Supplementary Information

DBU-catalyzed Metal-free C-O Bond Cleavage of Lignin Model Compounds under Mild Conditions

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SUPPORTING INFORMATION

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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

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.

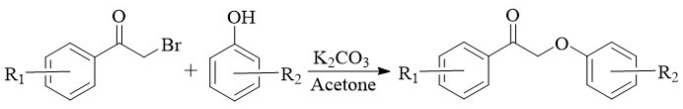
The products were identified and quantified using gas chromatography-mass spectrometry (GC-MS) and an Agilent 7890A/5975C instrument equipped with an HP-5 MS column (30 m in length, 0.25 mm in diameter). Conversion and yield were determined using p-xylene as the internal standard.

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 DMSO using internal reference (the residue proton peaks of DMSO at 2.5 ppm) on Bruker 400 spectrometer. Liquid ^{13}C NMR was recorded at 100.6 MHz in DMSO using residual DMSO as internal reference (the residue proton peaks of DMSO at 40.03 ppm).

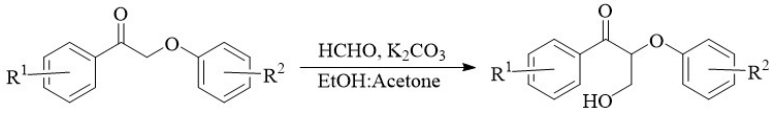
2. Synthesis of lignin model compounds and details of NMR Characterization

2.1 Synthesis of lignin models



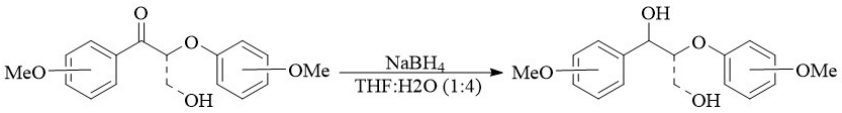
Scheme S1 synthetic ketone lignin model.

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 (1 mmol) is dissolved in a solution of K_2CO_3(1.5 mmol, 0.207 g) and phenol (1 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=3:1) 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.

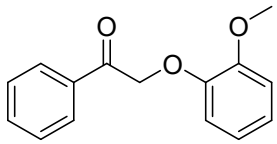


Scheme S3 synthetic lignin model compounds.

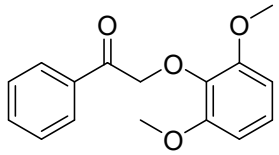
The resulting compound (3.5 mmol, 0.847 g) from the previous step was dissolved in the mixture of THF and H_2O (v:v=5:1, total 25 mL), and sodium borohydride (7 mmol, 0.26 g) was added portionwise to maintain a gentle evolution of gas. Then, the mixture was stirred for 6 h at room temperature. The reaction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

2.2 detailed NMR characterization of model compounds.

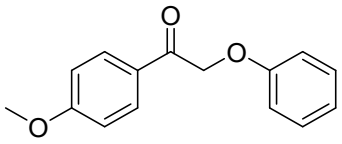
2-(2-methoxyphenoxy)-1-phenylethan-1-one: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 7.4 Hz, 1H), 5.54 (s, 2H), 3.77 (d, *J* = 12.0 Hz, 3H).
^{13}C NMR (101 MHz, DMSO) δ 195.19, 149.47, 147.91, 134.94, 134.20, 129.28, 128.35, 121.85, 121.01, 119.63, 116.04, 114.22, 112.96, 71.23, 56.03.



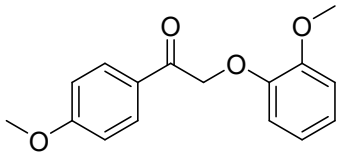
2-(2,6-dimethoxyphenoxy)-1-phenylethan-1-one: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 46.9 Hz, 3H), 7.01 (s, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 5.15 (s, 2H), 3.72 (s, 6H).
^{13}C NMR (101 MHz, DMSO) δ 195.40, 153.20, 136.48, 135.26, 133.90, 129.14, 128.57, 124.40, 106.08, 75.22, 56.30.



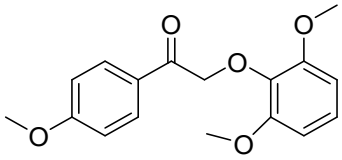
1-(4-methoxyphenyl)-2-phenoxyethan-1-one: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (d, *J* = 9.1 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.94 (t, *J* = 7.7 Hz, 3H), 5.49 (s, 2H), 3.86 (s, 3H).
^{13}C NMR (101 MHz, DMSO) δ 192.92, 163.55, 157.99, 157.32, 130.22, 129.37, 129.33, 127.33, 120.78, 118.76, 115.21, 114.58, 114.03, 69.77, 55.57.



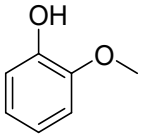
2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 7.02 – 6.77 (m, 4H), 5.45 (s, 2H), 3.82 (d, *J* = 29.1 Hz, 6H).
^{13}C NMR (101 MHz, DMSO) δ 193.01, 163.52, 149.00, 147.53, 130.24, 127.37, 121.30, 120.52, 114.00, 113.70, 112.47, 70.52, 55.55, 55.53.



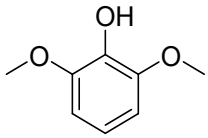
2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.05 (dd, *J* = 19.2, 8.6 Hz, 3H), 6.69 (d, *J* = 8.4 Hz, 2H), 5.08 (s, 2H), 3.81 (d, *J* = 44.6 Hz, 9H).
^{13}C NMR (101 MHz, DMSO) δ 193.20, 163.30, 152.79, 136.03, 130.50, 127.69, 123.90, 113.88, 105.62, 74.58, 55.85, 55.50.



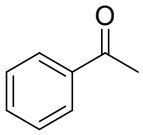
2-methoxyphenol: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.91 (s, 1H), 7.03 – 6.68 (m, 4H), 3.77 (s, 3H).
^{13}C NMR (101 MHz, DMSO) δ 147.67, 146.60, 120.94, 119.27, 115.61, 112.17, 55.38.



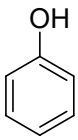
2,6-dimethoxyphenol: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (s, 1H), 6.79 – 6.46 (m, 3H), 3.74 (s, 6H).
^{13}C NMR (101 MHz, DMSO) δ 148.23, 135.71, 118.16, 105.73, 55.94.



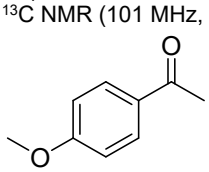
acetophenone: ^{1}H NMR (400 MHz, DMSO-d6) δ 7.90 (dd, J = 8.4, 1.6 Hz, 3H), 7.55 (t, J = 6.6 Hz, 1H), 7.48-7.39 (m, 3H).
^{13}C NMR (101 MHz, DMSO-d6) δ 198.18, 137.26, 133.46, 129.00, 128.54, 39.92, 26.89.



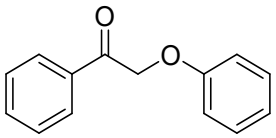
phenol: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.36 (s, 1H), 7.18 (dd, *J* = 8.6, 7.2 Hz, 2H), 6.92 – 6.64 (m, 3H).
^{13}C NMR (101 MHz, DMSO) δ 157.83, 129.83, 119.28, 115.73.



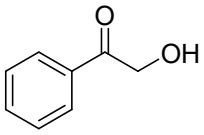
methyl 4-methoxybenzoate: ^{1}H NMR (400 MHz, DMSO-d6) δ 7.93 (d, J = 8.9 Hz, 2H), 7.05 (d, J = 8.9 Hz, 2H), 3.84 (d, J = 7.2 Hz, 6H).
^{13}C NMR (101 MHz, DMSO) δ 166.35, 163.57, 131.66, 122.30, 114.44, 55.91, 52.21.



2-phenoxy-1-phenylethan-1-one: ^{1}H NMR (400 MHz, DMSO-d6) δ 8.29 – 7.89 (m, 2H), 7.63 (dt, J = 49.1, 7.6 Hz, 3H), 7.44 – 7.14 (m, 2H), 6.96 (dd, J = 14.7, 7.7 Hz, 3H), 5.57 (s, 2H).
^{13}C NMR (101 MHz, DMSO) δ 194.61, 157.91, 134.42, 133.75, 129.39, 128.81, 127.85, 120.85, 114.60, 70.02.



2-hydroxy-1-phenylethan-1-one：^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, *J* = 6.9 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 5.11 (t, *J* = 5.8 Hz, 1H), 4.82 (d, *J* = 5.5 Hz, 2H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 199.64, 135.05, 133.86, 129.24, 128.01, 65.81.



3. Mechanism study

3.1 Controlled experiments

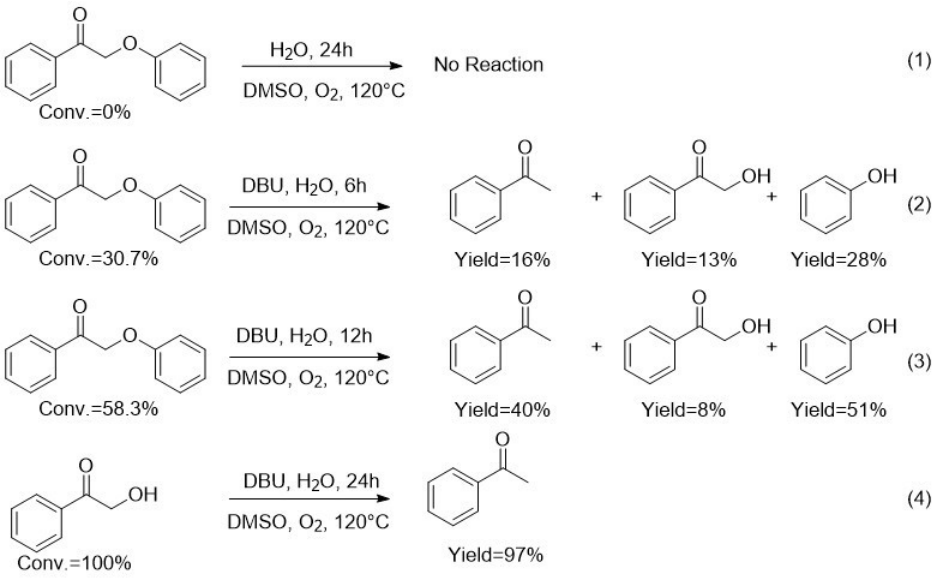


Figure S1. Mechanism study and controlled experiments.

