Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary information for

Acid promoted C–C bond oxidative cleavage of β-O-4 and β-1 lignin models to esters over copper catalyst

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1. Detection of reaction gas phase product

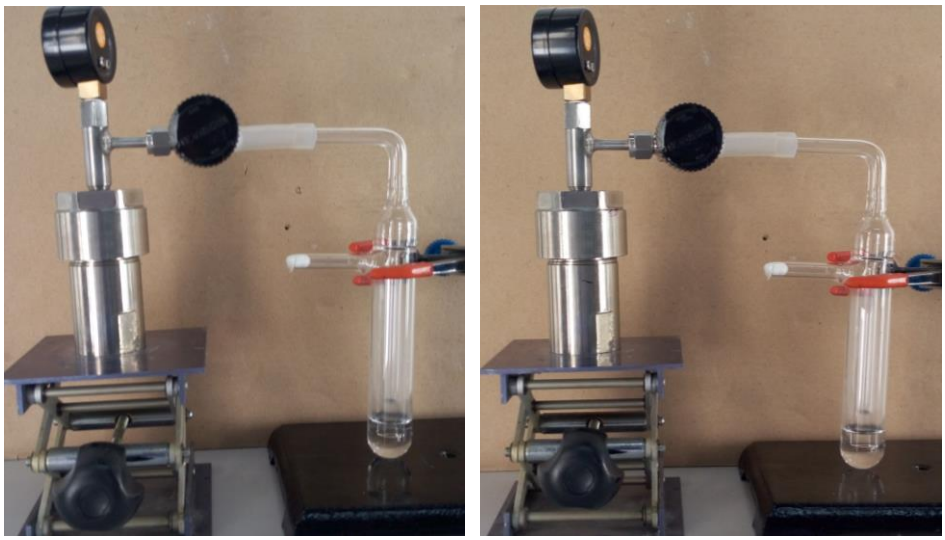


Fig. S1. Limewater images before (left) and after (right) introduction of the reaction gas phase. The limewater was not cloudy, indicating that the reaction gas phase nearly contains no CO_2.

2. GC detection of the liquid phase product

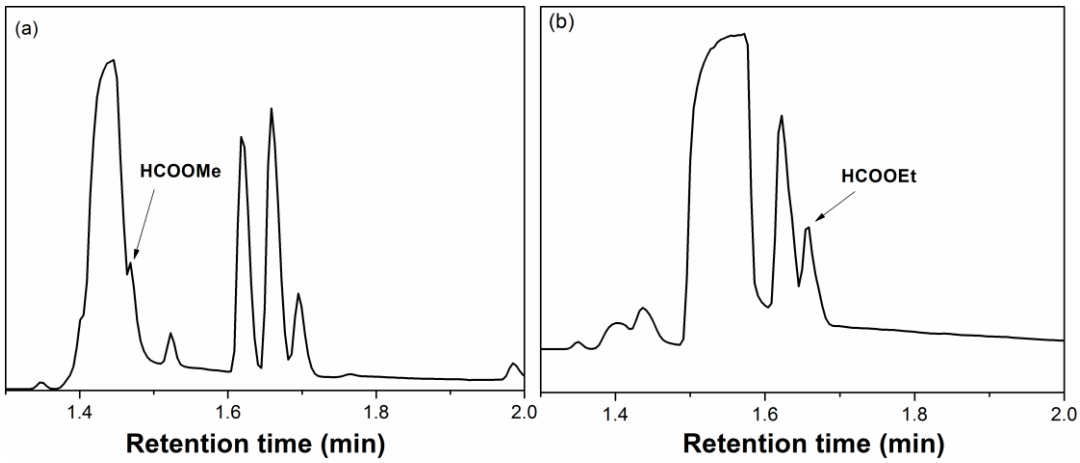
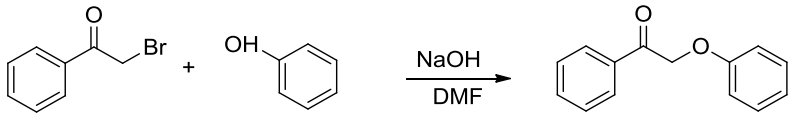


Fig. S2. GC spectra of the oxidation of lignin model 2 in methanol (a) and ethanol (b).

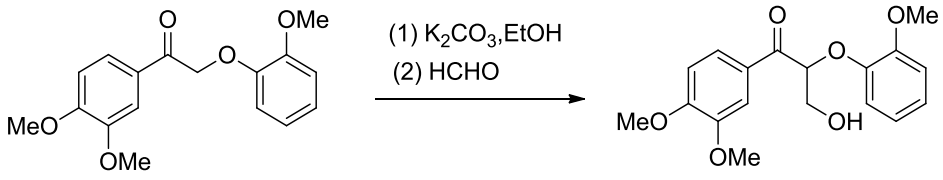
3. Synthesis of model compounds and detailed NMR characterization

Procedure for preparation of 2-phenoxy-1-phenylethanone



2-Phenoxy-1-phenylethanone was prepared by the literature procedures.[1] A 350 mL pressure bottle was charged with phenol (6.9 g, 73 mmol) and K_2CO_3 (10.4 g, 75 mmol) in acetone (150 mL) in Ar atmosphere and stirred at RT for 30 min. To this solution, 2-bromoacetophenone (14.0 g, 70 mmol) was added, the resulting suspension was stirred at RT for 16 h, after which the suspension was filtered and concentrated *in cacuo*. The solid was dissolved in ethyl acetate and washed with NaOH aqueous (5%, 30 ml) and water (30 ml). The organic phase was dried over anhydrous Na_2SO_4. The crude product was recrystallized from ethanol to give 2-phenoxy-1-phenylethanone as a white solid in 87% yield. Spectral data were in accordance with those previously reported. For the other methoxyl substituted 2-phenoxy-1-phenylethanone, the preparation procedure is the same as described above, except that using different stating materials.

