Supporting Information

Photocatalyzed Oxidative Cleavage of C≡C Bond to Carbonyl Compounds by a Recyclable Homogeneous Carbon Nitrides Semiconductor/Aqueous System

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General Methods

All chemicals were commercially available and used without further purification. Analytical thin-layer chromatography was performed on glass plates that were precoated with silica gel impregnated with a fluorescent indicator (254 nm). The plates were visualized by exposure to ultraviolet light. All solvents were obtained from commercial suppliers. ^{1}H NMR spectra were recorded on a Bruker DRX (400 MHz) and ^{13}C NMR spectra were recorded on a Bruker DRX (100 MHz) spectrometer, using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Mass spectra were recorded on a Finnigan TSQ Quantum-MS instrument in the electrospray ionization (ESI) mode. All reactions were carried out in oven-dried glassware under an oxygen atmosphere, unless stated otherwise. For quantitative flash chromatography, technical grade solvents were used.

Characterization of KNaPHI-II

1、Synthesis of KNaPHI

KNaPHI were prepared by grinding 12mmol of melamine with a mixture of 10mmol KOH and 5mmol NaOH and heating it in a lid-covered crucible at a rate of 5 ℃/min up to 330 ℃ in a muffle furnace, then it was kept for 2h at the reached temperature before being withdrawn from the furnace. The obtained solid was powdered and mixed with 100mL of deionized water and stir for 2 h. Followed by a 0.45 μm PTFE syringe filtered and being put inside a cellulose membrane and dialyzed for 24 h. Eventually, the resulting liquid was gradually evaporated at 80 ℃ for 24 h. The target product in the form of light yellow powder was obtained by grinding, which was recorded as KNaPHI-I. Other samples with different potassium sodium ratio were denoted as follow:

KNaPHI-II: KOH 10mmol + NaOH 8.75mmol;（K/Na=1:1.15）

KNaPHI-III: KOH 5mmol + NaOH 10mmol;（K/Na=1:2）

KNaPHI-IV: KOH 15mmol + NaOH 6mmol;（K/Na=2.5:1）

2、Preparation of acid (3a):

The catalyst KNaPHI 20 mg was accurately weighed on an electronic balance and added to a clean and dry 25 mL Schlenk reaction tube with a rotor, the tube was evacuated, the air in the tube was replaced with oxygen three times and then filled

with oxygen; stirring was turned on and phenylacetylene (1 mmol), deionized 2 mL H_2O were added to the oxygen-filled reaction tube with a syringe, and an oxygen-filled balloon was inserted at the stopper of the reaction tube to equalize the pressure in the tube and protect the reaction to proceed smoothly; the reaction was carried out continuously for 6 h under the illumination of a UV-LEDs (365nm 7W 227mw/cm^2) and the distance of the reaction vial from the light is about 6 centimeters. After the reaction, the solvent was removed under reduced pressure. Purification of the crude product was achieved by flash column chromatography using petrol n-hexane /ethyl acetate (1:1) as eluent, and the collected product was evaporated and concentrated in the oven (60℃) for further drying and weighing.

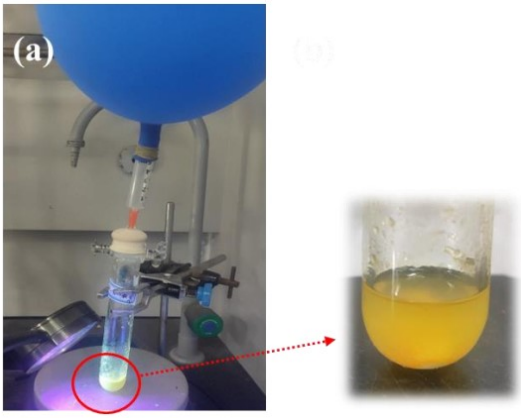
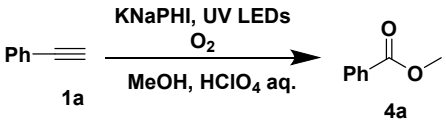


