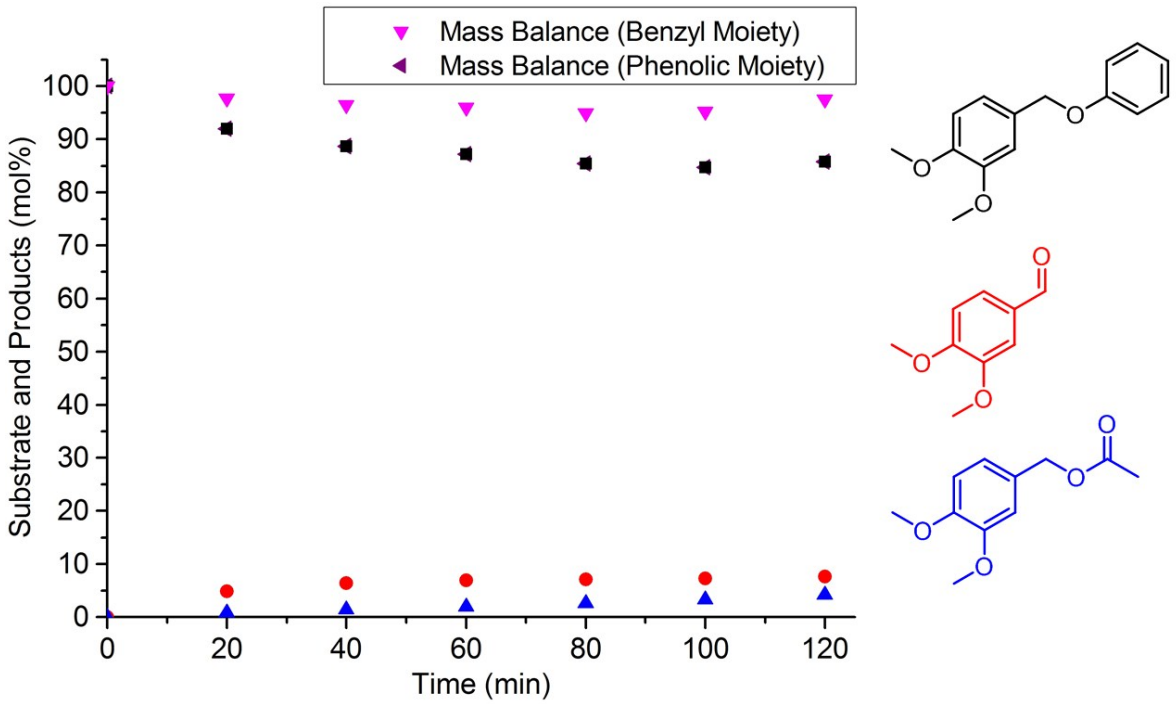


Figure S3. Time-course profile of the catalytic oxidation of A2.

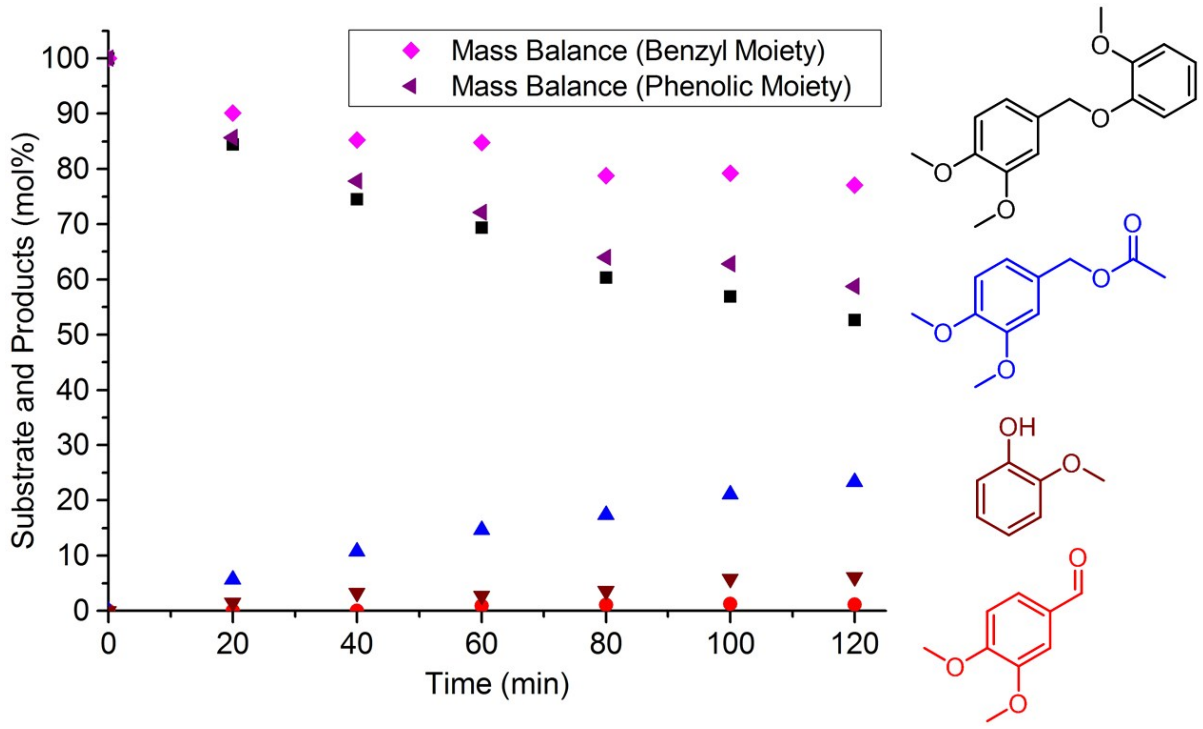


Figure S4. Time-course profile of the catalytic oxidation of A3.

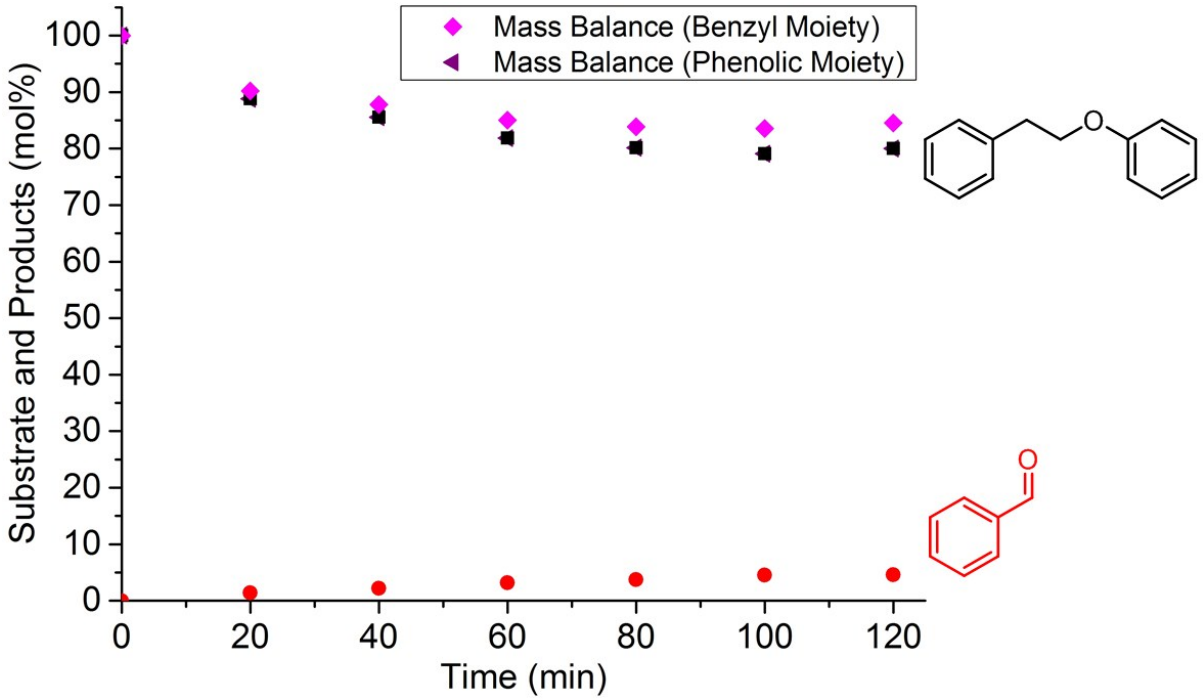


Figure S5. Time-course profile of the catalytic oxidation of B1.

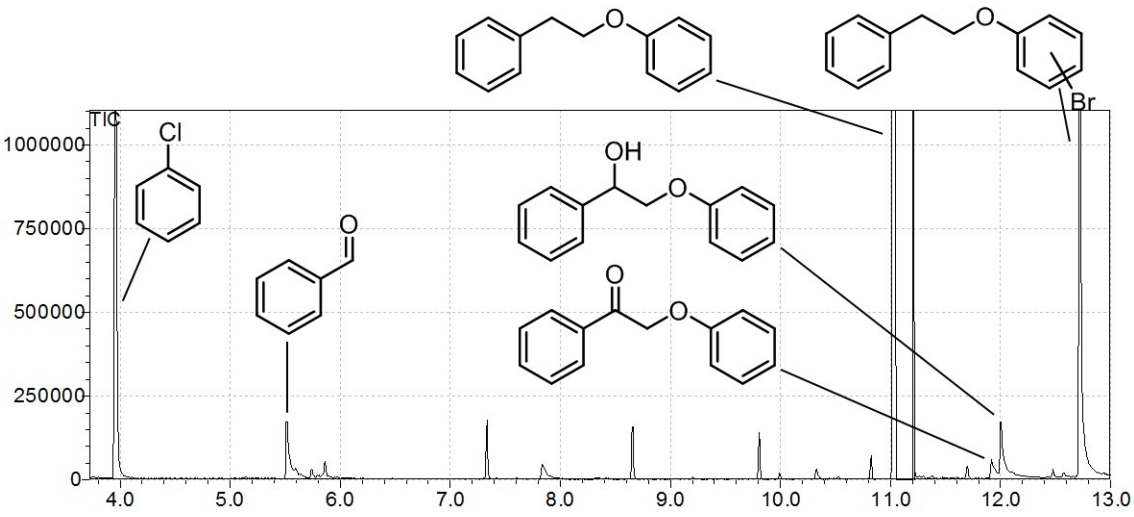


Figure S6. GC-MS chromatogram of the sample taken at 120 minutes of the catalytic oxidation of B1. Unlabelled peaks correspond to species attributed to either the solvent or the silica column. The concentration of the peak corresponding to the substrate was too high and saturated the detector at approx. 11.0–11.3 min.

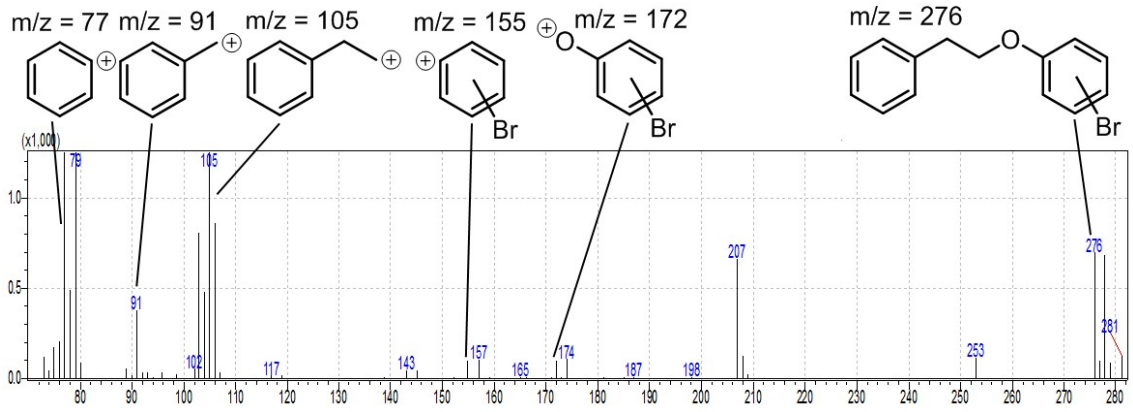


Figure S7. Fragmentation pattern of the species attributed to the peak at approx. 12.7 min in Figure S6. The peaks at m/z = 207 and 253 correspond to species attributed to the silica column.

