Supporting Information

Photocatalytic Oxidation of Lignin Model Compounds to Benzaldehyde and Phenol: A Preliminary Study on Extracted Lignin

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1. General

1.1 Materials

All reagents and solvents were purchased from Accela, Adamas, Innochem, Psaitong and Aladdin. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

1.2 Instrumentation

Blue LED lamps, radiators, fan, regulated DC power supplies and quartz reaction tubes used in the photocatalytic reaction were purchased from Shenzhen Xindaxin Photoelectric Technology Co., Ltd.

Products were purified by flash chromatography on silica gel. Analysis of crude reaction mixture was performed on an Agilent 7820A GC System with a HP-INNOWAX capillary column (30 m×0.25 mm×0.32 μm) and an FID detector. The following GC temperature program was used: 60 °C is maintained for 2 minutes, rises to 150 °C at 10 °C/min, and finally rises to 300°C at a rate of 20°C/min, and hold for 4 minutes. Nitrogen was used as a carrier gas. The injector temperature was held at 250 °C.

GC-MS analysis was carried out on a SHIMADZU GC-MSQP 2010 with a DB-5 capillary column (30 m×0.25 mm×0.32 μm).

^{1}H NMR spectra were recorded in $CDCl_3$ or DMSO using internal reference (the residue proton peaks of $CDCl_3$ at 7.26 ppm and DMSO at 2.5 ppm) on Bruker 400 spectrometer. Liquid ^{13}C NMR was recorded at 100.6 MHz in $CDCl_3$ using residual $CDCl_3$ as internal reference (the residue proton peaks of $CDCl_3$ at 77.02 ppm and DMSO at 40.03 ppm).

Powder X-ray diffraction (PXRD) analysis was performed using a D / MAX-2500 diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 1.5405 Å). The working voltage of the instrument is 40 kV, the voltage is 150 mA, the scanning rate is 10°/min, the step size is 0.02°, and the data in the range of 0-50° are collected.

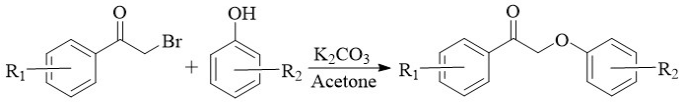
Fourier Transform Infrared Spectroscopy (FT-IR) spectra were collected on PerkinElmer Spectrum 100 spectrometer.

Scanning electron microscopy (SEM) were conducted on a Hitachi JSM-7610F field emission scanning electron microscope.

The pore structure of the sample was characterized using a Quantachrome Nova Station A gas adsorption analyzer (Quantachrome Instruments, USA) with Quantachrome ASiQwin v3.01 for data acquisition and processing. Prior to testing, 0.1197 g of the sample was placed in a 1 cc cell without outgassing. Nitrogen adsorption-desorption isotherms were measured at 77.3 K (liquid nitrogen bath), with adsorption/desorption pressure tolerance of 0.100/0.100, equilibrium time of 60/60 sec, equilibrium timeout of 240/240 sec, relative pressure (P/P_0) range of 0.026–1.09, and total test duration of 294.2 min. The specific surface area was calculated via the multi-point BET method (r=0.999882), while the BJH method was used to analyze adsorption/desorption branch data, yielding pore volume, pore diameter, and specific surface area.

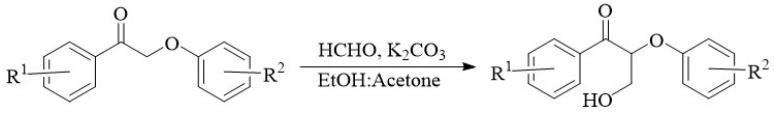
The sample NH3-TPD test was performed using an AutoChem II 2920 chemisorption instrument (Micromeritics, USA, with AutoChem v4.0 software) ; the 0.100 g (40-60 mesh) sample was weighed in a U-shaped quartz tube, desorbed at 300 °C for 120 min in He gas (50 mL/min) and cooled to 50 °C, and then adsorbed by 10 % NH3-He mixed gas (30 mL/min) for 60 min, purged by He gas for 90 min, and then heated from 50 °C to 800 °C at a rate of 10 °C/min. The NH3 desorption signal was detected by TCD, and the intensity of acidic sites was determined by software baseline correction and peak area integration.

2. Synthesis of lignin models



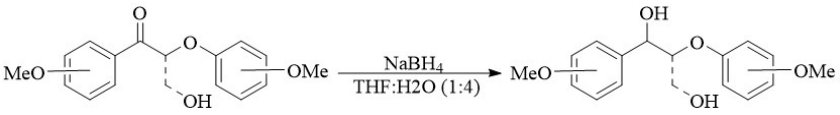
Scheme S1 synthetic ketone lignin model.

The synthesis reaction was carried out in a 150 mL round glass flask containing a condenser. 2-phenoxyacetophenone were synthesized by the reaction of the corresponding phenol with 2-bromoacetophenone according to the reported procedure[1]. Typically, 2-bromoacetophenone (5 mmol) is dissolved in a solution of K_2CO_3(7.5 mmol, 1.036 g) and phenol (5 mmol) in acetone (50 mL) and loaded in a reactor. The reaction mixture is then stirred at reflux temperature for 5 hours, filtered and vacuumized. The residue was purified by column chromatography with petroleum ether: ethyl acetate(v:v=4:1) a stirring. For the other methoxy substituted 2-phenoxy-1-phenylethanone, the preparation procedure is the same as described above, except of using different stating materials.



Scheme S2 synthetic 3-hydroxy-2-phenoxy-1-phenylpropan-1-one.

According to the reaction process of the previous step in **Scheme S1**, to a stirring suspension of K_2CO_3 (0.6 g, 4.3 mmol) in ethanol:acetone (v:v=1:1, total 20 mL) and 2-phenoxyacetophenones (0.78 g, 4 mmol) at rt, a water solution of formaldehyde (36.5~38wt%, 0.6 mL, 7.3 mmol) was added. After 4 h, the reaction mixture was filtered to remove K_2CO_3 and concentrated in vacuo to get a solid product. The crude product was purified with petroleum ether: ethyl acetate (v:v=3:1) to obtain the required 2-phenoxyacetophenone, on silica gel to obtain 3-hydroxy-1,2-diphenylpropan-1-one in 90% yield.



Scheme S3 synthetic lignin model compounds.

The resulting compound (3.5 mmol, 0.847 g) from the previous step was dissolved in the mixture of THF:H_2O (v:v=5:1, total 25 mL), and sodium borohydride (7 mmol, 0.26 g) was added portionwise to maintain a gentle evolution of gas. Then, the mixture was stirred for 6 h at room temperature. The reaction mixture was quenched

with saturated aqueous NH_4Cl (50 mL) and diluted with 30 mL water. The aqueous portion was extracted with ethyl acetate (3×30mL). The organic parts were combined, dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by column chromatography with hexane:ethyl acetate (v:v=2:1).

3. Reaction equipment and experiment

3.1 Experimental installation

The degradation experiments were carried out in a photochemical reactor with two 20W blue LEDs from Shenzhen Chundaxin Optoelectronics, with a spectral distribution of 400 nm-410 nm, and borosilicate glass tubes were used without filters. The distance between the reaction tube and the LED is 30mm

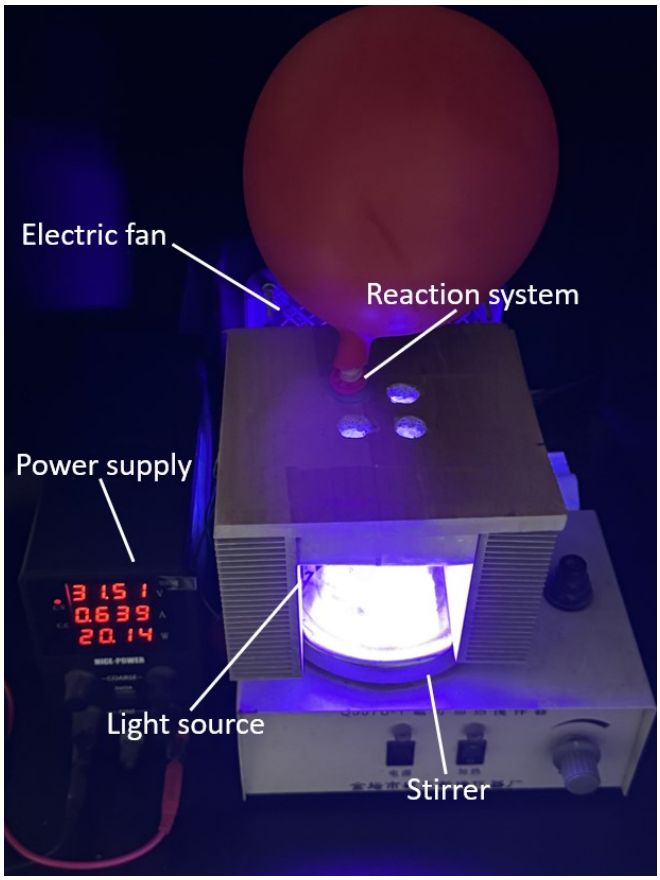
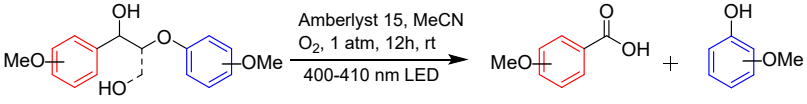


Figure S1 The experimental instruments of the light-promoted reactions.

3.2 Photocatalytic cleavage of lignin model compounds



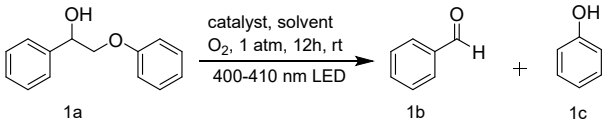
Scheme S4. Cleavage of lignin model compound.

The general procedure of the reaction: the photocatalytic equipment is composed of two 400-410 nm LED series. The constant voltage steady current power supply voltage is 32 V, the electric current is 1.25 A, and the power is 40 W. Feed was added to a 10mL quartz reaction tube and an oxygen balloon was mounted and stirred on a photocatalytic device while the device was cooled by a fan. After 12 hours, the reaction solution was diluted and extracted with dichloromethane. The yield of the obtained product was determined by GC with dodecane as internal standard. The conversion and yield were calculated according to the formula (1)-(2). The main products of the reaction were purified by silica gel column chromatography, and $CDCl_3$ was used as solvent for NMR detection.

$$Conversion(\%) = \frac{C_0}{C_R} \times 100\#(1)$$

$$Yield(\%) = \frac{C_E}{C_0} \times 100\#(2)$$

In the equation, C_0 and C_R are the molar number of lignin model compounds at the initial time and R time, respectively, and C_E is the molar number of the generated product.

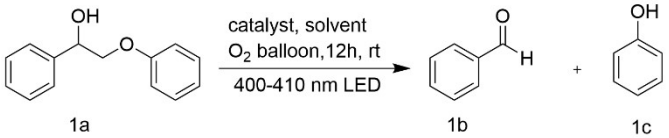


Scheme S5. Specific examples of photocatalytic lignin model compounds

Substrate 1a (214 mg, 1 mmol, 1.0 equiv) in 2 mL of MeCN was added with Amberlyst 15 (27.8 mg, 0.2 mmol, 0.2 equiv). Then solution system stirred at room temperature in a glass test tube under oxygen balloon (1 bar) and irradiated with blue LED (400-410 nm, 40W). The reaction was completed at 12 hours through TLC monitoring. The mixture was extracted with CH_2Cl_2 (25 mL×3). The organic parts were combined, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting residue was purified by flash chromatography over silica gel (PE/EA = 3:1) to give 1b (97.5 mg, 92% isolated yield) and 1c (83.7 mg, 89% isolated yield).

3.3 Screening of parameters for oxidative cleavage of lignin model compound

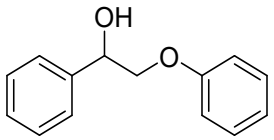
Table S1. Screening of parameters for oxidative cleavage of lignin model compound



Entry	Catalyst	Solvent	Yield 1b (%)	Yield 1c (%)	Conv. (%)
1	Amberlyst 15	MeCN	92	89	95
2	Amberlyst 16	MeCN	76	80	81
3	Amberlyst 35	MeCN	43	38	49
4	Amberlyst 36	MeCN	46	35	50
5	HCl (6 M)	MeCN	24	18	33
6	H_2SO_4(40%w)	MeCN	37	21	42
7	HBF_4 (70%w)	MeCN	30	21	35
8	Amberlyst 15	acetone	48	42	53
9	Amberlyst 15	MeOH	69	48	74
10	Amberlyst 15	H_2O	0	0	0
11[a]	Amberlyst 15	MeCN	51	42	55
12[b]	Amberlyst 15	MeCN	32	26	36
13[c]	Amberlyst 15	MeCN	0	0	0

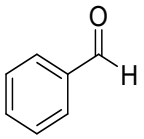
Reaction conditions: substrate 1a (0.1 mmol), catalyst (0.2 eq), solvent (2 mL), O2 (1 atm), room temperature for 12 h and irradiated with blue LED (400-410 nm, 20 W). ablue LED (365 nm, 20 W), bAir instead of O2, cAr instead of O2, Yield of products isolated via column chromatography.

3.4 Spectroscopic Data



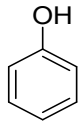
2-Phenoxy-1-phenyl-ethanol (**1a**)

Data for 1a: 1H NMR (400 MHz, Chloroform-d) δ 7.39 (d, J = 6.9 Hz, 2H), 7.36 – 7.16 (m, 5H), 6.95 – 6.86 (m, 1H), 6.85 (dd, J = 7.7, 1.5 Hz, 2H), 5.05 (dt, J = 9.0, 2.7 Hz, 1H), 4.04 (dd, J = 9.6, 3.2 Hz, 1H), 3.94 (t, J = 9.2 Hz, 1H), 2.72 (d, J = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-d) δ 158.43, 139.70, 129.56, 128.57, 128.18, 126.29, 121.34, 114.70, 73.35, 72.61, 1.01.



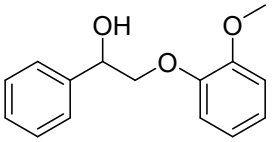
Benzaldehyde (**1b**)

Data for **1b**: ^{1}H NMR (400 MHz, CDCl3) δ 10.02 (s, 1H), 7.91 – 7.84 (m, 2H), 7.64 – 7.58 (m, 1H), 7.56 – 7.50 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 192.53, 171.59, 136.41, 134.52, 133.72, 130.20, 129.78, 129.44, 129.03, 128.50, 77.43, 77.11, 76.79.



