Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Contents

1 General Information

All chemicals were commercially available and purchased from Aladdin (Shanghai, China) and were used as received without any further purification. All chemicals used were of analytical grade. ^{1}H NMR and ^{13}C NMR spectrum were recorded on a Bruker Avance-400 instrument, 400 MHz for ^{1} H NMR and 100 MHz for ^{13}C NMR, with $CDCl_3$ or DMSO-d_6 as solvent in all cases. All chemical shifts (δ) were quoted in parts per million (ppm) and reported relative to an internal tetramethylsilane (TMS, δ 0.00) standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t =triplet, q =quartet, m = multiplet. Yields of products were measured by HPLC analysis using SHIMADZU instrument equipped with a column Wonda Sil C18-WR 5μm.

2 General Procedures

2.1 General procedure for the oxidation of aldehydes using H_2O_2 as the oxidant

A reaction vessel was charged with water 5ml, aldehyde was introduced to form a final concentration of 10 or 5 mM, and hydrogen peroxide (4ml) was dropwisely added to the reaction vessel. After completion of the addition of hydrogen peroxide, the reaction was allowed to proceed for 8 hours in a shaker incubator (160rpm/min). After reactions completed, samples were taken out for HPLC analysis.

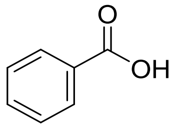
2.2 General procedures oxidation of aldehydes using O2 as the oxidant

A closed reaction vessel, charged with water 5 mL, aldehyde was introduced to form a final concentration of 10 or 5 mM. Oxygen was flushed into the vessel and sealed with a balloon filled with oxygen. After that, the reaction mixture was heated to 37 ^{o}C and kept for 24h in shaker incubator (160rpm/min). After reaction completed, samples were taken for further HPLC analysis.

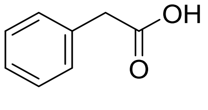
2.3 General procedure for scalable preparation of carboxylic acids

A closed reaction vessel, charged with water 20 mL, aldehyde was introduced to form a final concentration of 5mM. Oxygen was simply flushed into the vessel and sealed with a balloon filled with enough oxygen. After that, the reaction mixture was heated to 37 °C and kept for 24h in shaker incubator (160rpm/min). After reaction completed, pH of the mixture was made at 10.0, and the reaction mixture was cooled to -20°, which was then kept in a freeze dryer till all water was removed. The resulted powder was introduced with 1mL water to dissolve and pH of the solution was made at 5.0 with sulphuric acid. Which was then extracted with ethyl acetate (3 × 5 ml). The organic layer was isolated and combined, dried over anhydrous $MgSO_4$, and the organic solvents were removed under vacuum to give crude product, which was then chromatographed to afford pure product.

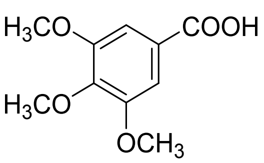
3 Characterization data for all products.



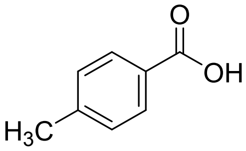
Benzoic acid **(1a):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (*s*, 1H), 8.20 (*d*, *J* = 7.2 Hz, 2H), 7.68 (t, *J* = 7.44 Hz, 1H) 7.68 (*t*, *J* = 7.92 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 172.60, 133.89, 130.28, 129.39, 128.55.



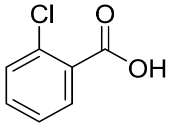
*Phenylacetate***(1b):** ^{1}H NMR (400 MHz, DMSO) δ 12.35 (*s*, H), 7.29 (m, 5H), 3.59 (s, 2H); ^{13}C NMR (100MHz, DMSO) δ 173.19, 135.50, 129.85, 128.71, 127.05, 41.18.



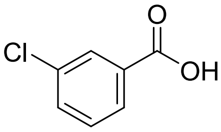
3,4,5-Trimethoxybenzoic acid(**1c**): ^{1} H NMR (400 MHz, DMSO) δ 12.95 (*s*, H), 7.25 (*s*, 2H), 3.84 (*s*, 6H), 3.74(*s*, 3H) ; ^{13} C NMR (100MHz, DMSO) δ 167.40, 153.11, 141.81, 126.38, 106.98, 60.55, 56.35.



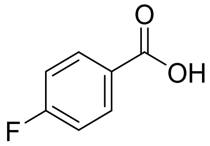
4-Methylbenzoic acid (**1d**): ^{1}H NMR (400 MHz, DMSO) δ 12.80(*s*, 1H), 7.84 (*d*, *J* = 6.48 Hz, 2H), 7.29 (*d*, *J* = 7.88 Hz, 2H) 2.36 (*s*, 3H); ^{13}C NMR (100MHz, DMSO) δ 167.80, 143.46, 129.80, 129.55, 128.52, 21.55, 126.75.



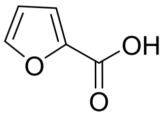
2-Chlorobenzoic acid(**1e**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09(*d*, *J* = 7.44 Hz, 1H), 7.50 (*m*, 1H), 7.40(*m*, 1H), 7.31(*m*, 1H) ^{13}C NMR (100MHz, $CDCl_3$) δ 171.09, 134.83, 133.65, 132.54, 131.56, 128.46, 126.75.



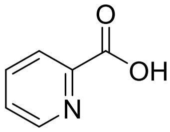
3-Chlorobenzoic acid(**1f**): ^{1}H NMR (400 MHz, DMSO) δ 13.34 (*s*, 1H), 7.79 (*m*, 2H), 7.70(m, 1H), 7.55(*t*, *J* = 8.08 Hz, 1H); ^{13}C NMR (100MHz, DMSO) δ 166.54, 133.82, 133.37, 133.15, 131.30, 129.30, 128.37.



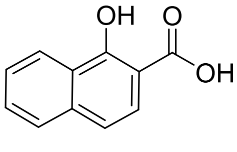
4-Fluorobenzoic acid (**1g**): ^{1}H NMR (400 MHz, DMSO) δ 13.06 (s, 1H), 8.01 (dd, *J* = 5.64, 5.6 Hz, 1H), 7.32 (t, *J* = 8.88 Hz, 1H); ^{13}C NMR (100MHz, DMSO) δ 166.85, 166.63, 164.14, 132.61, 132.52, 127.84, 127.81, 116.18 , 115.96.



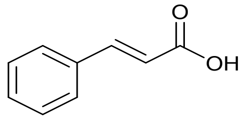
2-Furoic acid(**1h**): ^{1}H NMR (400 MHz, DMSO) δ 7.90 (dd, *J* = 1.64, 0.76 Hz, 1H), 7.22 (dd, *J* = 3.48, 0.76 Hz, 1H), 6.64 (dd, *J* = 3.44, 1.72 Hz, 1H) ; ^{13}C NMR (100MHz, DMSO) δ 159.81, 147.44, 145.38, 118.16, 112.52.



2-Picolinic acid(**1i**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.68 Hz, 1H), 8.32 (d, *J* = 7.76 Hz, 1H), 8.04 (td, *J* = 7.72, 1.64 Hz, 1H), 7.76(m, 1H), 7.31(s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 164.69, 148.10, 146.70, 138.60, 127.83, 124.26.



2-Hydroxy-1-naphthotic acid(**1j**): ^{1}H NMR (400 MHz, DMSO) δ 12.82 (s, 1H), 8.57 (d, *J* = 8.68 Hz, 1H), 7.99 (t, *J* = 9.08 Hz, 1H), 7.86(t, *J* = 7.76 Hz, 1H), 7.56(m, 1H) 7.36(m, 1H) 7.22(m, 1H); ^{13}C NMR (100MHz, DMSO) δ172.99, 160.78, 135.26, 131.99, 129.19, 128.47, 12.39, 125.02, 123.81, 119.33, 108.52.