Standard conditions: substrate (0.5 mmol), DBU (3.0 eq), H_2O (1.0 eq), 2.0 mL DMSO, O_2 atmosphere, 120 ℃, 24 h.

3.2 Radical Trapping Experiments

When employing TEMPO or BHT as radical trappers, the reaction were mostly inhibited, which suggested radical species might involves during the reaction. Yield of 5a was determined by GC:

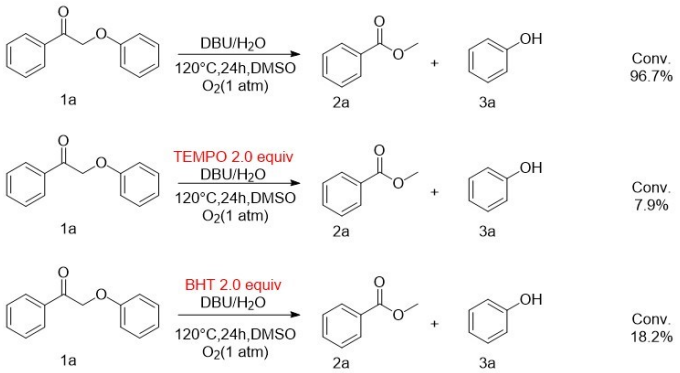
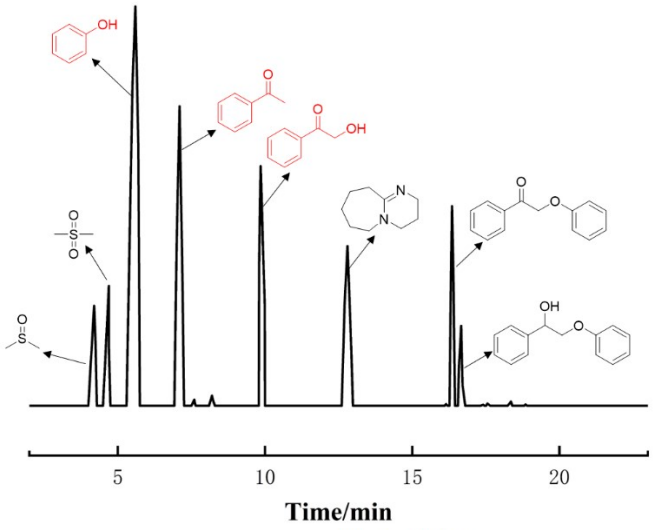
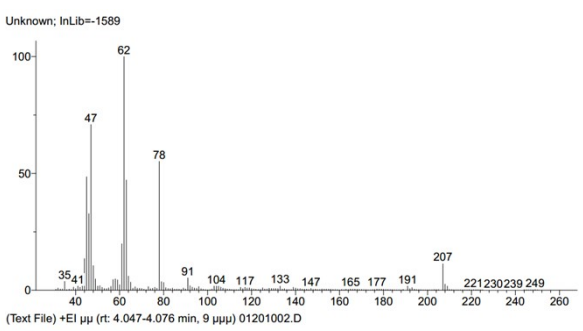


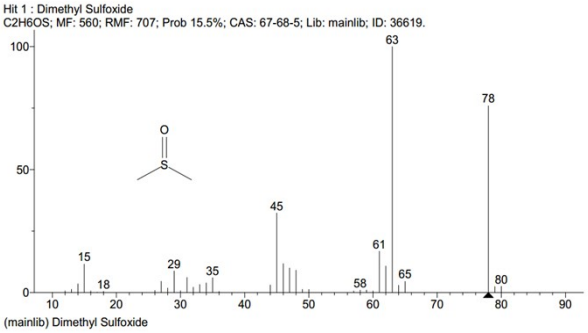
Figure S2 Radical Trapping Experiments.

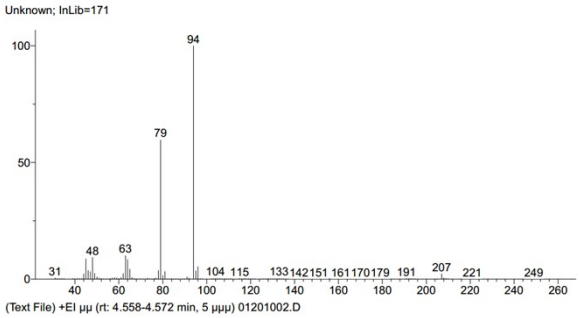
4. The type of data

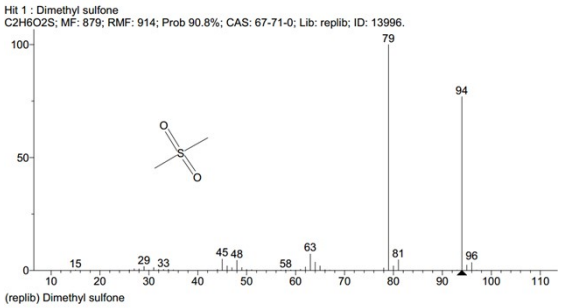
4.1 GC-MS analysis

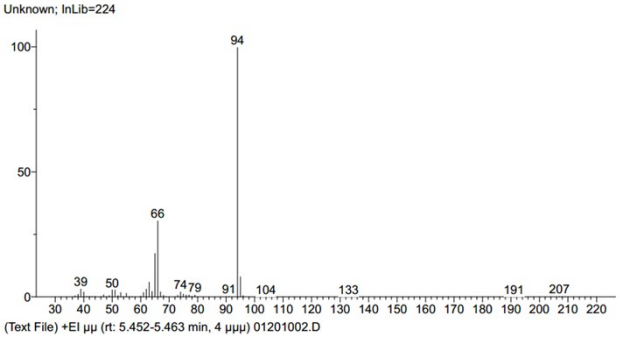


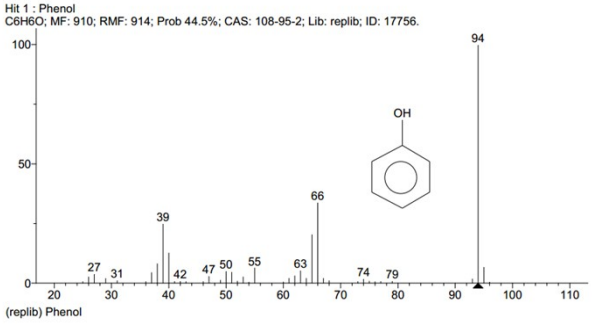












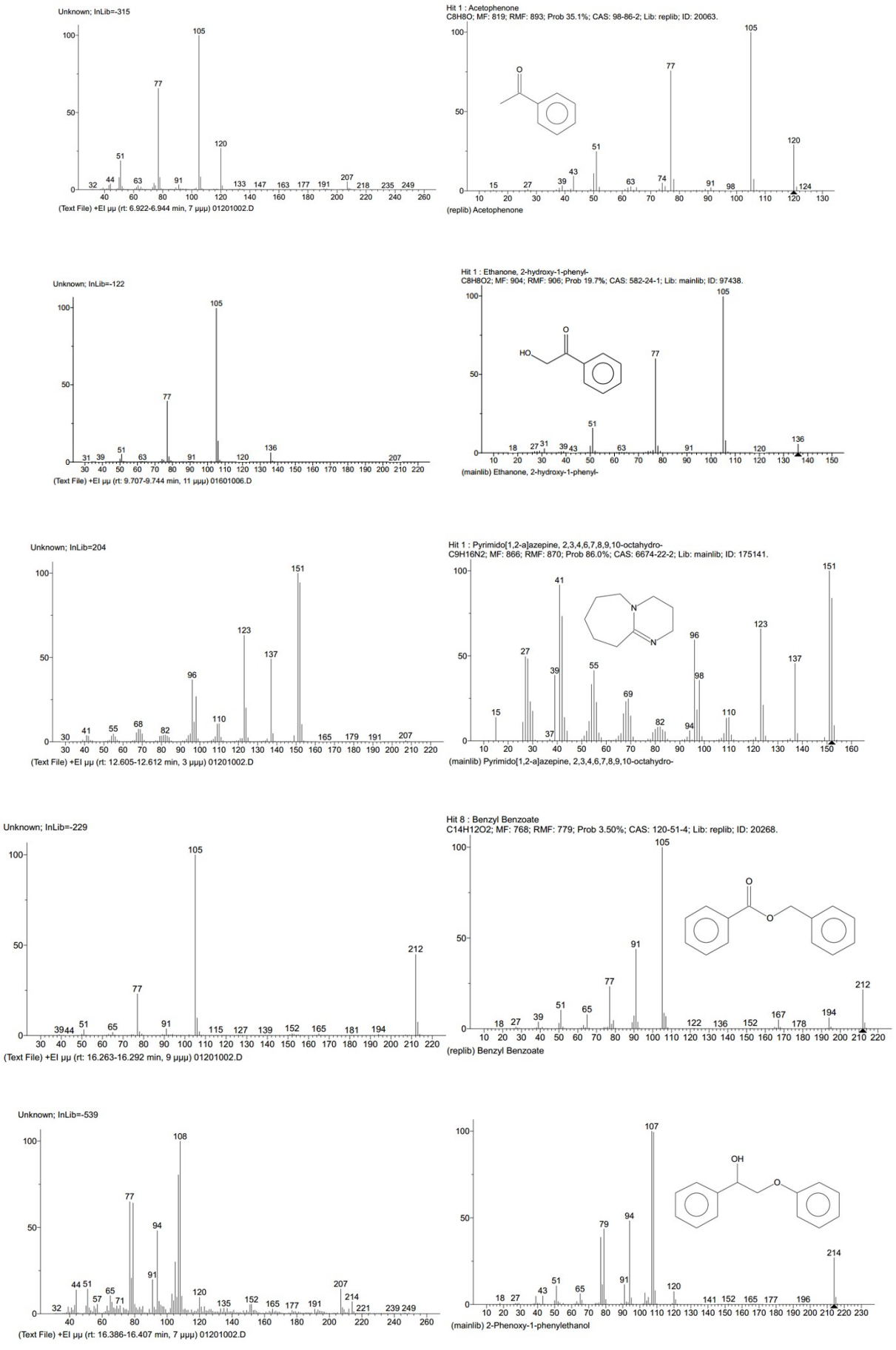
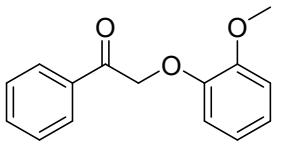


Figure S3 GC-MS analysis.