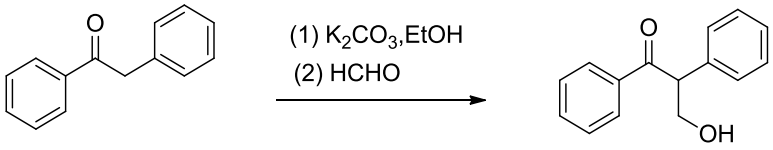
Procedure for preparation of 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one



1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one was prepared by the literature procedures.[1] To a stirring suspension of K_2CO_3 (0.6 g, 4.3 mmol) and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone (1.2 g, 4 mmol) in ethanol: acetone (v/v = 1:1, 20 mL), a water solution of formaldehyde (36.5-38%) (0.6 mL, 7.3 mmol) was added at room temperature. After 4 h the reaction mixture

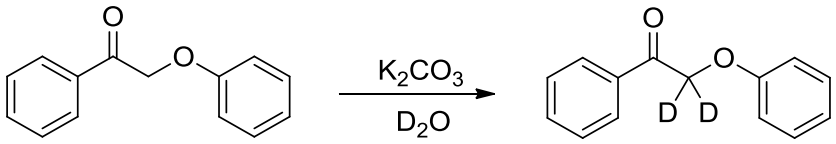
was concentrated *in vacuo* to get a solid product. The solid was purified by column chromatography (pentane/ethyl acetate, 1:1) to yield 1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one as a pale yellow solid (1.19 g, 3.6 mmol) in 90% yield. ^{1}H NMR (400 MHz, CD_3CN) δ = 7.75 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.04 – 6.89 (m, 3H), 6.89 – 6.73 (m, 2H), 5.56 (dd, *J* = 5.5, 4.3 Hz, 1H), 3.99 (td, *J* = 6.0, 3.3 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H), 3.72 (q, *J* = 5.9 Hz, 1H), 3.23 (dd, *J*=7.9, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ = 195.86, 154.61, 150.46, 149.73, 147.68, 128.88, 123.96, 122.89, 121.30, 117.90, 116.26, 113.28, 111.50, 111.31, 82.55, 63.63, 56.22, 56.01, 55.98.

Procedure for preparation of 3-hydroxy-1,2-diphenylpropan-1-one



3-hydroxy-1,2-diphenylpropan-1-one was prepared as follows: To a stirring suspension of K_2CO_3 (0.6 g, 4.3 mmol) and 1,2-diphenylethanone (0.78 g, 4 mmol) in ethanol: acetone (v/v = 1:1, 20 mL), a water solution of formaldehyde (36.5-38%) (0.6 mL, 7.3 mmol) was added at room temperature. After 4 h the reaction mixture was concentrated *in vacuo* to get a solid product. The solid was purified by column chromatography (pentane/ethyl acetate, 1:1) to yield 3-hydroxy-1,2-diphenylpropan-1-one. ^{1}H NMR (400 MHz, CD_3CN) δ = 7.97 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.58 – 7.49 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.18 (m, 5H), 4.88 (dd, *J* = 8.0, 5.6 Hz, 1H), 4.20 (ddd, *J* = 10.7, 8.0, 6.0 Hz, 1H), 3.83 – 3.72 (m, 1H), 2.92 (t, *J* = 6.0 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ = 199.91, 137.64, 137.42, 133.74, 129.49, 129.26, 129.15, 129.09, 127.93, 64.66, 56.37.

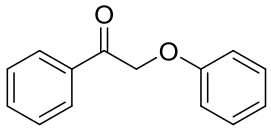
Procedure for synthesis of synthesis of the deuterated compounds



2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone (0.50 g 9.19 mmol) was added to a vial with anhydrous K_2CO_3 (0.126 g, 0.92 mmol) and 5 mL of D_2O. The vial was caped. The reaction ran at 100 ℃ for 24 h. The D_2O was decanted and replaced by fresh one. The reaction was maintained for additional 24 h at 100 ℃. Then the solid was washed to remove the K_2CO_3 residues. Finally, the solid was dried under vacuum to give deuterated compounds as a light yellow solid in 95% yield.

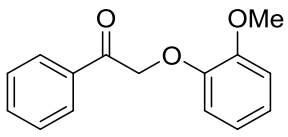
(1) Dawange, M.; Galkin, M. V.; Samec, J. S. M. *ChemCatChem* **2015**, *7*, 401-404.

2-phenoxy-1-phenylethanone



Prepared from 2-bromoacetophenone and phenol in 87% yield. White solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.08 – 8.00 (m, 2H), 7.73 – 7.64 (m, 1H), 7.56 (dd, *J* = 10.6 Hz, 4.8, 2H), 7.39 – 7.29 (m, 2H), 7.08 – 6.94 (m, 3H), 5.35 (s, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 194.29, 158.12, 134.68, 133.80, 129.54, 128.83, 127.94, 121.47, 114.64, 70.61.

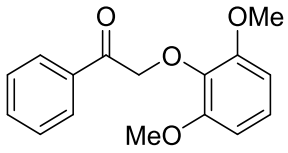
2-(2-methoxyphenoxy)-1-phenylethanone



Prepared from 2-bromoacetophenone and guaiacol in 71% yield. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 – 7.97 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.02 – 6.82 (m, 4H), 5.34 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz,

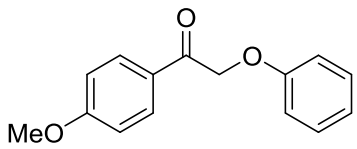
$CDCl_3$) δ = 194.59, 149.86, 147.57, 134.69, 133.74, 128.79, 128.12, 122.52, 120.81, 115.02, 112.27, 72.19, 55.93.

2-(2,6-dimethoxyphenoxy)-1-phenylethanone



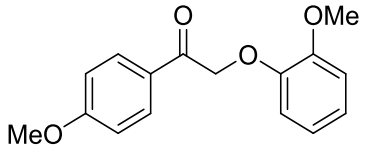
Prepared from 2-bromoacetophenone and 2,6-dimethoxyphenol in 43% yield. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.00 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 5.19 (s, 2H), 3.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.19, 153.20, 136.73, 135.24, 133.25, 128.54, 128.36, 124.06, 105.38, 75.44, 56.08.

1-(4-methoxyphenyl)-2-phenoxyethanone



Prepared from 2-bromo-1-(4-methoxyphenyl)ethanone and phenol in 83% yield. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.8 Hz, 2H), 7.27 (dd, *J* = 13.0 Hz, 4.4, 2H), 7.02 – 6.90 (m, 5H), 5.20 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.13, 164.06, 158.13, 130.58, 129.56, 127.70, 121.57, 114.82, 114.02, 70.76, 55.53.