Cinnamic acid(**1k**): ^{1}H NMR (400 MHz, DMSO); δ 7.84 (d, *J* = 8.00 Hz, 1H), 7.59(dt, *J* =6, 3.6 Hz, 1H), 7.45(m, 1H), 7.28(s, 1H), 6.50(d, *J* = 16.00 Hz, 1H); ^{13}C NMR (100MHz, DMSO) δ172.67, 147.12, 134.05, 130.77, 128.98, 128.40, 117.38.

4 ^{1}H NMR and ^{13}C NMR spectrum for product

^{1}H NMR spectra of benzoic acid ***(1a)***

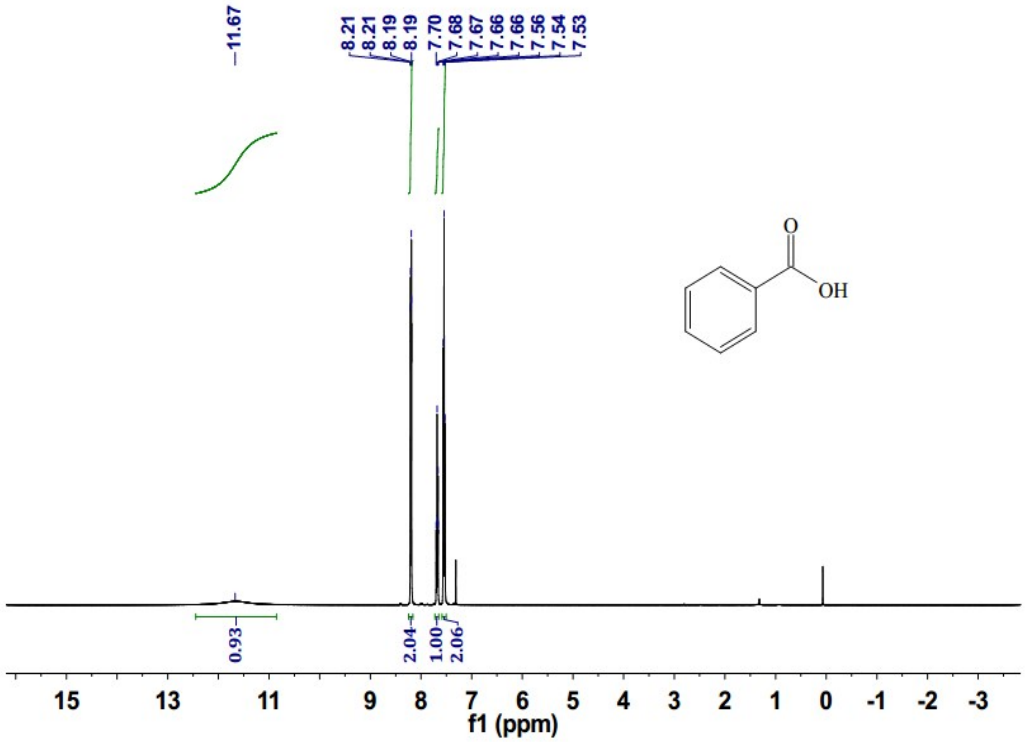


Fig.1 ^{1}H NMR spectra of benzoic acid

^{13}C NMR spectra of benzoic acid ***(1a)***

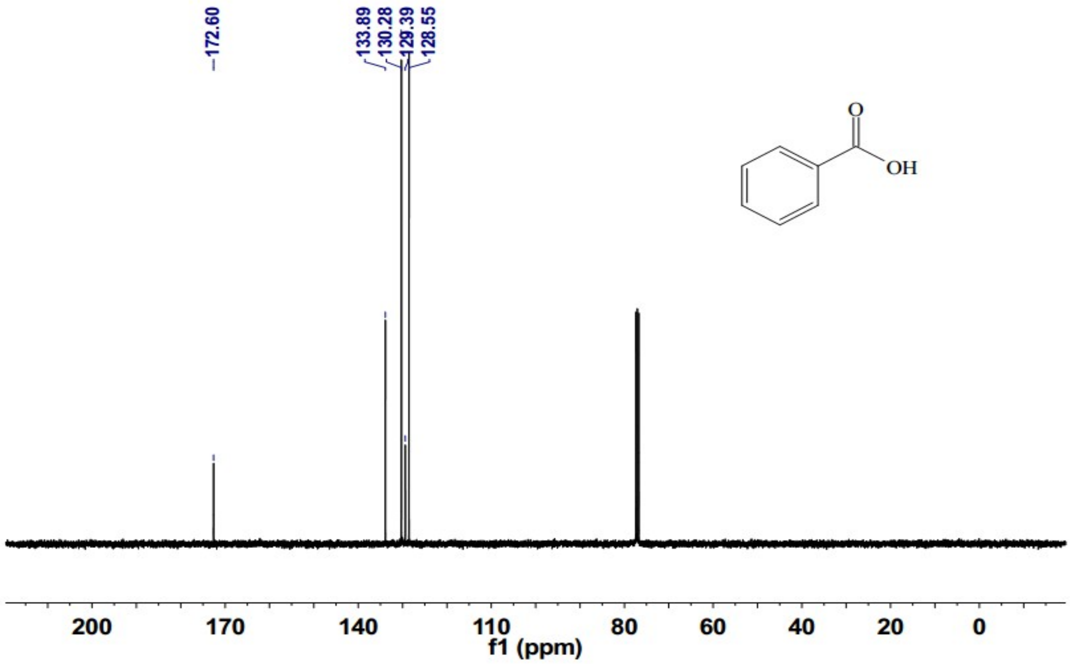


Fig.2 ^{13}C NMR spectra of benzoic acid