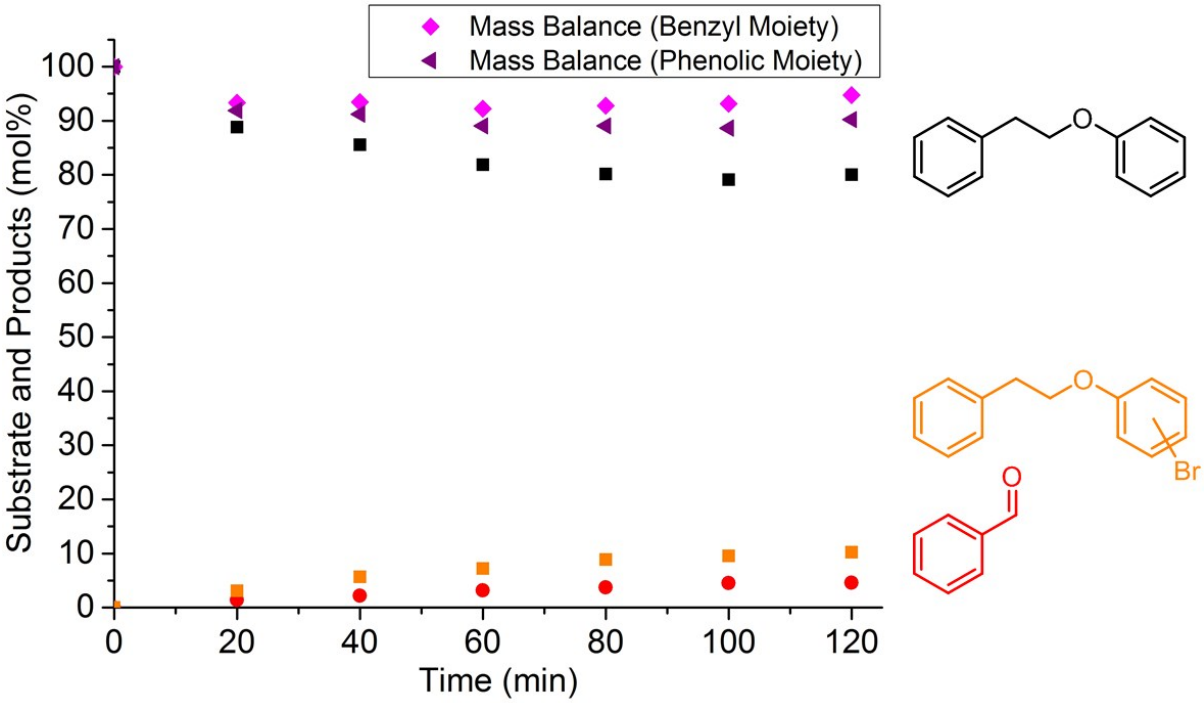


Figure S8. Time-course profile of the catalytic oxidation of B1, including the time-course profile of the bromide product by assuming it has a similar GC signal response as the substrate. The mass balance of the reaction is 96% and 91% for the benzyl and phenolic moieties respectively when including the estimated yield of the brominated substrate.

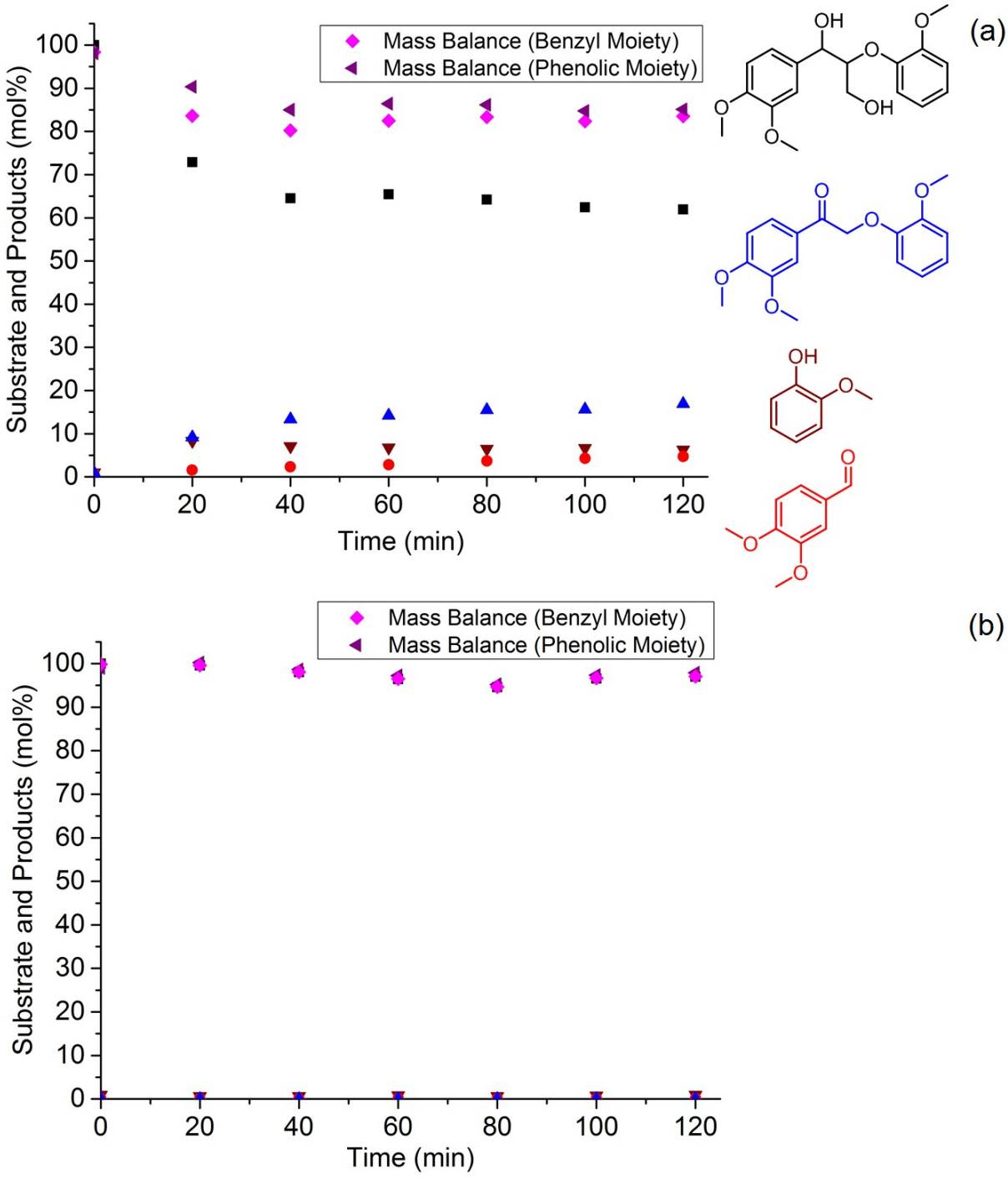


Figure S9. (a) Time-course profile of the catalytic oxidation of B2, **(b)** time-course profile of the heating of B2 in acetic acid solvent at 70 °C for 2 h.

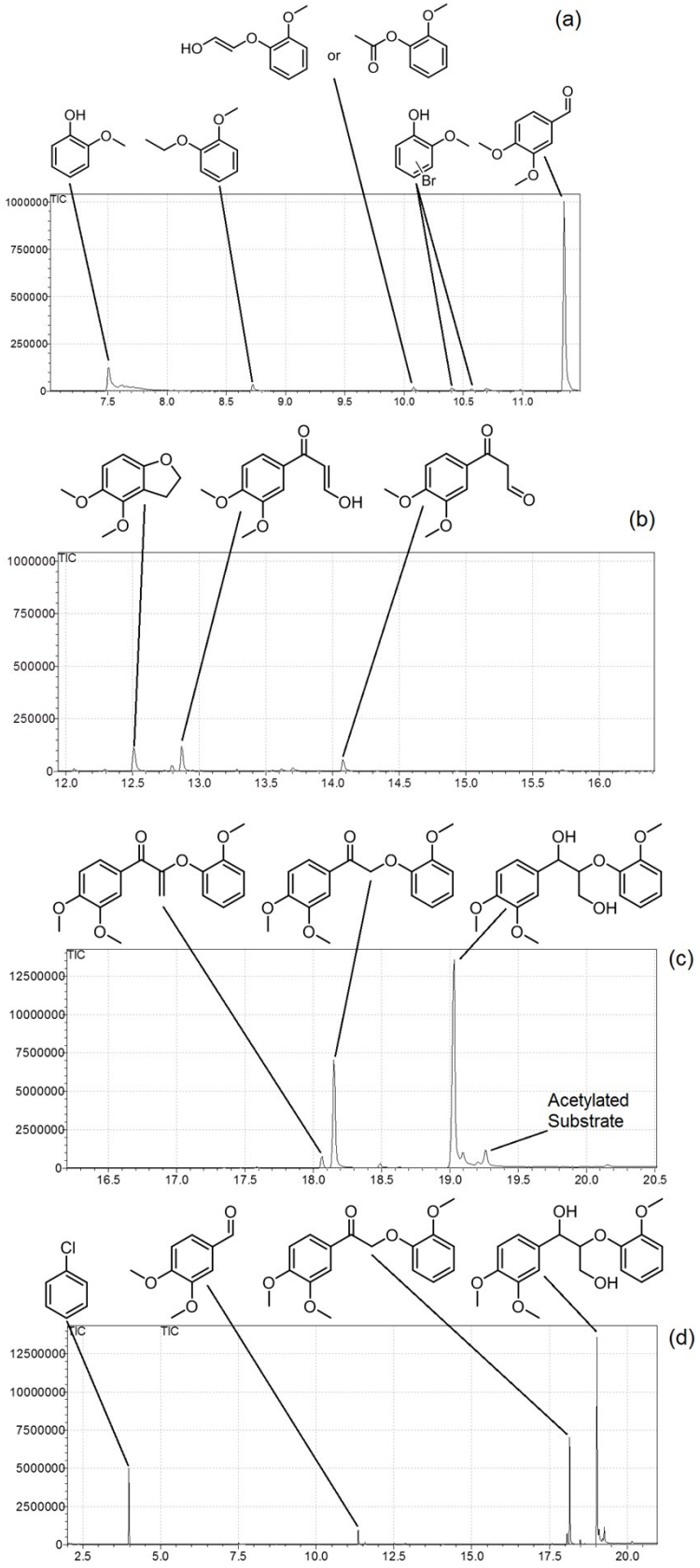


Figure S10. (a-d) GC-MS chromatograms of the sample taken at 120 minutes of the catalytic oxidation of B2. Several of the low intensity ion peaks could not be reliably identified by the NIST library, however, structures based on the m/z ratio are proposed.

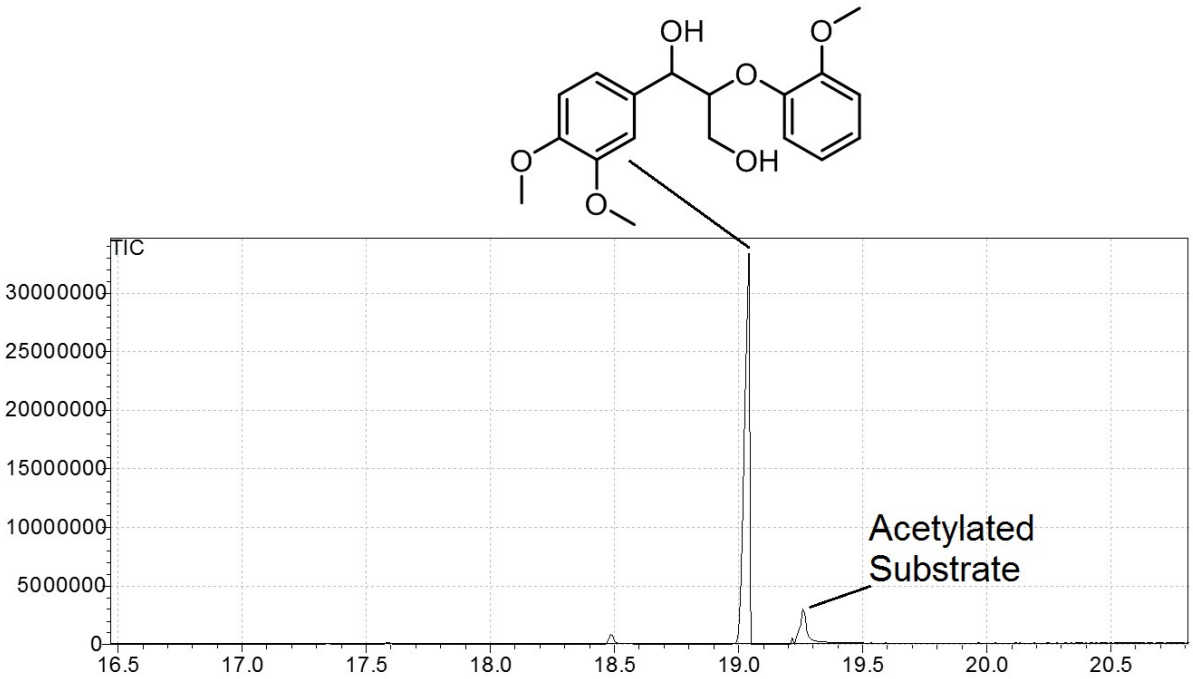


Figure S11. GC-MS chromatograms of the sample taken at 120 minutes of the heating of B2 in acetic acid. The concentration of the peak corresponding to the substrate was high to saturate the detector at approx. 19.05–19.3 min.