5.^{1}H NMR and ^{13}C NMR spectra of compounds



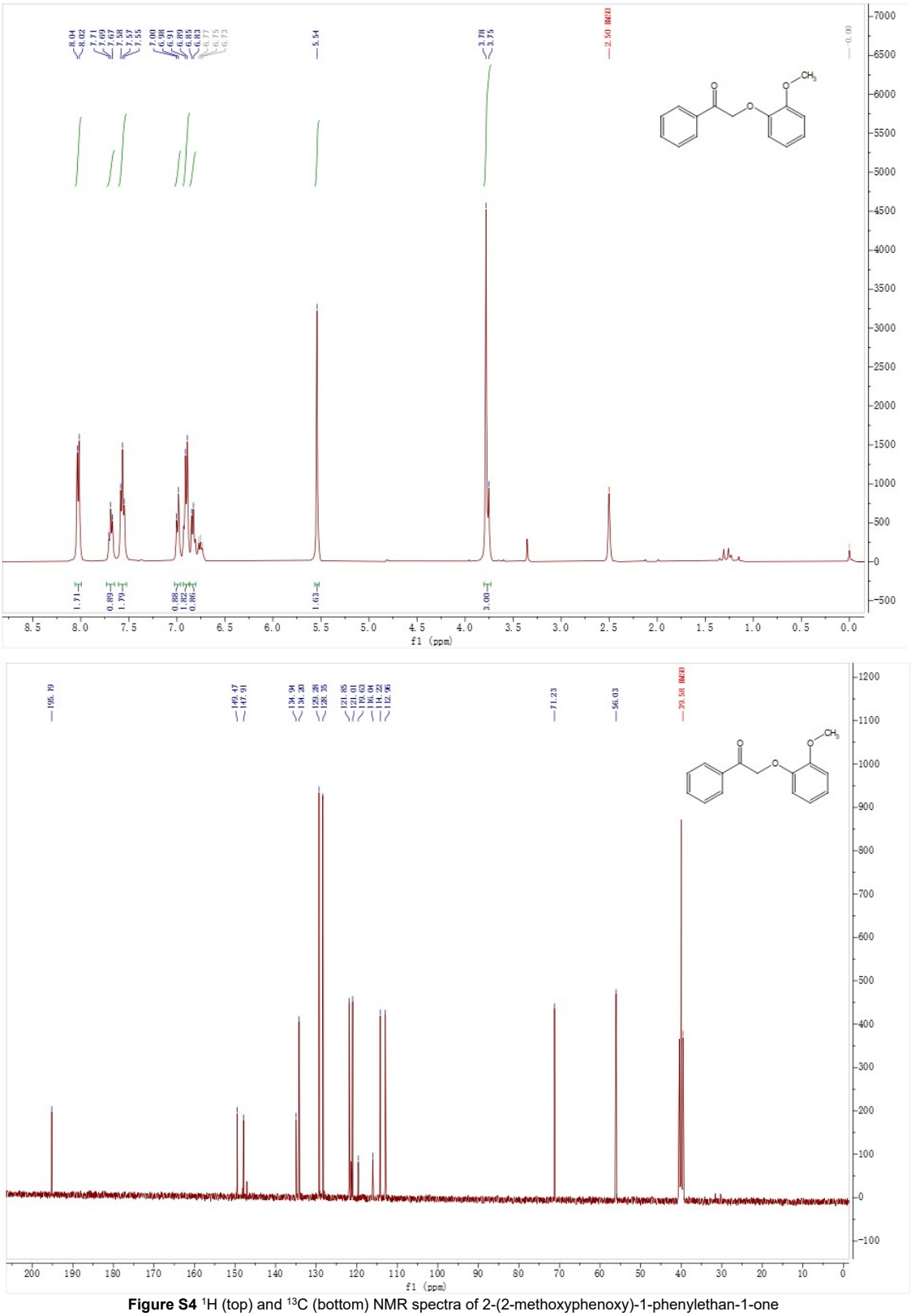
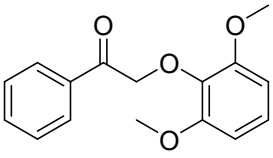
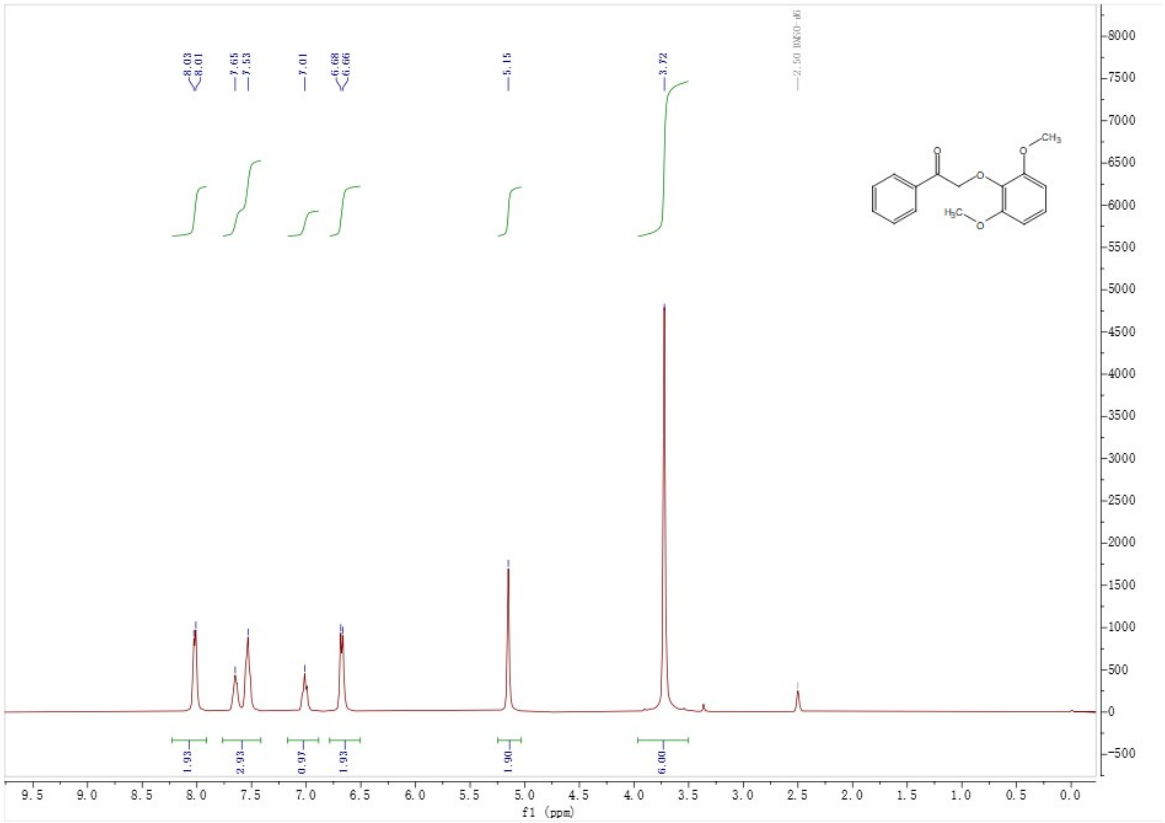


Figure S4 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(2-methoxyphenoxy)-1-phenylethan-1-one





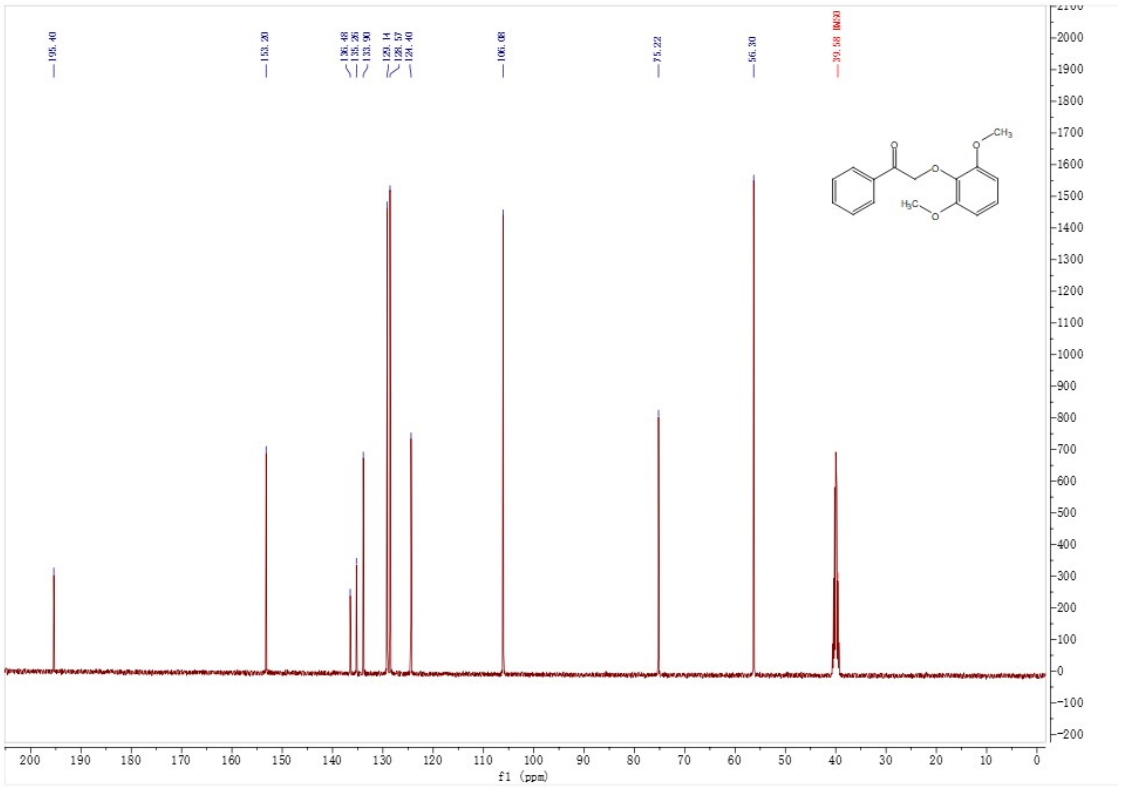
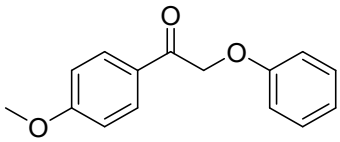


Figure S5 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(2,6-dimethoxyphenoxy)-1-phenylethan-1-one.