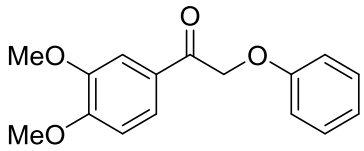
2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone



Prepared from 2-bromo-1-(4-methoxyphenyl)ethanone and guaiacol in 88% yield. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 – 7.96 (m, 2H), 7.00 – 6.81 (m,

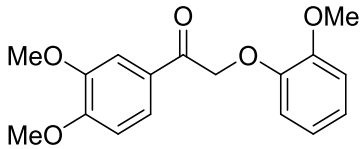
6H), 5.27 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.15, 163.97, 149.78, 147.67, 130.52, 127.75, 122.34, 120.81, 114.79, 113.96, 112.22, 72.02, 55.93, 55.51.

1-(3,4-dimethoxyphenyl)-2-phenoxyethanone



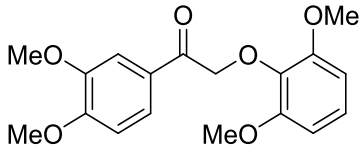
Prepared from 2-bromo-1-(3,4-dimethoxyphenyl)ethanone and phenol in 85% yield. Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (dd, *J* = 8.4 Hz, 1.9, 1H), 7.56 (d, *J* = 1.9 Hz, 1H), 7.35 – 7.23 (m, 2H), 7.03 – 6.86 (m, 4H), 5.21 (s, 2H), 3.93 (d, *J* = 8.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.18, 158.13, 153.93, 149.30, 129.57, 127.81, 122.86, 121.58, 114.82, 110.41, 110.19, 70.73, 56.03.

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



Prepared from 2-bromo-1-(3,4-dimethoxyphenyl)ethanone and guaiacol in 92% yield. Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (dd, *J* = 8.4 Hz, 1.9, 1H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.02 – 6.82 (m, 5H), 5.29 (s, 2H), 3.98 – 3.86 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.30, 149.76, 149.23, 147.63, 127.89, 122.80, 122.37, 120.83, 114.76, 112.20, 110.50, 110.16, 72.08, 56.11, 56.01, 55.92.

2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanone

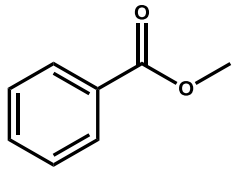


Prepared from 2-bromo-1-(3,4-dimethoxyphenyl)ethanone and 2,6-dimethoxyphenol in 93% yield. Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (dd, *J* = 8.4

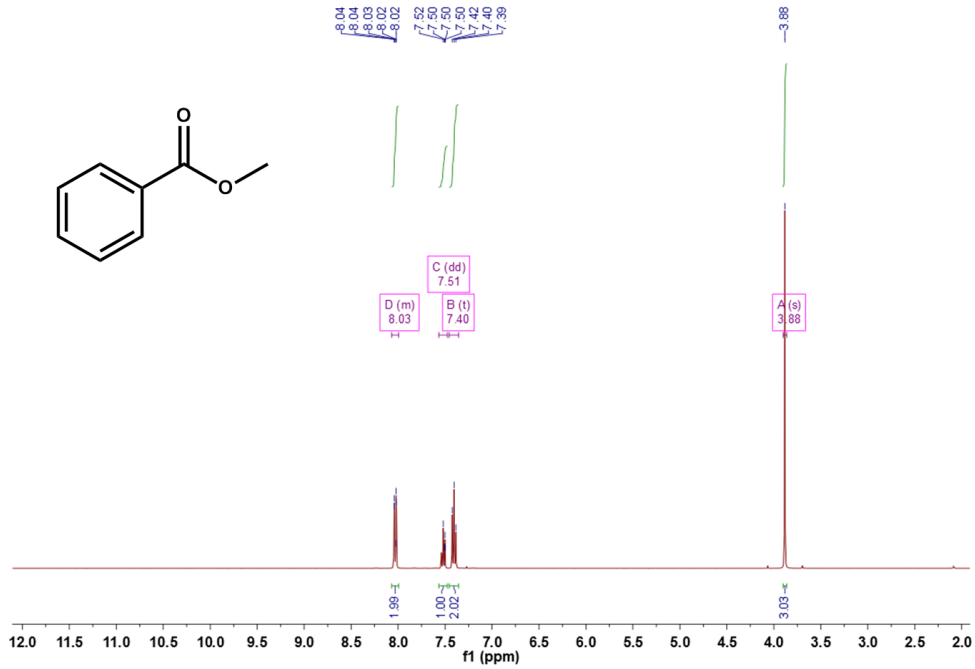
Hz, 1.9, 1H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.01 (t, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 5.15 (s, 2H), 3.94 (s, 6H), 3.81 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.71, 153.42, 153.27, 149.01, 136.72, 128.42, 124.06, 123.08, 110.72, 110.08, 105.38, 75.30, 56.09.