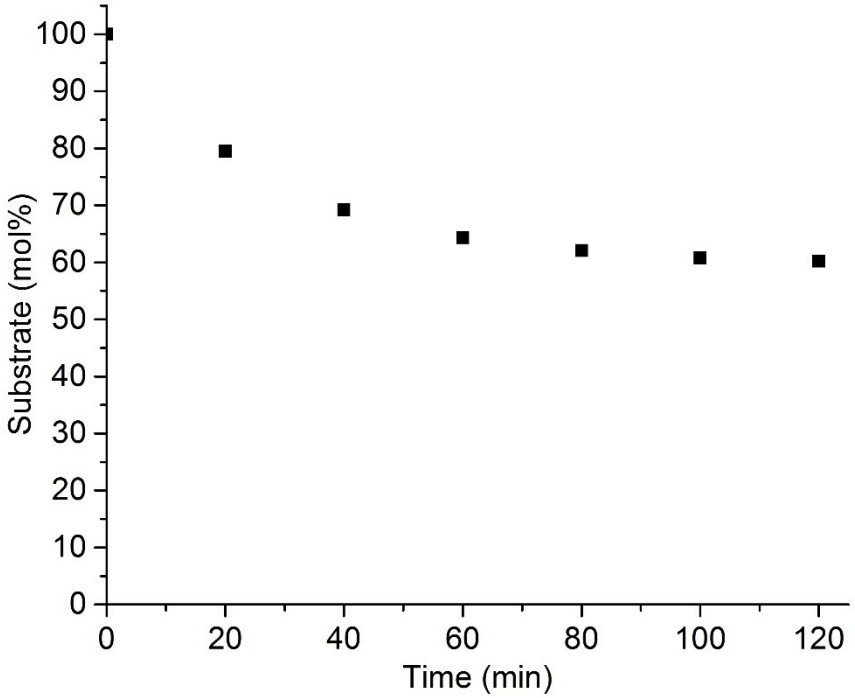


Figure S12. Time-course profile of the catalytic oxidation of phenol.

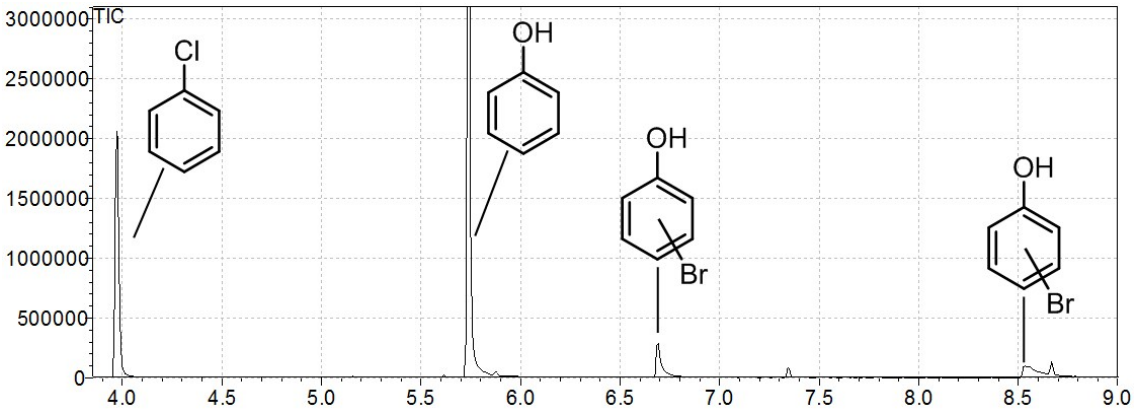


Figure S13. GC-MS chromatogram of the sample taken at 120 minutes of the catalytic oxidation of phenol. Unlabelled peaks correspond to species attributed to either the solvent or the silica column.

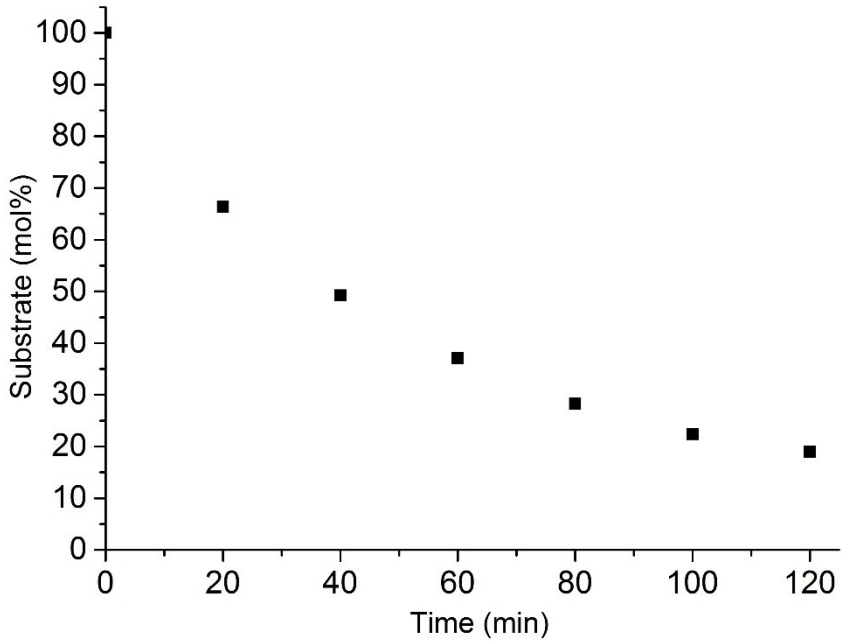


Figure S14. Time-course profile of the catalytic oxidation of guaiacol.

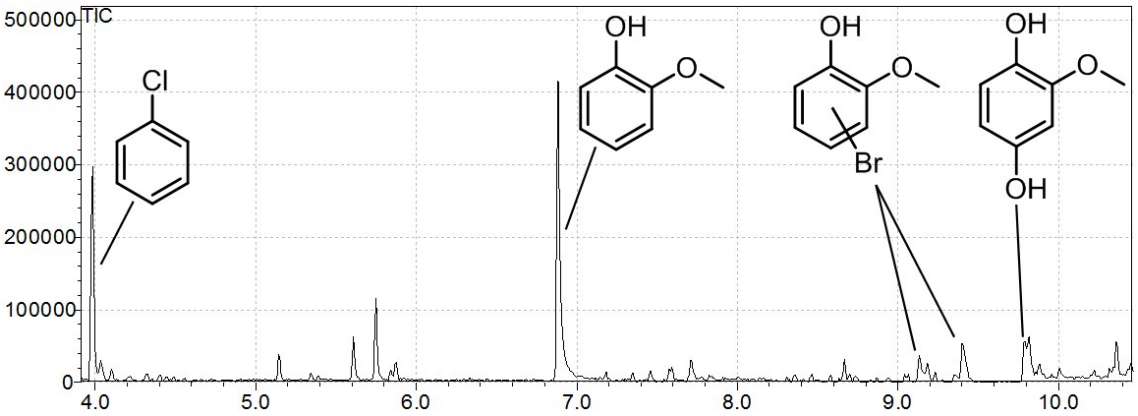


Figure S15. GC-MS chromatogram of the sample taken at 120 minutes of the catalytic oxidation of guaiacol. Unlabelled peaks correspond to species attributed to either the solvent or the silica column.

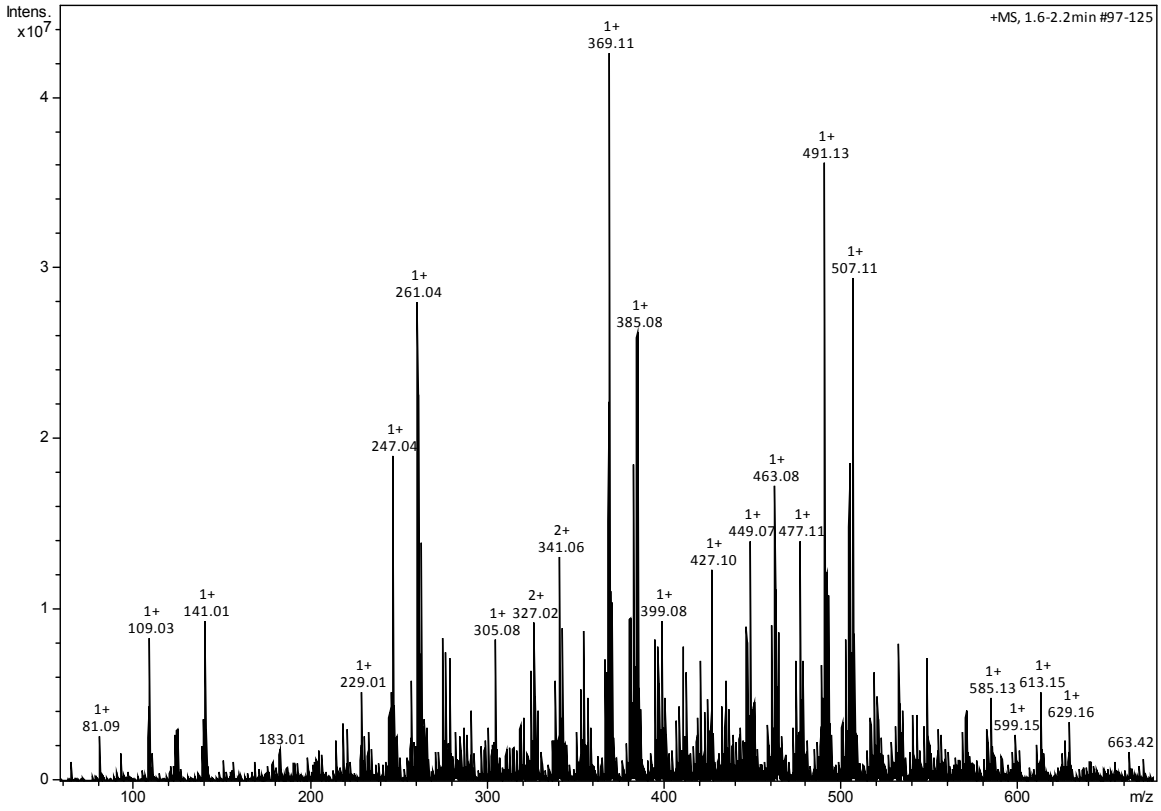


Figure S16. APCI mass spectrum of material recovered from the catalytic oxidation of guaiacol. Multiple species are observed including ions with a m/z ratio consistent with a structure of methoxycatechol (*m/z* = 141.06), guaiacol dimer (*m/z* = 247.04), trimer (*m/z* = 369.16), tetramer (*m/z* = 491.13) and pentamer (*m/z* = 613.15).

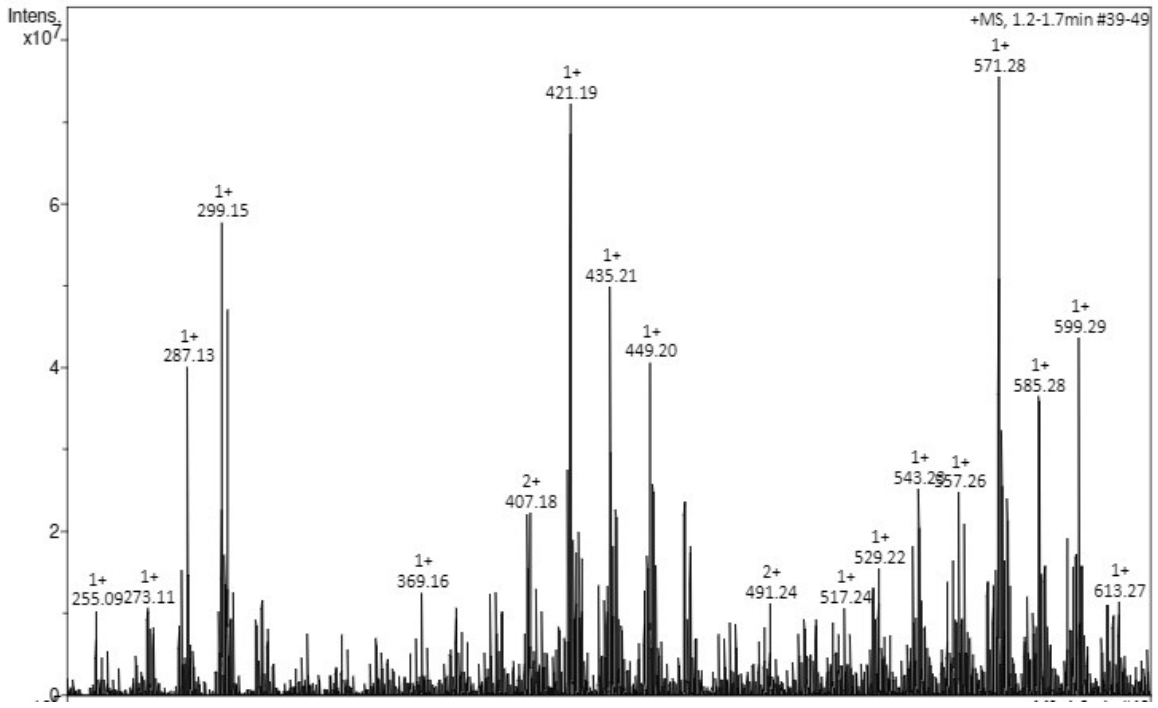


Figure S17. APCI mass spectrum of material recovered from the catalytic oxidation of A3. Multiple oligomeric species are observed composed of structures consistent with guaiacyl (*m/z* = 122) and benzyl fragments (*m/z* = 150).