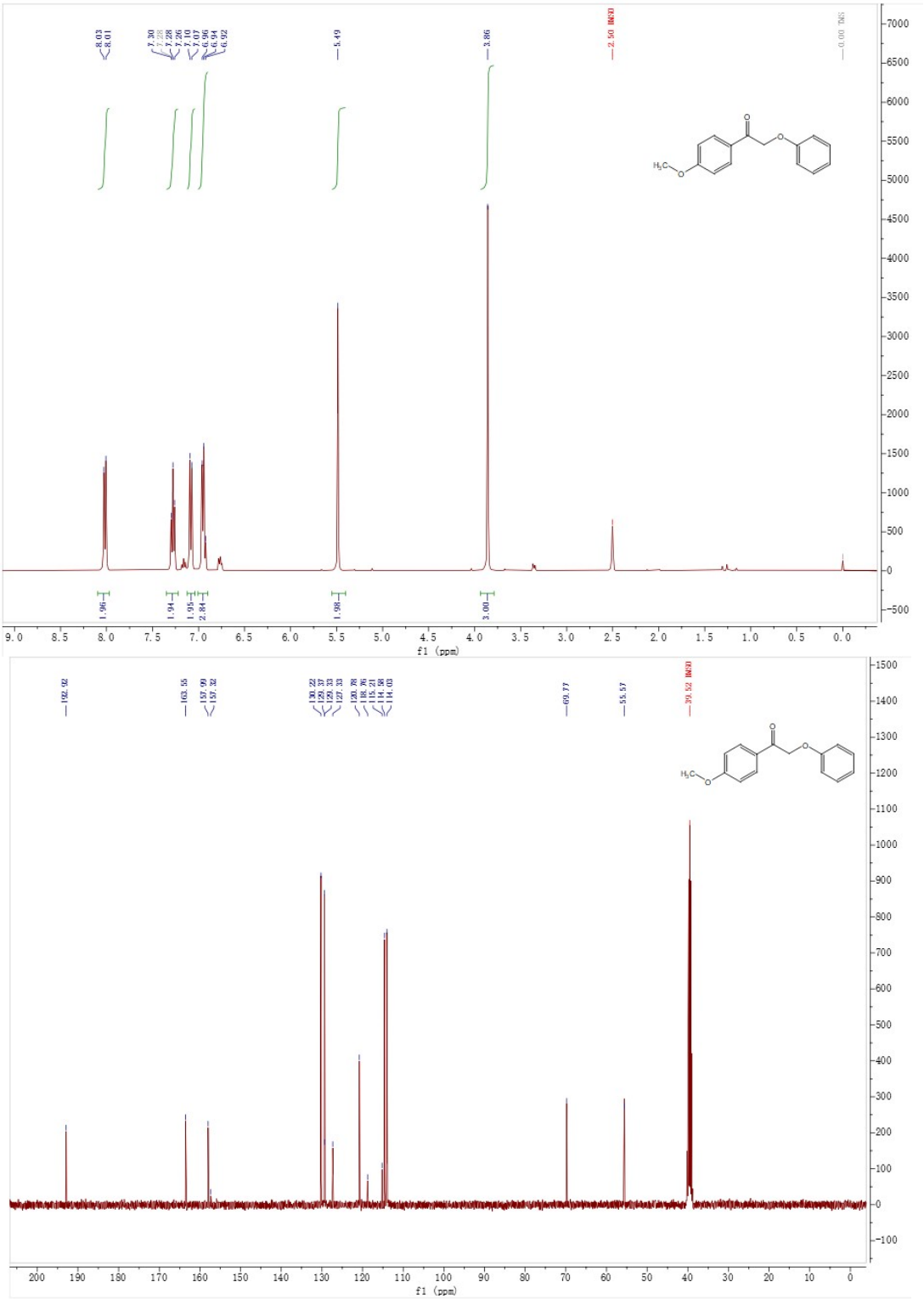
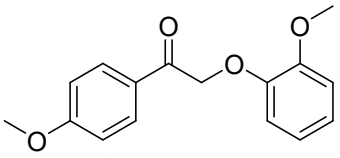
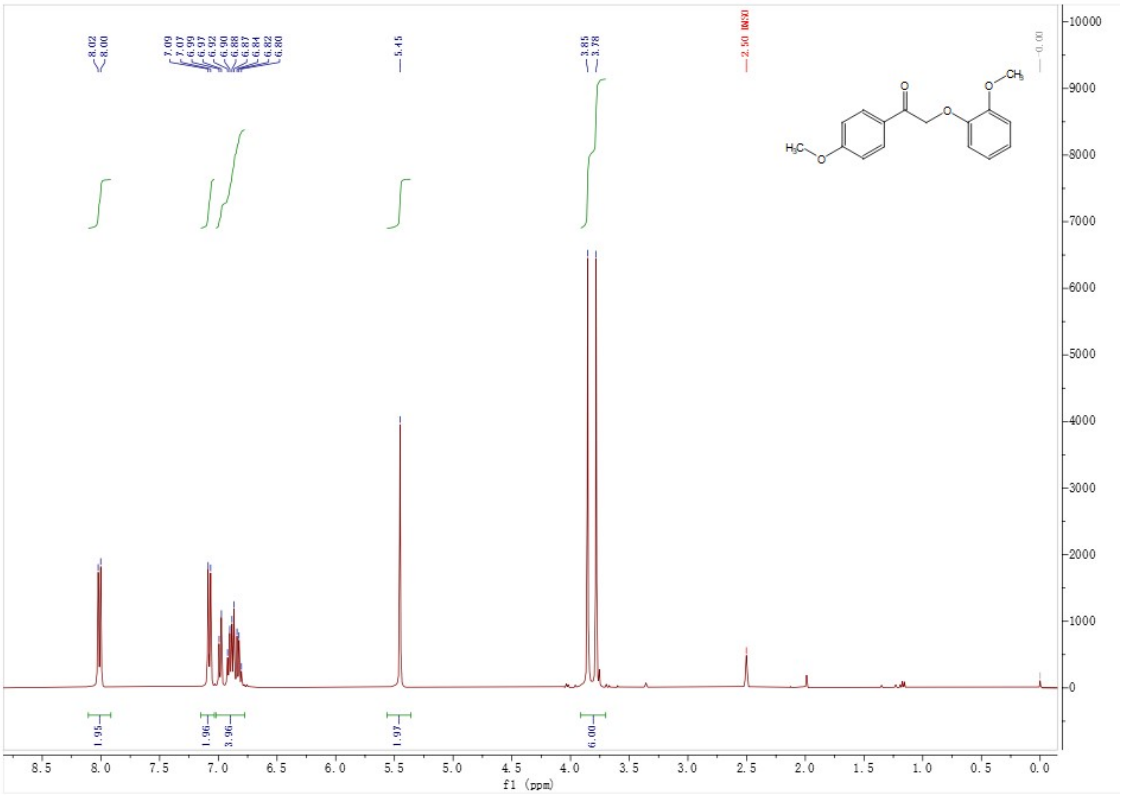


Figure S6 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-(4-methoxyphenyl)-2-phenoxyethan-1-one.