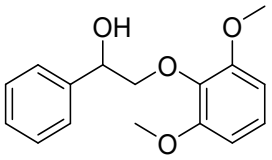
Phenol (**1c**)

Data for **1c**: ^{1}H NMR (500 MHz, Chloroform-d) δ 7.33 – 7.26 (m, 2H), 7.02 – 6.95 (m, 1H), 6.92 – 6.85 (m, 2H), 5.03 (s, 1H); ^{13}C NMR (126 MHz, Chloroform-d) δ 155.46, 129.75, 120.90, 115.37.



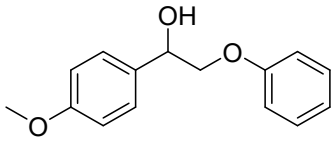
2-(2-methoxyphenoxy)-1-phenylethan-1-ol (**2**)

Data for **2**: ^{1}H NMR (500 MHz, Chloroform-d) δ 7.48 (d, J = 7.4 Hz, 2H), 7.38 (dt, J = 30.3, 7.2 Hz, 3H), 7.04 (ddd, J = 8.0, 7.1, 1.8 Hz, 1H), 6.98 (td, J = 8.3, 1.7 Hz, 2H), 6.96 – 6.90 (m, 1H), 5.15 (dt, J = 9.8, 2.4 Hz, 1H), 4.23 (dd, J = 10.1, 2.9 Hz, 1H), 4.02 (t, J = 9.8 Hz, 1H), 3.93 (s, 3H), 3.49 (d, J = 2.1 Hz, 1H);^{13}C NMR (126 MHz, CDCl3) δ 150.24, 139.52, 128.54, 128.07, 126.33, 122.67, 121.15, 116.19, 112.07, 77.31, 77.06, 76.80, 76.45, 72.38, 55.91, 0.04.



2-(4-chlorophenoxy)-1-phenylethan-1-ol (**3**)

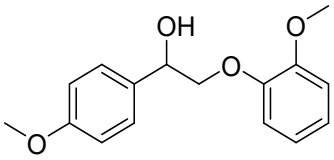
Data for **3**: ^{1}H NMR (500 MHz, Chloroform-d) δ 7.46 – 7.40 (m, 2H), 7.40 – 7.34 (m, 2H), 7.31 (s, 5H), 7.08 (t, J = 8.4 Hz, 1H), 6.65 (d, J = 8.4 Hz, 2H), 5.00 (d, J = 9.8 Hz, 1H), 4.56 (d, J = 1.6 Hz, 1H), 4.45 (dd, J = 11.0, 2.7 Hz, 1H), 3.92 (s, 6H), 3.76 (dd, J = 11.0, 10.0 Hz, 1H); ^{13}C NMR (126 MHz, CDCl3) δ 153.30, 128.36, 127.73, 126.35, 124.13, 105.20, 80.09, 77.31, 77.05, 76.80, 72.47, 56.14.



1-(4-methoxyphenyl)-2-phenoxyethan-1-ol (**4**)

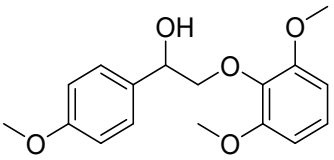
Data for **4**: ^{1}H NMR (600 MHz, Chloroform-d) δ 7.38 (d, J = 8.7 Hz, 2H), 7.29 (dd, J = 8.7, 7.2 Hz, 2H), 7.00

– 6.95 (m, 1H), 6.94 – 6.91 (m, 4H), 5.08 (d, J = 7.8 Hz, 1H), 4.08 (dd, J = 9.6, 3.2 Hz, 1H), 4.00 (t, J = 9.2 Hz, 1H), 3.82 (s, 3H), 2.73 (d, J = 2.3 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 159.70, 158.55, 131.91, 129.70, 127.71, 121.42, 114.79, 114.14, 73.43, 72.35, 55.47.



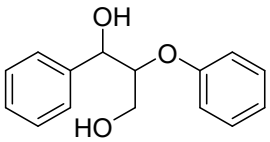
2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethan-1-ol (**5**)

Data for **5**: ^{1}H NMR (500 MHz, Chloroform-d) δ 7.39 – 6.82 (m, 9H), 5.06 (d, J = 8.4 Hz, 1H), 4.15 (d, J = 12.7 Hz, 1H), 3.96 (t, J = 9.8 Hz, 1H), 3.85 (d, J = 39.8 Hz, 6H), 3.44 (s, 1H); ^{13}C NMR (126 MHz, CDCl3) δ 159.47, 150.23, 148.05, 131.66, 127.60, 122.59, 121.12, 116.11, 113.96, 112.05, 77.32, 77.06, 76.81, 76.38, 71.98, 55.90, 55.35, 29.77, 0.04.



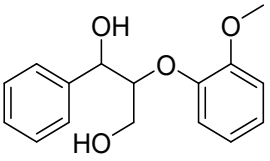
2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl) ethan-1-ol (**6**)

Data for **6**: ^{1}H NMR (500 MHz, Chloroform-d) δ 7.31 (d, J = 8.8 Hz, 3H), 7.04 (t, J = 8.4 Hz, 1H), 6.87 (d, J = 8.7 Hz, 2H), 6.61 (d, J = 8.4 Hz, 2H), 4.91 (d, J = 12.0 Hz, 1H), 4.48 (s, 1H), 4.37 (dd, J = 11.0, 2.7 Hz, 1H), 3.90 – 3.63 (m, 9H), 1.57 (s, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 159.23, 153.30, 136.82, 131.59, 127.60, 124.09, 113.80, 105.18, 80.08, 77.32, 77.06, 76.81, 72.04, 56.13, 55.31, 0.04.



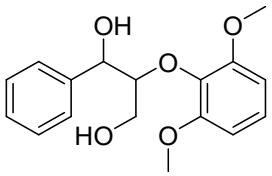
2-phenoxy-1-phenylpropane-1,3-diol (**7**)

Data for **7**: ^{1}H NMR (500 MHz, Chloroform-d) δ 7.48 – 7.24 (m, 7H), 7.04 – 6.89 (m, 3H), 5.09 (ddd, J = 34.9, 6.0, 3.3 Hz, 1H), 4.44 (dt, J = 6.6, 4.2 Hz, 1H), 4.00 – 3.77 (m, 1H), 3.59 (ddd, J = 11.8, 7.2, 4.0 Hz, 1H), 2.81 (dd, J = 13.2, 3.4 Hz, 1H), 1.81 (dd, J = 7.3, 5.4 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 157.99, 157.48, 140.13, 139.56, 129.68, 129.60, 128.55, 128.48, 128.27, 127.93, 127.39, 126.87, 126.15, 122.00, 121.88, 116.55, 116.48, 83.05, 81.83, 73.92, 61.17, 61.04.



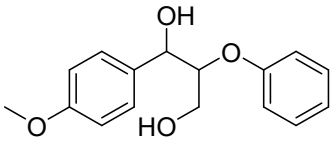
2-(2-methoxyphenoxy)-1-phenylpropane-1,3-diol (**8**)

Data for **8**: ^{1}H NMR (500 MHz, Chloroform-d) δ 7.48 – 6.88 (m, 10H), 5.08 – 5.02 (m, 1H), 4.09 – 4.03 (m, 1H), 3.91 (d, J = 12.1 Hz, 3H), 3.63 (dd, J = 12.6, 3.2 Hz, 1H), 3.49 (dd, J = 12.5, 4.0 Hz, 1H). ^{13}C NMR (126 MHz, CDCl3) δ 151.80, 151.41, 147.62, 146.83, 139.79, 139.67, 128.60, 128.50, 128.29, 127.75, 127.18, 126.07, 124.44, 124.40, 121.75, 121.72, 121.32, 121.23, 112.28, 112.23, 89.61, 87.59, 77.32, 77.07, 76.81, 74.17, 72.97, 61.06, 60.63, 55.96, 31.67, 29.71, 0.04.



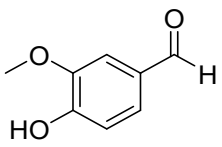
2-(2,6-dimethoxyphenoxy)-1-phenylpropane-1,3-diol (**9**)

Data for **9**: ^{1}H NMR (500 MHz, Chloroform-d) δ 7.45 – 7.39 (m, 2H), 7.33 – 7.26 (m, 3H), 7.26 – 7.19 (m, 1H), 7.04 – 6.97 (m, 1H), 6.58 (t, J = 8.3 Hz, 2H), 5.10 – 5.01 (m, 1H), 4.33 (d, J = 1.4 Hz, 1H), 3.92 – 3.81 (m, 7H), 3.52 (dt, J = 12.4, 3.3 Hz, 1H), 3.32 (dd, J = 9.9, 3.7 Hz, 1H), 3.24 (ddd, J = 12.4, 9.8, 2.5 Hz, 1H). ^{13}C NMR (126 MHz, CDCl3) δ 153.61, 153.29, 140.18, 139.46, 135.33, 134.97, 128.43, 128.36, 128.05, 127.45, 127.39, 125.84, 124.56, 105.35, 88.89, 86.99, 77.34, 77.08, 76.83, 74.29, 72.85, 60.56, 60.46, 56.20, 0.05.



1-(4-methoxyphenyl)-2-phenoxypropane-1,3-diol (**10**)

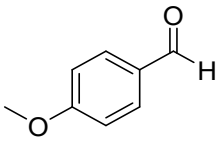
Data for **10**: ^{1}H NMR (500 MHz, Chloroform-d) δ 8.09 (d, J = 8.9 Hz, 1H), 7.28 (d, J = 5.7 Hz, 1H), 7.03 – 6.90 (m, 3H), 5.33 (s, 1H), 4.16 (qd, J = 12.0, 5.2 Hz, 1H), 3.90 (s, 2H), 1.46 (d, J = 8.5 Hz, 4H), 1.38 – 1.25 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-d) δ 159.65, 159.37, 158.13, 157.68, 132.41, 131.68, 129.80, 129.70, 128.24, 127.60, 127.52, 122.08, 121.91, 116.64, 116.59, 114.08, 113.99, 83.26, 81.92, 73.89, 73.70, 61.40, 61.14, 55.35.



2-Methoxy-4-formylphenol (Vanillin)

Data for Vanillin: ^{1}H NMR (400 MHz, CDCl3) δ 9.83 (d, J = 1.8 Hz, 1H), 7.43 (t, J = 3.9 Hz, 2H), 7.05 (dd, J

= 8.4, 1.9 Hz, 1H), 6.39 (d, J = 1.9 Hz, 1H), 3.96 (d, J = 1.9 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 190.99, 151.77, 147.21, 129.87, 127.57, 114.44, 108.84, 77.37, 77.06, 76.74, 56.13, -0.03.

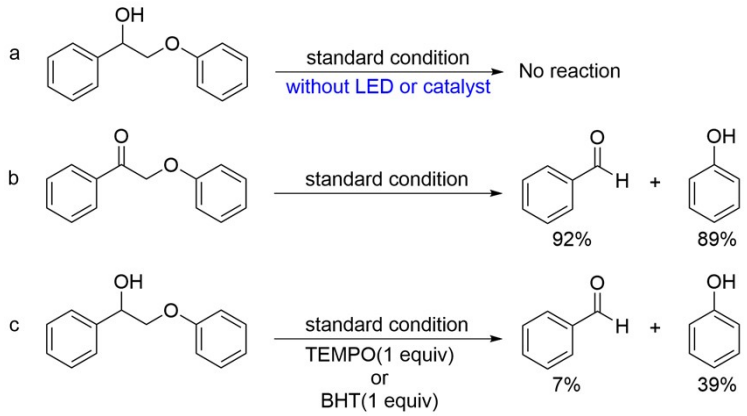


4-methoxybenzaldehyde (p-Anisaldehyde)

Data for p-Anisaldehyde: ^{1}H NMR (400 MHz, CDCl3) δ 9.88 (s, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.00 (d, J = 8.3 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 190.81, 164.62, 131.97, 129.95, 121.94, 114.32, 113.65, 77.45, 77.13, 76.81, 55.56.

4. Mechanistic Experiments

4.1 Control experiments



Scheme S6. Controlled experiments.

Standard conditions: substrate (0.1 mmol), Amberlyst 15 (0.2 eq), MeCN (2.0 mL), 1 atm O2, rt, 12 h, 40W blue LED (400-410nm).

Table S2. Effect of catalyst amount on reaction.

Entry	Catalyst dosage (equivalent)	The amount of substance(mmol)	mass (g)	Conv. (%)	Yield 1b (%)	Yield 1c (%)
1	0	0	0	0	0	0
2	0.05	0.005	0.016	40	23	23
3	0.1	0.01	3.144	80	41	52
4	0.15	0.015	4.716	89	73	74
5	0.2	0.02	6.288	95	92	89
6	0.25	0.025	7.860	93	89	86
7	0.3	0.03	9.432	93	90	87
8	0.35	0.035	11.004	92	88	86
9	0.4	0.04	12.576	92	90	87

Reaction time 12 h, the other reaction conditions are the same as Table s1.

Table S3. Effect of reaction time on reaction.

Entry	Time (h)	Conv. (%)	Yield 1b (%)	Yield 1c (%)
1	0	0	0	0

2	1	20	15	12
3	2	27	18	17
4	3	30	20	21
5	4	35	22	23
6	5	43	27	25
7	6	49	33	30
8	7	54	42	41
9	8	62	52	54
10	9	80	62	66
11	10	88	70	72
12	11	92	83	85
13	12	95	92	89
14	13	95	90	88
15	14	96	90	88
16	15	96	89	87

4.2 Electron paramagnetic resonance (EPR) spectroscopy experiments

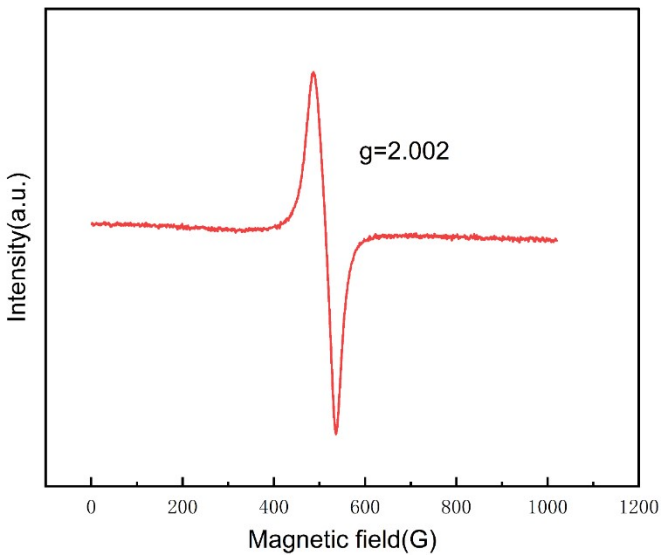


Figure S2. Electron paramagnetic resonance (EPR) spectra. Center Field: 500.00 G (adjusted to match the peak position in the spectrum), Sweep Width: 1000.0 G, Power: 6.325 mW, Power Atten: 15.0 dB, Frequency: 9.830200 GHz, Sweep Time: 30.00 s, Modulation Amplitude: 1.000 G, Modulation Frequency: 100.00 kHz.