Fig. S1 The photochemical set (a) UV-LED and (b) Sunlight

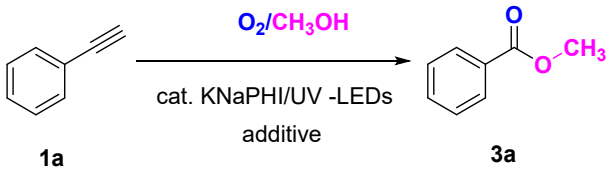
3、Preparation of Methyl benzoate



A 25 mL clean and dry Schlenk reaction tube with a magnetic stirring rotor was equipped with styrene **1a** (1 mmol), KNaPHI (20 mg), $HClO_4$ (0.4 mL, 50 wt% aqueous) in MeOH (2 mL). The mixture was irradiated with a UV-LEDs (365nm 7W 227mw/cm2) and the distance of the reaction vial from the light is about 6 centimeters with an oxygen ball for 6 h. The temperature of the reaction mixture is about 26 ℃ and the distance of the reaction vial from the light is about 4 centimeters. After the reaction, the solvent was removed under reduced pressure. Purification of the crude product was achieved by flash column chromatography using petrol n-hexane/ethyl acetate (8:1~16:1) as eluent, and the collected product was evaporated and concentrated in the oven (60 ℃) for further drying and weighing.

4、Optimization of the Esterification reaction conditions

Table S1 Optimization of the Esterification reaction conditions



1a **3a**

Entry	Cat.	Solvent	additive	Yield/%[b] **3a**
1	KNaPHI-II(20mg)	MeOH	-	trace
2	KNaPHI-II (20mg)	MeOH	Na_2CO_3	NR
3	KNaPHI-II (20mg)	MeOH	Cs_2CO_3	NR
4	KNaPHI-II (20mg)	MeOH	*t*BuOK	NR
5	KNaPHI-II (20mg)	MeOH	DBU	30
6	KNaPHI-II (20mg)	MeOH	H_2SO_4	20
7	KNaPHI -II(20mg)	MeOH	HCl	45
8	KNaPHI-II (20mg)	MeOH	HNO_3	25
9	KNaPHI-II (20mg)	MeOH	$HClO_4$	70
10	KNaPHI-II (20mg)	MeOH	H_3PO_4	24
11	KNaPHI-II (20mg)	MeOH	CF_3SO_3H	38
12	KNaPHI-II (20mg)	MeOH	$H_3O_{40}PW_{12}$	NR
13[c]	KNaPHI-II (20mg)	MeOH/H_2O	$HClO_4$	23
14[d]	KNaPHI-II (20mg)	MeOH/MeCN	$HClO_4$	70
15	CN620 (20mg)	MeOH	$HClO_4$	62
16[e]	-	MeOH	$HClO_4$	NR
17[f]	KNaPHI-II (20mg)	MeOH	$HClO_4$	NR

[a] Reaction conditions: **1a** (1 mmol), KNaPHI-II 20mg, 2 mL MeOH, and 2 equv. of acid in an O_2 atmosphere, under 7W UV-LED irradiation for 6 h. [b] Isolated yield.

[c] MeOH/H_2O=5:1 [d] MeOH/MeCN=1:2. [e] No photocatalyst. [f] Without light.

5、Characterization of KNaPHI-II

The morphology of the sample was observed by SEM and TEM (Fig.S3, a, b). The morphology of the synthesized sample is lamellas, indicating that we successfully synthesized KNaPHI-II through a simple roast method.

The X-ray diffraction (XRD) patterns, obtained on an X-ray diffractometer (Bruker D8 Advance) using Cu Kα radiation, were used to characterize the crystalline phase of the sample KNaPHI-II. XRD patterns (Fig.S3, c) was determined to provide the phase structures information for KNaPHI-II. It had distinct diffraction peaks at 27.4° which can be indexed to graphitic materials as the (002) crystal plane of CN.

And the peak intensity of 27.4°-27.8° is very strong, which is produced by stacking each layer on each other.

The cyclic voltammetry (50 mVs^{-1}, 0.1 M $TBAPF_6$ in acetonitrile) study of the K,Na-PHI sample is showing the HOMO and LUMO positions at 1.2 V and -1.91 V versus normal hydrogen electrode (NHE), respectively (Fig.S3, d).

Analyzed from a synthetic point of view, the presence of hydroxide in the melt catalyzes the condensation of melamine, thus lowering the synthesis temperature of this catalyst to 330 °C. The two main stages of mass loss are attributed to H_2O evolution and melamine deamination, respectively. The analysis of the thermogravimetric results of KNaPHI-II (Fig.S3, e), showed that the decomposition starts only about 600 °C.

In addition, it can be seen that the photoluminescence excitation wavelength of KNaPHI-II is 360 nm (Fig.S3, f).