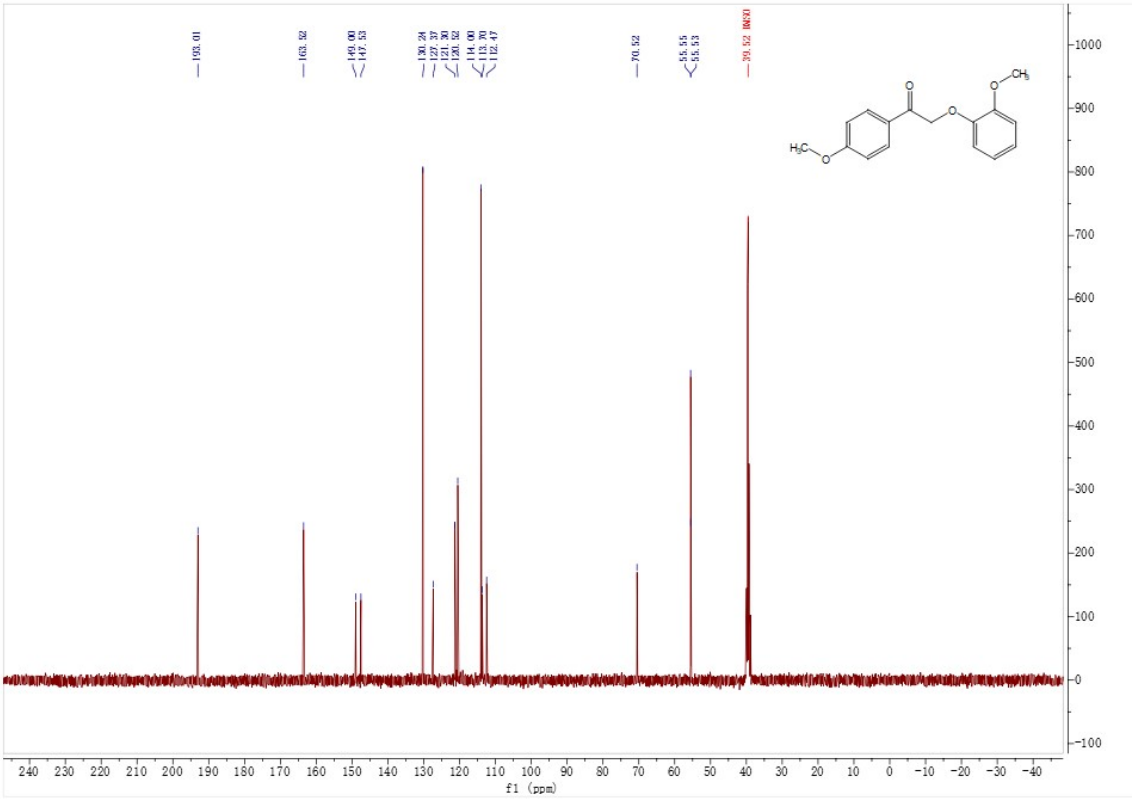
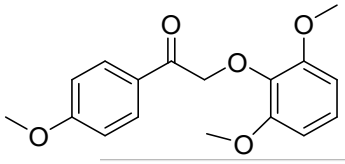
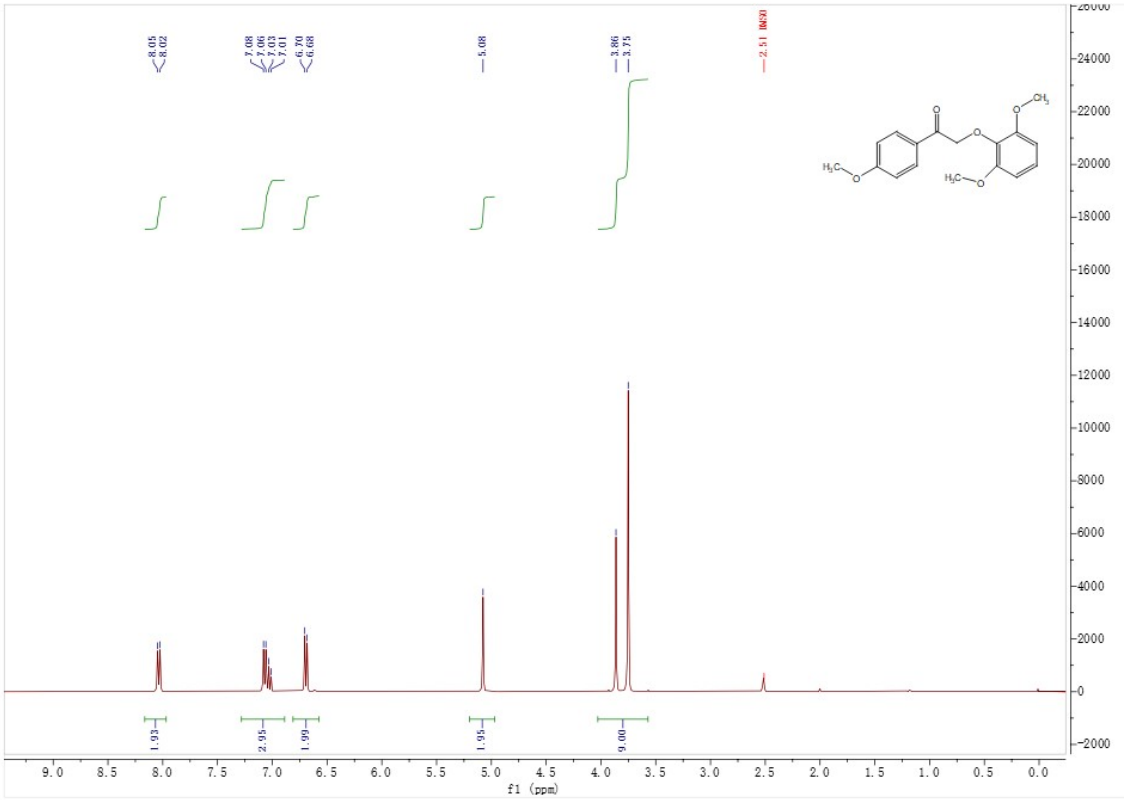


Figure S7 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one.





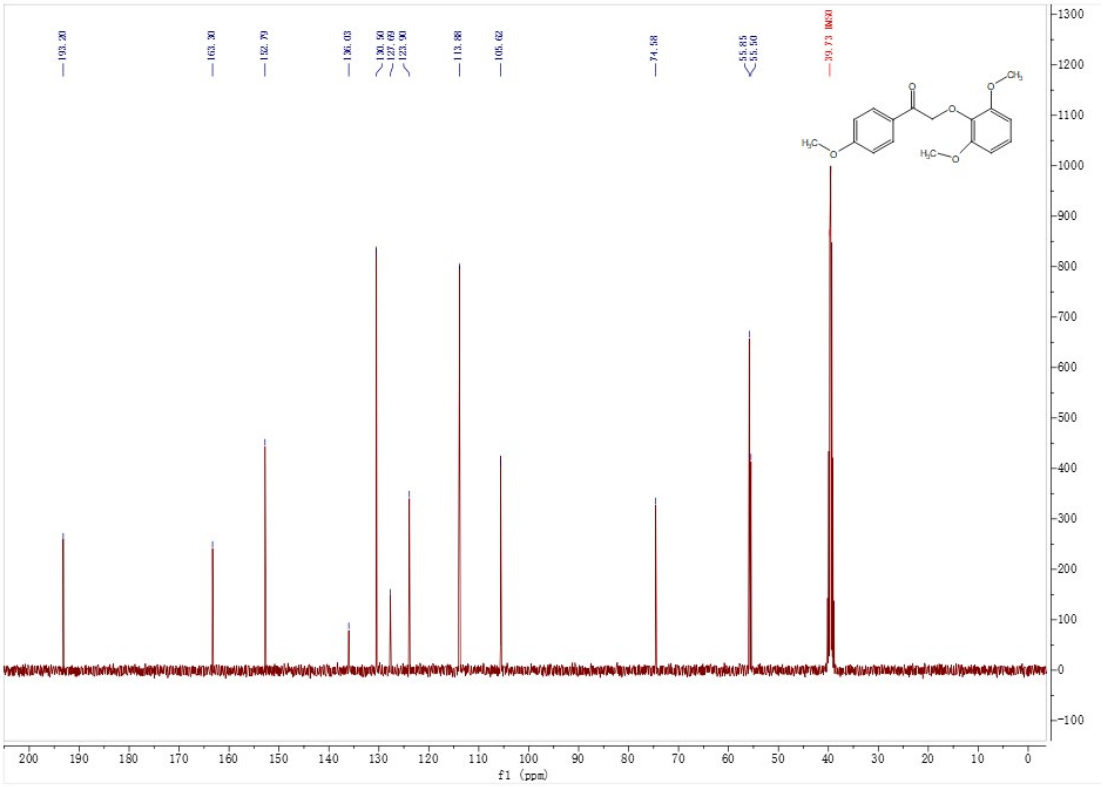
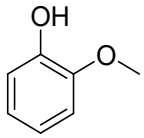
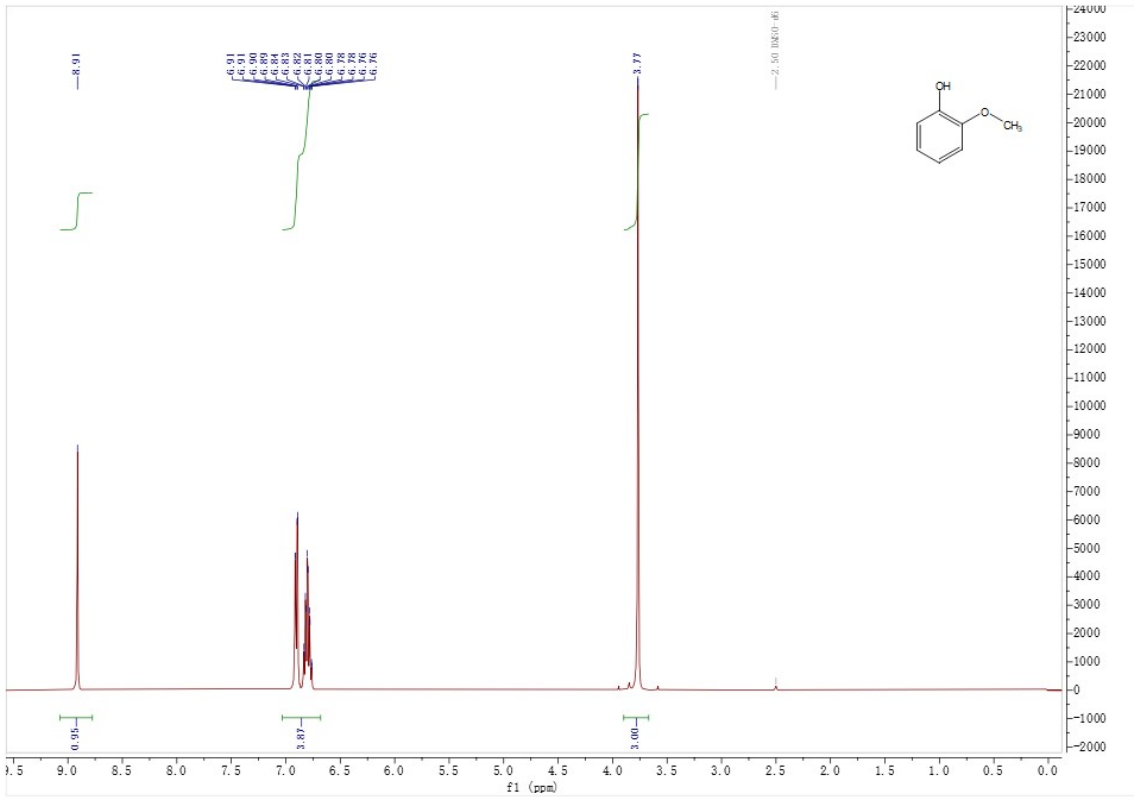


Figure S8 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one.