4.3 Detection of CO_2

Under the environment of pure oxygen, tail gas was collected and detected by GC.

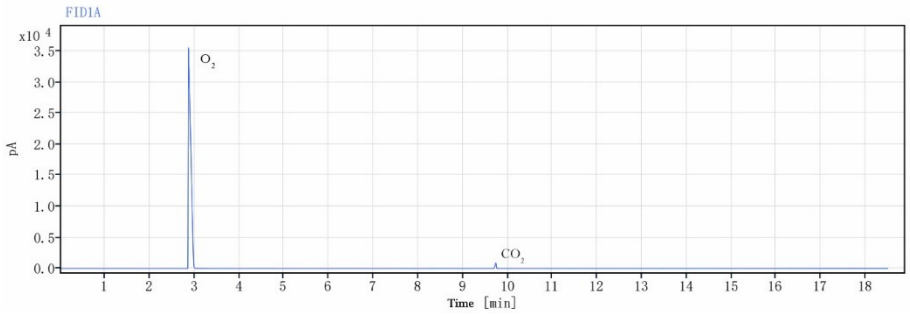


Figure S3. GC profile of the gas phase of the reaction solution.

4.4 Carbon mass balance

In order to verify the quantitative reliability of the depolymerization reaction of β-O-4 LMC and clarify the source of the yield deviation between benzaldehyde (1b) and phenol (1c), the carbon flow direction of the reaction was systematically analyzed by carbon mass balance calculation, qualitative and quantitative analysis of by-products and separation loss verification.

$$Carbon\ recovery\ rate(\%) = \frac{\sum Carbon\ Mass\ of\ Each\ Product\ (mg)}{Initial\ Carbon\ Mass\ of\ Substrate(mg)} \times 100\%\#(3)$$

Table S4. Carbon Distribution of Main Products and By-Products

Form of Carbon Existence	Substance Name	Molar Yield (%)	Number of C Atoms	Carbon Mass (mg)	Carbon Fraction (%)
1b	Benzaldehyde	92	7	7.728	46.0
1c	Phenol	89	6	6.408	38.1
Quantified by-product	Benzoic acid (mild oxidation)	1.5	7	0.126	0.75
Quantified by-product	Benzyl alcohol (reduction by-product)	0.8	7	0.0672	0.4
Separation loss	Column chromatography adsorption/volatilization	-	-	1.4708	8.75
Total initial carbon of substrate	-	-	-	16.8	100
Total recovered carbon	-	-	-	15.792	94.0%

Standard conditions: substrate (0.1 mmol), Amberlyst 15 (0.2 eq), MeCN (2.0 mL), 1 atm O2, rt, 12 h, 40W blue LED (400-410nm). Carbon mass of each product = molar amount of product × number of C atoms in product × 12 g/mol; initial carbon mass of substrate = 16.8 mg (fixed value).

5. Degradation of natural lignin

5.1 Extraction of lignin

We charged a round bottom flask with 10.3 g poplar sawdust, 50 mL 1,4-dioxane, and 1.75 mL HCl (37wt%), and heated to reflux at 85 °C in oil bath for 3 h. After cooling to rt, the mixture was added with 3.36 g sodium bicarbonate ($NaHCO_3$), stirred for another 30 min, after which it was filtered and washed with 10 mL of dioxane. Then the solution was concentrated at 40 °C under reduced pressure. The resulting dark-brown oil was diluted with 30 mL ethyl acetate (EtOAc) and added dropwise to 500 mL of hexane to precipitate the lignin. After filtration, the collected lignin was washed with hexane (50 mL). The recovered lignin was dried overnight at rt in a desiccator to afford 1.36 g poplar lignin[2]. At the same time, it was subjected to two-dimensional nuclear magnetic HSQC detection (Figure.S4).

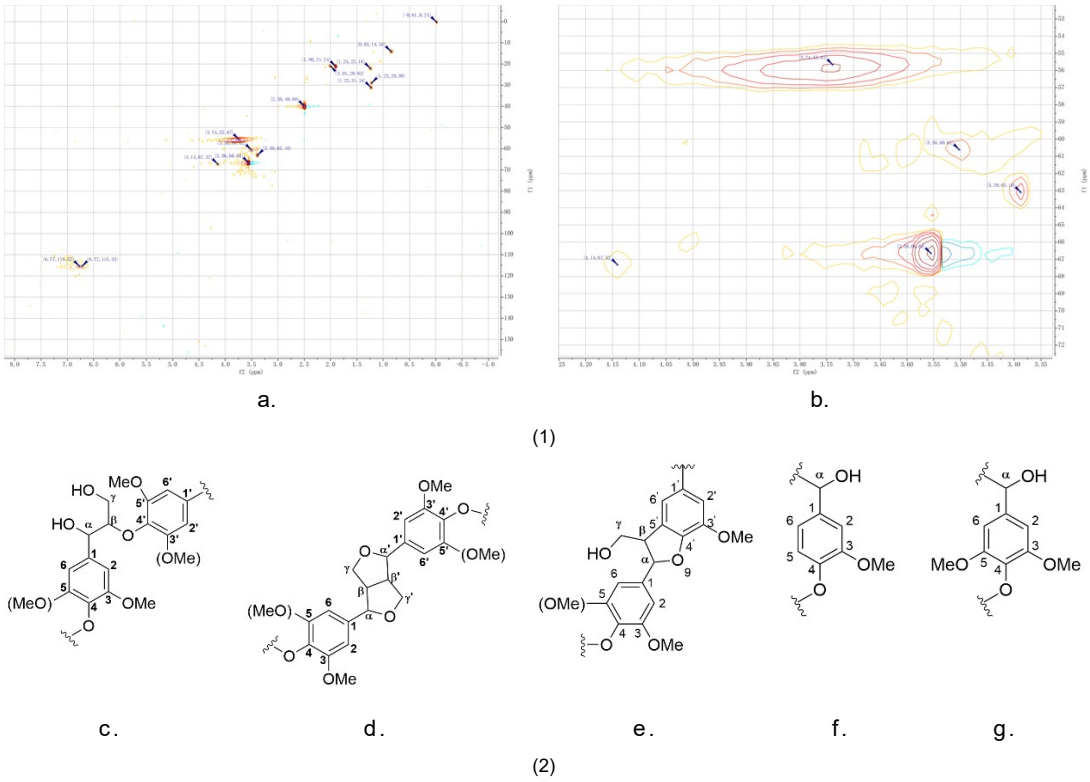
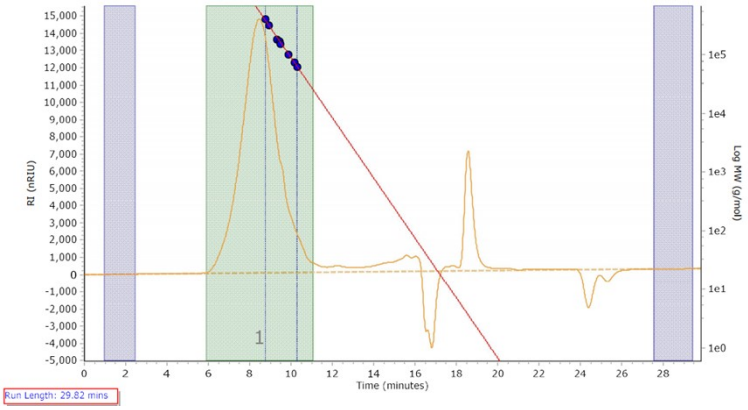
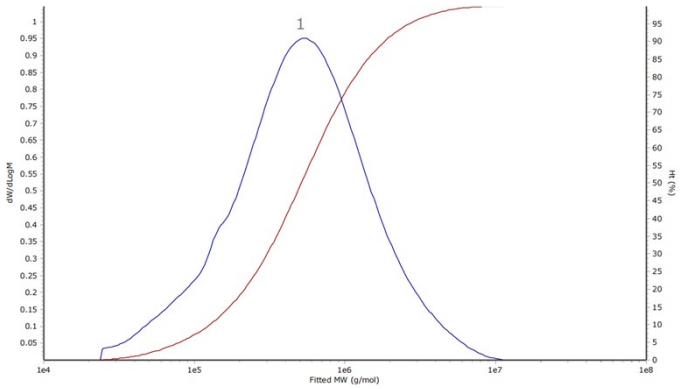


Figure S4. (1) HSQC results. (2) Several lignin structural units analyzed: c. β-O-4 linkages, d. β-β resinol structural units, e. β-5 units, f. Guaiacyl (G) units, g. Syringyl (S) units

5.2 Gel Permeation Chromatography (GPC) test results of poplar lignin samples



a.



b.

Figure S5. Gel Permeation Chromatography (GPC) test

Polystyrene was used as the standard, NMP was used as the mobile phase, the sample concentration was 2mg / ml, the flow rate was 0.6ml / min, and the injection volume was 20μL. Agilent GPC/SEC Software (version A.02.02 [281]) and Instrument 1 instrument were used with RI concentration detector. The total running time of the sample was 29.82 minutes.

The calibration curve was y = -0.5129x + 10.07, and the linear correlation coefficient was-0.998921. The calibration molecular weight range was 61800-403200 g / mol, and the Mark-Houwink equation was used for auxiliary correction. The equation parameters were K = 14.100 × 10 Ω dL/g and α = 0.700.

Number average molecular weight (Mn) 12855 g / mol, weight average molecular weight (Mw) 18268 g / mol, peak molecular weight (Mp) 15308 g / mol, viscosity average molecular weight (Mv) 17149 g / mol, z average molecular weight (Mz) 19872 g / mol, z + 1 average molecular weight (Mz+1) 23652 g / mol, polydispersity index (PD) 2.096.

5.3 Depolymerization of lignin

A total of 100 mg poplar lignin and 20 mg Amberlyst 15 were placed in four test tubes, and 2 mL acetonitrile was added to each test tube. The reaction system was irradiated for 12 hours under two 400-410 nm LEDs. After the reaction, HCl was used for acidification, and the solid material was removed by suction filtration. The reaction product was extracted with CH_2Cl_2, and the product was detected by GC-MS and quantitatively analyzed by GC. The solid residue was dissolved in deuterated dimethyl sulfoxide for two-dimensional nuclear magnetic HSQC detection (Figure.S6).

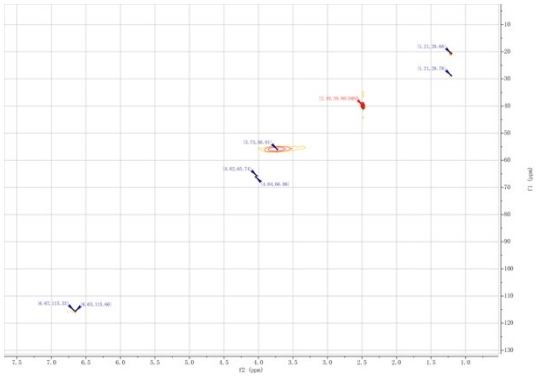
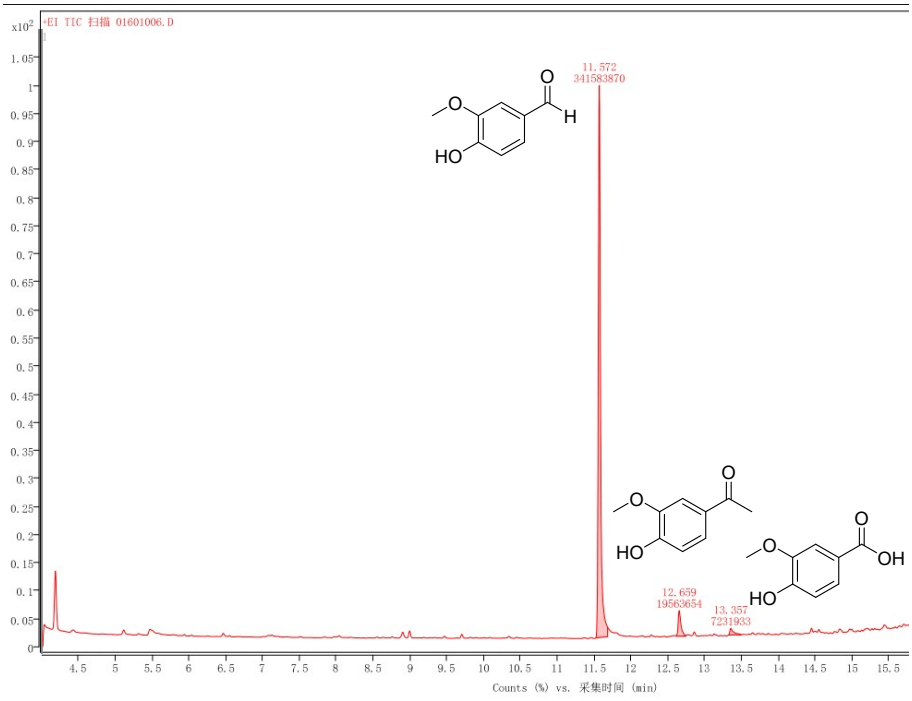


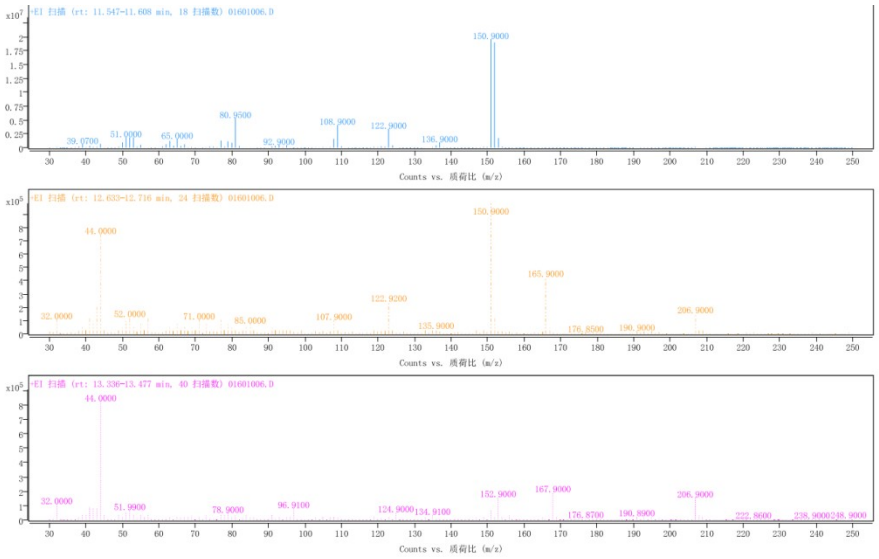
Figure S6. HSQC results

Figure S7 Depolymerization of natural lignin.