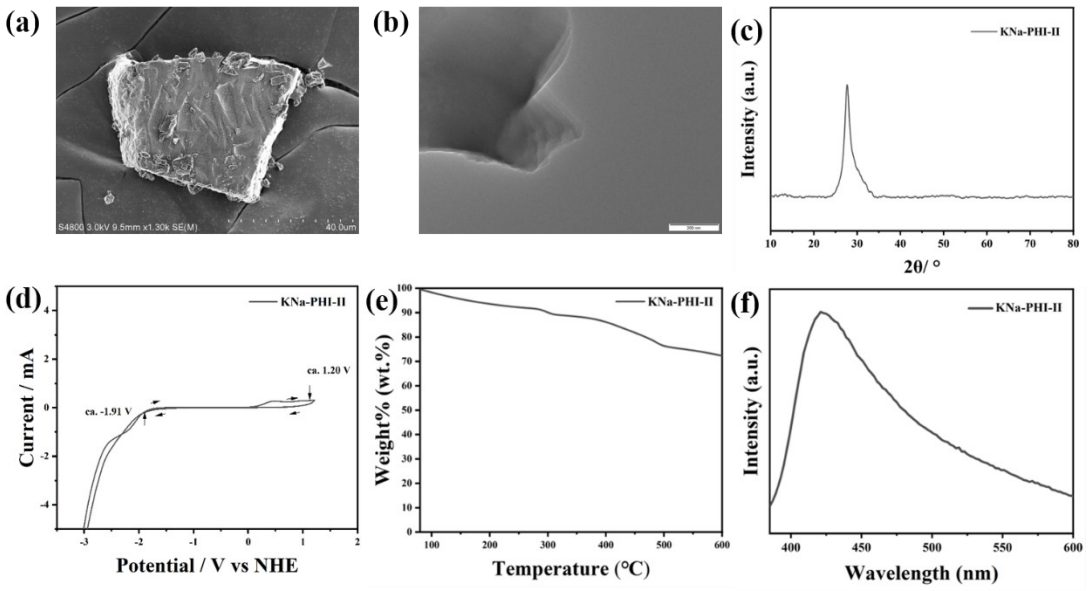
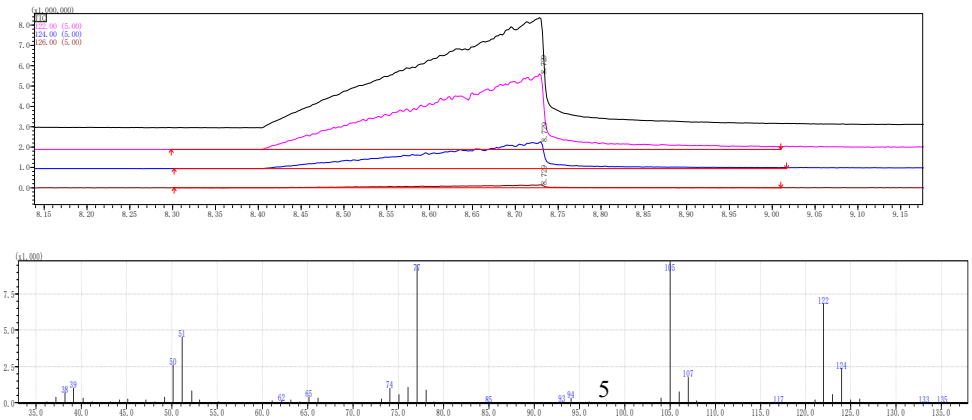
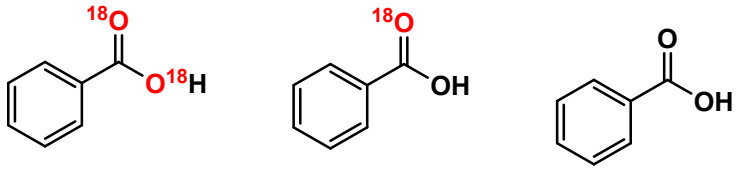


Fig. S2 (a) SEM; (b) TEM; (c) XRD; (d) CV; (e) TGA; (f) PL of KNaPHI-II

6、Isotope labeling experiment:

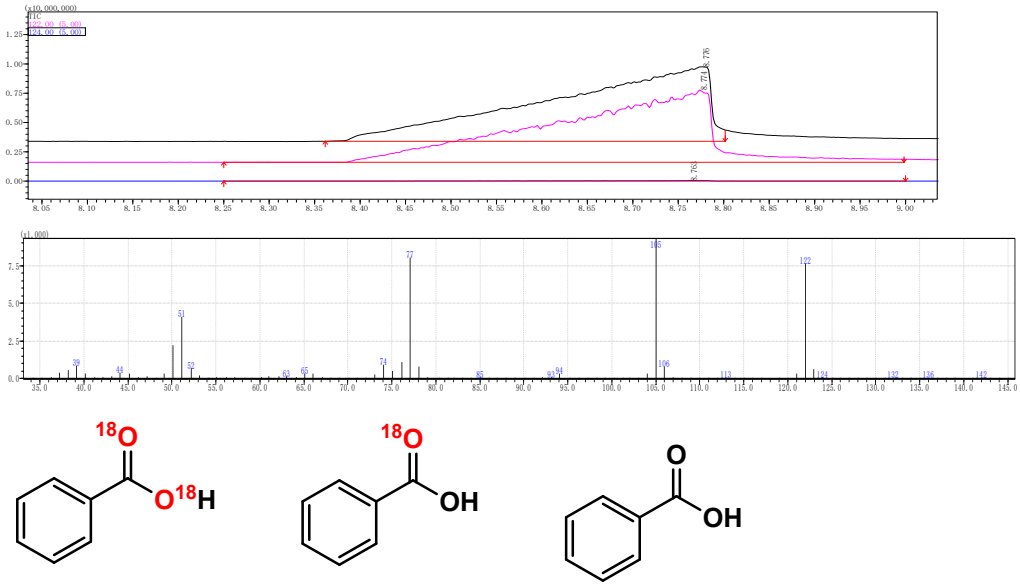
6.1 The H_2O^{18} isotope experiment





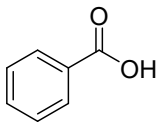
S126: S124 : S122 = 0.07: 1.0 ： 1.6

6.2 The $^{18}O_2$ isotope experiment

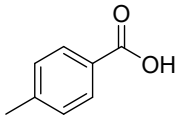


S126: S124 : S122 = 0.05: 1.0 ： 1.1

Characterization data[1,2]

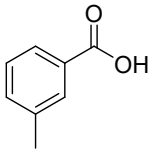


benzoic acid (**3a**). White solid (108mg, 89%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.95 (s, 1H), 7.97 (d, J = 8.3 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 167.51, 133.72, 130.95, 130.22, 129.47, 128.63, 127.79. ESI-MS: m/z =122[M+1]$^+$. Calc. for: $C_7H_6O_2$, C, 68.85; H, 4.95.

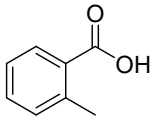


4-methylbenzoic acid (**3b**). White solid (122mg, 90%). ^{1}H NMR (400 MHz, DMSO-

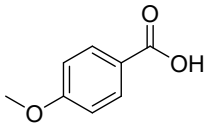
d_6) δ 12.77 (s, 1H), 7.84 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 167.49, 143.12, 130.31, 128.64, 128.22, 21.81. ESI-MS: m/z =136[M+1]$^+$. Calc. for: $C_8H_8O_2$, C, 70.58; H, 5.92.



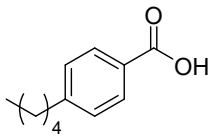
3-methylbenzoic acid (**3c**). White solid (118mg, 87%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.85 (s, 1H), 7.76 (s, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1 H), 7.36 (t, J = 7.6 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 167.56, 137.95, 134.30, 130.85, 129.27, 127.67, 125.77, 21.49. ESI-MS: m/z =136[M+1]$^+$. Calc. for: $C_8H_8O_2$, C, 70.58; H, 5.92.



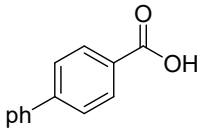
2-methylbenzoic acid (**3d**). White solid (111mg, 82%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.79 (s, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.45-7.41 (m, 1H), 7.27 (t, J = 8.4 Hz, 2H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 168.82, 139.17, 132.50, 130.89, 129.54, 126.64, 125.10, 21.94. ESI-MS: m/z =136[M+1]$^+$. Calc. for: $C_8H_8O_2$, C, 70.58; H, 5.92.



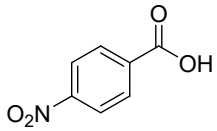
4-methoxybenzoic acid (**3e**). White solid (138mg, 91%). ^{1}H NMR (400 MHz, DMSO- d_6) δ 12.60 (s, 1H), 7.90 (d, J = 8.9 Hz, 2H), 6.98 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.19, 162.96, 132.32, 123.13, 114.69, 56.17. ESI-MS: m/z =152[M+1]$^+$. Calc. for: $C_8H_8O_3$, C, 63.15; H, 5.30.



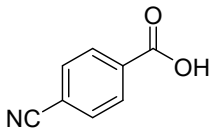
4-pentylbenzoic acid (**3f**). White liquid (168mg, 88%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.75 (s, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 2.63 – 2.57 (m, 2H), 1.59 – 1.51 (m, 2H), 1.31 – 1.20 (m, 4H), 0.83 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.32, 147.72, 130.20, 129.23, 128.53, 128.32, 127.59, 35.07, 30.88, 30.31, 21.91, 13.22. ESI-MS: m/z =192[M+1]$^+$. Calc. for: $C_{12}H_{16}O_2$, C, 74.97; H, 8.39.