^{1}H NMR spectra of phenylacetate ***(1b)***

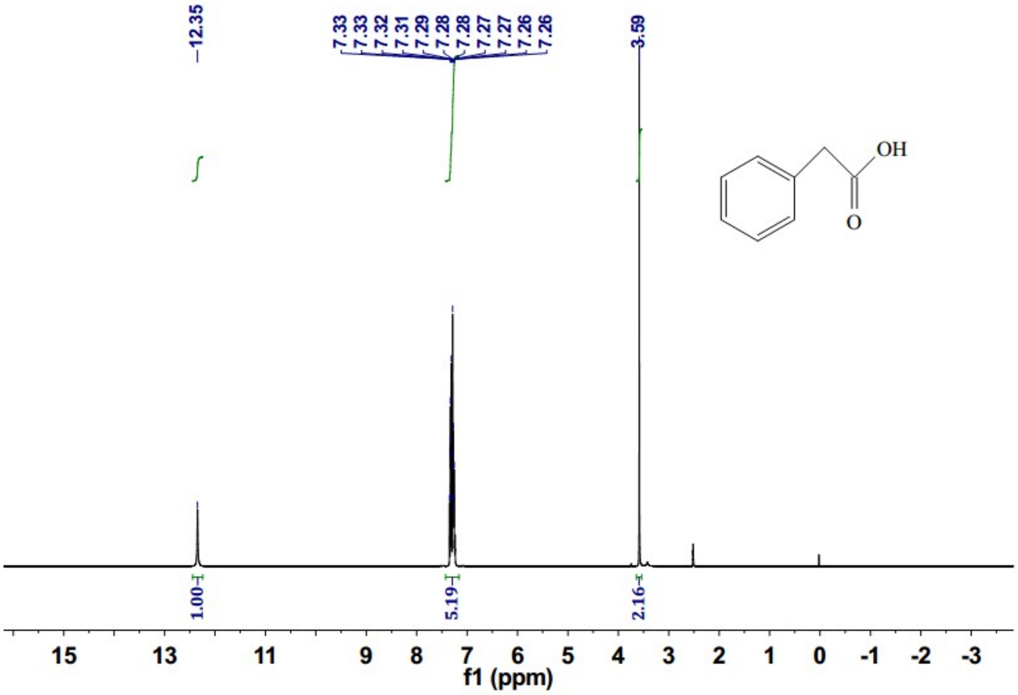


Fig.3 ^{1}H NMR spectra of phenylacetate

^{13}C NMR spectra of phenylacetate ***(1b)***

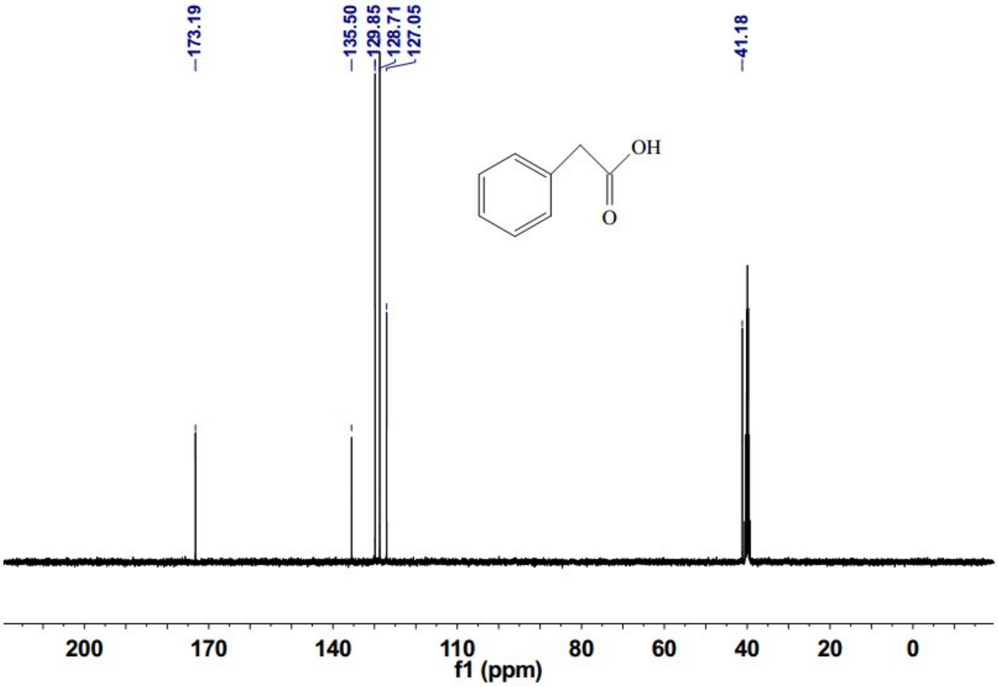


Fig.4 ^{13}C NMR spectra of phenylacetate

*1H NMR spectra of 3,4,5-trimethoxybenzoic acid (**1c**)*

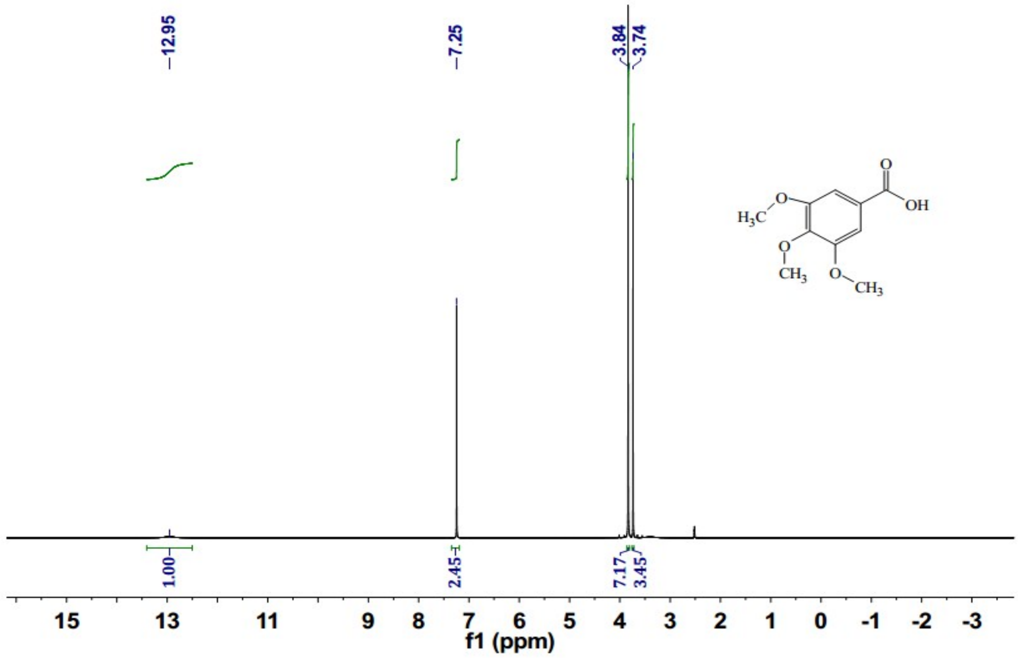


Fig.5 ^{1}H NMR spectra of 3,4,5-trimethoxybenzoic acid

*^{13}C NMR spectra of 3,4,5-trimethoxybenzoic acid (**1c**)*

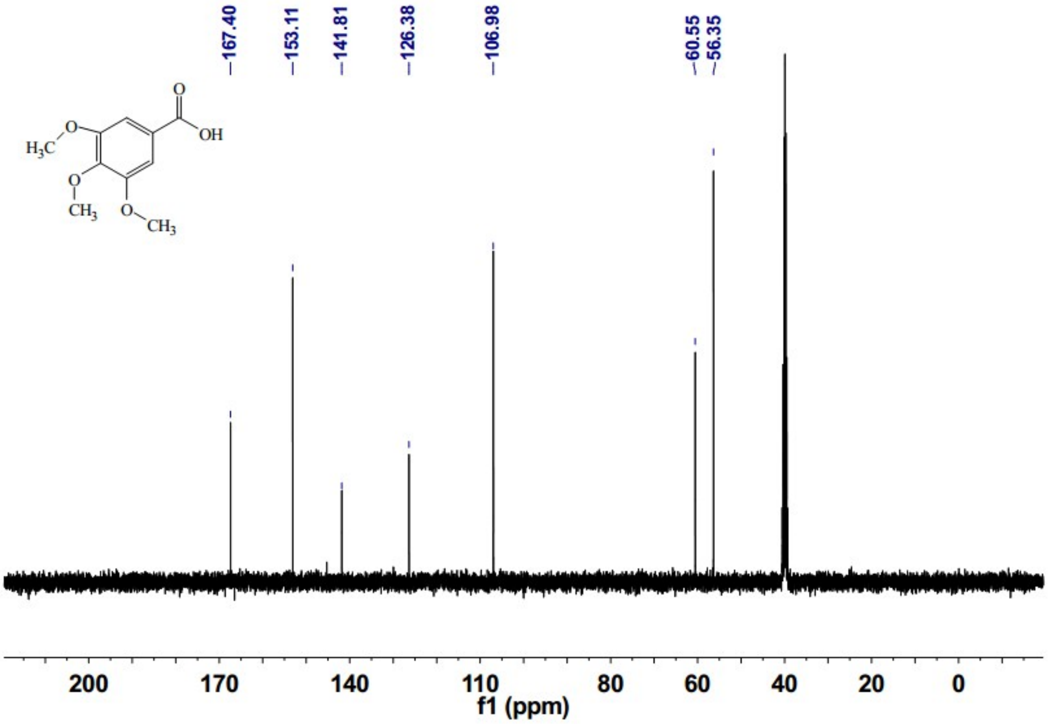


Fig.6 ^{13}C NMR spectra of 3,4,5-trimethoxybenzoic acid