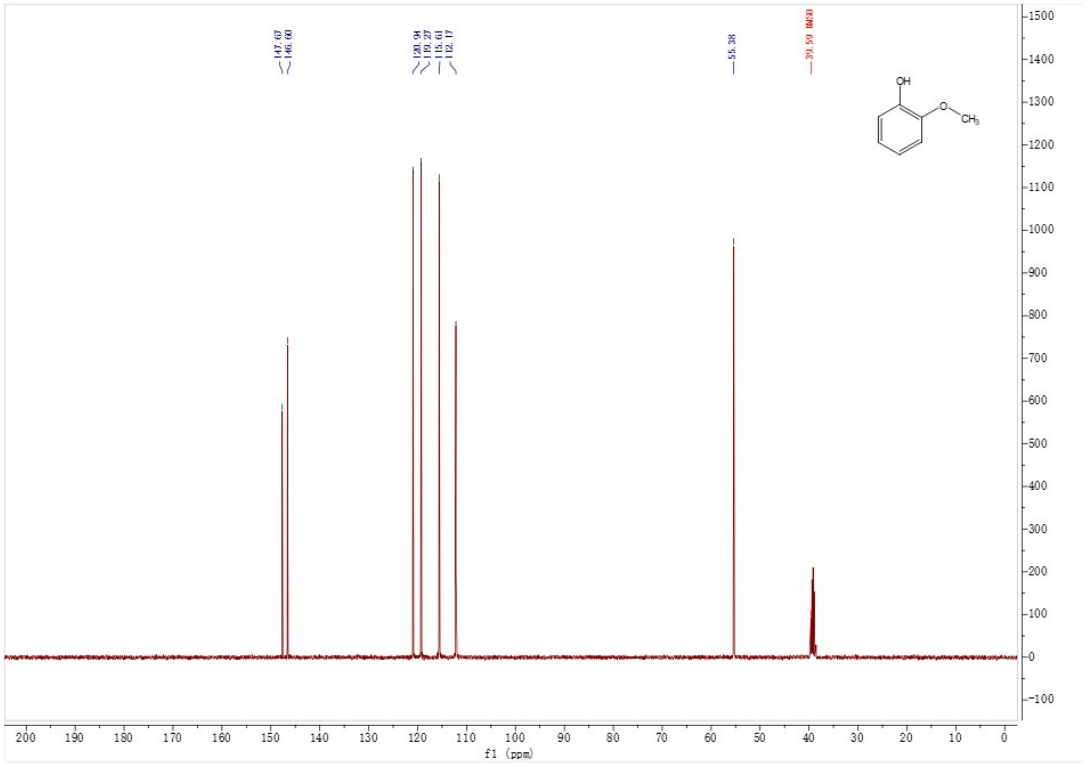
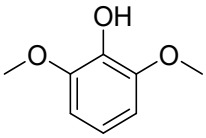


Figure S9 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-methoxyphenol.



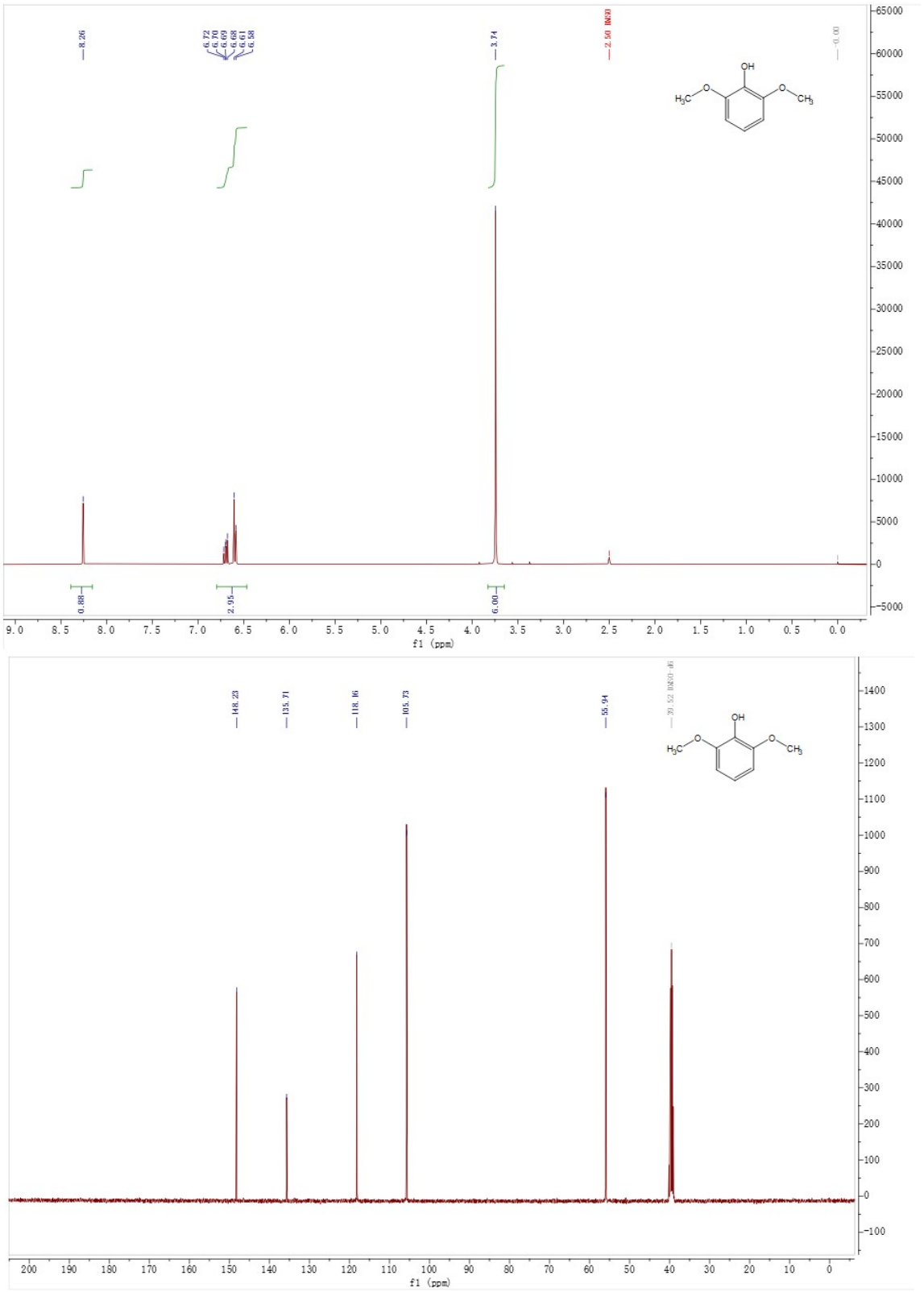


Figure S10 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2,6-dimethoxyphenol.

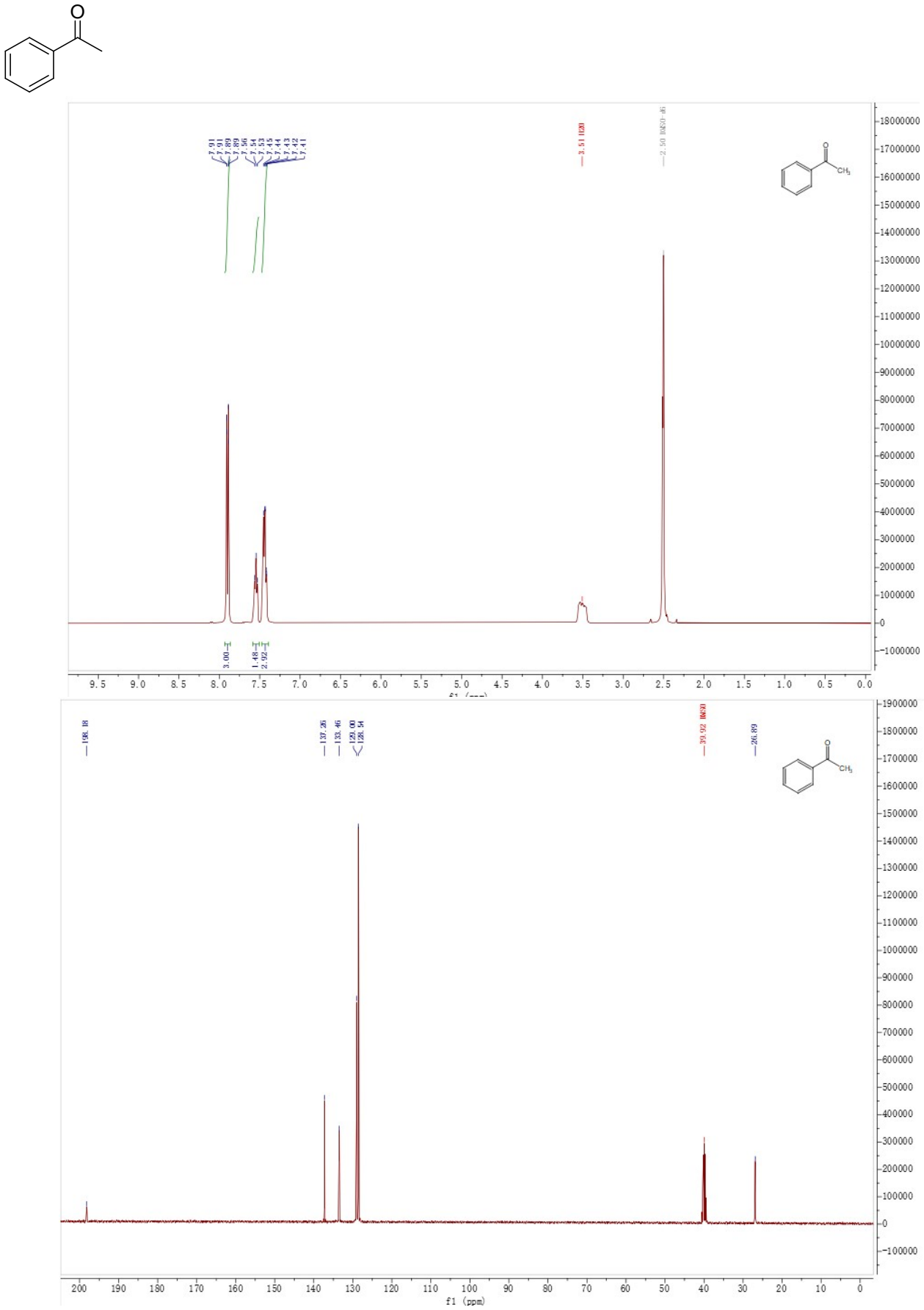
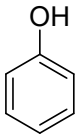


Figure S11 ^{1}H (top) and ^{13}C (bottom) NMR spectra of acetophenone.