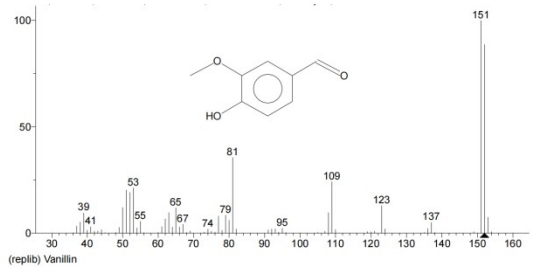
5.4 GC-MS analysis of real lignin depolymerization products



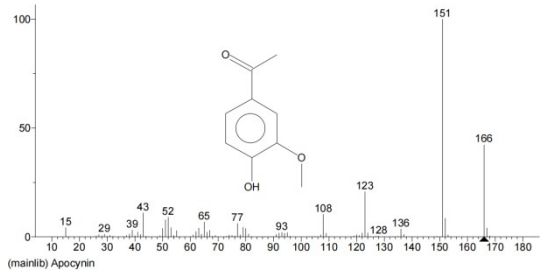
a



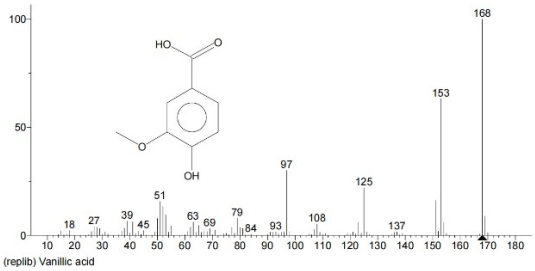
b



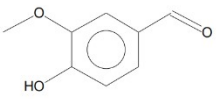
c



d

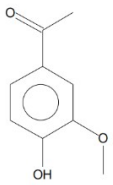


e



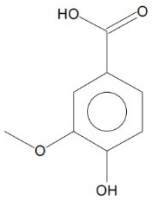
Name: Vanillin
Formula: $C_8H_8O_3$
MW: 152 Exact Mass: 152.047344 CAS#: 121-33-5 NIST#: 379339 ID#: 30209 DB: replib

f



Name: Apocynin
Formula: $C_9H_{10}O_3$
MW: 166 Exact Mass: 166.062994 CAS#: 498-02-2 NIST#: 352840 ID#: 175929 DB: mainlib

g

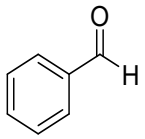


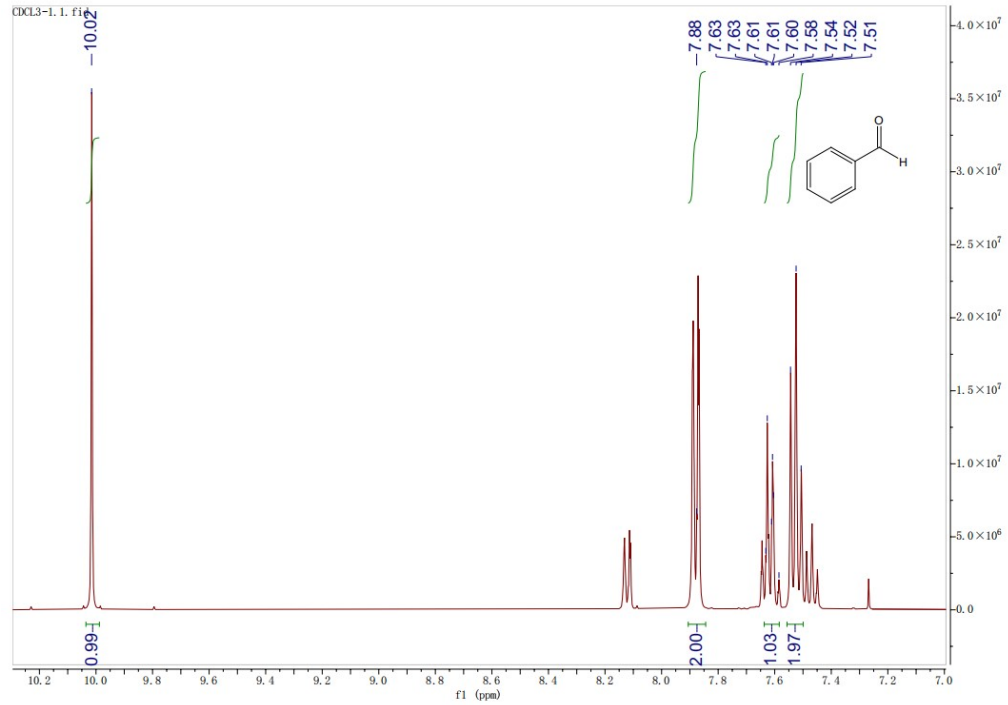
Name: Vanillic acid
Formula: $C_8H_8O_4$
MW: 168 Exact Mass: 168.042258 CAS#: 121-34-6 NIST#: 6514 ID#: 32831 DB: replib

h

Figure S8 GC-MS analysis of natural lignin depolymerization.

6. ^{1}H NMR and ^{13}C NMR spectra of compounds





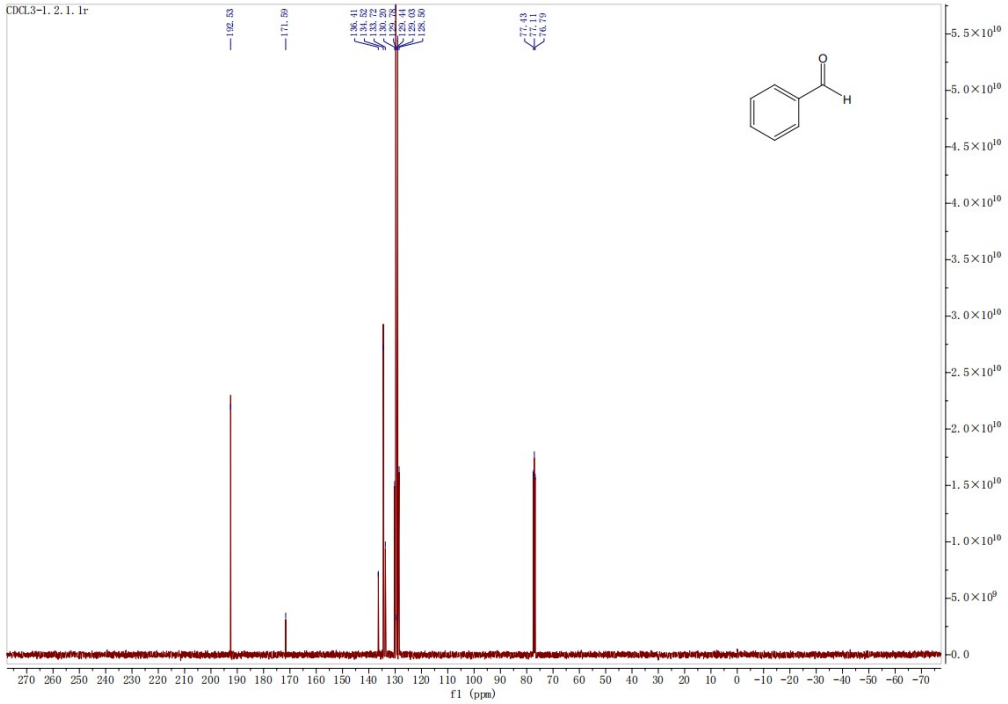


Figure S9 ^{1}H (top) and ^{13}C (bottom) NMR spectra of Benzaldehyde.

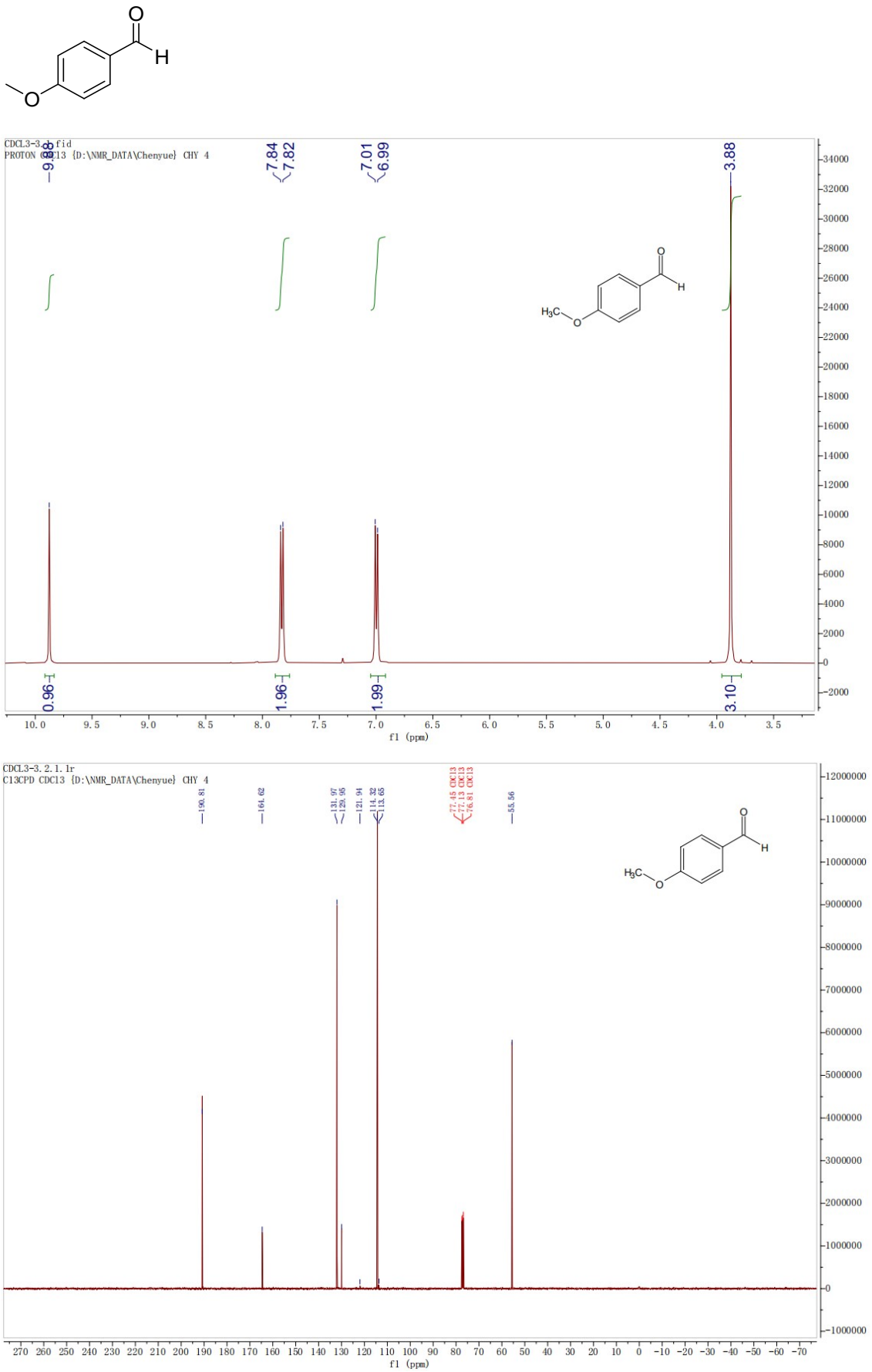


Figure S10 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 4-methoxybenzaldehyde.