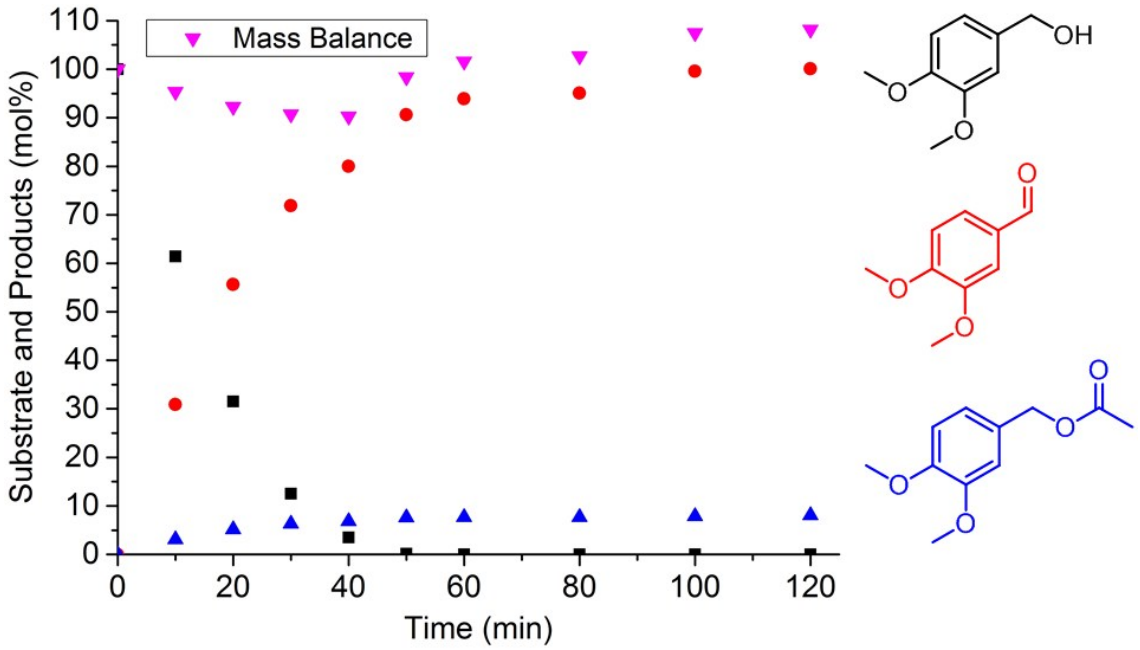


Figure S18. Time-course profile of the catalytic oxidation of 3,4DMB-OH.

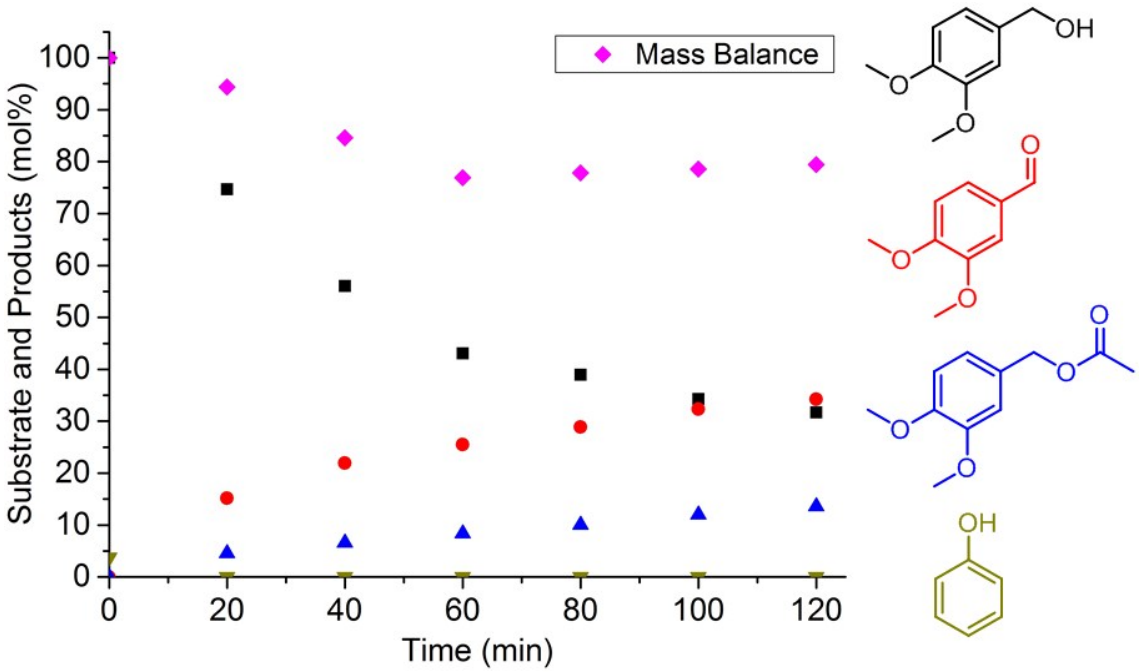


Figure S19. Time-course profile of the catalytic oxidation of 3,4DMB-OH in the presence of phenol (5 mol%).

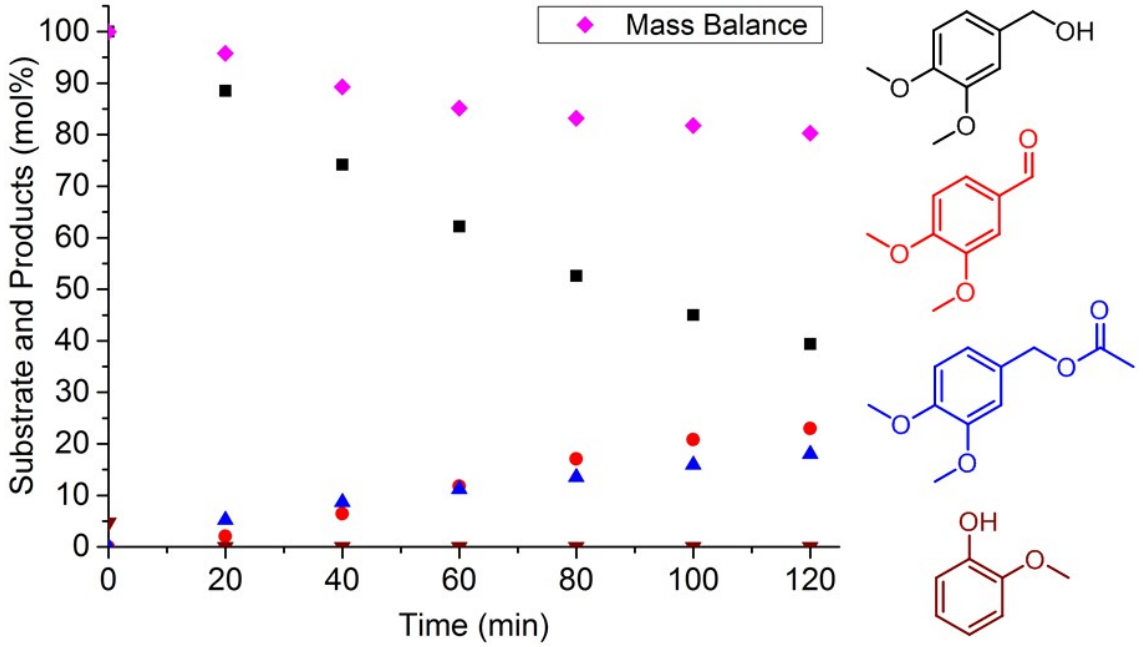


Figure S20. Time-course profile of the catalytic oxidation of 3,4DMB-OH in the presence of guaiacol (5 mol%).

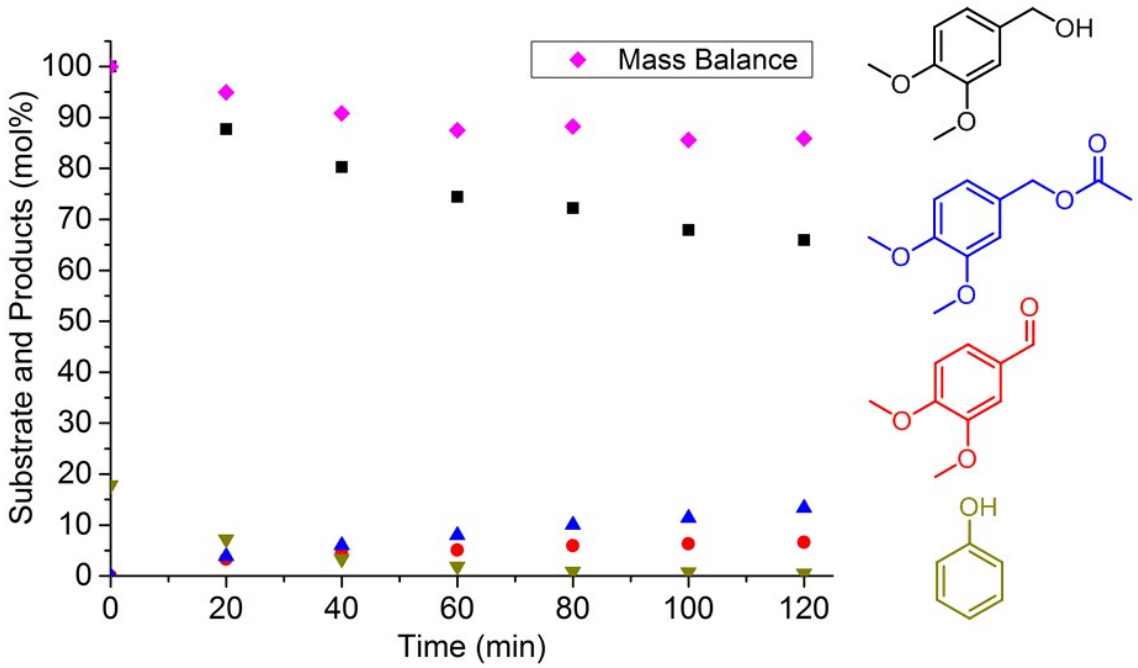


Figure S21. Time-course profile of the catalytic oxidation of 3,4DMB-OH in the presence of phenol (20 mol%).

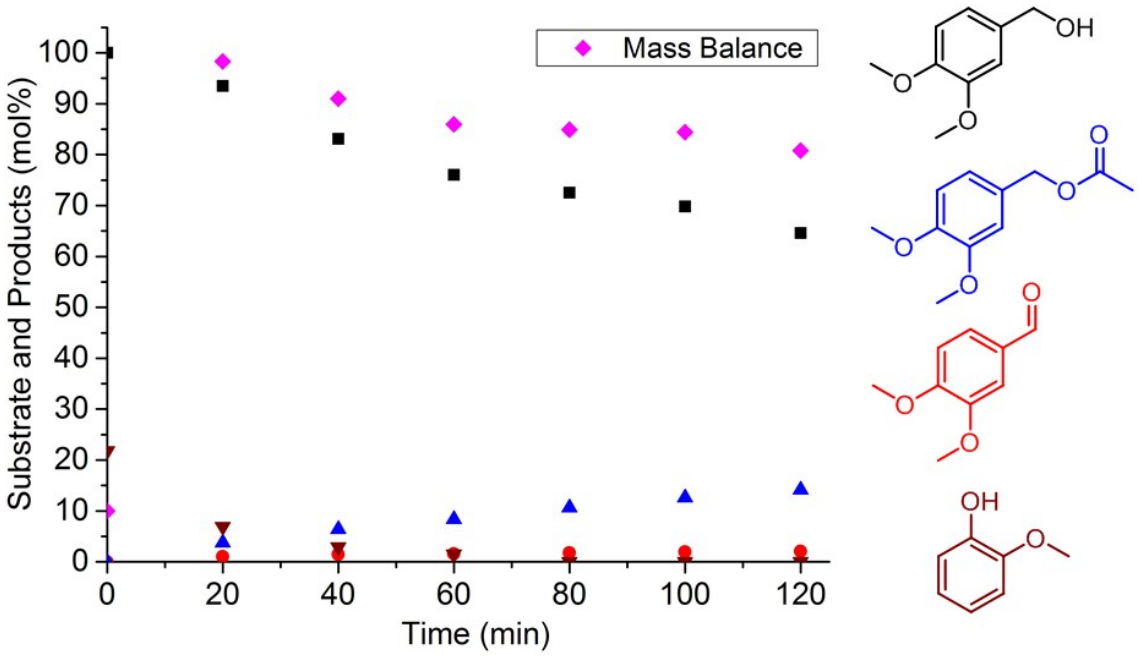


Figure S22. Time-course profile of the catalytic oxidation of 3,4DMB-OH in the presence of guaiacol (20 mol%).

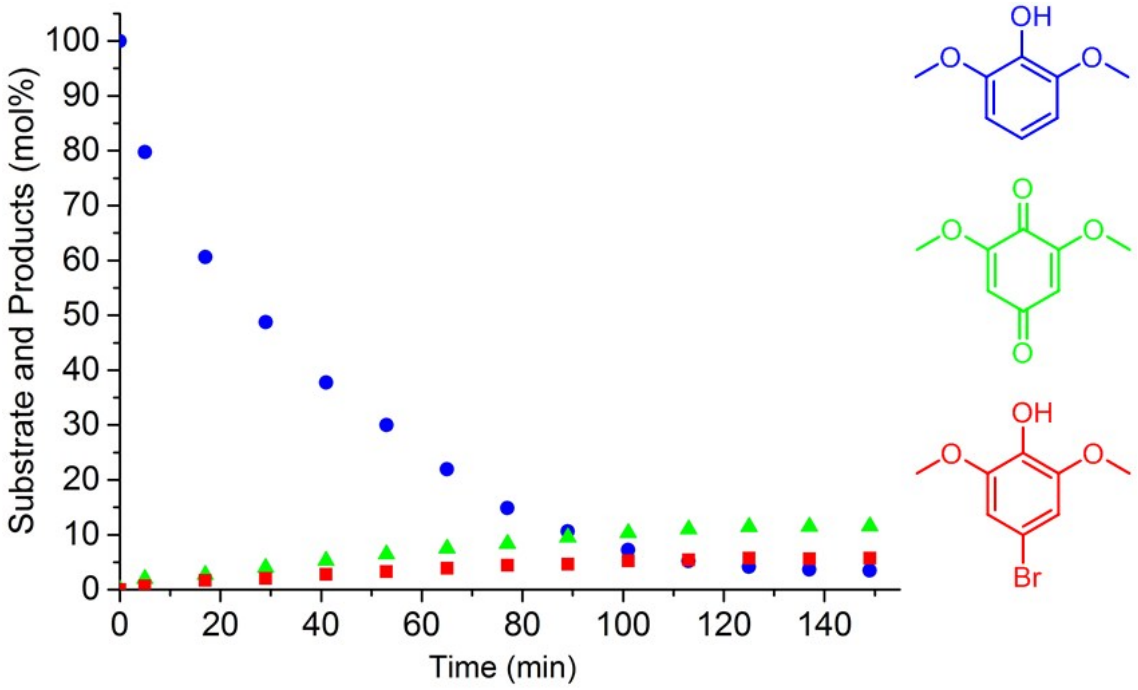


Figure S23. Time-course profile of the catalytic oxidation of syringol over 2.5 h.