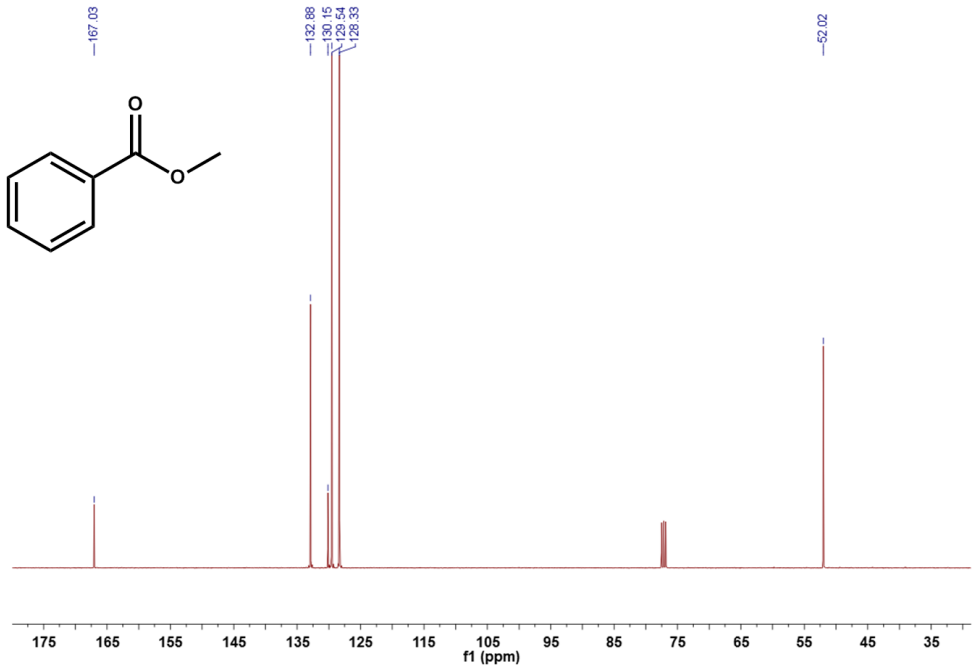
4. NMR spectra of the product

Methyl benzoate

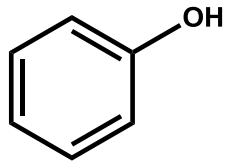


^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (m, 2H), 7.51 (dd, J=5.0, 3.7, 1H), 7.40 (t, J=7.7, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.03, 132.88, 130.15, 129.54, 128.33, 52.02.

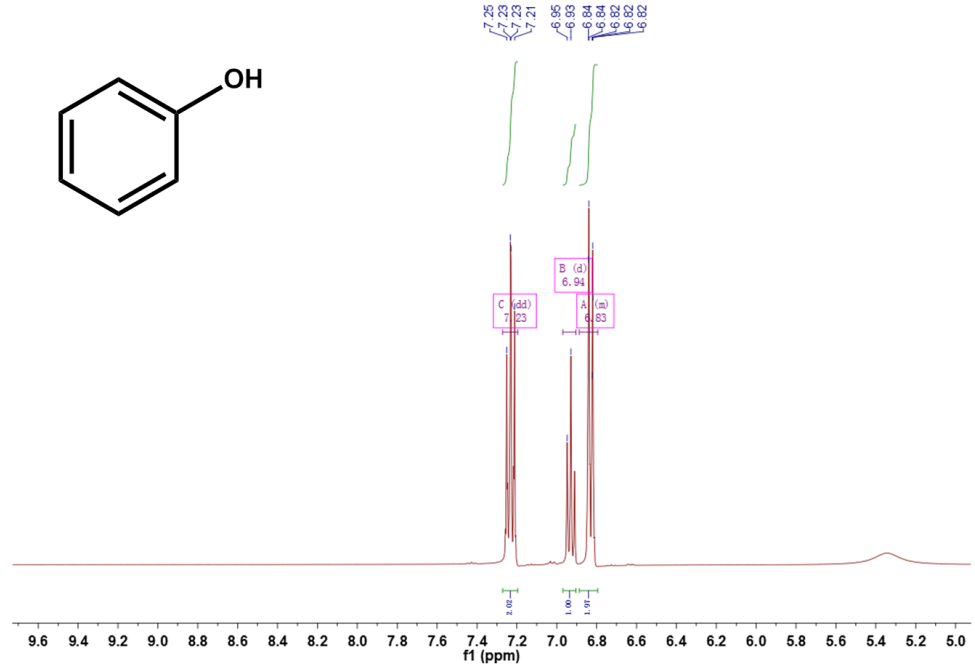


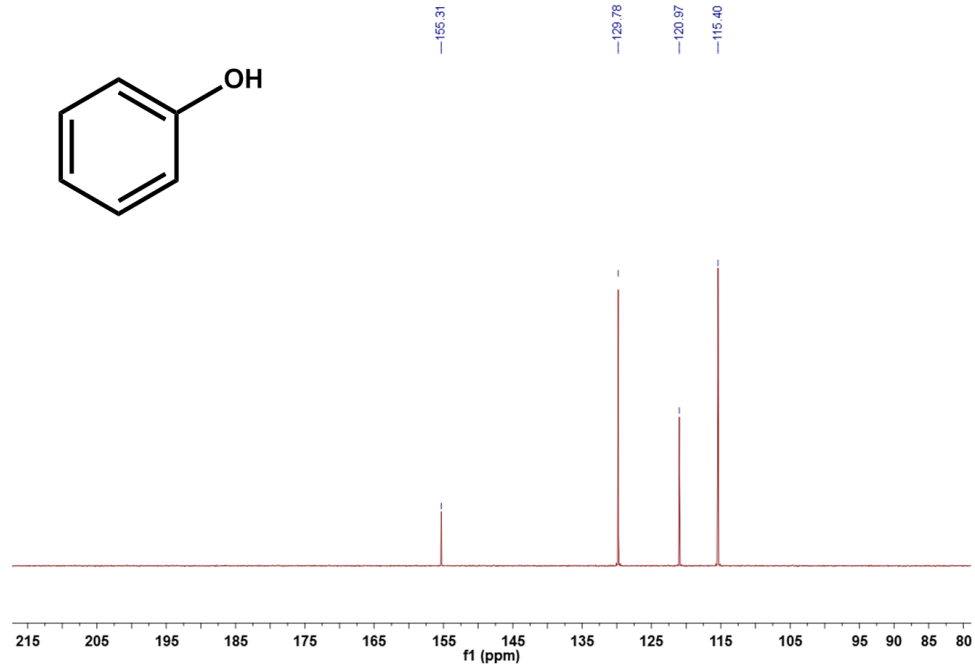


Phenol

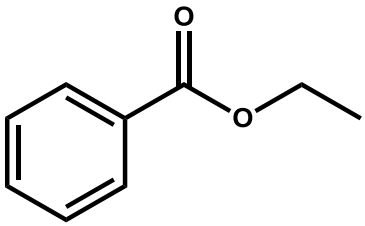


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (dd, *J*=8.5, 7.5, 2H), 6.94 (d, *J*=7.4, 1H), 6.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.31, 129.78, 120.97, 115.40.