*^{1}H NMR spectra of 4-methylbenzoic acid **(1d)***

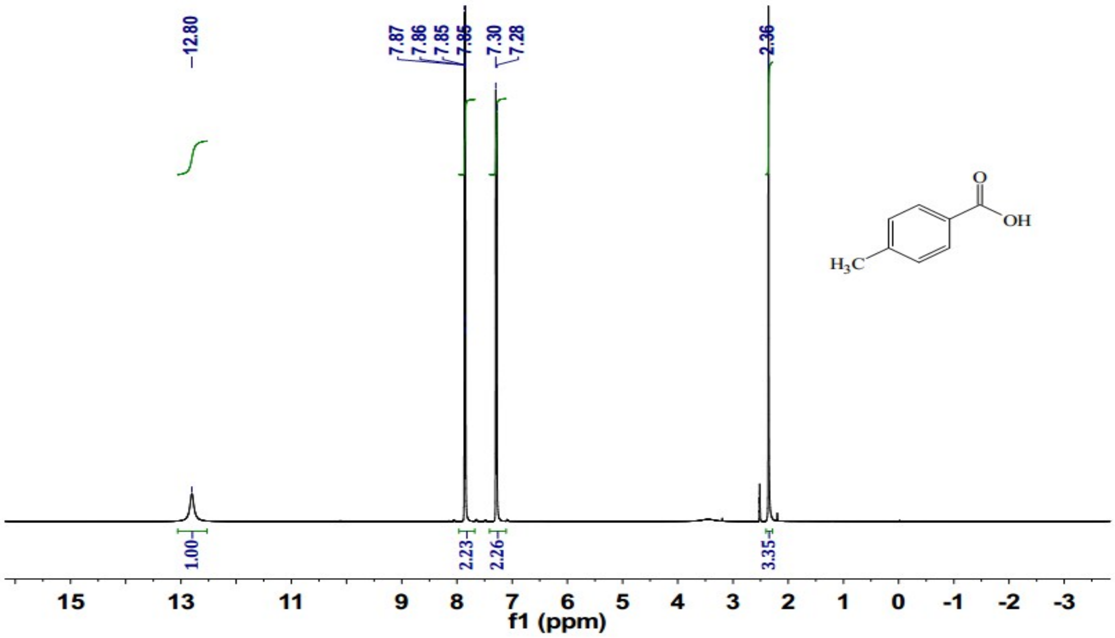


Fig.7 ^{13}H NMR spectra of 4-methylbenzoic acid

*^{13}C NMR spectra of 4-methylbenzoic acid **(1d)***

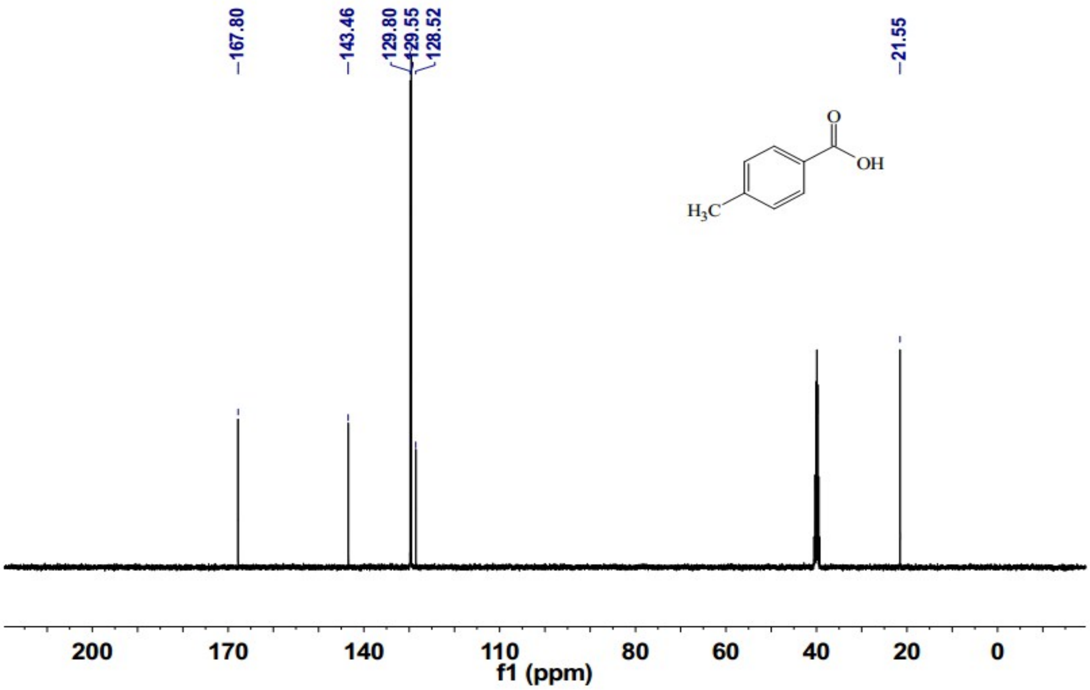


Fig.8 ^{13}C NMR spectra of 4-methylbenzoic acid

*^{1}H NMR spectra of 2-chlorobenzoic acid (**1e**)*

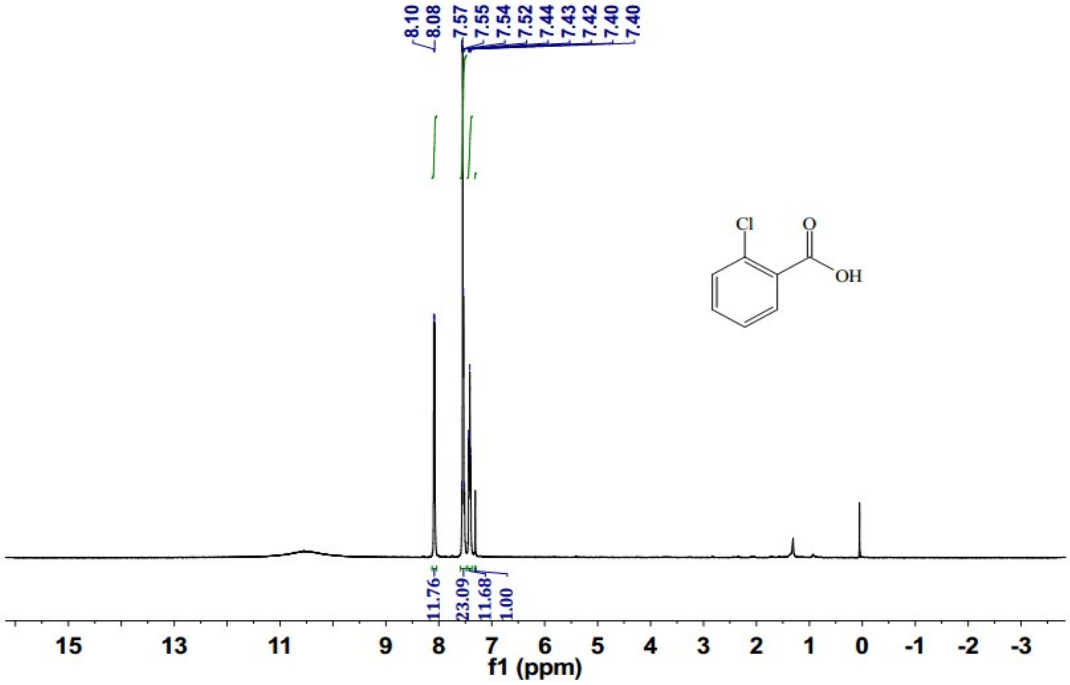


Fig.9 ^{1}H NMR spectra of 2-chlorobenzoic acid

*^{13}C NMR spectra of 2-chlorobenzoic acid (**1e**)*

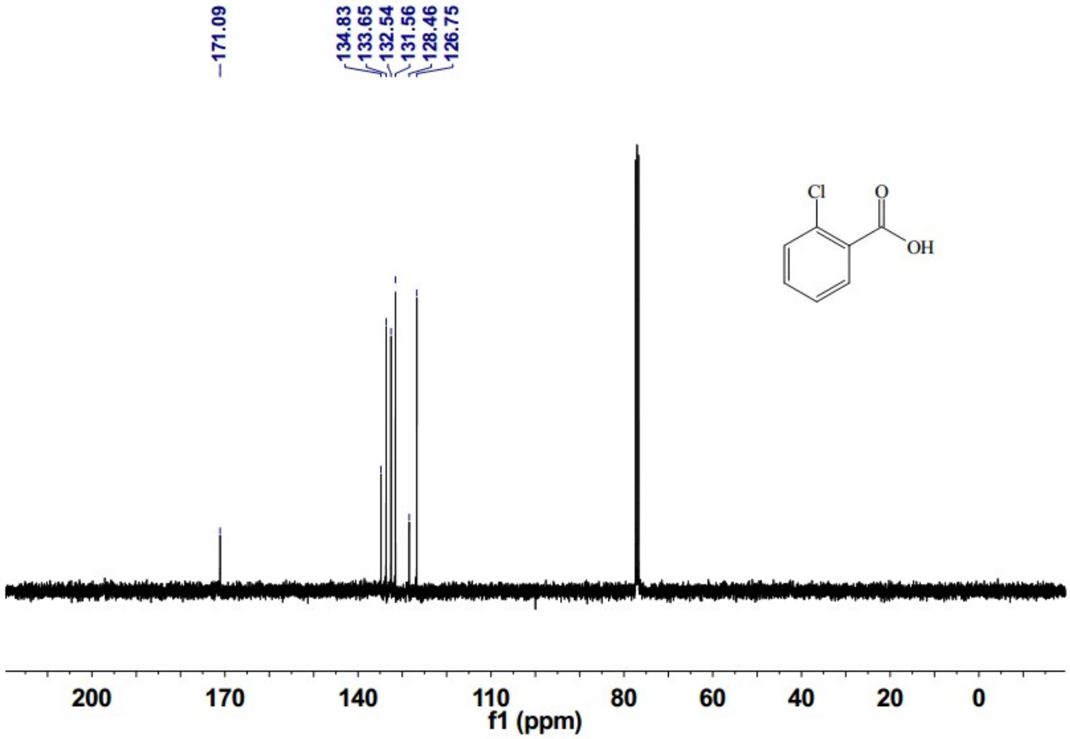


Fig.10 ^{13}C NMR spectra of 2-chlorobenzoic acid