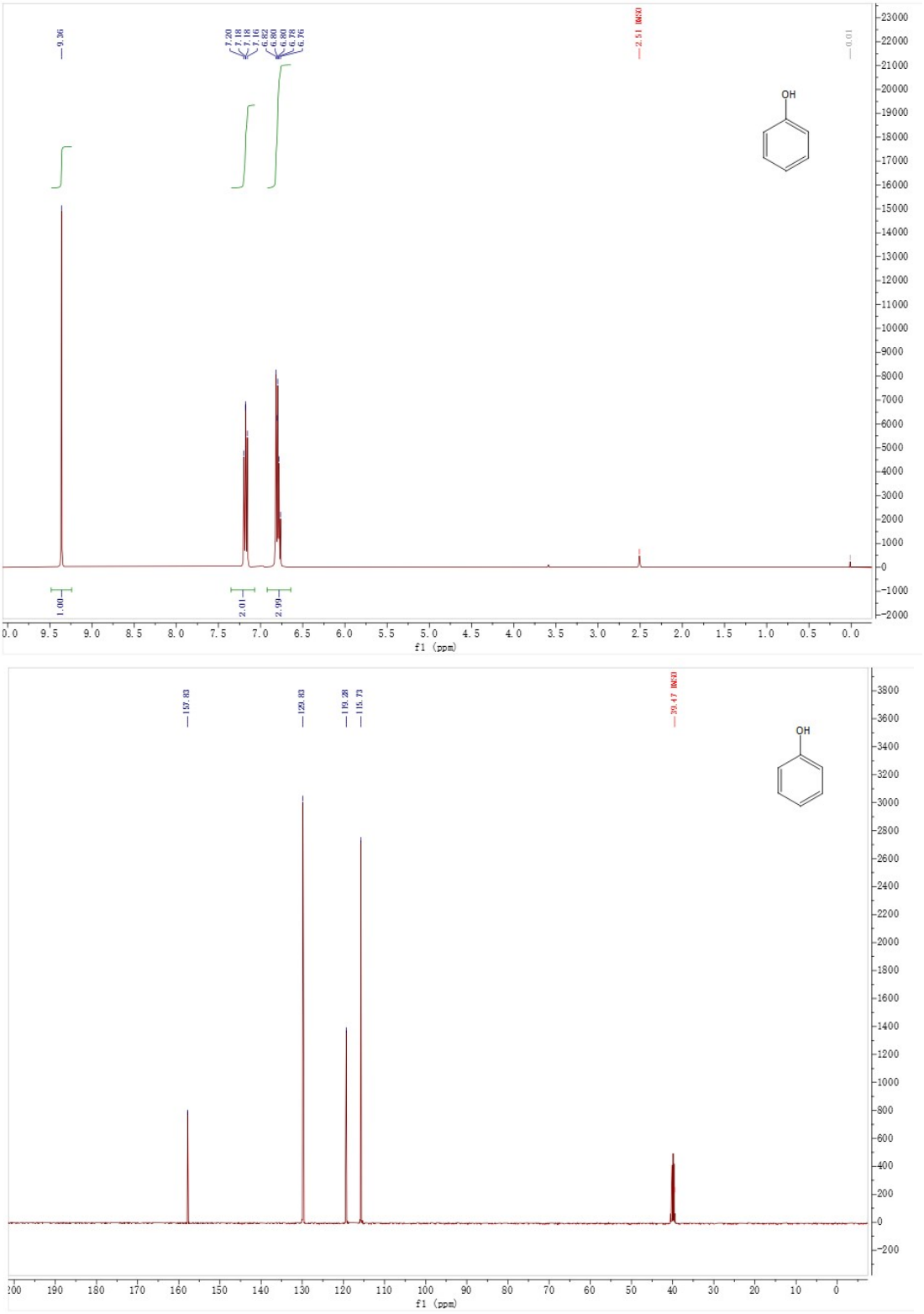
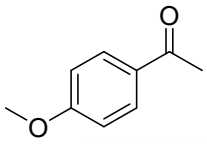


Figure S12 ^{1}H (top) and ^{13}C (bottom) NMR spectra of phenol.



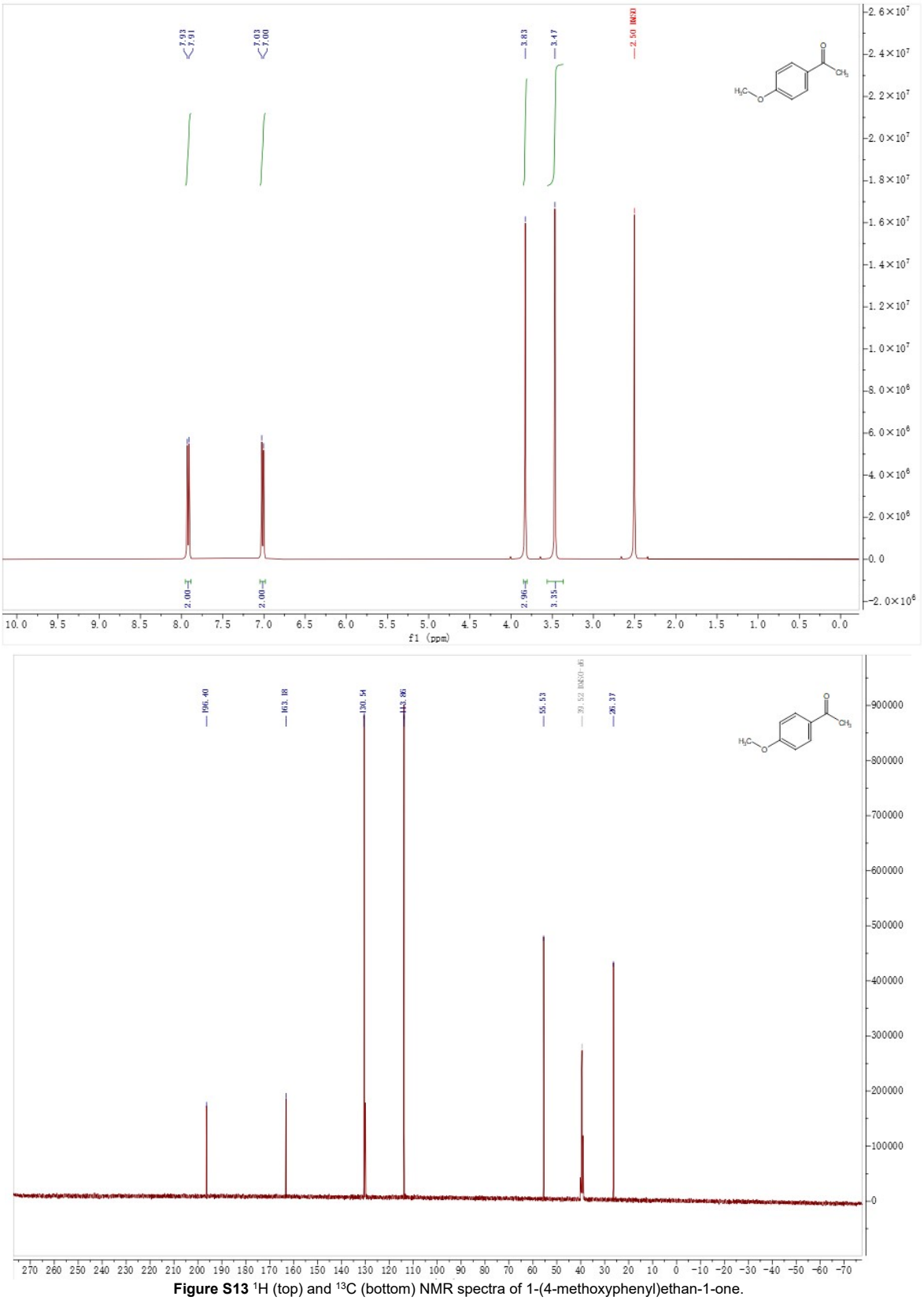
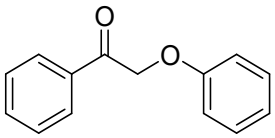
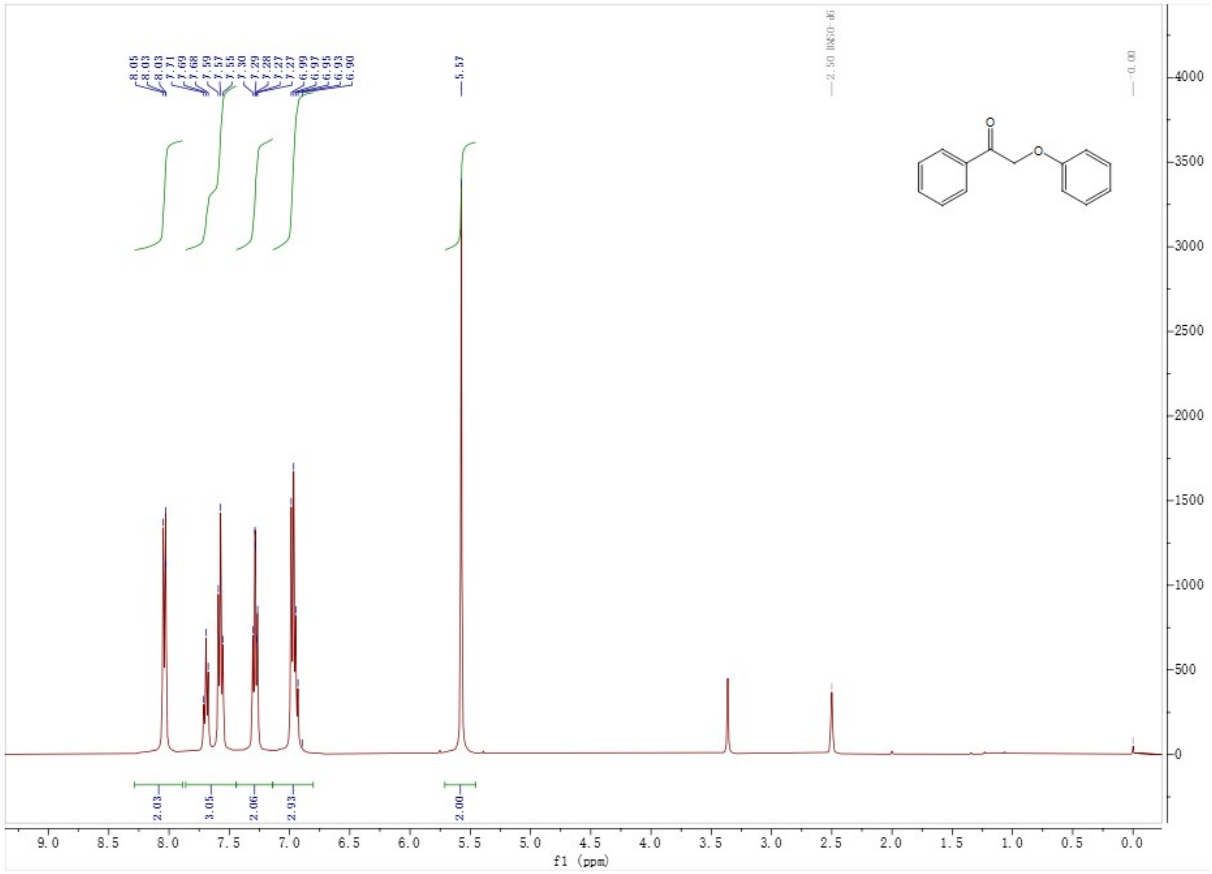