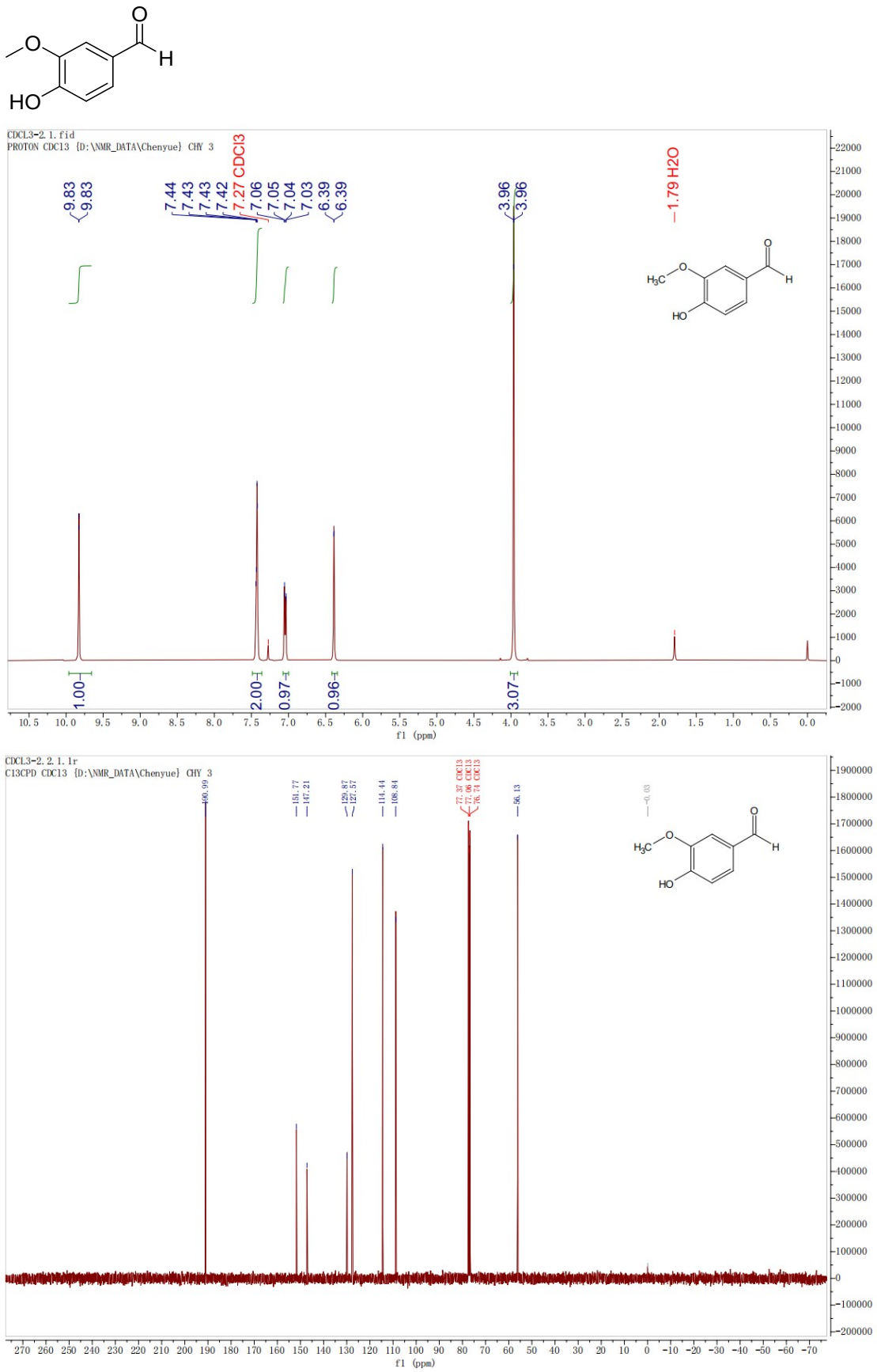


Figure S11 ^{1}H (top) and ^{13}C (bottom) NMR spectra of Vanillin.

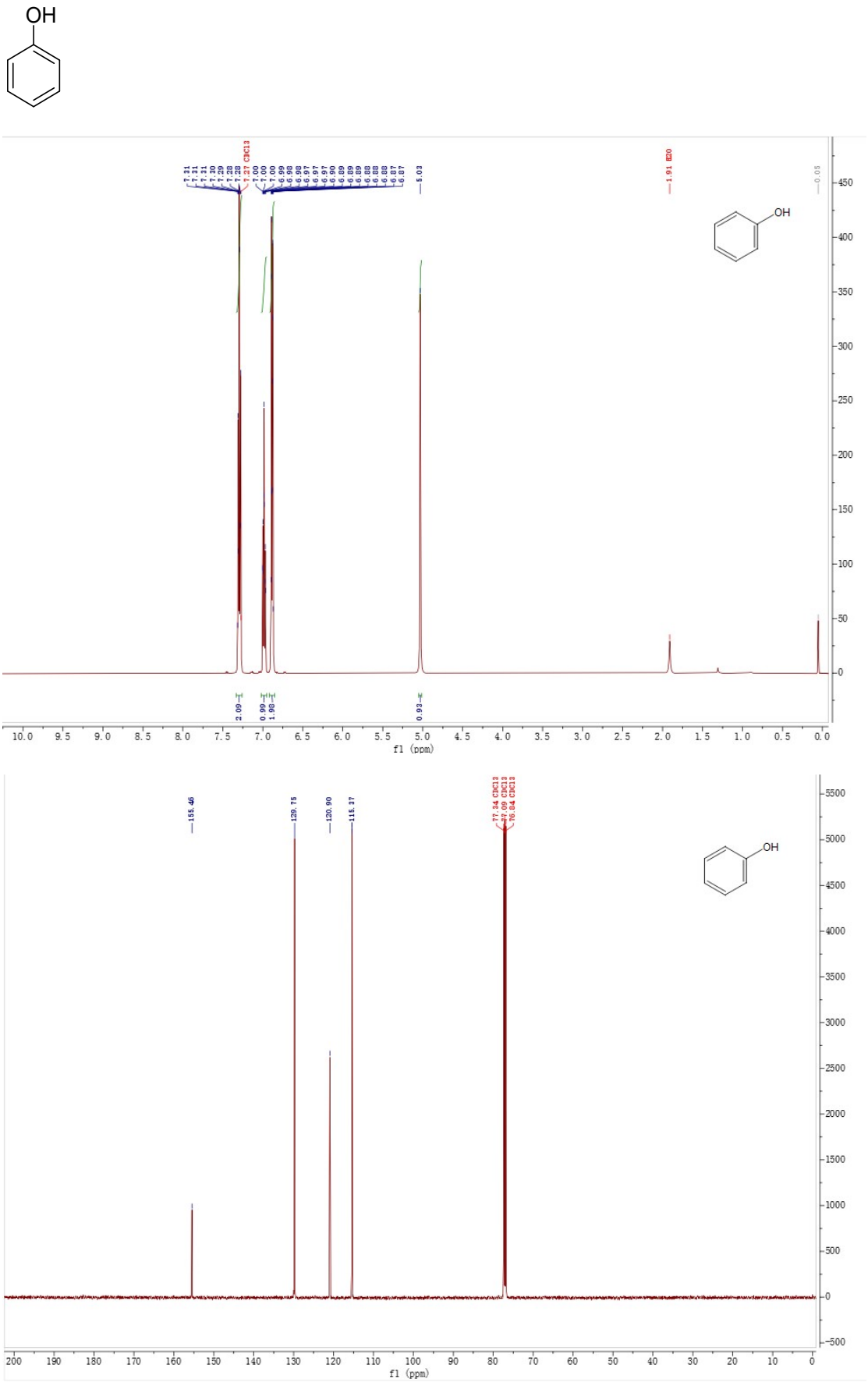


Figure S12 ^{1}H (top) and ^{13}C (bottom) NMR spectra of Phenol.

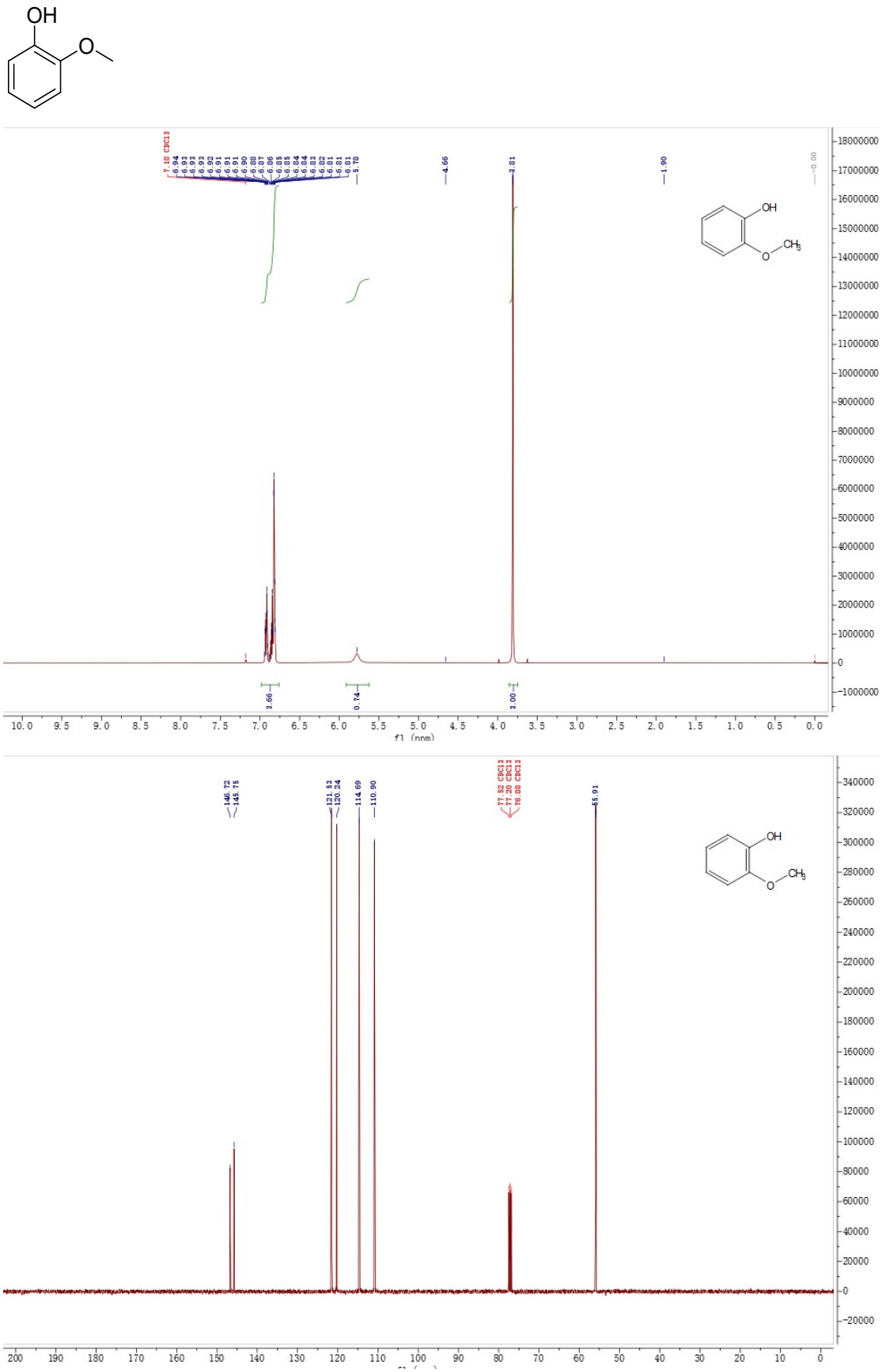
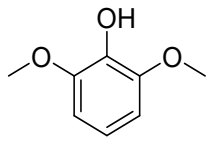
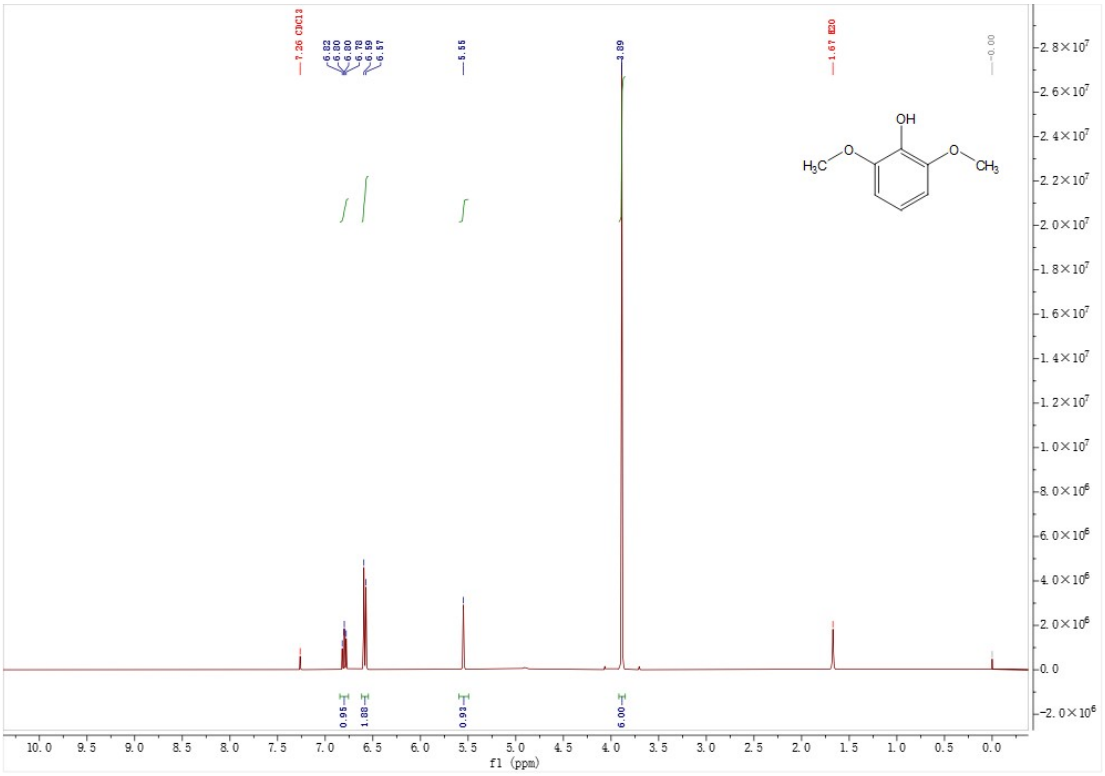


Figure S13 ^{1}H (top) and ^{13}C (bottom) NMR spectra of Guaiacol.





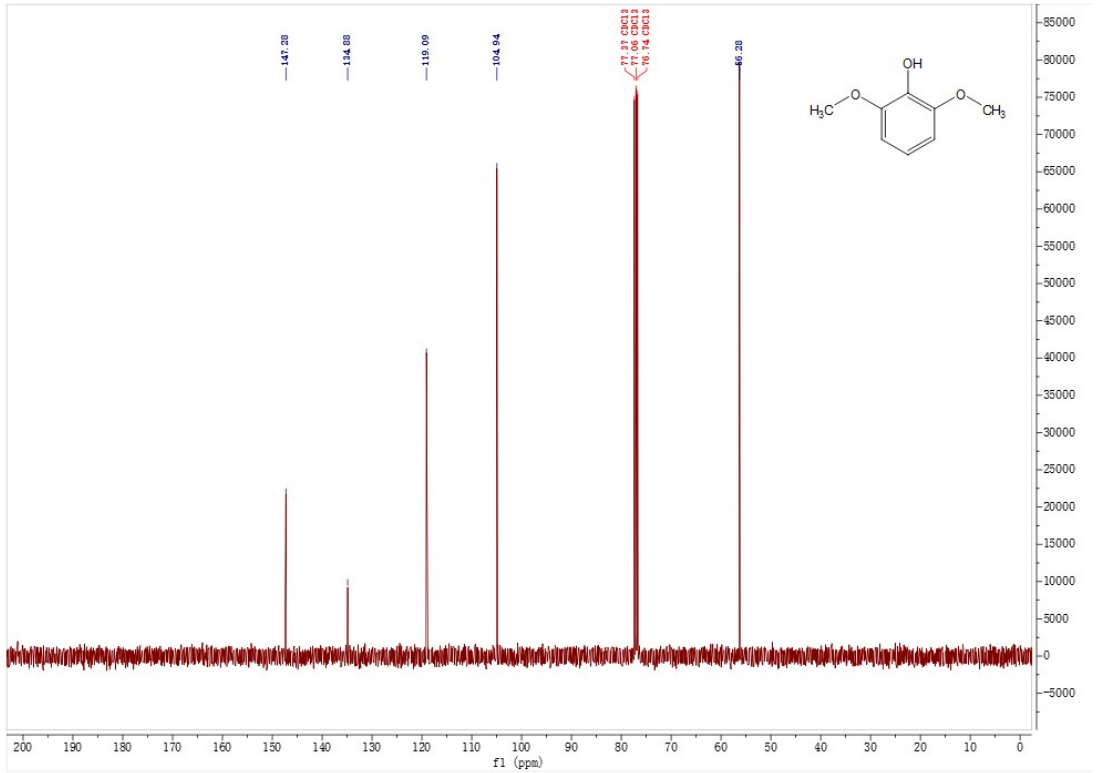


Figure S14 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2,6-Dimethoxyphenol.