*^{1}H NMR spectra of 3-chlorobenzoic acid (**1f**)*

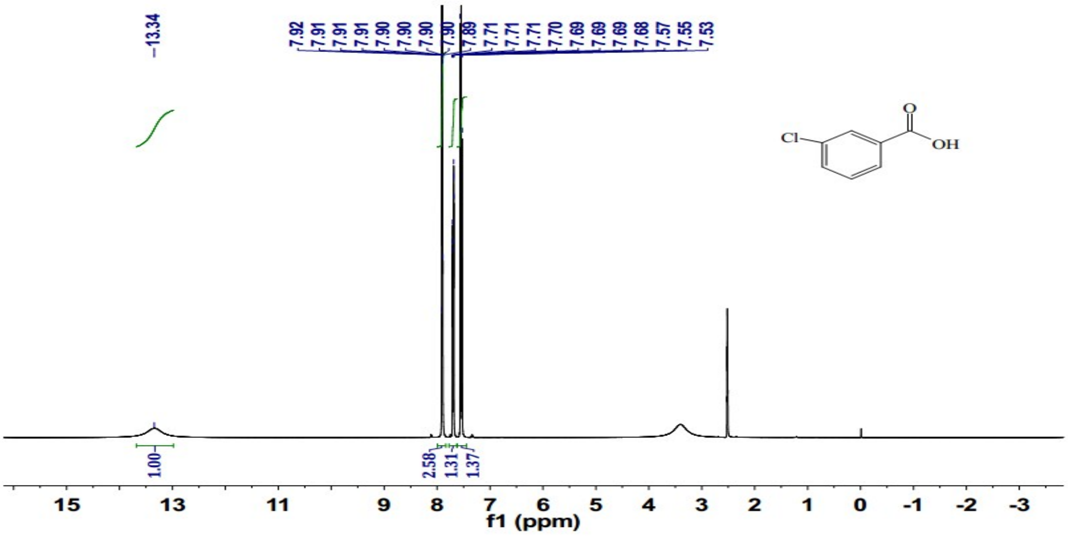


Fig.11 ^{1}H NMR spectra of 3-chlorobenzoic acid

*^{13}C NMR spectra of 3-chlorobenzoic acid (**1f**)*

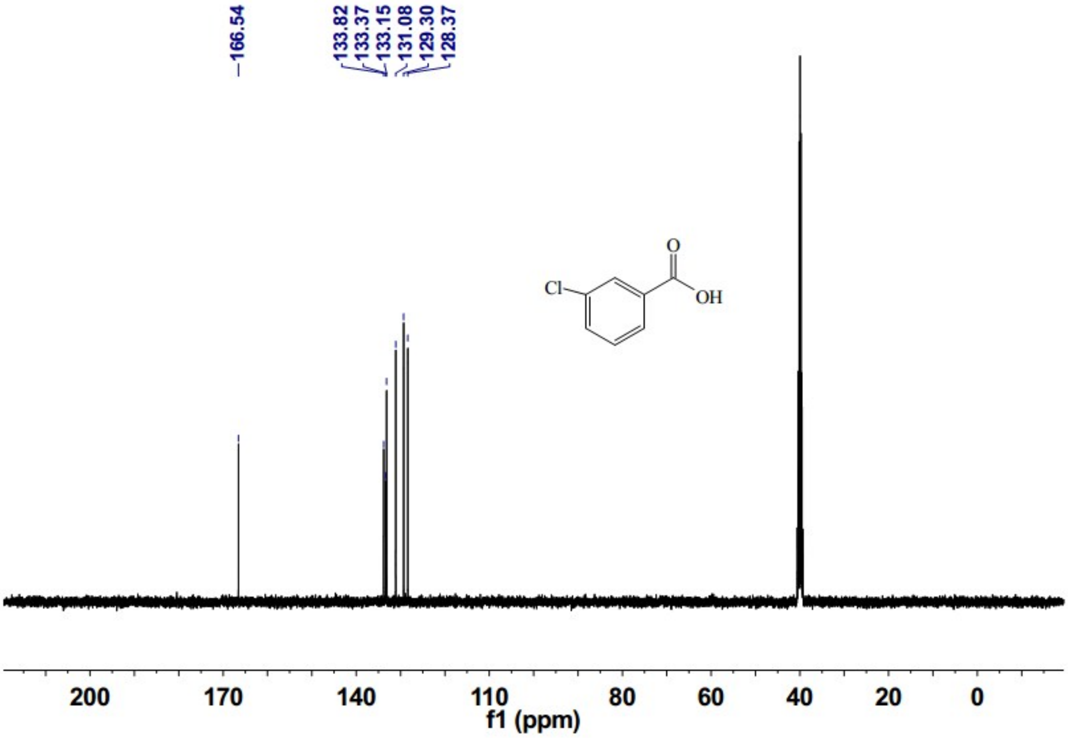


Fig.12 ^{13}C NMR spectra of 3-chlorobenzoic acid

*^{1}H NMR spectra of 4-fluorobenzoic acid (**1g**)*

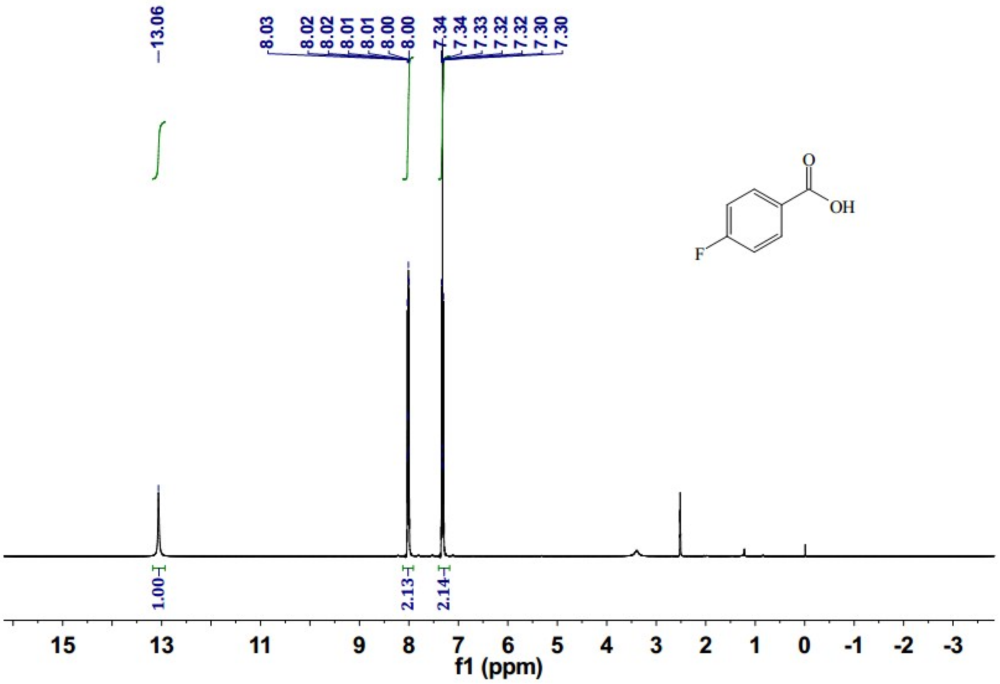


Fig.13 ^{1}H NMR spectra of 4-fluorobenzoic acid

*^{13}C NMR spectra of 4-fluorobenzoic acid (**1g**)*

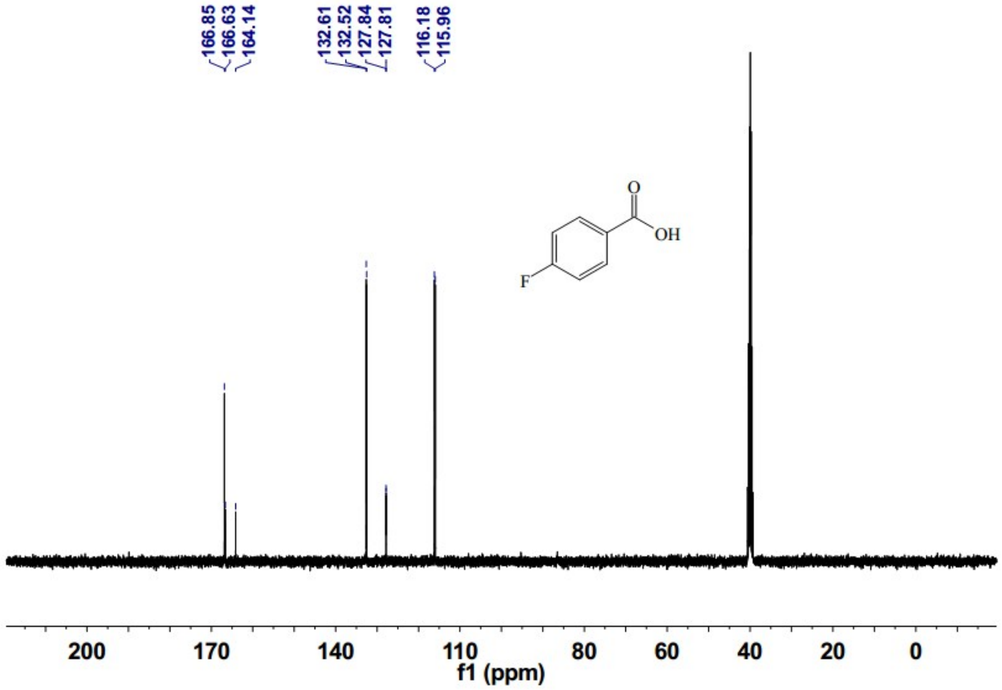


Fig.