Figure S13 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-(4-methoxyphenyl)ethan-1-one.





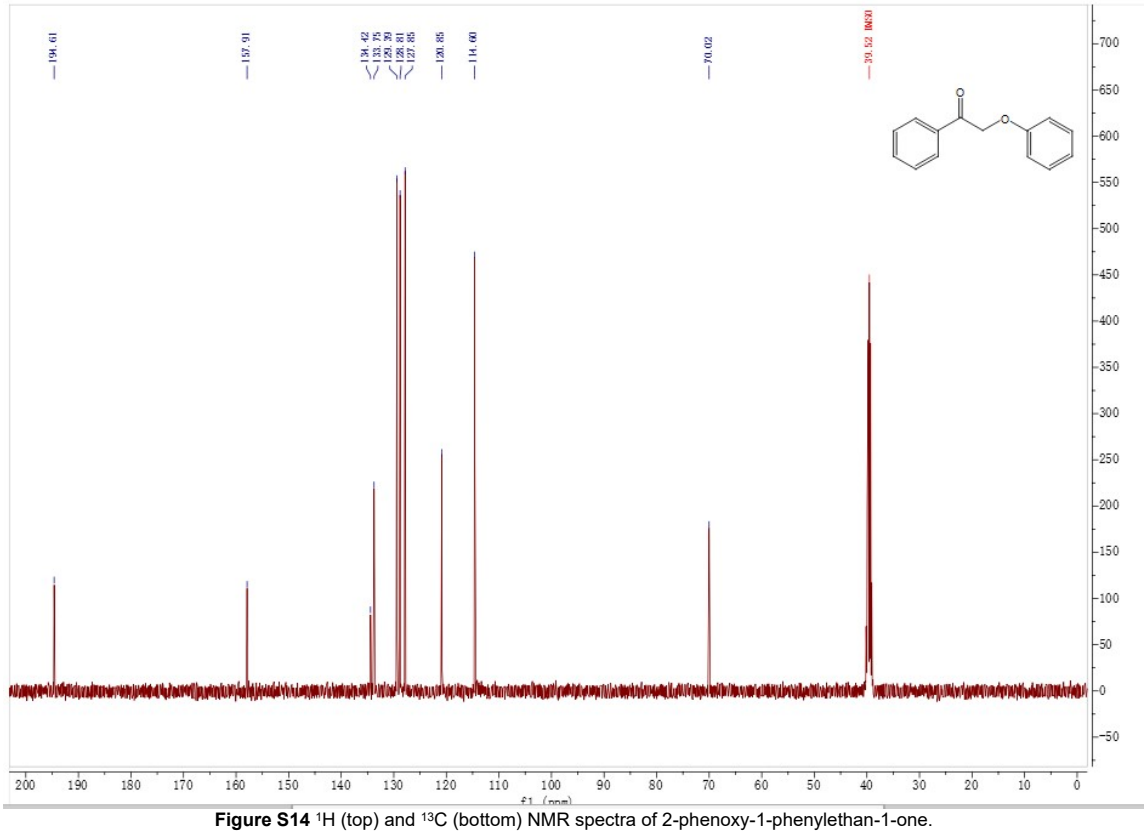
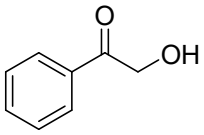


Figure S14 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-phenoxy-1-phenylethan-1-one.



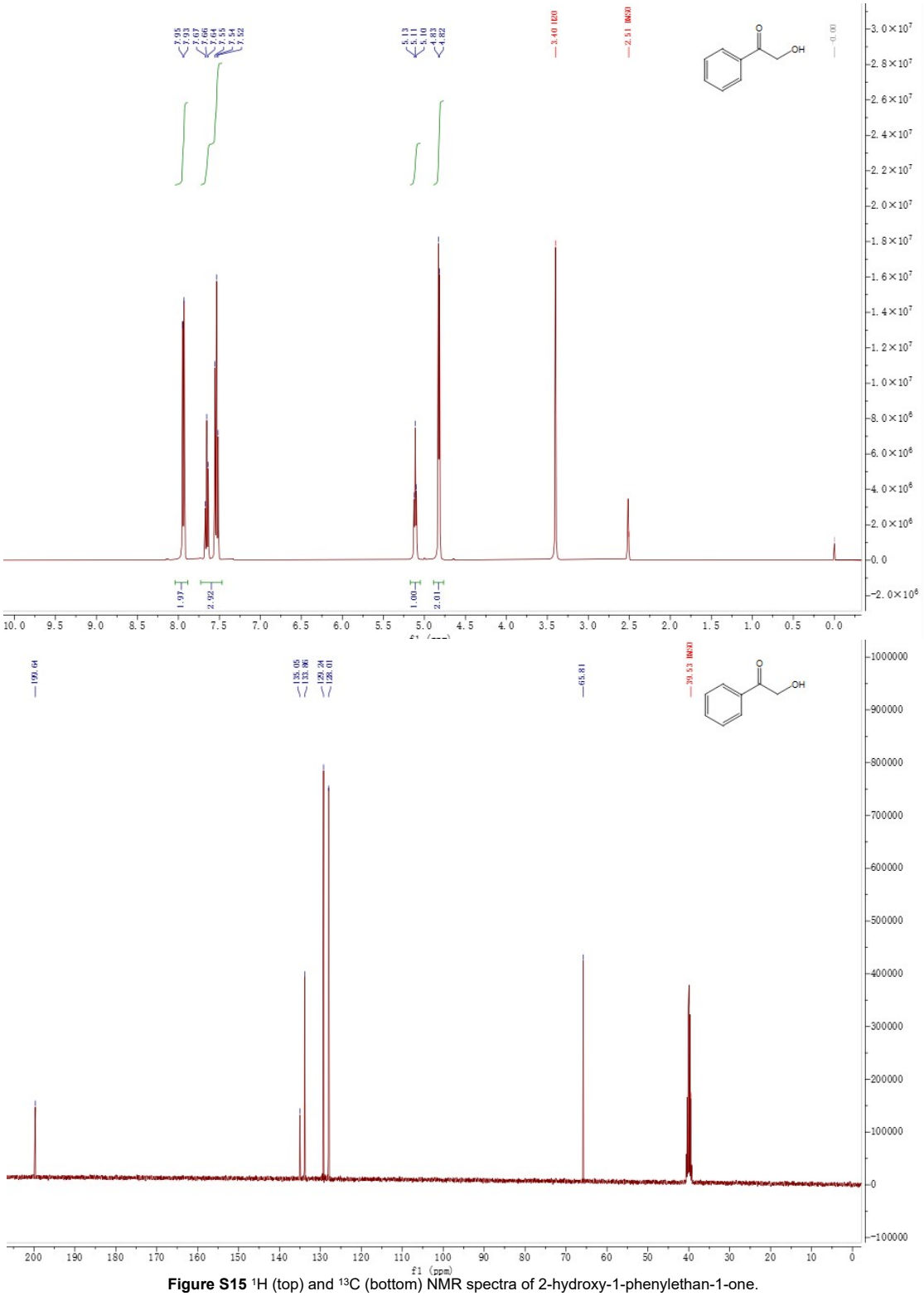


Figure S15 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-hydroxy-1-phenylethan-1-one.

6. References

[1] S. A. Kim, S. E. Kim, Y. K. Kim and H. Y. Jang, *ACS Omega*, 2020, **5**, 31684-31691.