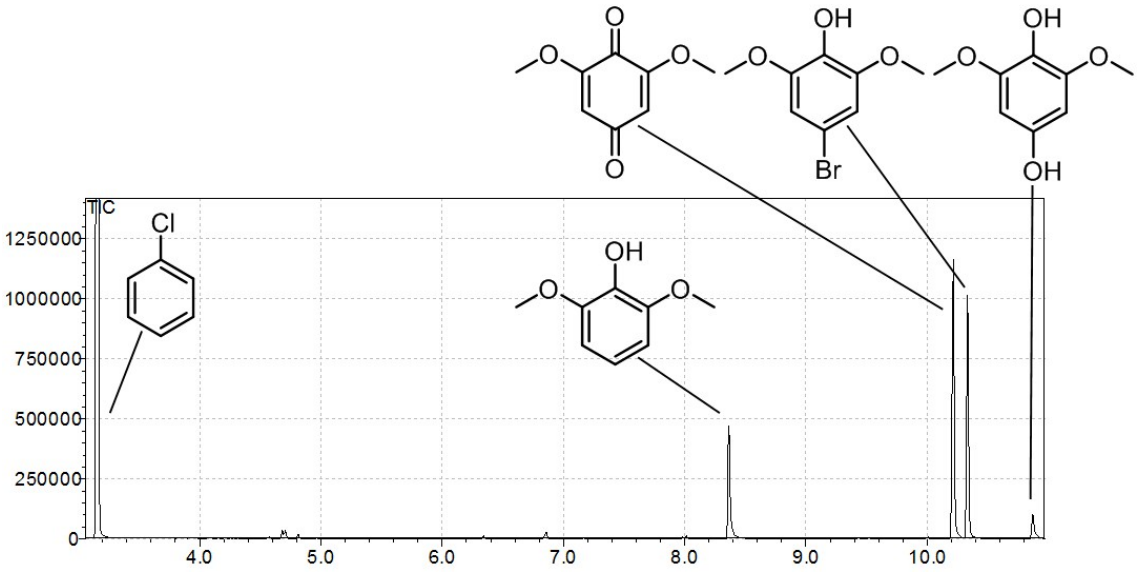


Figure S24. GC-MS chromatogram of the sample taken at 144 minutes of the catalytic oxidation of syringol. Unlabelled peaks correspond to species attributed to either the solvent or the silica column.

Characterisation data for 3,3',5,5'-tetramethoxy-4,4'-diphenoquinone (coerulignone)

Melting Point: 283 °C

Selected MS/APCI data: m/z (%) = 305 (100 $[M + H]^+$).

Elemental Microanalysis – Calc.(%) for $C_{16}H_{16}O_6$ (304.29 g mol^{-1}): C 63.15, H 5.30.

Found: C 63.08, H 5.23.

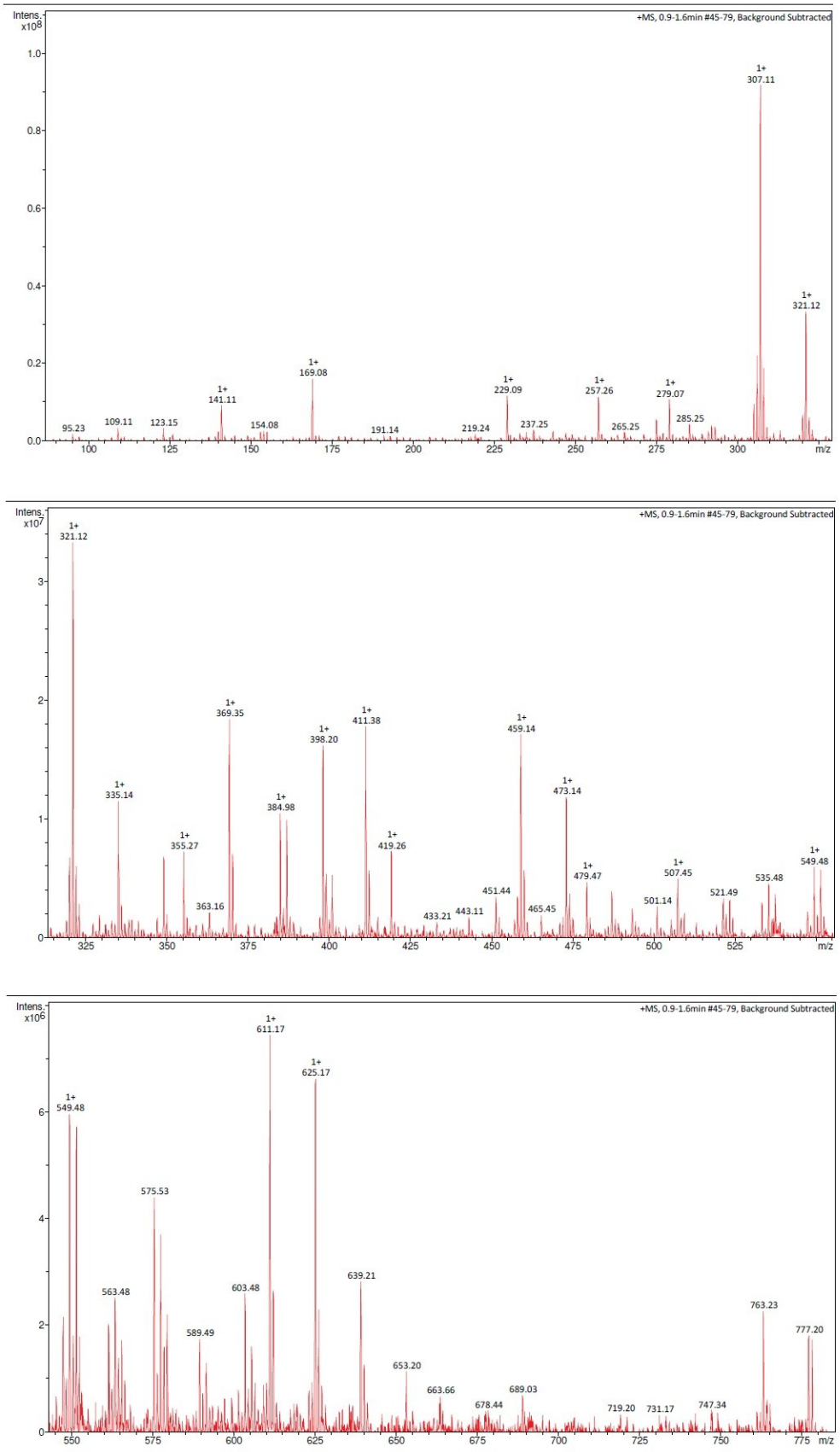


Figure S25. APCI mass spectrum of material recovered from the catalytic oxidation of syringol. Multiple oligomeric species are observed composed of structures consistent with syringyl (*m/z* = 152) moieties, *e.g. m/z* = 307, 459, 611, 763.

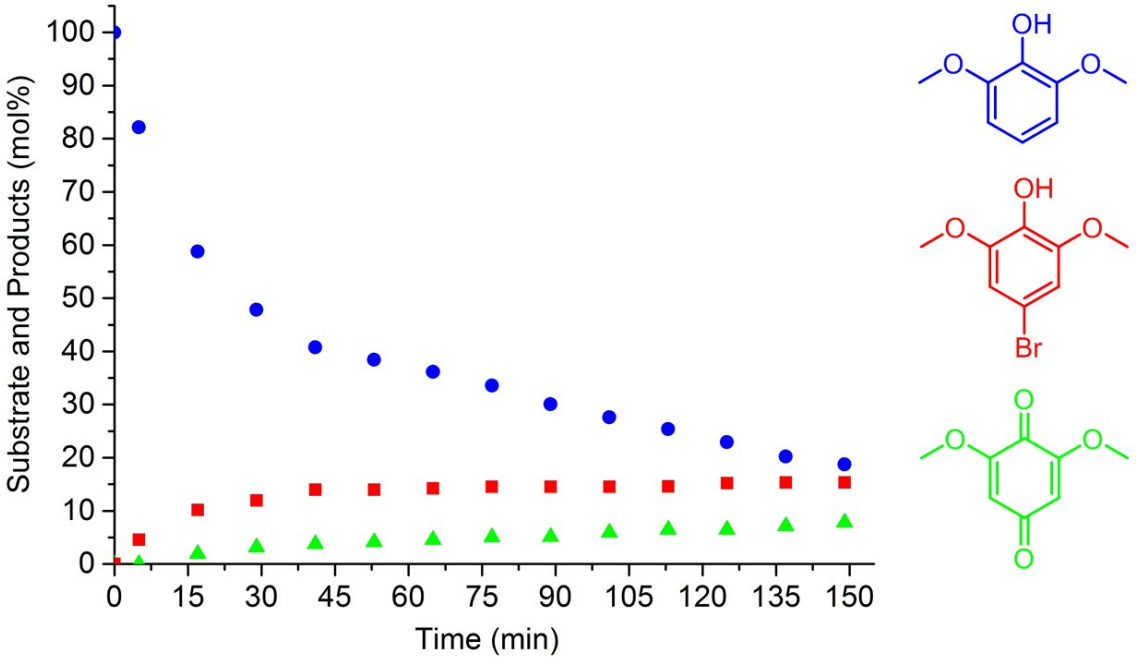


Figure S26. Time-course profile of the catalytic oxidation of syringol in the absence of Co catalyst. The change in the time-course profile of syringol is due to the sequestration of bromide (> 90% after 29 min) to form the catalytically inactive 4Br2,6DMP. The recovered residue accounted for 38% of the initial mass of substrate.

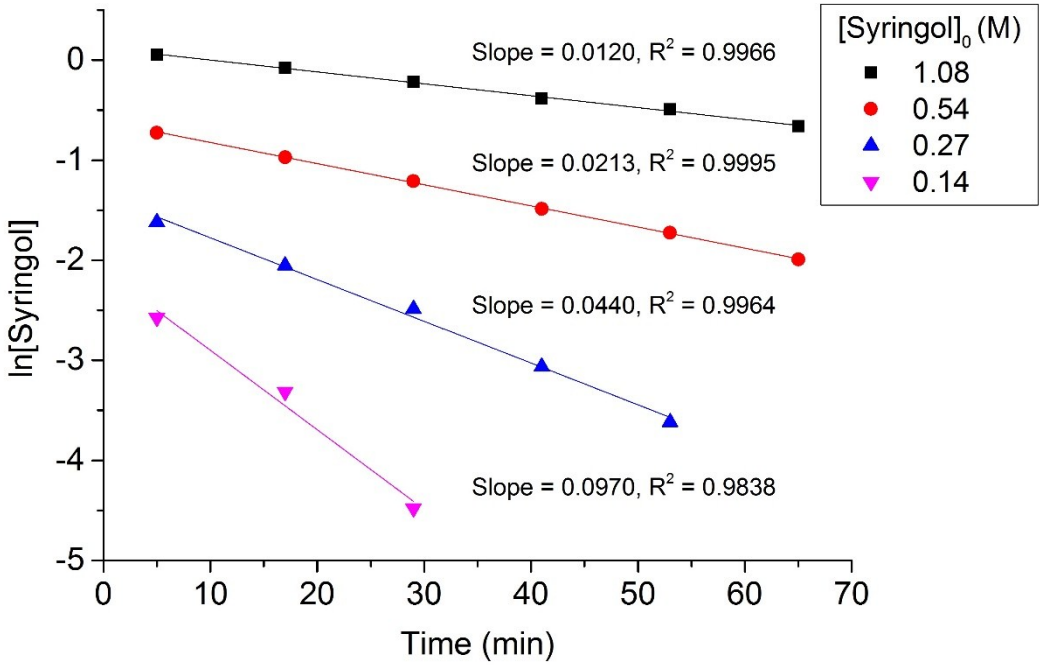


Figure S27. Plot of the natural logarithm of syringol concentration *vs* time from the catalytic oxidation of syringol by $Co/Br^-/H_2O_2$ with different initial concentrations of syringol (1 h of peroxide addition). The pseudo-first order rate constant for syringol conversion is derived from the slope of ln[syringol] *vs* time. The data points plotted are for the initial part of the reaction. When the syringol concentration decreases below 10% of its starting value the plots deviate from linear behaviour.