14 ^{13}C NMR spectra of 4-fluorobenzoic acid

*^{1}H NMR spectra of 2-furoic acid (**1h**)*

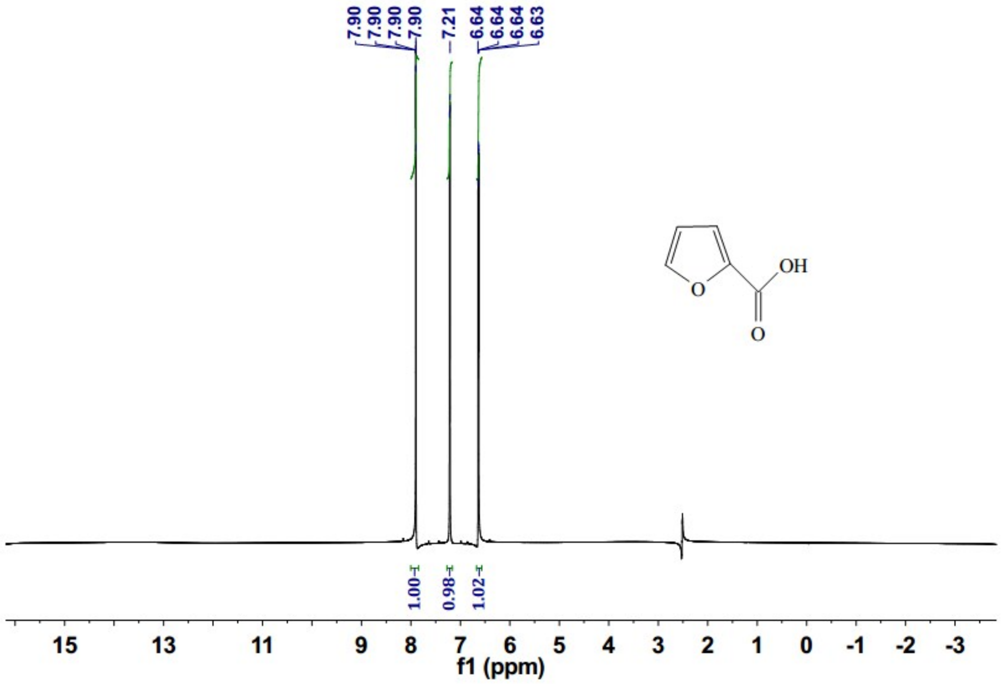


Fig.15 ^{1}H NMR spectra of 2-furoic acid

*^{13}C NMR spectra of 2-furoic acid (**1h**)*

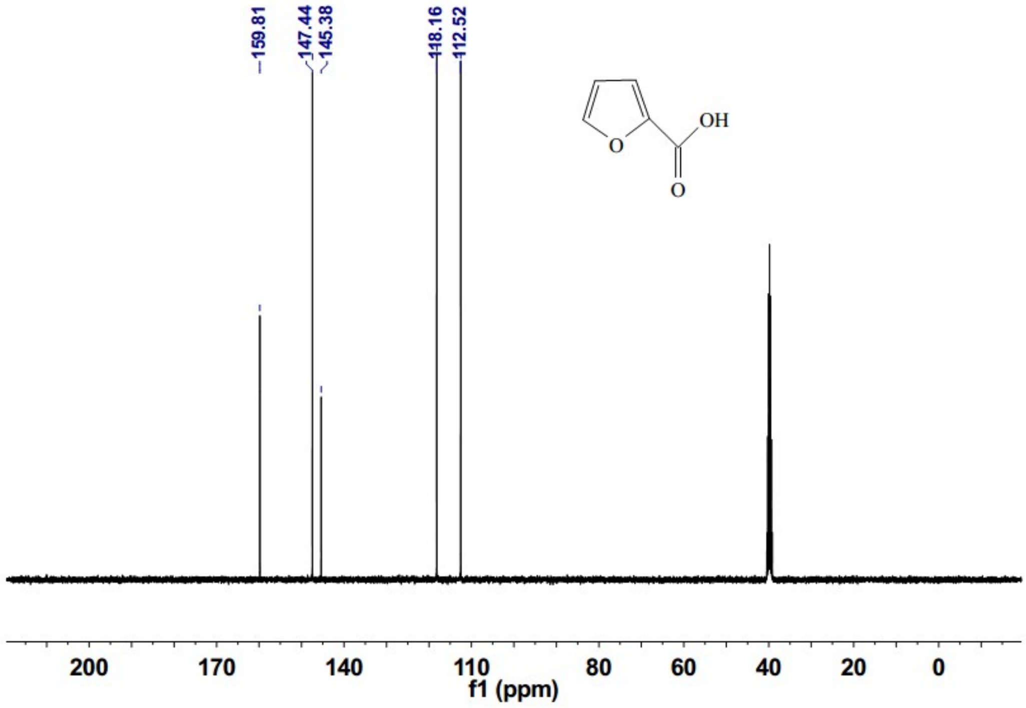


Fig.16 ^{13}C NMR spectra of 2-furoic acid

*^{1}H NMR spectra of 2-picolinic acid (**1i**)*

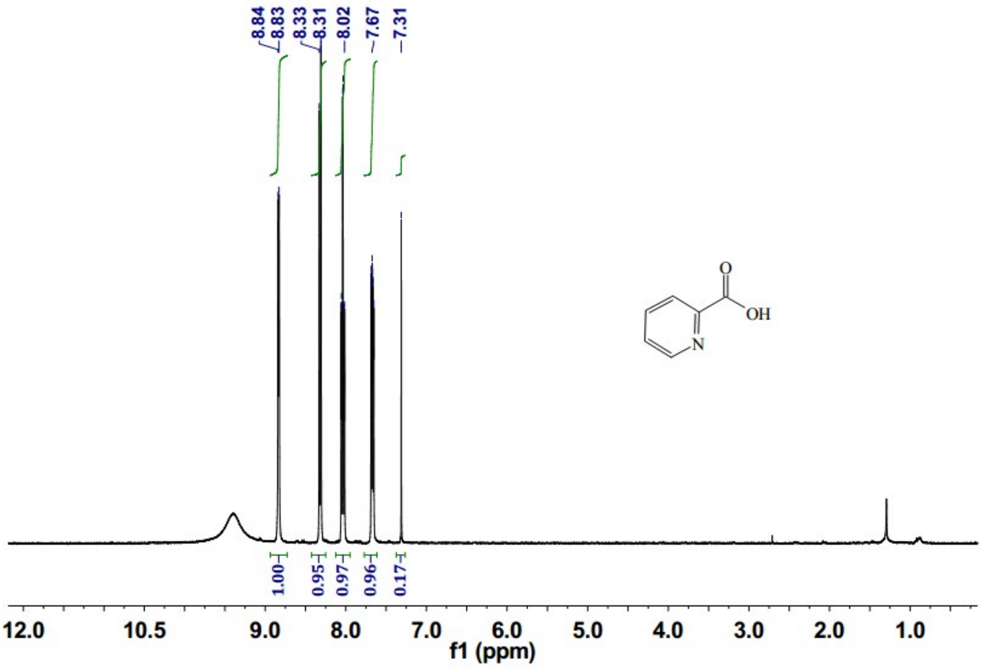