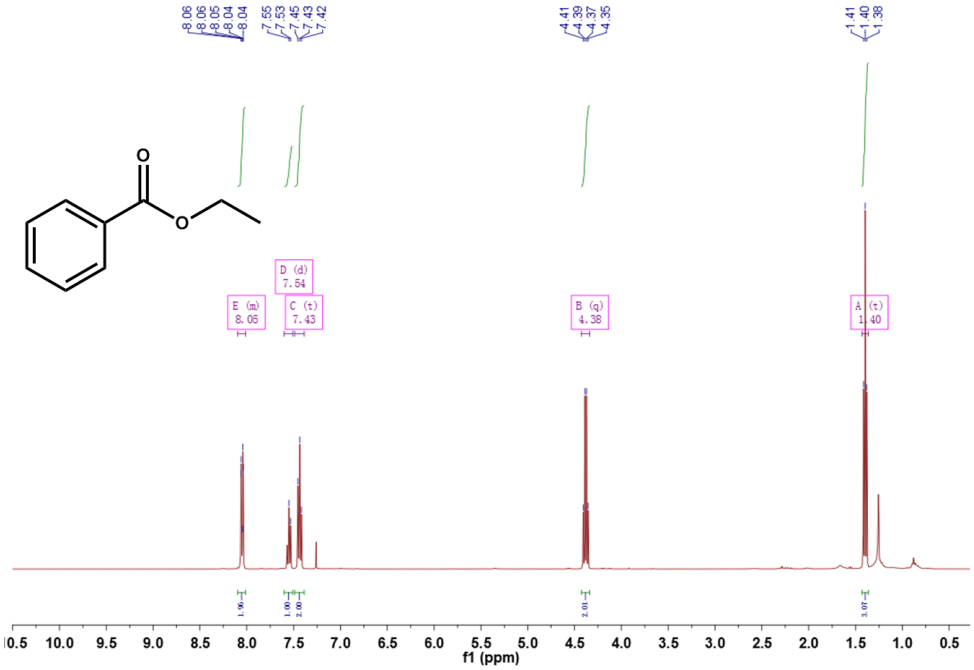


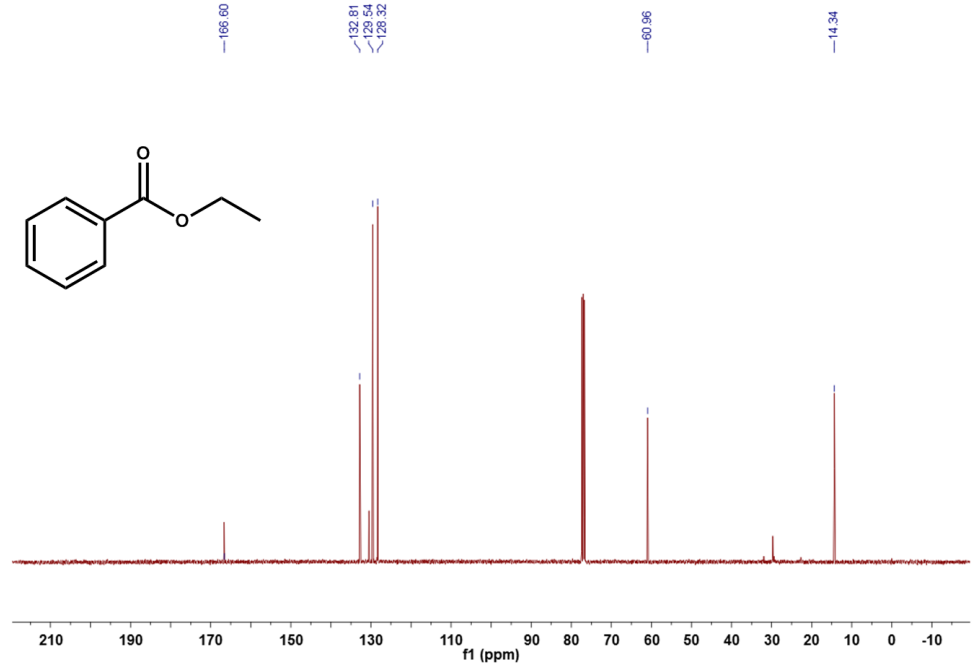


Ethyl benzoate

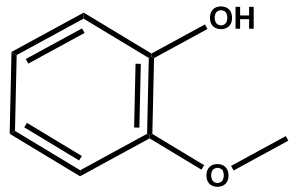


^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (m, 2H), 7.54 (d, *J*=7.4, 1H), 7.43 (t, *J*=7.6, 2H), 4.38 (q, *J*=7.1, 2H), 1.40 (t, *J*=7.1, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.60, 132.81, 129.54, 128.32, 60.96, 14.34.