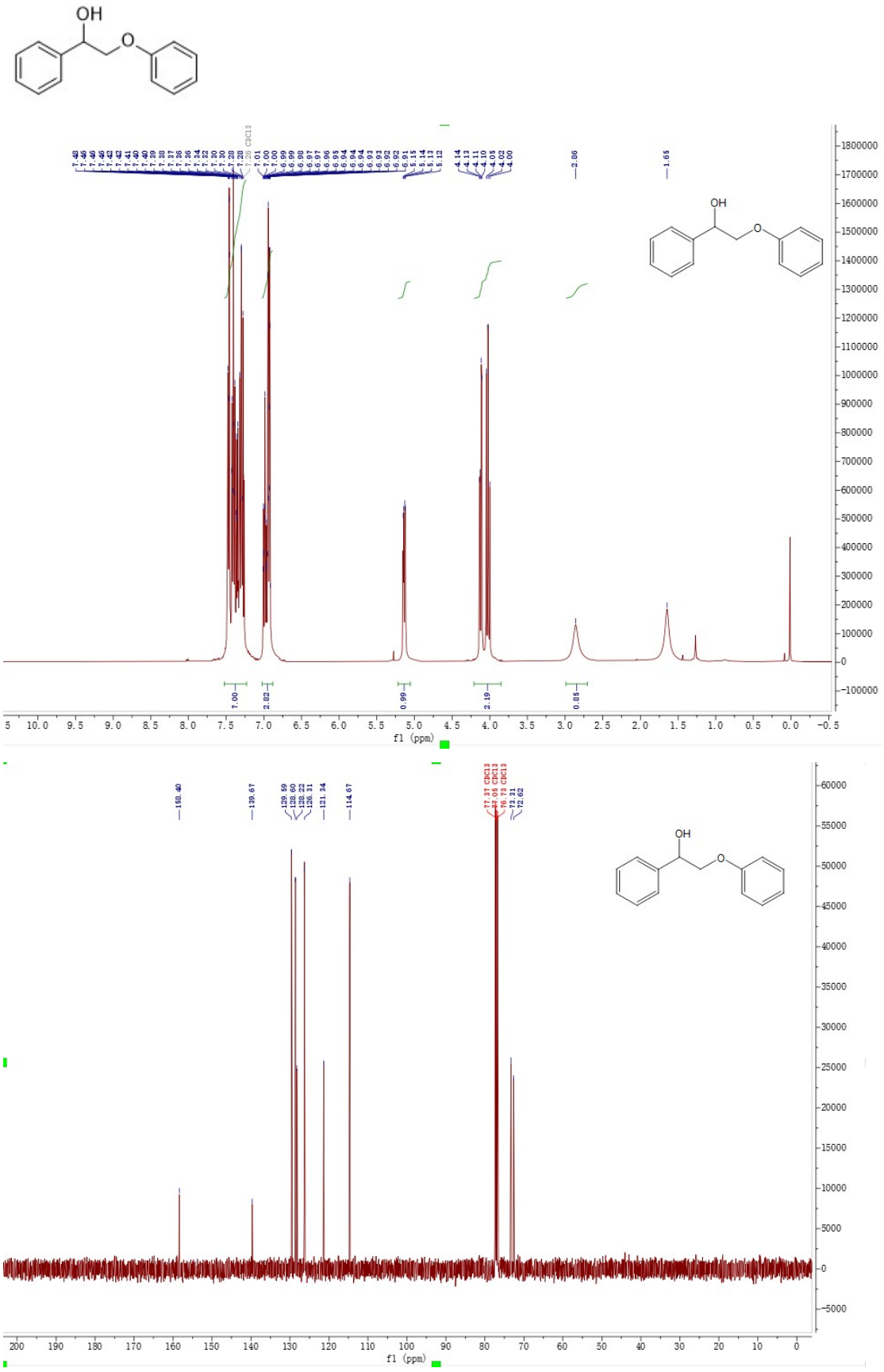


Figure S15 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-Phenoxy-1-phenyl-ethanol.

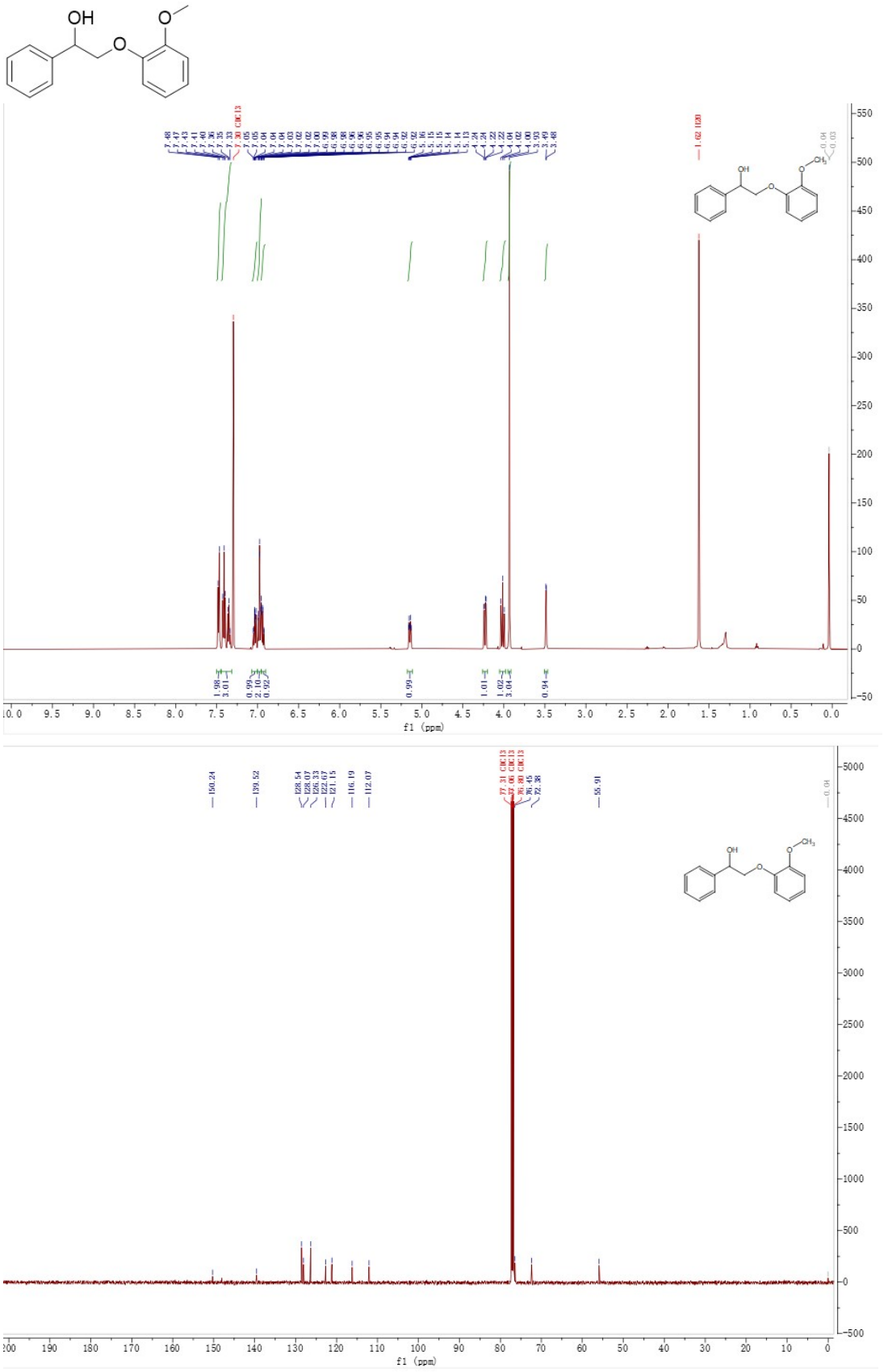


Figure S16 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(2-methoxyphenoxy)-1-phenylethan-1-ol.

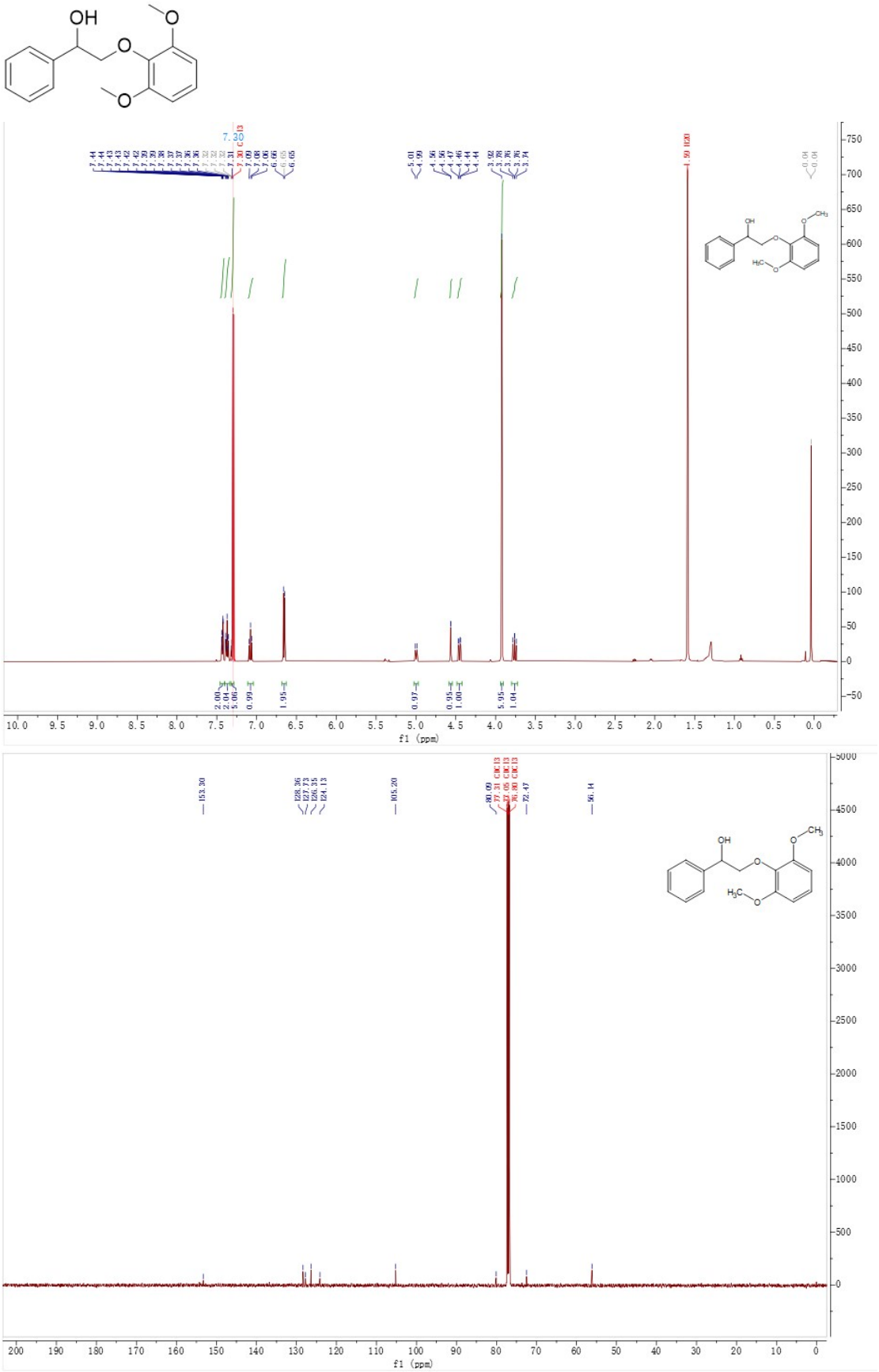


Figure S17 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-chlorophenoxy)-1-phenylethan-1-ol.