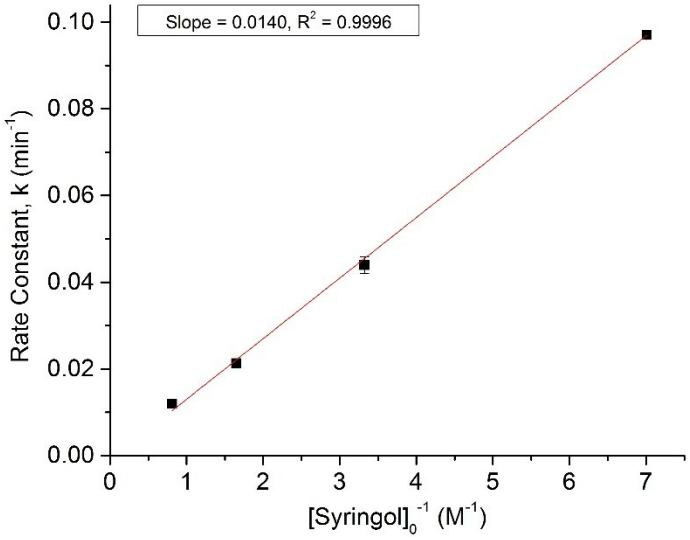


Figure S28. Plot of the pseudo-first order rate constants for syringol conversion *vs* the inverse initial syringol concentration.

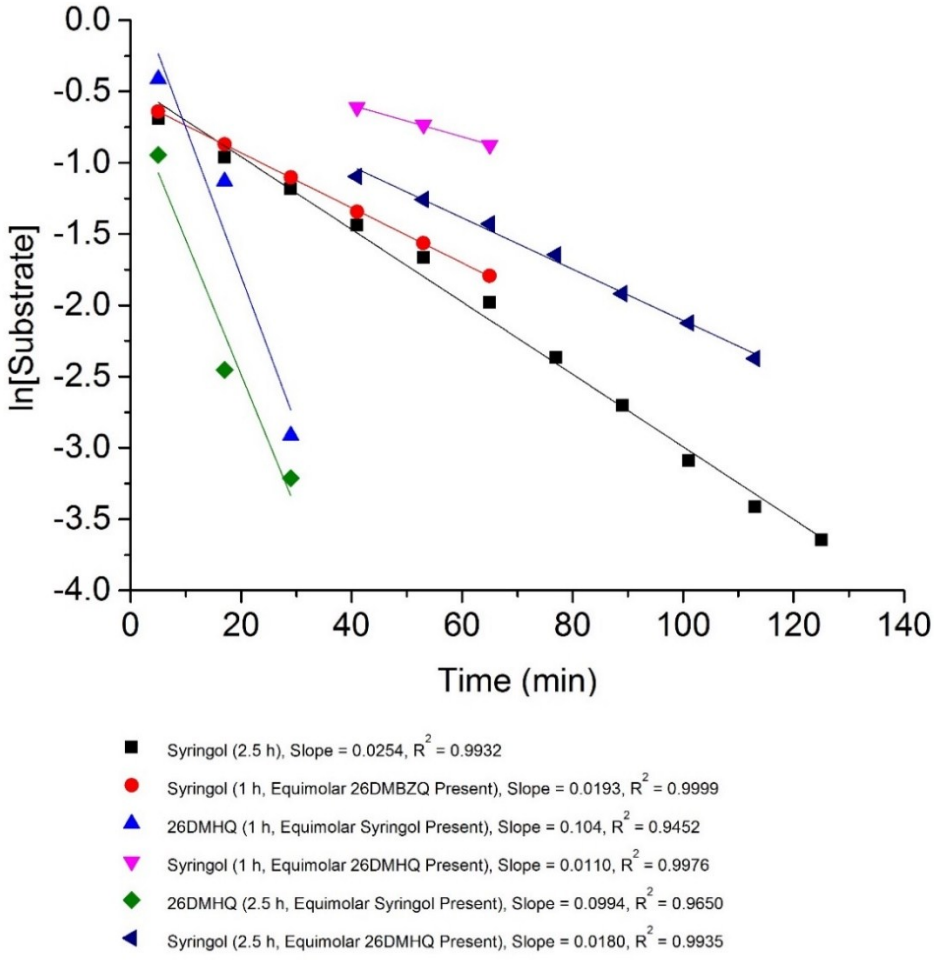


Figure S29. Plot of the natural logarithm of substrate *vs* time for reactions involving syringol in the presence of equimolar 2,6DMBZQ or 2,6DMHQ. Rate constants (slopes) were extracted from applying linear regression to the data points. The plotted data represents either the time during peroxide addition or until the reaction had gone to completion.

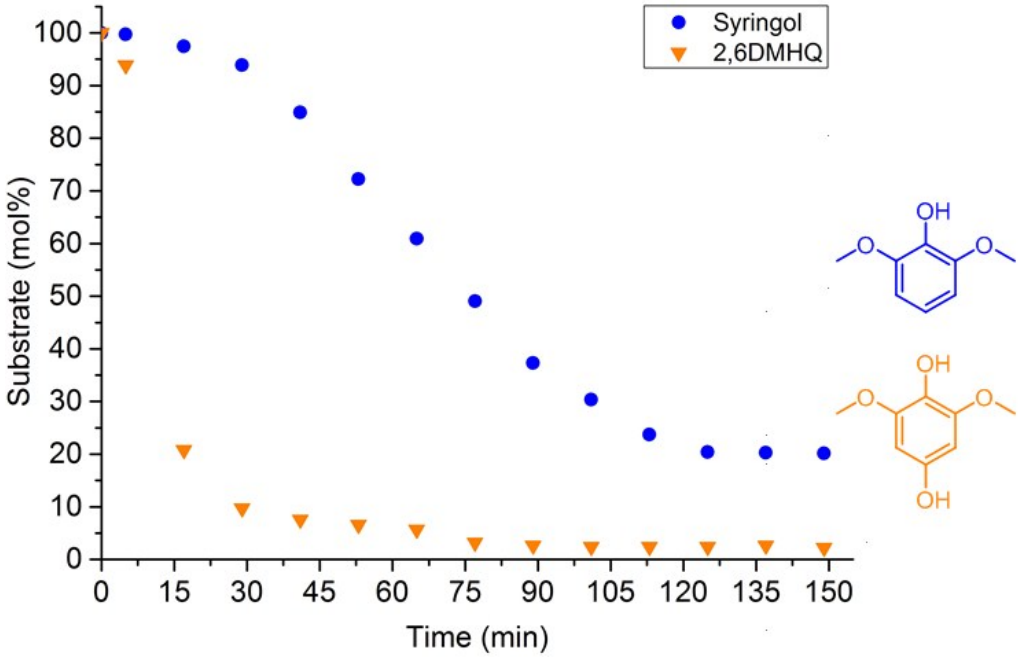


Figure S30. Time course profile of the catalytic oxidation of equimolar syringol and 2,6DMHQ over 2.5 h.

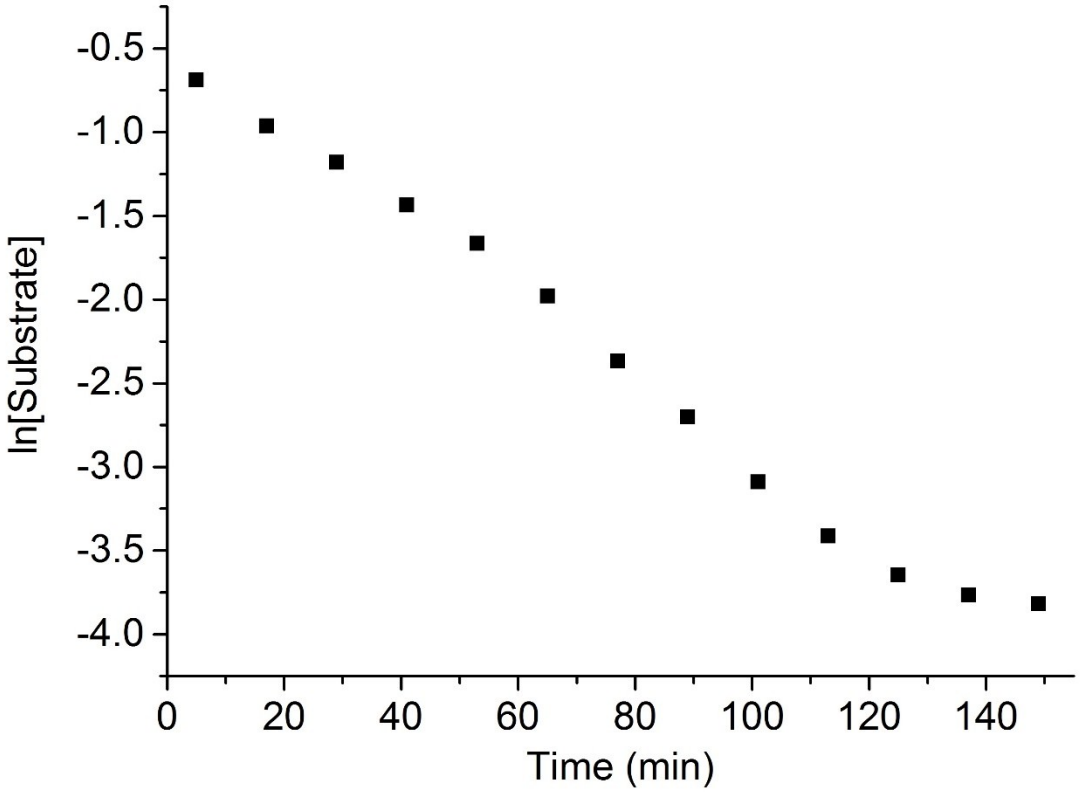


Figure S31. Plot of the natural logarithm of substrate *vs* time for the catalytic oxidation of syringol over 2.5 h. The reaction profile of the substrate *vs* time is plotted in Fig. S23.

Figure S32. GC-MS chromatogram of the sample taken at 65 minutes of the catalytic oxidation of 2,6DMBZQ. Unlabelled peaks correspond to species attributed to either the solvent or the silica column.

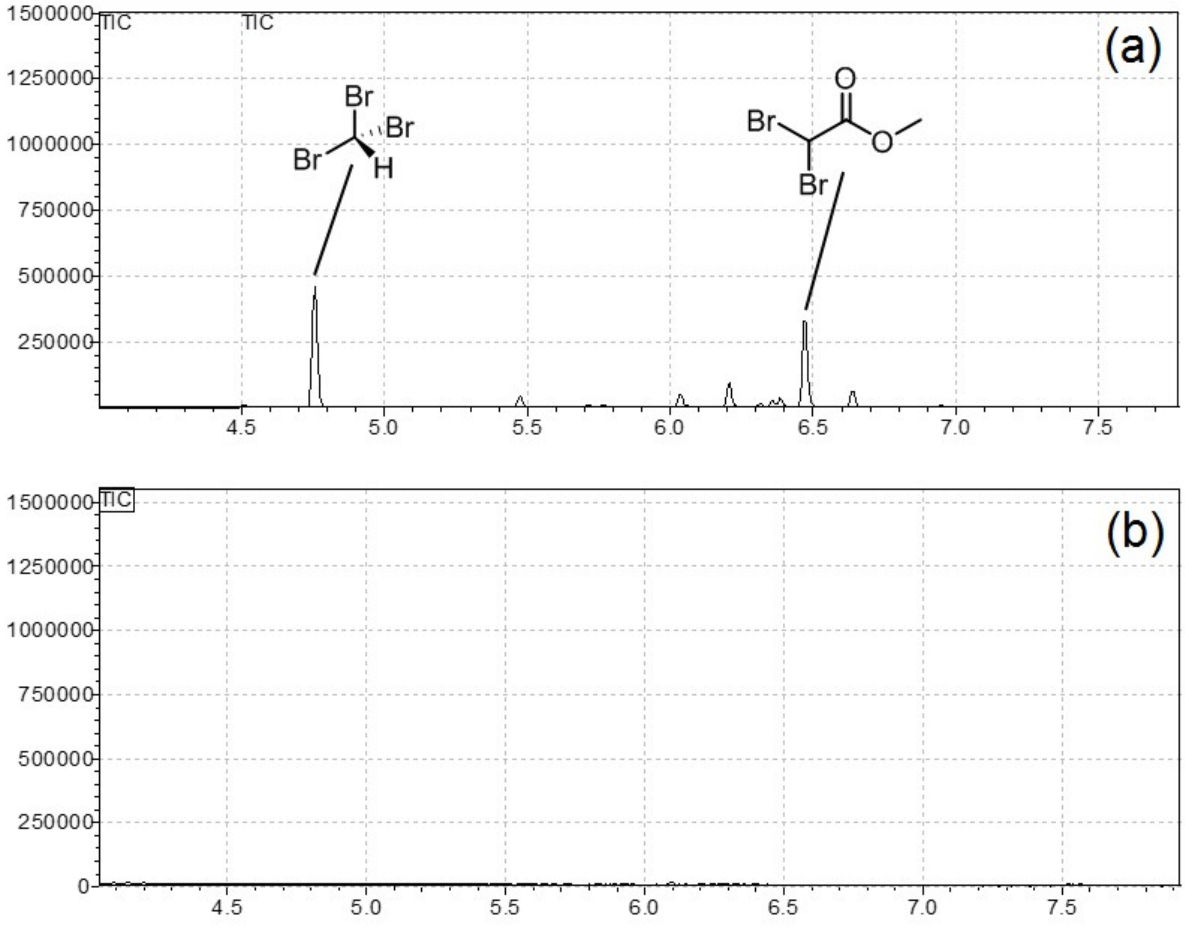


Figure S33. (a) GC-MS chromatogram of the sample taken at 65 minutes of the catalytic oxidation of coerulignone **(b)** and a blank reaction (no substrate). Unlabelled peaks correspond to species attributed to either the solvent or the silica column.