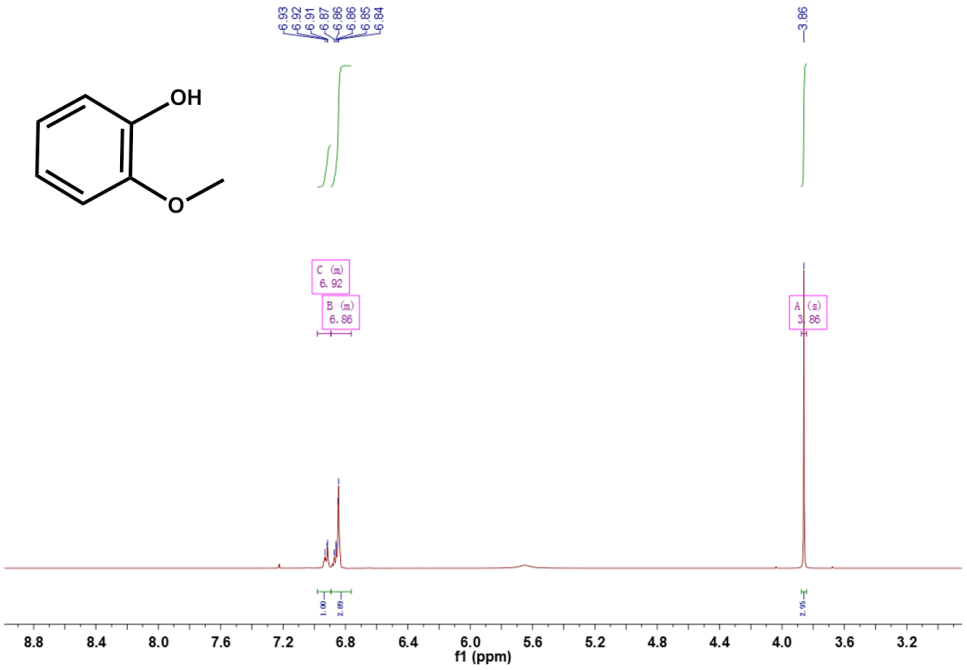


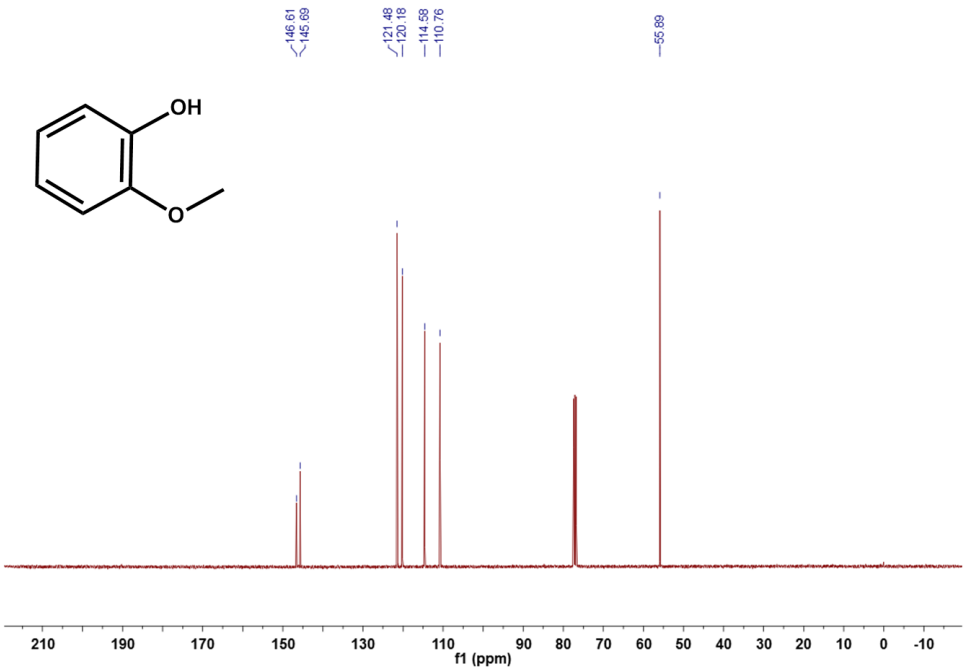


Guaiacol

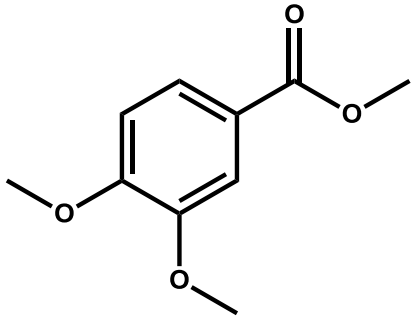


^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.92 (m, 1H), 6.86 (m, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.61, 145.69, 121.48, 120.18, 114.58, 110.76, 55.89.