Fig.17 ^{1}H NMR spectra of 2-picolinic acid

*^{13}C NMR spectra of 2-picolinic acid (**1i**)*

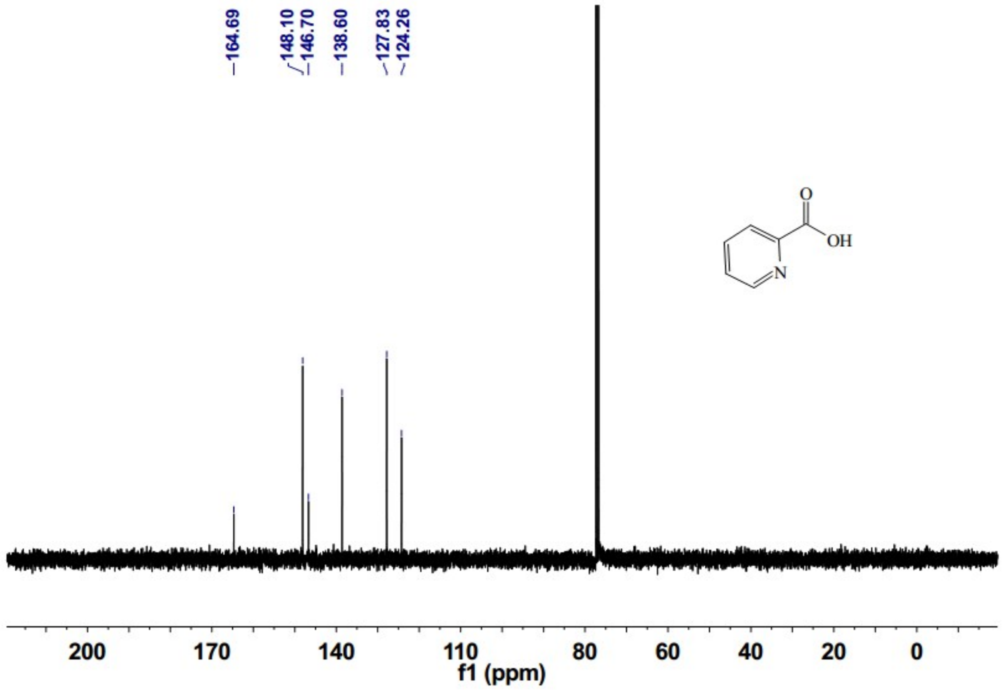


Fig.18 ^{13}C NMR spectra of 2-picolinic acid

*^{1}H NMR spectra of 2-hydroxy-1-naphthotic acid(**1j**)*

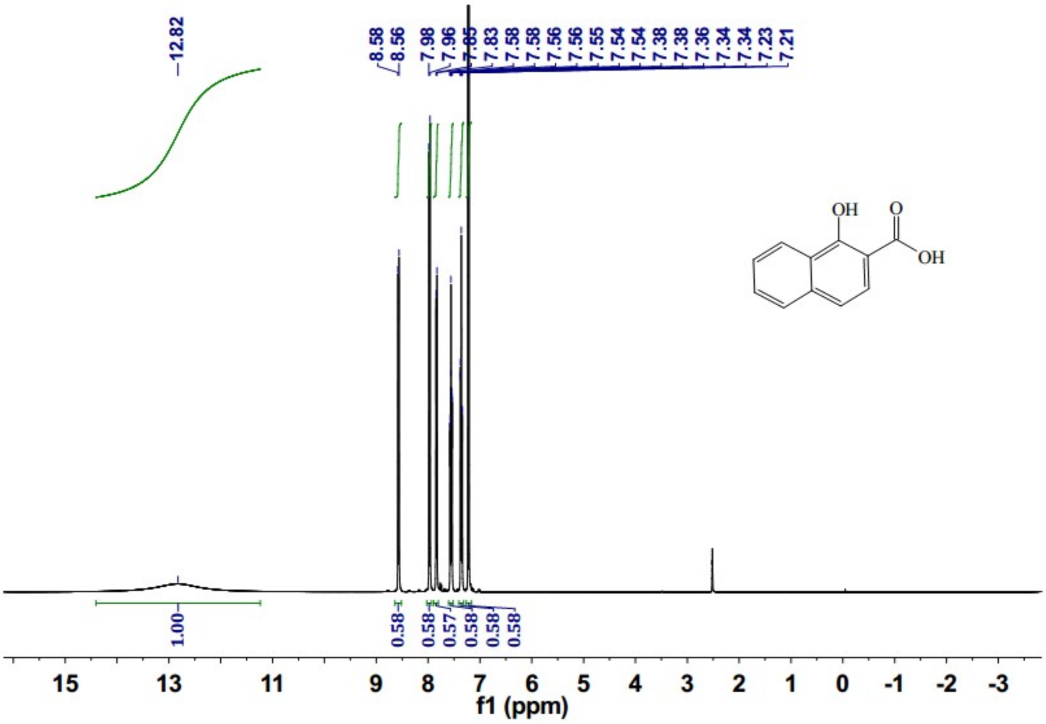


Fig.19 ^{1}H NMR spectra of 2-hydroxy-1-naphthotic acid

*^{13}C NMR spectra of 2-hydroxy-1-naphthotic acid(**j**)*