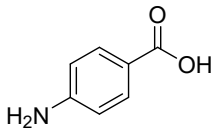
[1,1'-biphenyl]-4-carboxylic acid (**3g**). White solid (170mg, 86%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.02 (s, 1H), 8.05 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 7.0 Hz, 2H), 7.46 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.28, 144.37, 139.11, 130.90, 129.76, 129.22, 128.26, 127.66, 126.00. ESI-MS: m/z =198[M+1]$^{+}$. Calc. for: $C_{13}H_{10}O_2$, C, 78.77; H, 5.09.



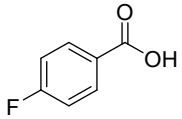
4-nitrobenzoic acid (**3h**). White solid. (123mg, 74%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.60 (s, 1H), 8.26 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.85, 150.04, 136.43, 131.53, 129.84, 124.57, 122.82. ESI-MS: m/z =167[M+1]$^{+}$. Calc. for: $C_7H_5NO_4$, C, 50.31; H, 3.02.



4-cyanobenzoic acid (**3i**). White solid. (111mg, 76%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.49 (s, 1H), 8.04 (s, 2H), 7.90 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.14, 134.92, 133.53, 131.78, 130.86, 129.13, 118.25, 115.19. ESI-MS: m/z =147[M+1]$^{+}$. Calc. for: $C_8H_5NO_2$, C, 65.31; H, 3.43.

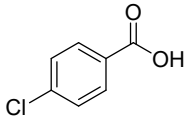


4-aminobenzoic acid (**3j**). White solid. (113mg, 83%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.94 (s, 1H), 7.65 (d, J = 8.7 Hz, 2H), 6.57 (d, J = 8.7 Hz, 2H), 5.84 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.72, 153.25, 132.24, 130.59, 117.11, 113.59, 111.96. ESI-MS: m/z =137[M+1]$^{+}$. Calc. for: $C_7H_7NO_2$, C, 61.31; H, 5.35.

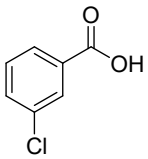


4-fluorobenzoic acid (**3k**). White solid. (114mg, 82%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.01 (s, 1H), 7.99 (dd, J = 8.9, 5.6 Hz, 2H), 7.27 (t, J = 8.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.50, 163.78, 133.01, 131.36, 127.48, 116.58, 114.67. ESI-

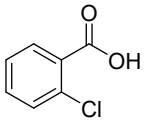
MS: m/z =140[M+1]$^+$. Calc. for: $C_7H_5FO_2$, C, 60.01; H, 6.60.



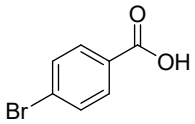
4-chlorobenzoic acid (**3l**). White solid. (137mg, 88%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.13 (s, 1H), 7.92 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.56, 137.91, 132.05, 130.34, 129.74, 129.59, 127.87. ESI-MS: m/z =156[M+1]$^+$. Calc. for: $C_7H_5ClO_2$, C, 53.70; H, 3.22.



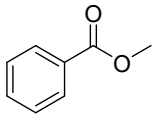
3-chlorobenzoic acid (**3m**). White solid. (132mg, 85%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.27 (s, 1H), 7.86-7.88 (m, 2H), 7.64-7.61 (m, 1H), 7.48 (t, J = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.11, 133.46, 132.92, 131.32, 129.68, 128.08, 127.08. ESI-MS: m/z =156[M+1]$^+$. Calc. for: $C_7H_5ClO_2$, C, 53.70; H, 3.22.



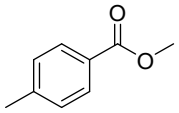
2-chlorobenzaldehyde (**3n**). White solid. (124mg, 80%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.35 (s, 1H), 7.80 – 7.77 (m, 1H), 7.52 – 7.47 (m, 2H), 7.40-7.36 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.88, 133.46, 131.77, 131.56, 130.13, 128.08, 126.39. ESI-MS: m/z =156[M+1]$^+$. Calc. for: $C_7H_5ClO_2$, C, 53.70; H, 3.22.



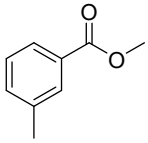
4-bromobenzoic (**3o**). White solid. (174mg, 87%).^{1}H NMR (400 MHz, DMSO-d_6) δ 13.14 (s, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.67, 132.52, 132.12, 130.88, 130.46, 130.07, 126.92. ESI-MS: m/z =200[M+1]$^+$. Calc. for: $C_7H_5BrO_2$, C, 41.83; H, 2.51.