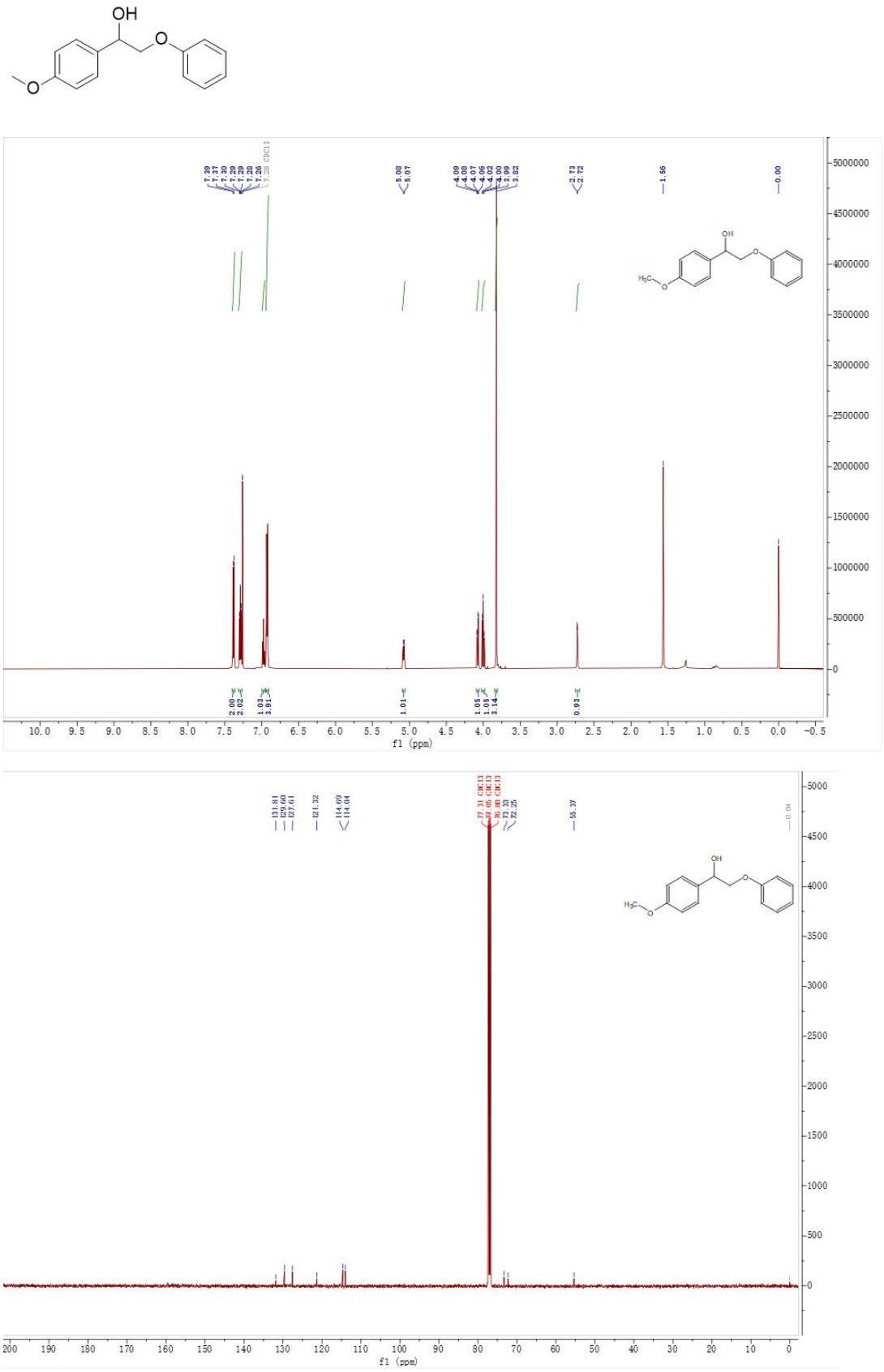
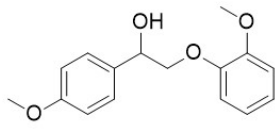
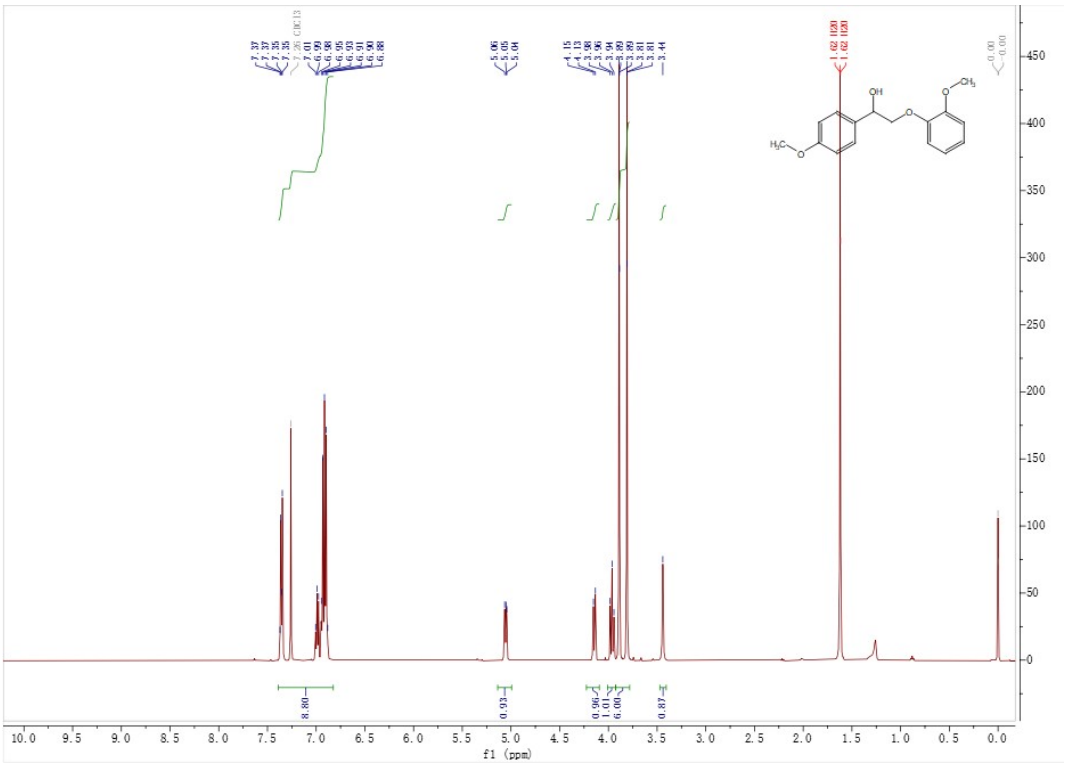


Figure S18 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-(4-methoxyphenyl)-2-phenoxyethan-1-ol.





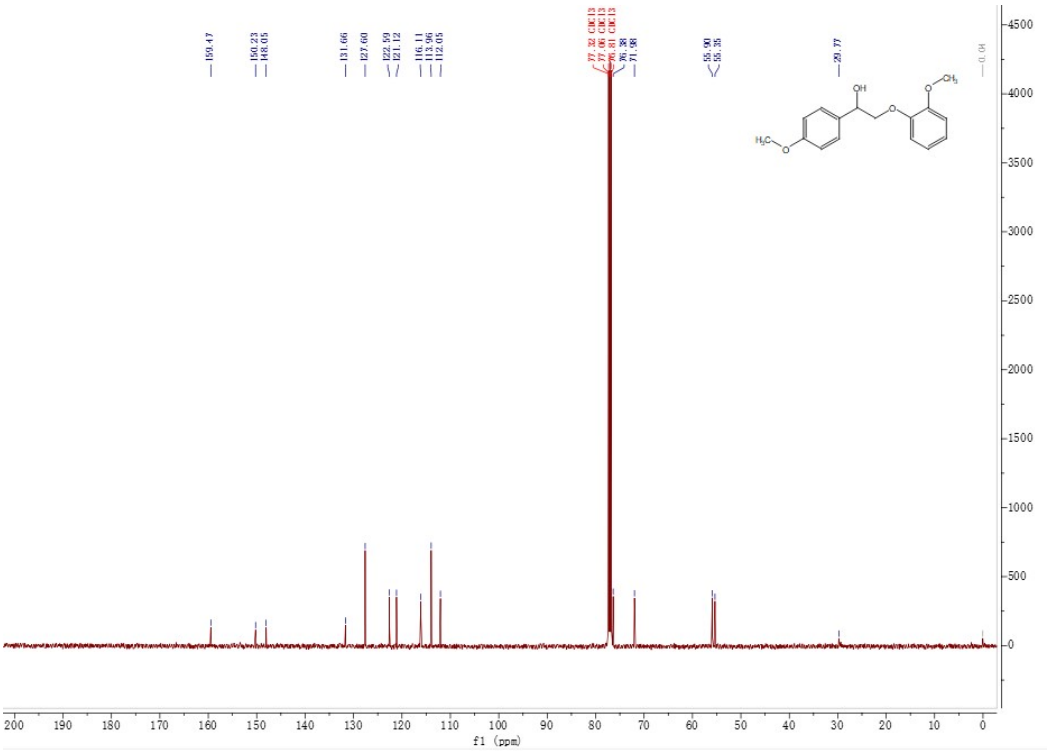


Figure S19 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethan-1-ol.

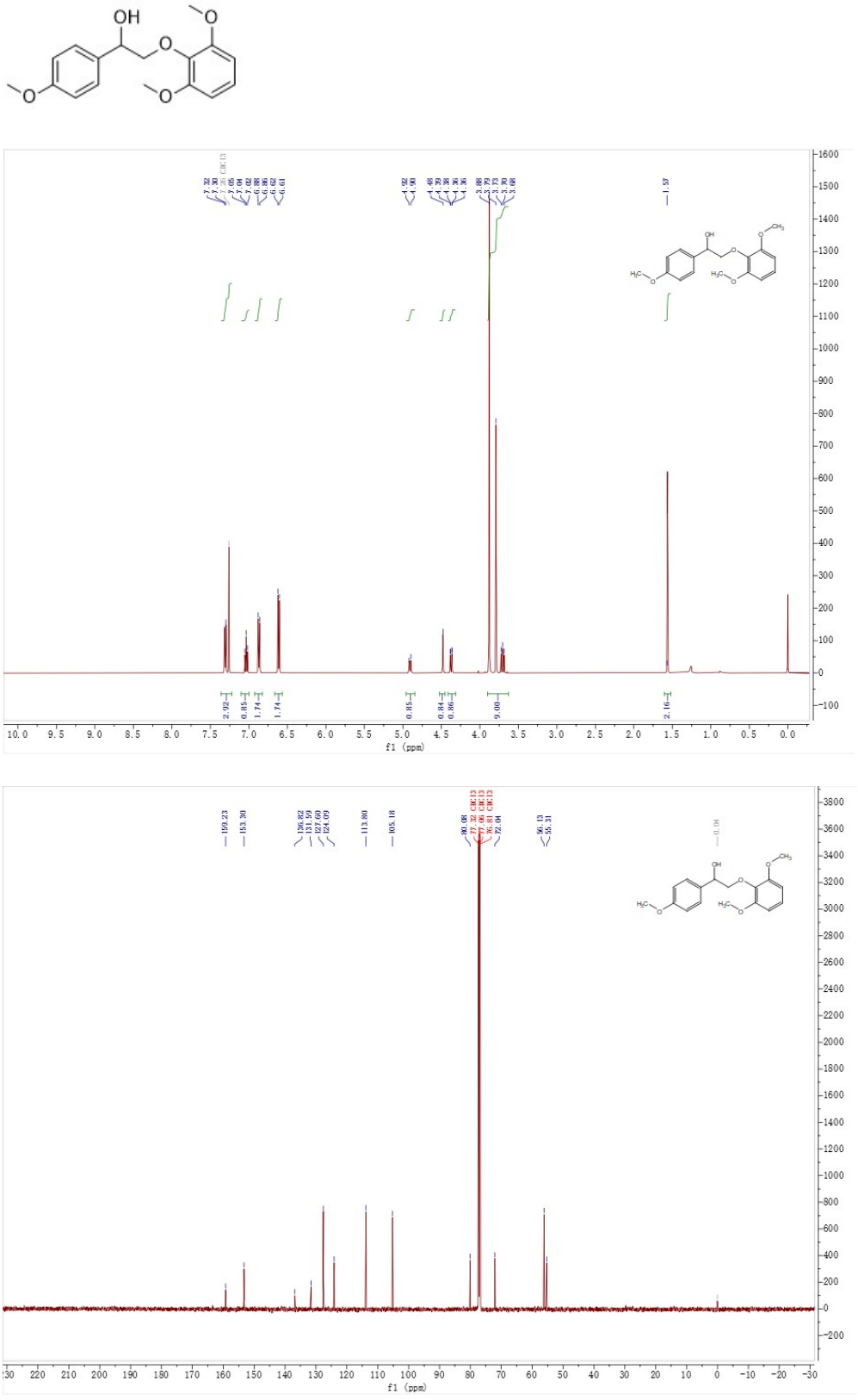


Figure S20 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl) ethan-1-ol.