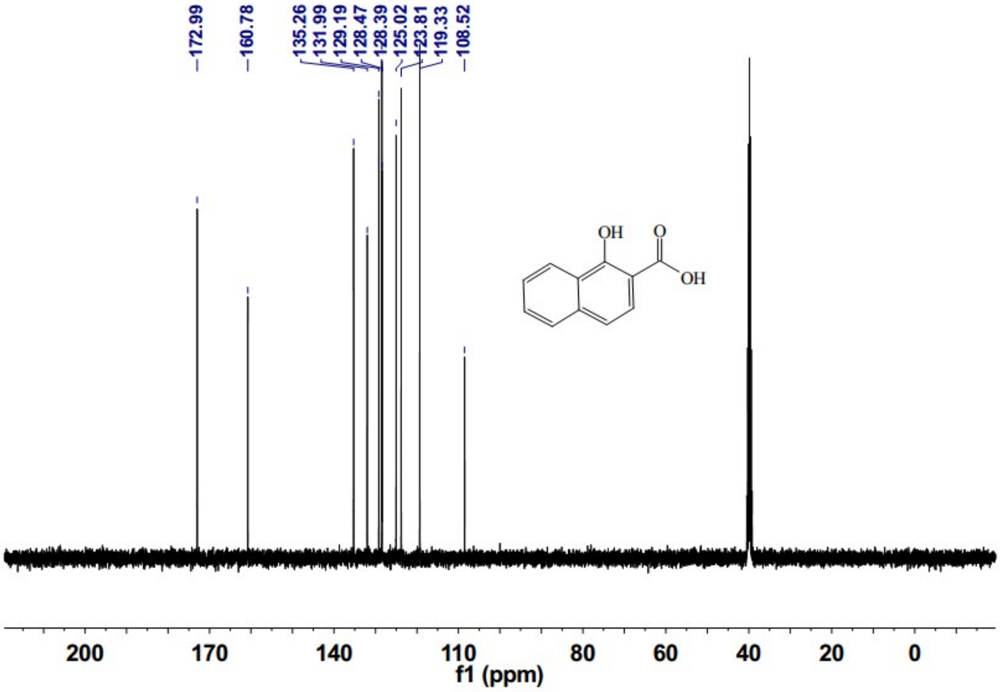


Fig.

20 ^{13}C NMR spectra of 2-hydroxy-1-naphthotic acid

*^{1}H NMR spectra of Cinnamc acid(**1k**)*

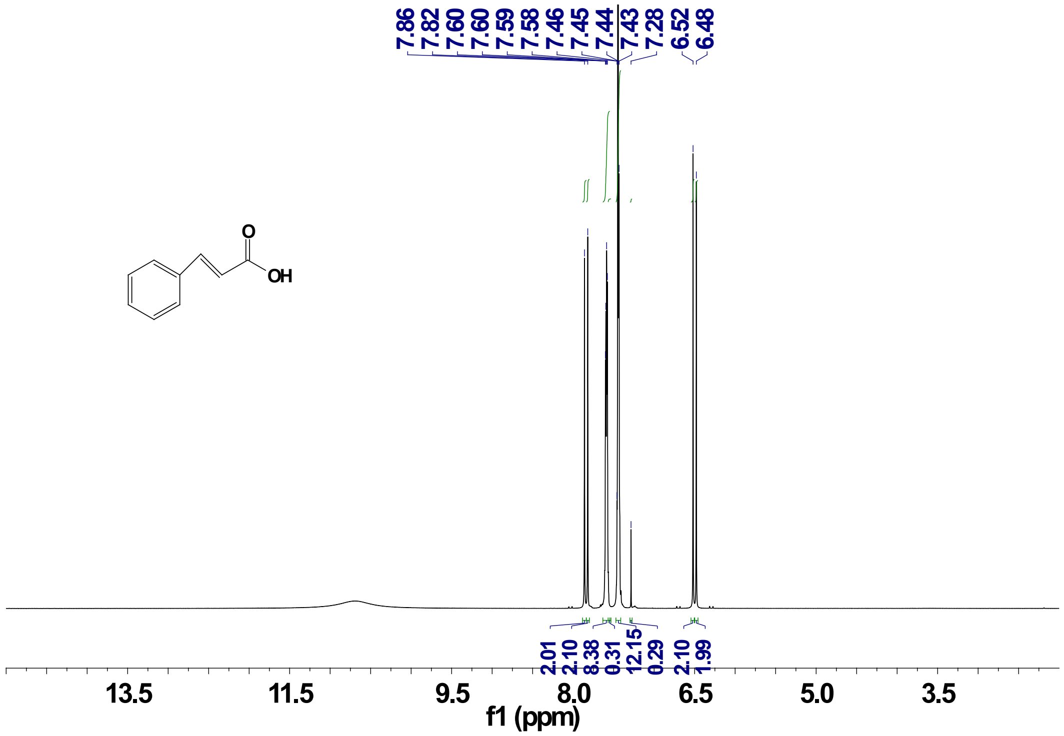


Fig.21 ^{1}H NMR spectra of Cinnamc acid

*^{13}C NMR spectra of Cinnamic acid(**1k**)*

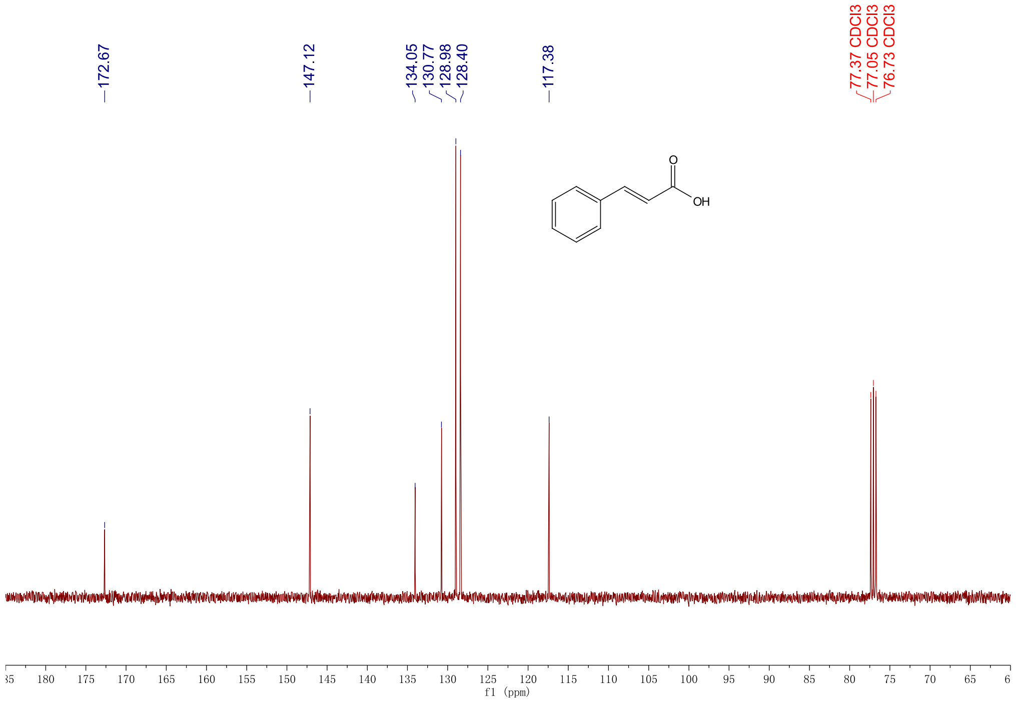


Fig.22 ^{13}C NMR spectra of Cinnamc acid