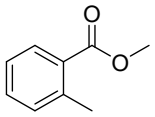
methyl benzoate (**4a**). Yellow liquid. (99mg, 73%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.98 (m, 2H), 7.56 – 7.48 (m, 1H), 7.40 (t, J = 7.6 Hz, 2H), 3.88 (d, J = 1.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 132.9, 130.2, 129.6, 128.3, 52.0. ESI-MS: m/z =136[M+1]$^+$. Calc. for: $C_8H_8O_2$, C, 70.58; H, 5.92.



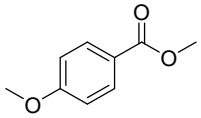
methyl 4-methylbenzoate (**4b**). Yellow liquid (111mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.4 Hz, 2H), 3.85 (s, 3H), 2.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 143.5, 129.6, 129.0, 127.4, 51.8, 21.5. ESI-MS: m/z =152$[M+1]^+$. Calc. for: $C_9H_{10}O_2$. C, 71.98; H, 6.71.



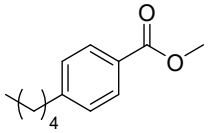
methyl 3-methylbenzoate (**4c**). White liquid (106mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.78 (m, 2H), 7.31 (dt, *J* = 14.9, 7.6 Hz, 2H), 3.89 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 138.1, 133.7, 130.1, 130.1, 128.3, 128.3, 126.7, 52.0, 21.2. ESI-MS: m/z =152$[M+1]^+$. Calc. for: $C_9H_{10}O_2$, C, 71.98; H, 6.71.



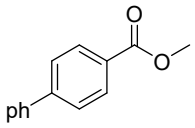
methyl 2-methylbenzoate (**4d**). White liquid (94mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.36 (td, *J* = 7.5, 1.4 Hz, 1H), 7.21 (dt, *J* = 7.2, 3.6 Hz, 2H), 3.86 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.01, 140.18, 131.96, 131.68, 130.58, 129.54, 125.69, 51.74, 21.71. ESI-MS: m/z =152$[M+1]^+$. Calc. for: $C_9H_{10}O_2$, C, 71.98; H, 6.71.



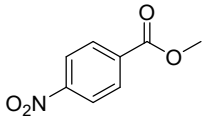
methyl 4-methoxybenzoate (**4e**). White solid. (131mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.80 (m, 2H), 6.90 – 6.80 (m, 2H), 3.78 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 163.5, 130.5, 130.2, 113.6, 55.4, 26.2. ESI-MS: m/z =167$[M+1]^+$. Calc. for: $C_9H_{10}O_3$. C, 65.05; H, 6.07.



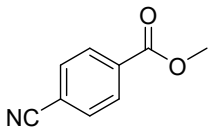
methyl 4-ethylbenzoate (**4f**). White solid. (138mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 2.68 – 2.62 (m, 2H), 1.63 (dt, *J* = 15.0, 4.8 Hz, 2H), 1.37 – 1.27 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 148.6, 129.6, 128.5, 127.6, 52.0, 36.0, 31.5, 30.9, 22.5, 14.0. ESI-MS: m/z =165$[M+1]^+$. Calc. for: $C_{10}H_{12}O_2$. C, 73.15; H, 7.37.



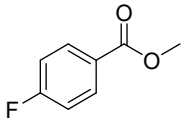
methyl [1,1'-biphenyl]-4-carboxylate (**4g**). White solid. (131mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.65 (dd, *J* = 15.1, 8.1 Hz, 4H), 7.43 (dt, *J* = 29.1, 7.2 Hz, 3H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 145.7, 140.0, 130.1, 129.0, 128.9, 128.2, 127.3, 127.1, 52.2. ESI-MS: m/z =213$[M+1]^+$. Calc. for:$C_{14}H_{12}O_2$. C, 79.23; H, 5.70.



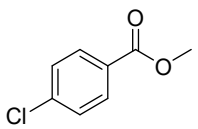
methyl 4-nitrobenzoate (**4h**). Yellow solid (81mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 8.18 (d, *J* = 8.8 Hz, 2H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 150.6, 135.5, 130.7, 123.5, 52.8. ESI-MS: m/z =182$[M+1]^+$. Calc. for: $C_8H_7NO_4$, C, 53.04; H, 3.90; N, 7.73.



methyl 4-cyanobenzoate (**4i**). White solid (69mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 133.9, 132.2, 130.1, 118.0, 117.4, 52.7. ESI-MS: m/z =162$[M+1]^+$. Calc. for: $C_9H_7NO_2$, C, 67.08; H, 4.38; N, 8.69.