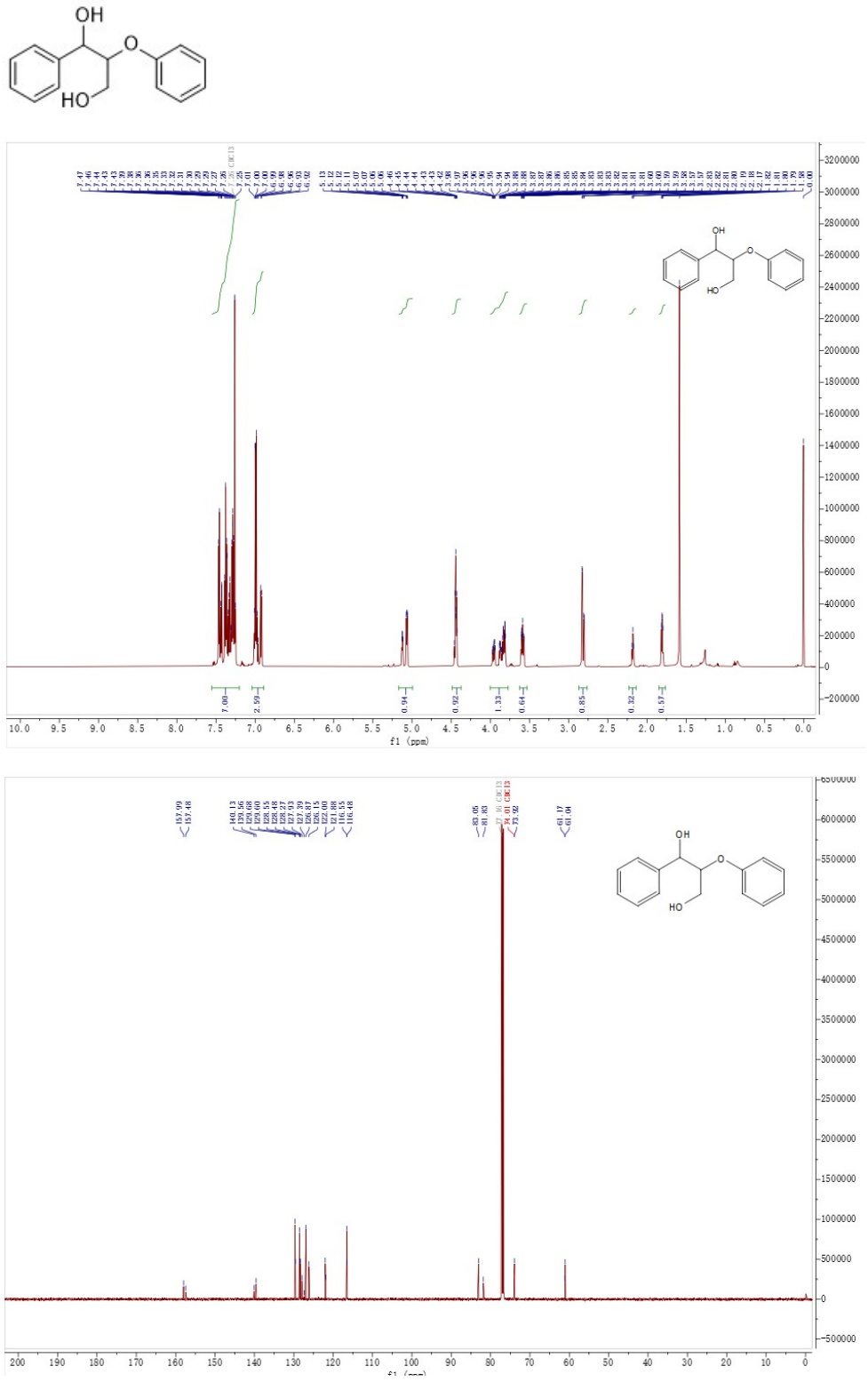
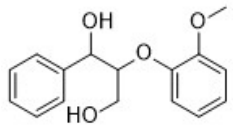
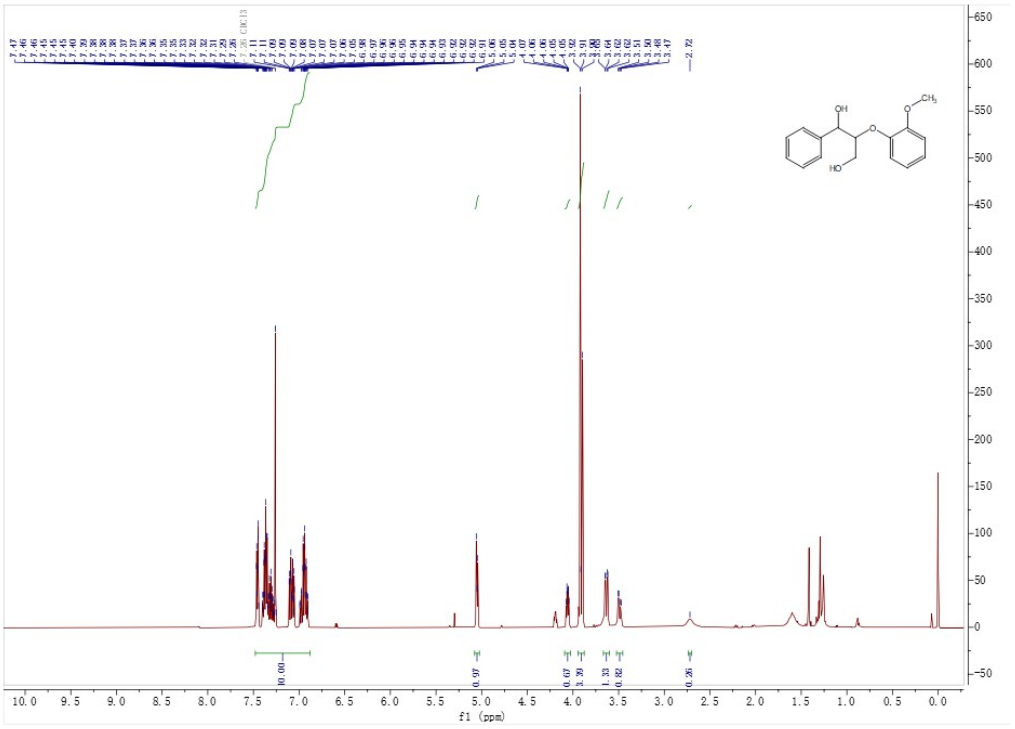


Figure S21 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-phenoxy-1-phenylpropane-1,3-diol.





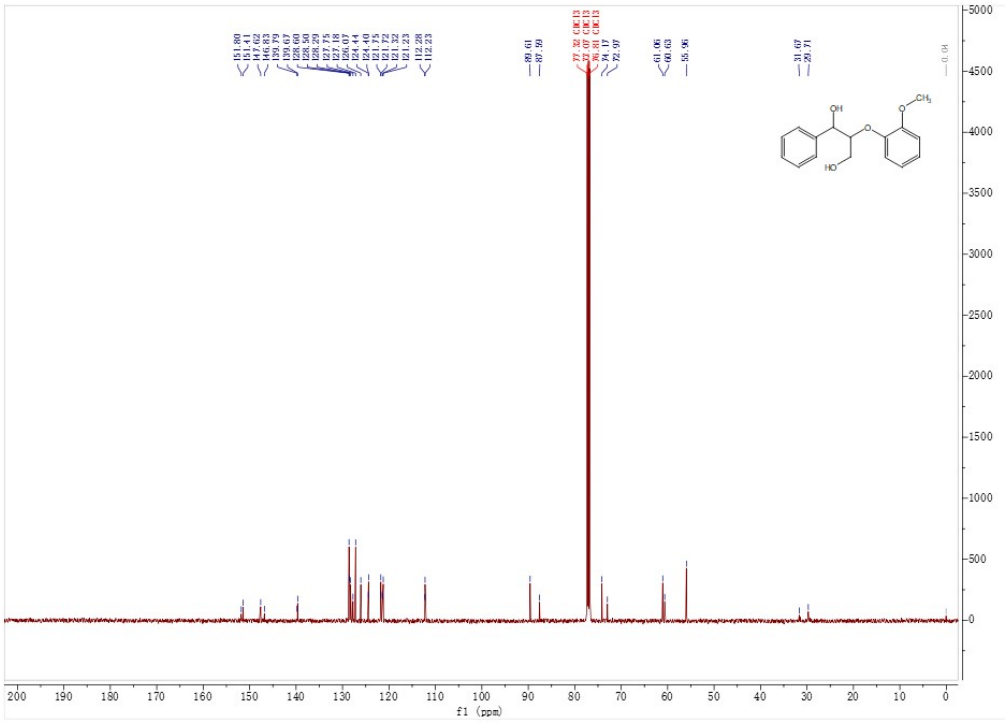


Figure S22 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(2-methoxyphenoxy)-1-phenylpropane-1,3-diol.

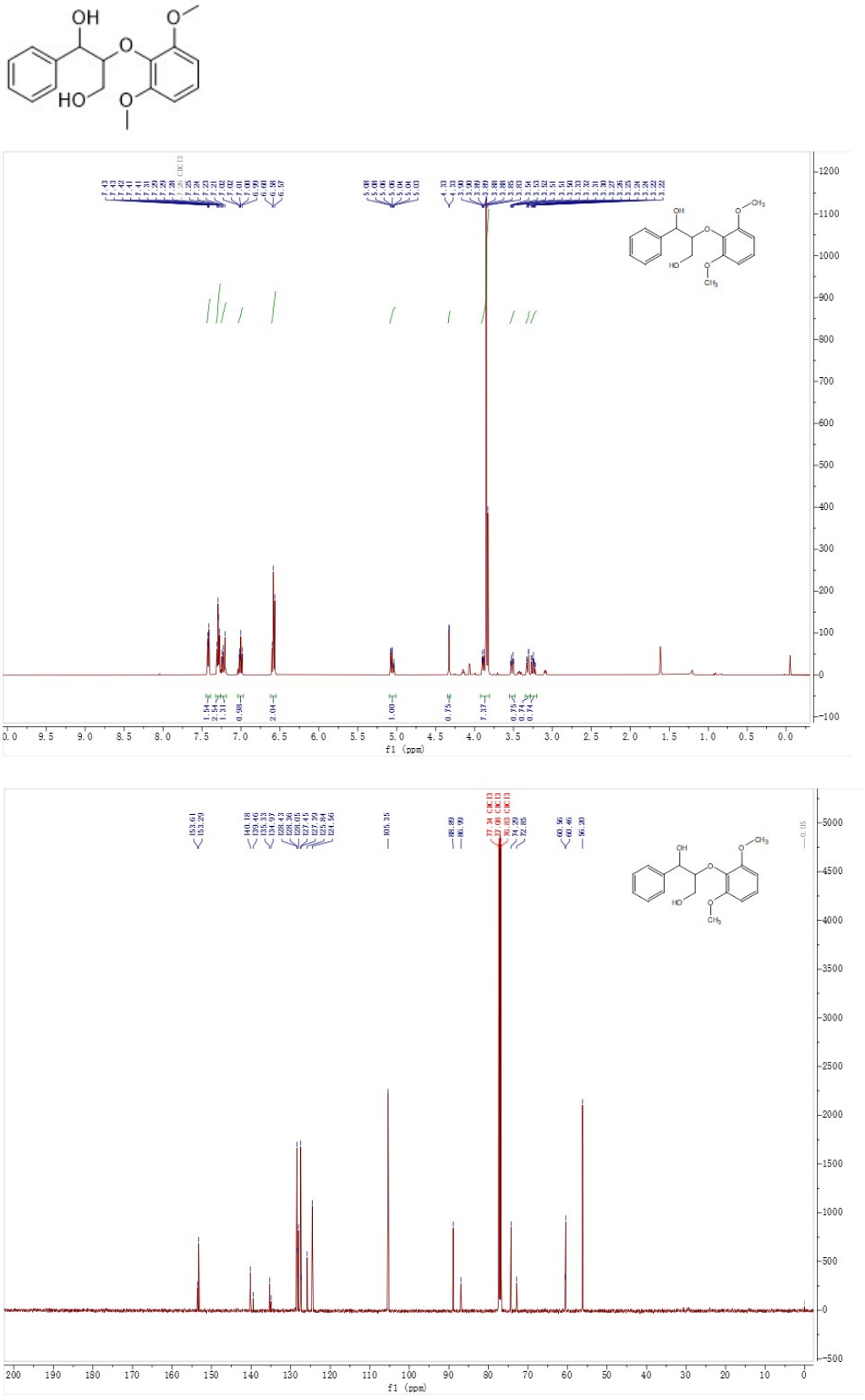


Figure S23 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(2,6-dimethoxyphenoxy)-1-phenylpropane-1,3-diol.

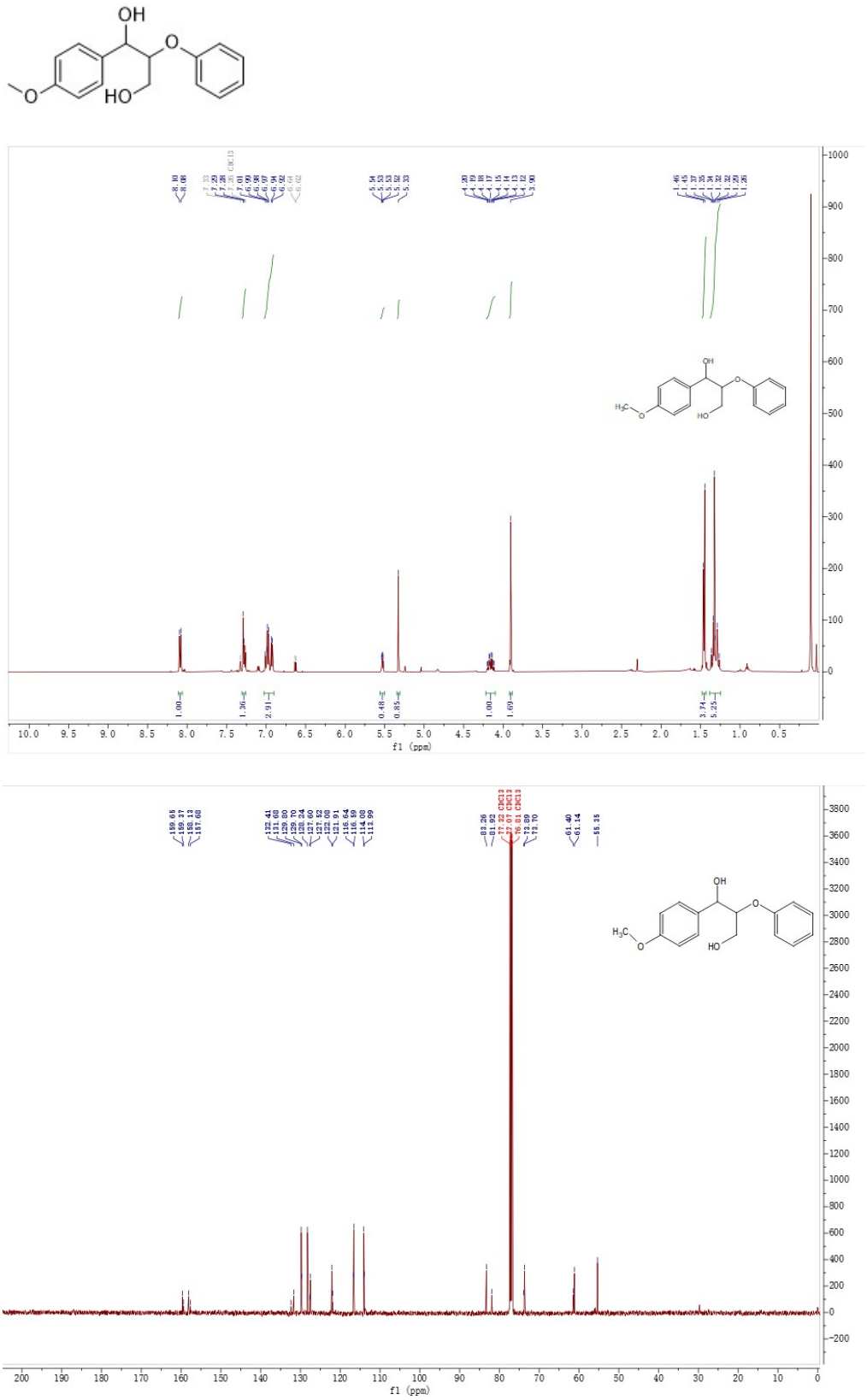


Figure S24 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-(4-methoxyphenyl)-2-phenoxypropane-1,3-diol.

7. References

1. S. A. Kim, S. E. Kim, Y. K. Kim and H. Y. Jang, *ACS Omega*, 2020, **5**, 31684-31691.
2. D. Huang, R. Li, P. Xu, T. Li, R. Deng, S. Chen and Q. Zhang, Chem. Eng. J., 2020, **402**, 126237.