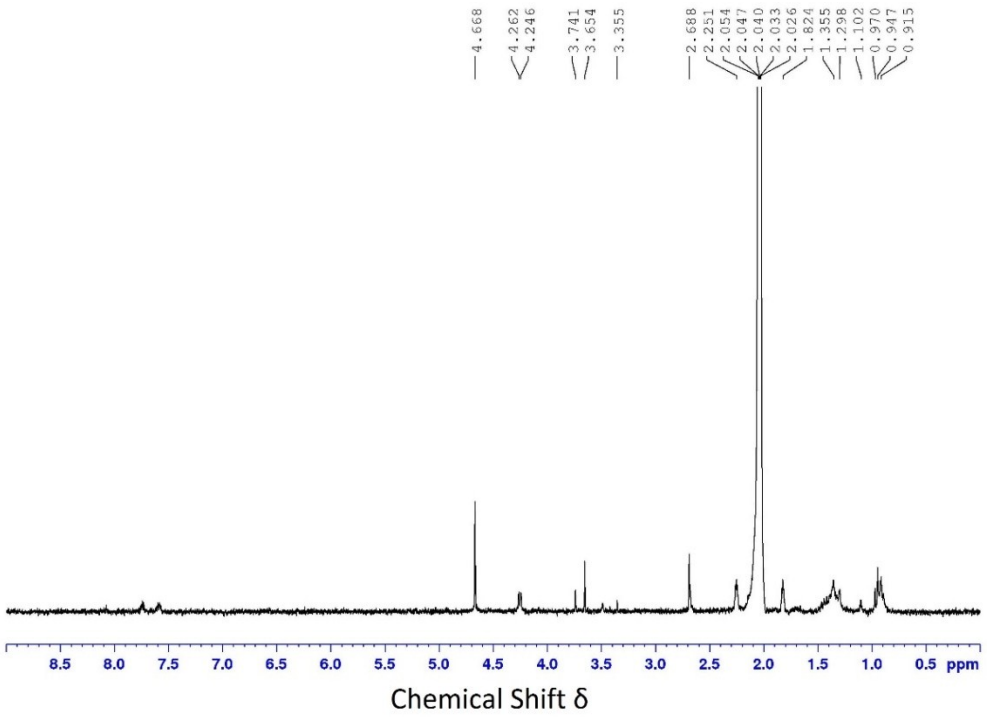


Figure S34. ^{1}H NMR spectrum of acetic acid-d_4 solvent. The residual solvent signal is centred on δ 2.04 ppm (C-D_3 quintent).

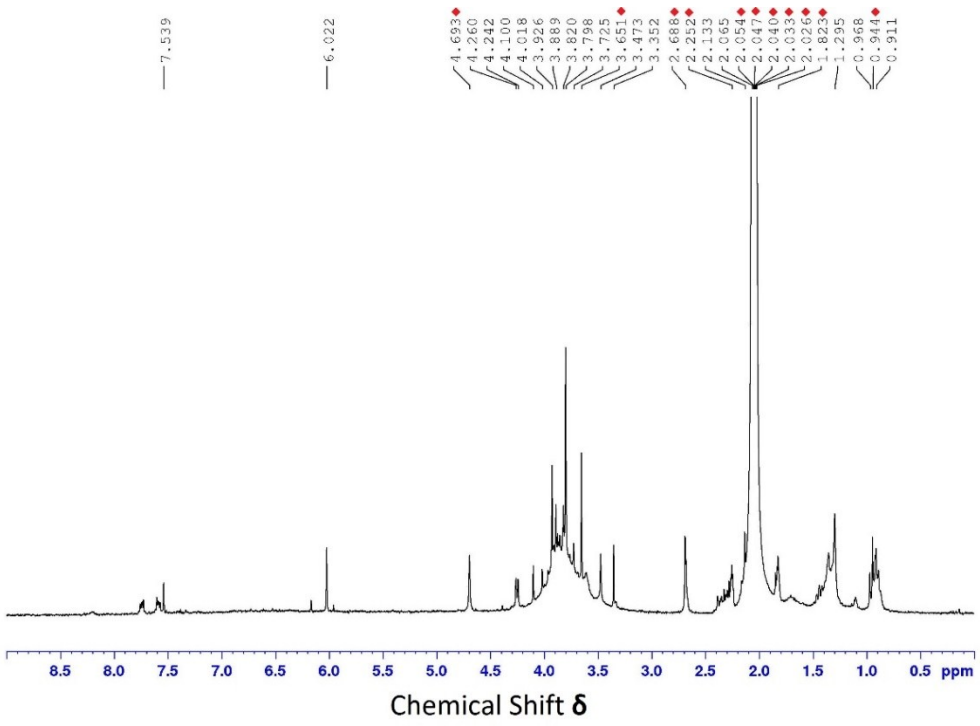


Figure S35. ^{1}H NMR spectrum in acetic acid-d_4 solvent of the residue collected from the catalytic oxidation of coerulignone. Signals identified from the NMR solvent (Fig. S32) are denoted with red diamonds. Compared to the neat NMR solvent, a collection of new signals are observed between δ 3 and 4.5 ppm indicative of Ar-O**H**, RCO_2-C**H**, Br-C**H** and Ar-O-C**H** environments. The signal at δ 6.022 ppm is potentially attributable to Ar-O**H** or Ar-**H**, and the signal at δ 7.539 ppm is potentially attributable to Ar-**H**.

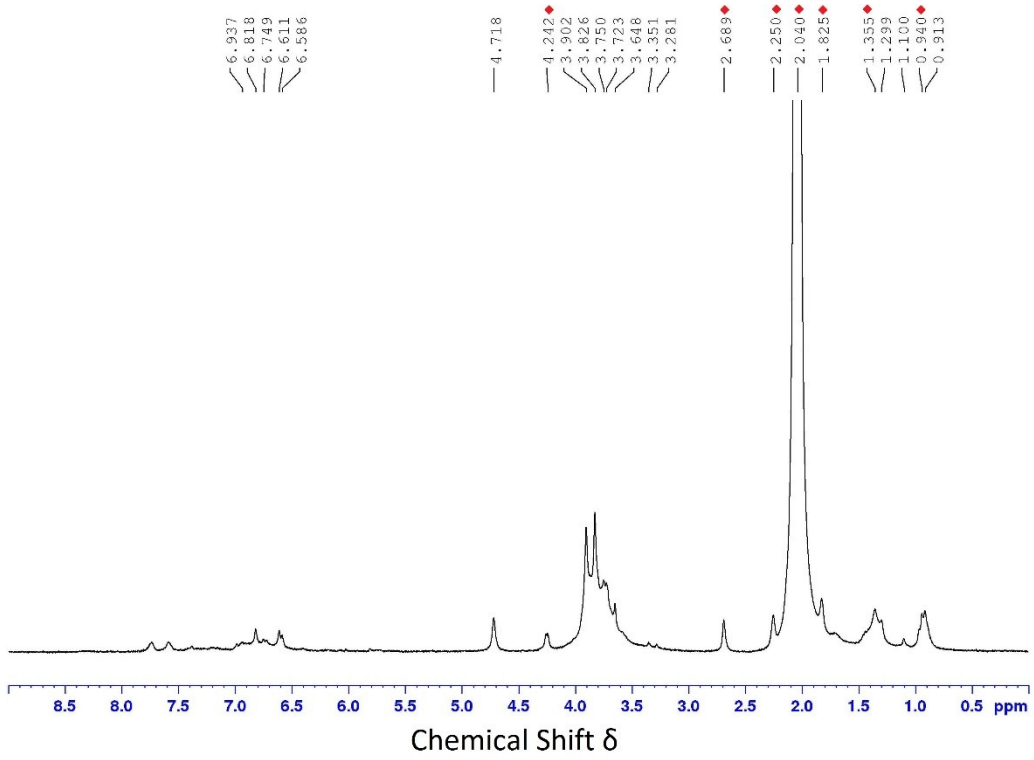


Figure S36. ^{1}H NMR spectrum in acetic acid-d4 solvent of the residue collected from the catalytic oxidation of syringol. Signals identified from the NMR solvent (Fig. S32) are denoted with red diamonds. Similar to the coerulignone residue, a collection of new signals are observed between δ 3 and 4.5 ppm indicative of Ar-O**H**, RCO_2-C**H**, Br-C**H** and Ar-O-C**H** environments. Compared to the coerulignone residue, an additional group of signals was observed between δ 6.5 and 7 ppm attributable to Ar-**H**.

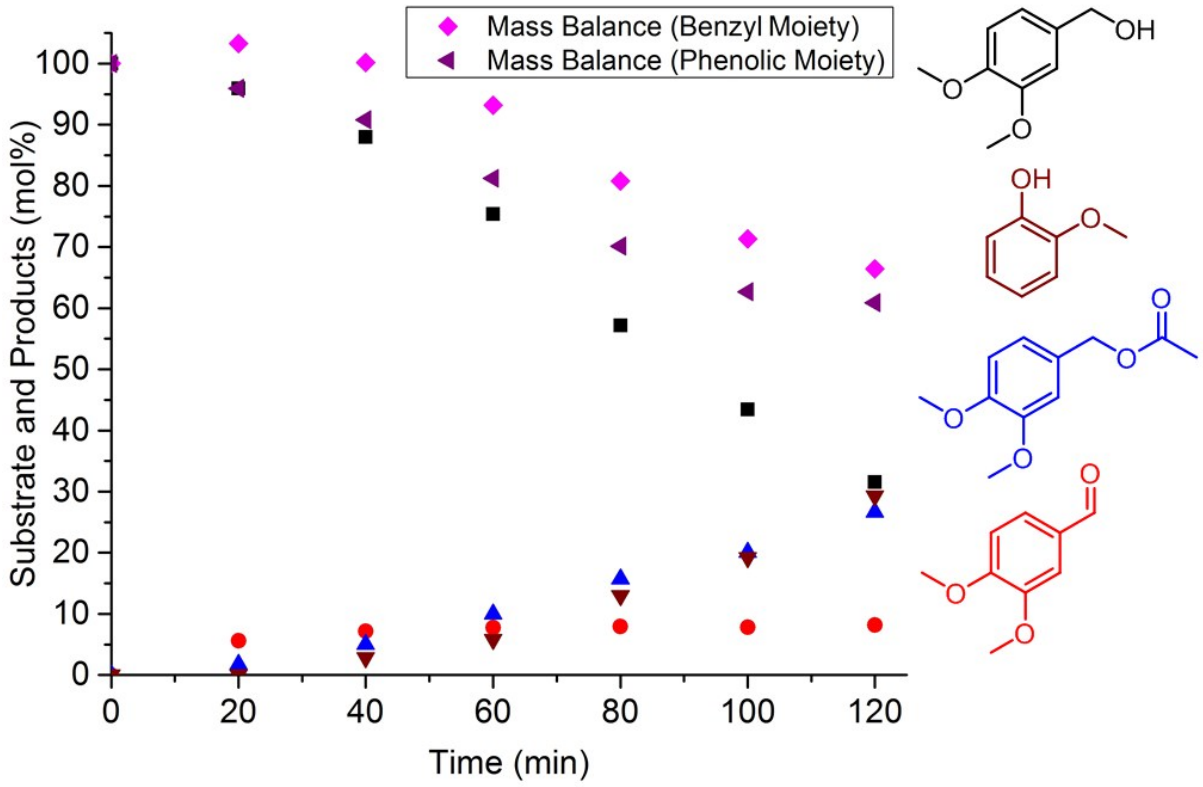


Figure S37. Time-course profile of the catalytic oxidation of A3 with substitution of bromide with equimolar NHPI.

Table S1. Comparison of substrate conversion, product yields and mass balances of the catalytic oxidation of A3 in the presence of either Br^- or NHPI as co-catalyst.