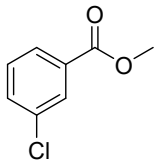


methyl 4-fluorobenzoate (**4k**). White solid (86mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.97 (m, 2H), 7.08 (dd, *J* = 12.1, 5.3 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 166.1, 164.5, 132.1, 132.1, 126.4, 126.4, 115.6, 115.4, 52.2. ESI-MS: m/z =155$[M+1]^+$. Calc. for: $C_8H_7FO_2$. C, 62.34; H, 4.58.

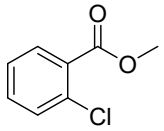


methyl 4-chlorobenzoate (**4l**). White solid (138mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 139.4, 130.9, 128.7, 128.6, 52.3. ESI-MS: m/z

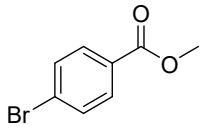
=171[M+1]$^+$. Calc. for: $C_8H_7ClO_2$. C, 56.33; H, 4.14.



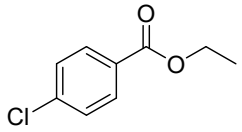
methyl 3-chlorobenzoate (**4m**). White solid (126mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, *J* = 1.8 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.46 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 134.5, 132.9, 131.8, 129.61, 127.7, 52.3. ESI-MS: m/z =171[M+1]$^+$. Calc. for: $C_8H_7ClO_2$. C, 56.33; H, 4.14.



methyl 2-chlorobenzoate (**4n**). White solid (117mg, 69%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.42 (dtd, *J* = 9.7, 8.0, 1.5 Hz, 2H), 7.33 – 7.27 (m, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 133.7, 132.6, 131.4, 131.1, 130.1, 126.6, 52.4. ESI-MS: m/z =171[M+1]$^+$. Calc. for: $C_8H_7ClO_2$. C, 56.33; H, 4.14.



methyl 4-bromobenzoate (**4o**). White solid (159mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 131.7, 131.1, 129.0, 128.1, 52.3. ESI-MS: m/z =214[M+1]$^+$. Calc. for:$C_8H_7BrO_2$. C, 44.68; H, 3.28.



ethyl 4-chlorobenzoate (**5l**). Yellow solid. (130mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.44 – 7.36 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 138.2, 130.0, 129.9, 127.9, 127.7, 127.6, 60.2, 51.3, 13.3. ESI-MS: m/z =185[M+1]$^+$. Calc. for: $C_9H_9ClO_2$, C, 58.55; H, 4.91.

References

[1] J. Ou, H. Tan, S. He, W. Wang, B. Hu, G. Yu, and K. Liu, *J. Org. Chem.*, 2021, **86**(21), 14974–14982.

[2] R. A. Molla, M. Iqubal, K. Ghosh, Kamaluddin and S. Islam, *Dalto Trans.*, 2015, **44**(14), 6546-6559.