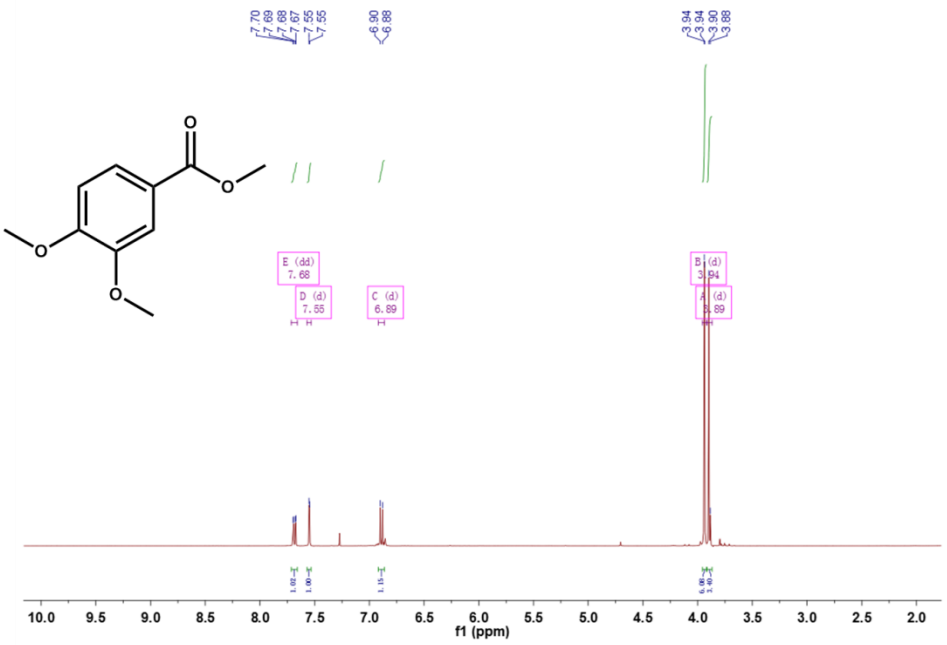




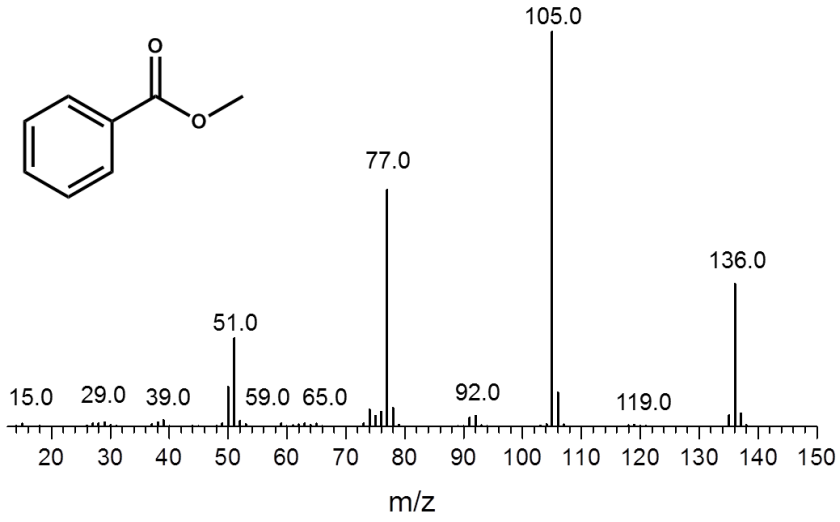
Methyl 3,4-dimethoxybenzoate

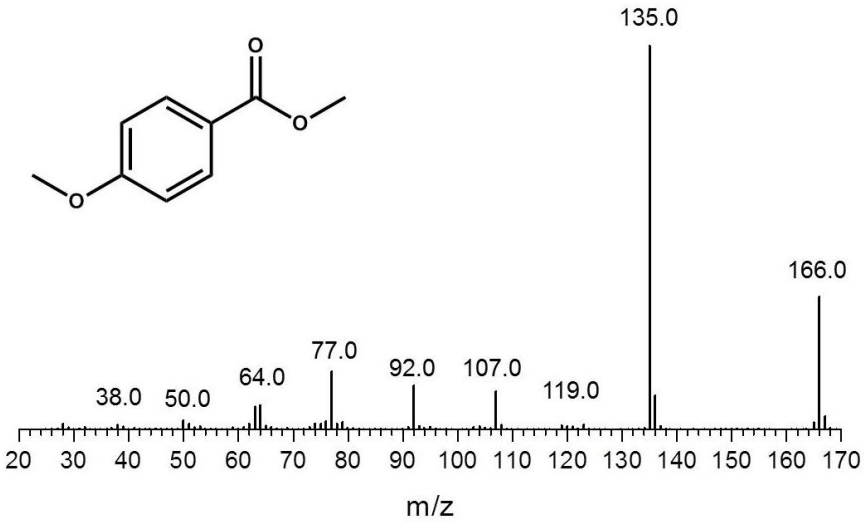


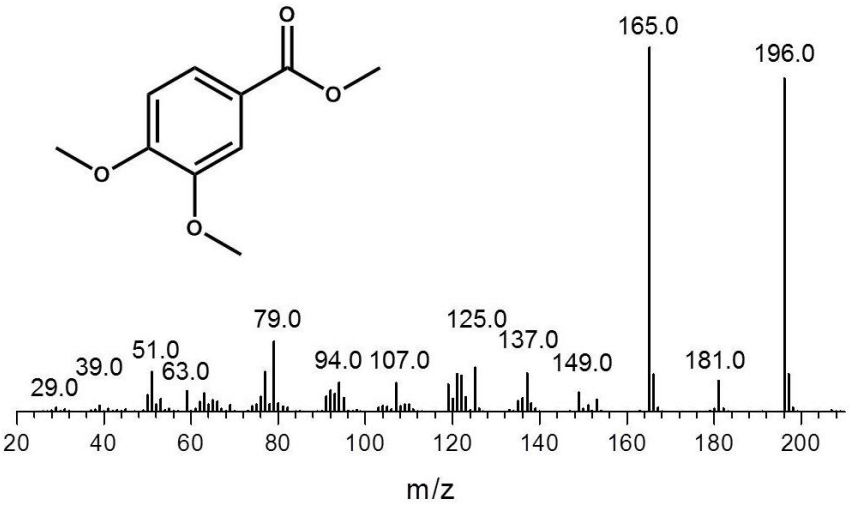
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (dd, *J*=8.4, 2.0, 1H), 7.55 (d, *J*=1.9, 1H), 6.89 (d, *J*=8.4, 1H), 3.94 (d, *J*=1.0, 6H), 3.89 (d, *J*=5.6, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.88, 152.93, 148.58, 123.57, 122.66, 111.92, 110.23, 56.01, 55.99, 52.00.