	Substrate	Products (yield mol%, selectivity %)			Mass Balance (mol%)	
Co-Catalyst	Conversion (mol%)	3,4-Dimethoxy Benzaldehyde	3,4-Dimethoxy Benzylacetate	Guaiacol	Benzyl Moiety	Phenolic Moiety
Br^-	47	1.2, 2.4	23, 49	6.1, 13	77	59
NHPI	68	8.2, 12	27, 39	29, 43	66	61

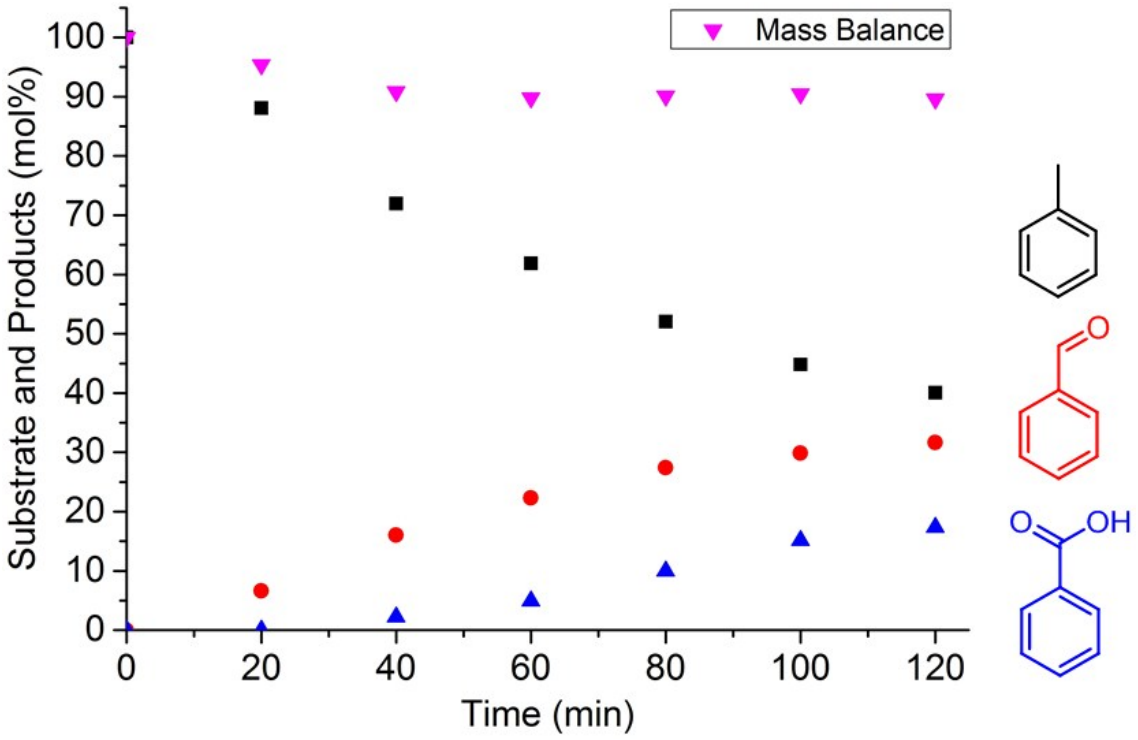


Figure S38. Time course profile of the catalytic oxidation of toluene with bromide as the co-catalyst. Small amounts of benzyl bromide and benzyl acetate were also detected (< 1%).

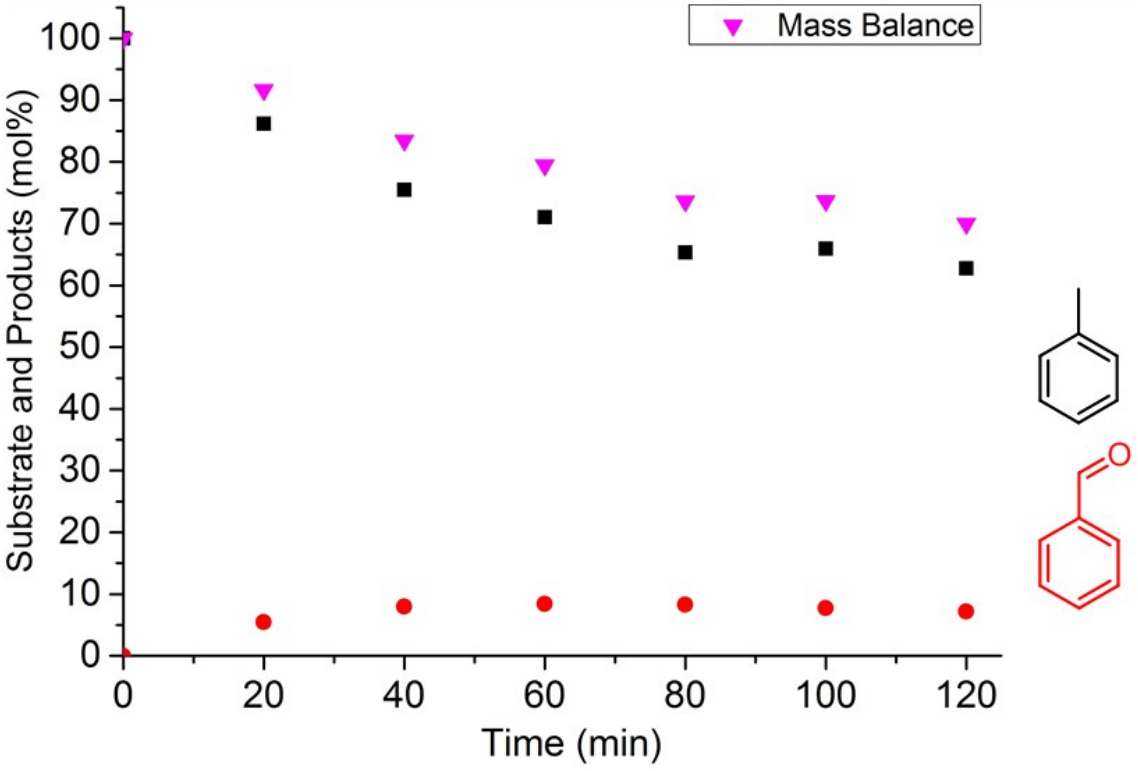


Figure S39. Time-course profile of the catalytic oxidation of toluene with replacement of bromide with equimolar NHPI. Benzoic acid could not be quantified for this time-course.

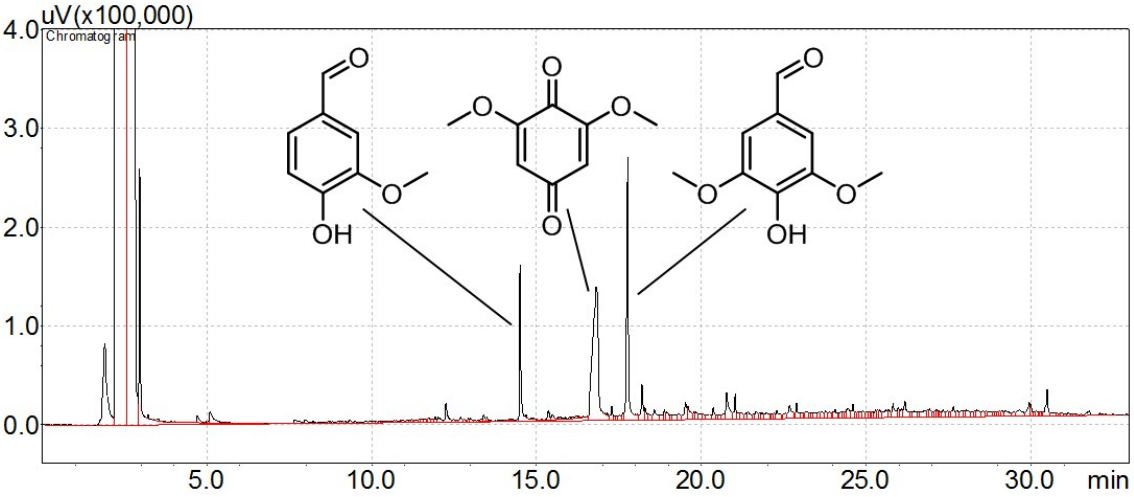


Figure 40. GC-FID chromatogram of the organic extract from the catalytic oxidation of Organosolv lignin with $Co/Br^{-}/H_2O_2$. The peak at ~ 2.5 min is the solvent front. Only the major products are labelled.

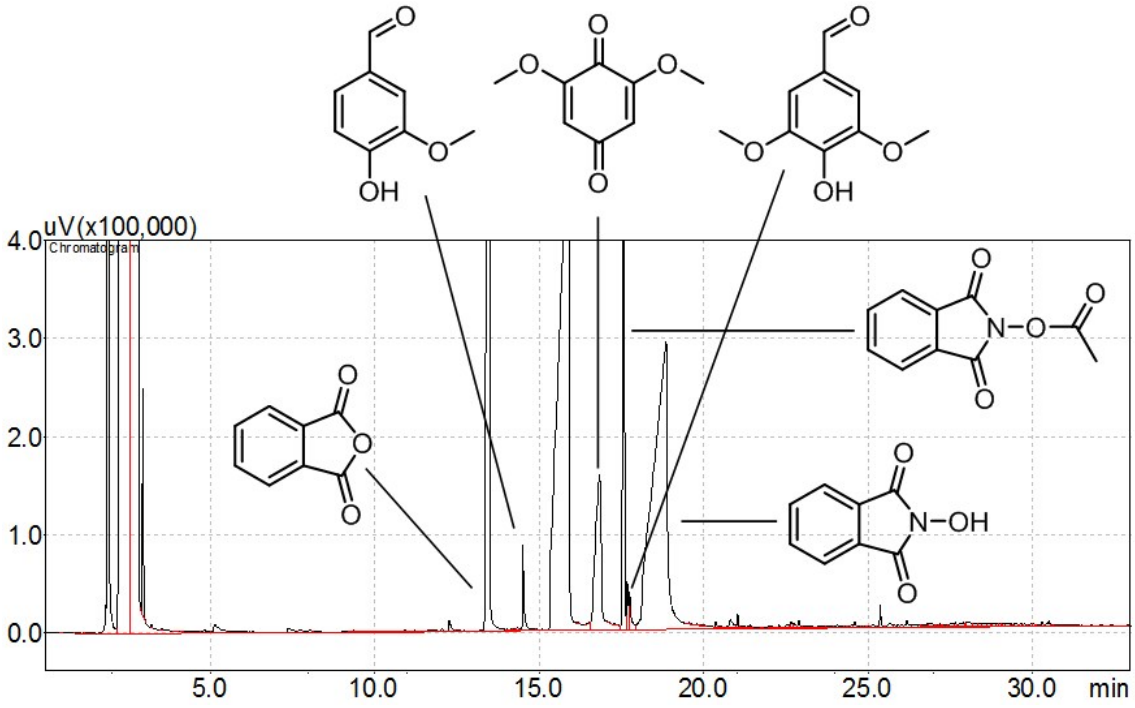


Figure 41. GC-FID chromatogram of the organic extract from the catalytic oxidation of Organosolv lignin with $Co/NHPI/H_2O_2$. The peak at ~ 2.5 min is the solvent front. Only the major products are labelled. The amount of phthalic anhydride present in the sample equates to approximately 20 wt% of the NHPI co-catalyst.

A. R. Gonçalves and U. Schuchardt, *Appl. Biochem. Biotechnol.*, 1999, 77, 127-132.

The results are for the oxidation of eucalyptus acetosolv lignin in the open system due to the similarity to the open system setup used in this work. In addition, eucalyptus is a hardwood similar to the source timber of the organosolv lignin used in in this work.

Table S2. Catalyst and solvent loading.

Catalyst	**Ratio (mol/mol)**	**mmols**	**Mass of Catalyst (g)**	**Catalyst Concentration (mM)**	**Solvent**	**Volume (L)**
Co	1	4.5	0.265	62	Acetic Acid	0.05
Mn	0.11	0.5	0.027	6.9	Acetic Anhydride	0.011
Br^-	0.55	2.5	0.198	34	Paraldehyde	0.011
Total		–	0.491	–	–	0.072

Oxidant = molecular oxygen. Temperature = 110 °C. Pressure = atmospheric. Time = 10 h.

Lignin (g) = 5.5
Lignin Loading (wt% of solvent) = 6.8
Lignin to Total Catalyst Ratio (wt/wt) = 11
Lignin to Metal Catalyst Ratio (wt/wt) = 19

Yield of Vanillin (wt% of initial lignin) = 1.1*

*Originally reported as combined mmols of vanillin and vanillic acid. This was converted to wt% of initial lignin using the molecular weight of vanillin for comparison to other results.

W. Partenheimer, *Adv. Synth. Catal.*, 2009, 351, 456-466.

The results are the highest reported yields for the oxidation of organosolv lignin, table 5, entry 1. The catalyst concentration was reported, but the solvent/reaction volume and mass of lignin in grams were not.

Table S3. Catalyst and solvent loading.

Catalyst	**Ratio (mol/mol)**	**Catalyst Concentration (mM)**	**Solvent**
Co	1	6.9	Acetic Acid
Mn	1	6.9	Water (8 wt%)
Zr	0.1	0.69	–
Br^-	2	13.8	–
Total		–	–

Oxidant = air. Temperature = 180 °C. Pressure = 138 bar. Time = 2 h.

Lignin Loading (wt% of solvent) = 8

Yield of Vanillin (wt% of initial lignin) = 0.99
Yield of Syringaldehyde (wt% of initial lignin) = 2.52

This work.

Table S4. Catalyst loading.

Catalyst	**Ratio (mol/mol)**	**mmols**	**Mass of Catalyst (g)**	**Catalyst Concentration (mM)**	**Solvent***	**Volume (L)**
Co	1	0.48	0.12	24	Acetic Acid	0.02
Br^-	4	2	0.238	100	–	–
Total		–	0.358	–	–	0.02

Oxidant = H_2O_2. Temperature = 70 °C. Pressure = atmospheric. Time = 2 h.

*Water is being continuously added to the reaction during the addition of hydrogen peroxide. After 1 h of reaction water constitutes 7.7 wt % of the solvent and after 2 h of reaction water constitutes 13 wt% of the solvent.

Lignin (g) = 1.67
Lignin Loading (wt% of solvent) = 7.4
Lignin to Total Catalyst Ratio (wt/wt) = 8.9
Lignin to Metal Catalyst Ratio (wt/wt) = 59

Yield of Vanillin (wt% of initial lignin) = 0.21
Yield of Syringaldehyde (wt% of initial lignin) = 0.54