5. Mass spectra of the product



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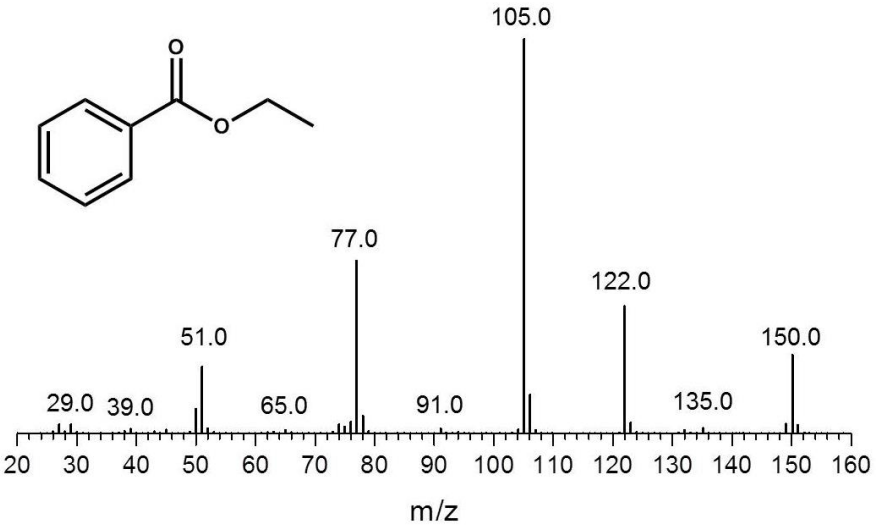
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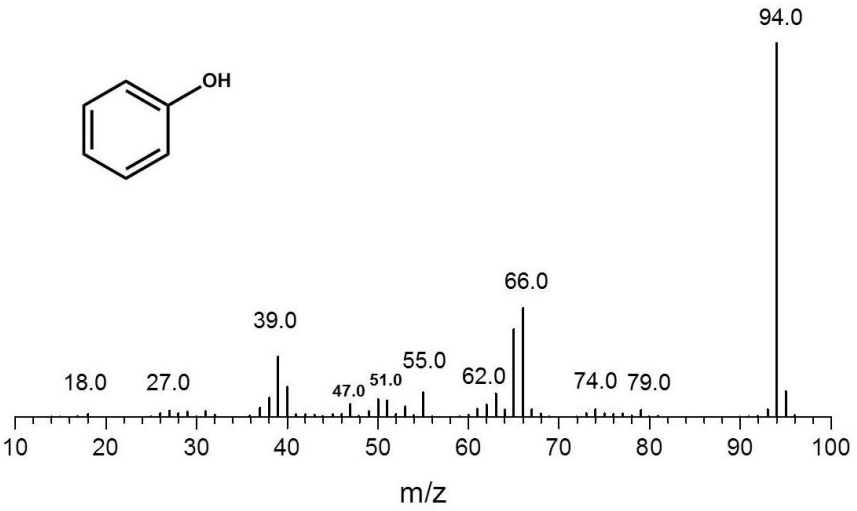
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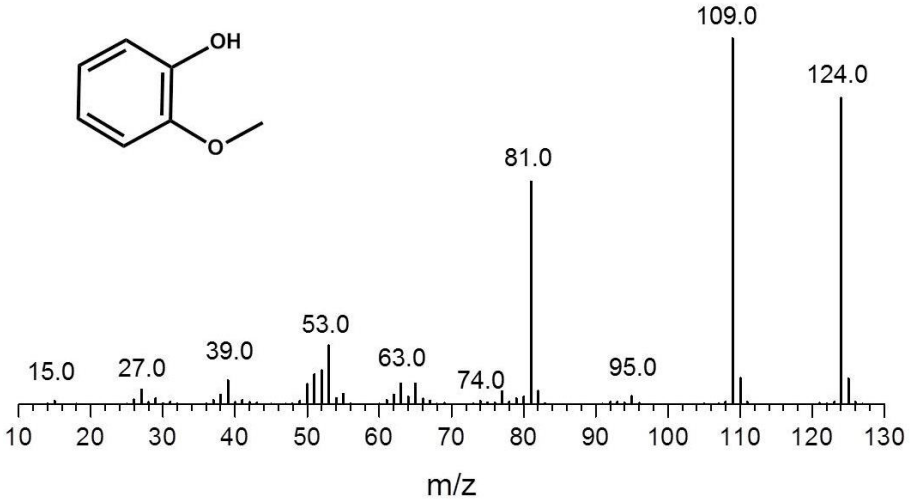
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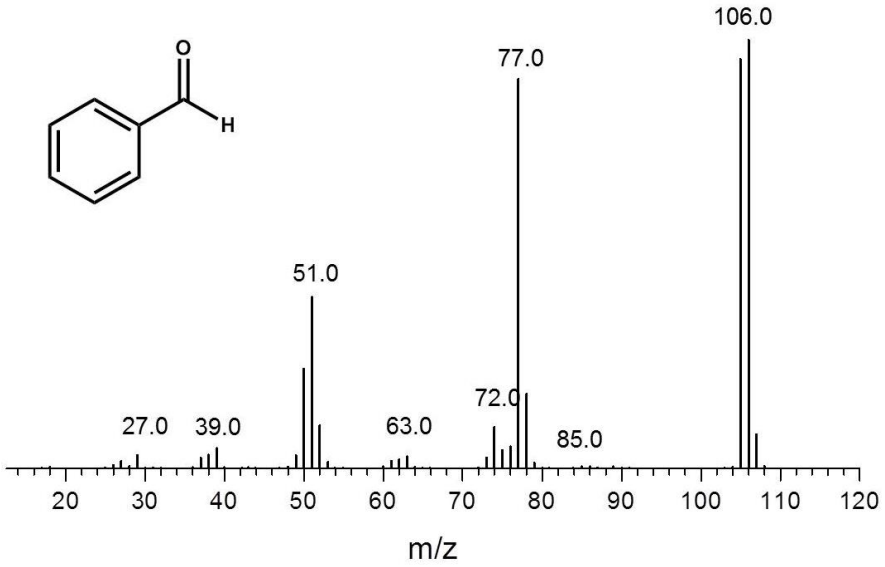
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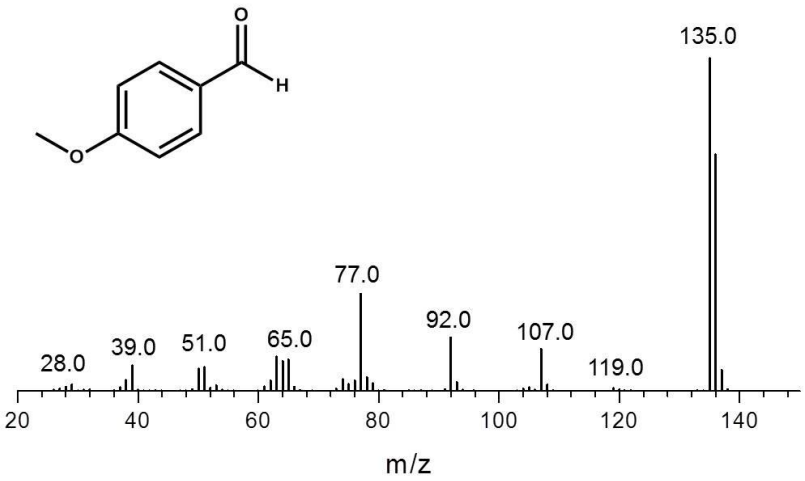
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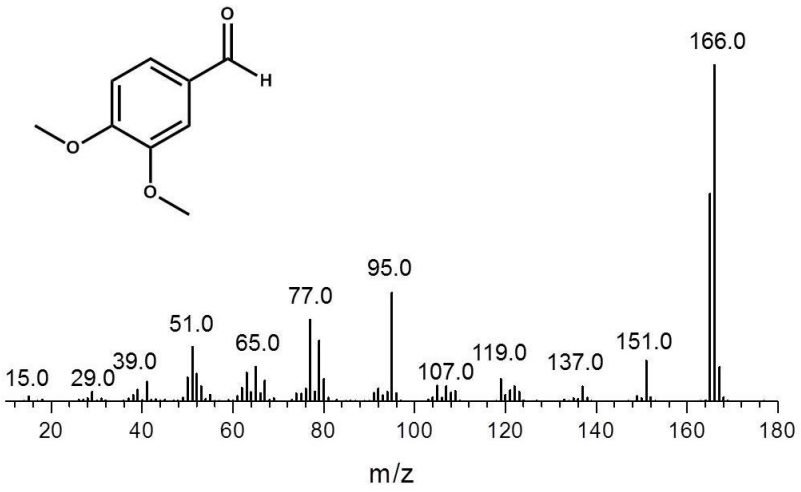
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