NMR Spectra

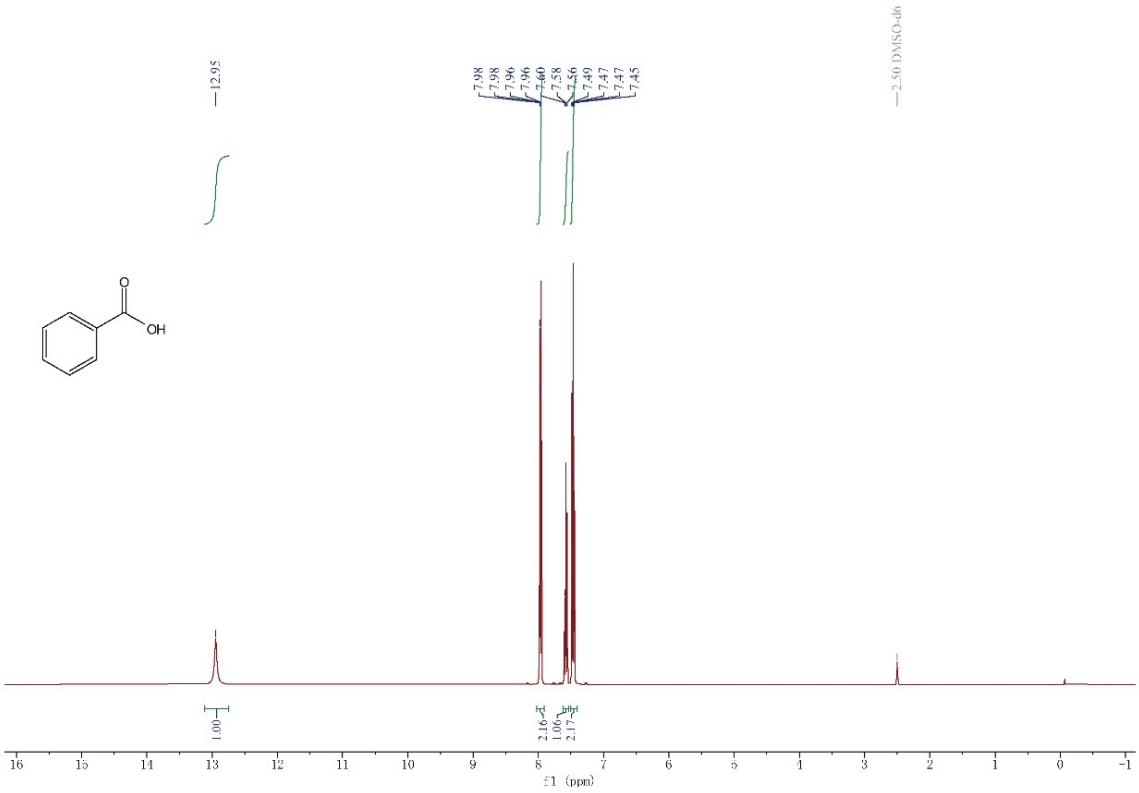


Fig.1 **3a** ^{1}H NMR

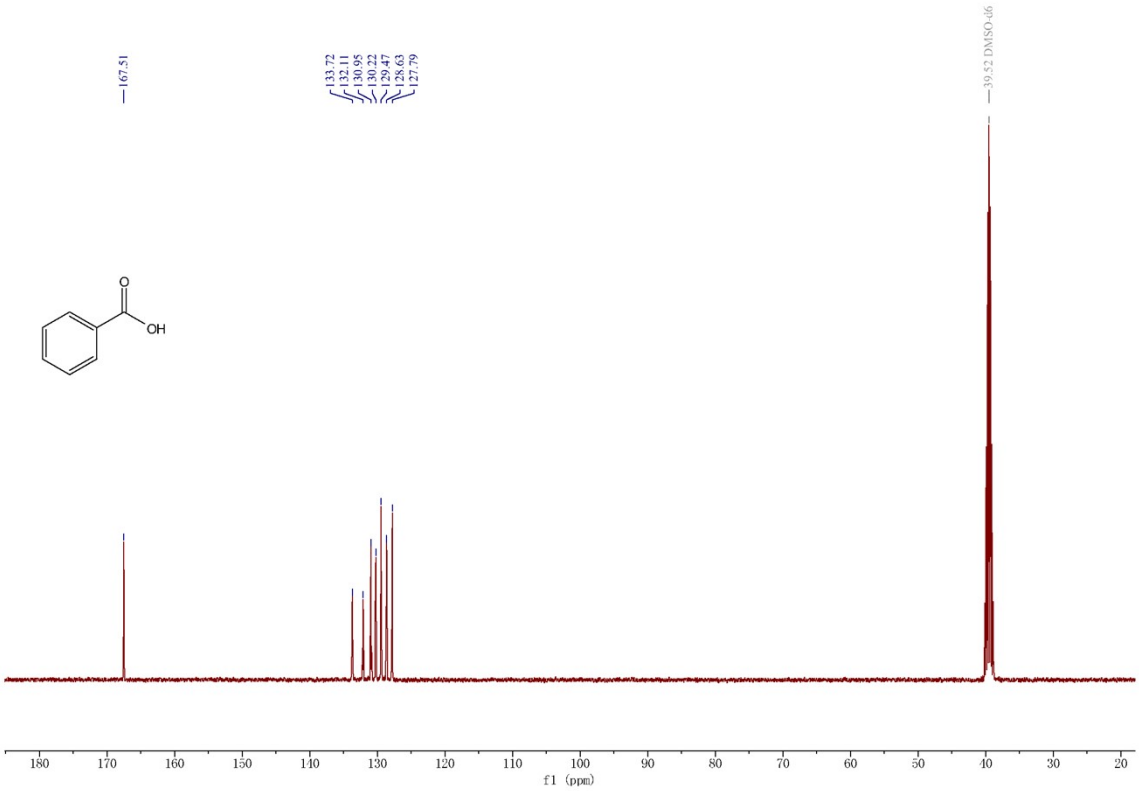


Fig.2 **3a** ^{13}C NMR

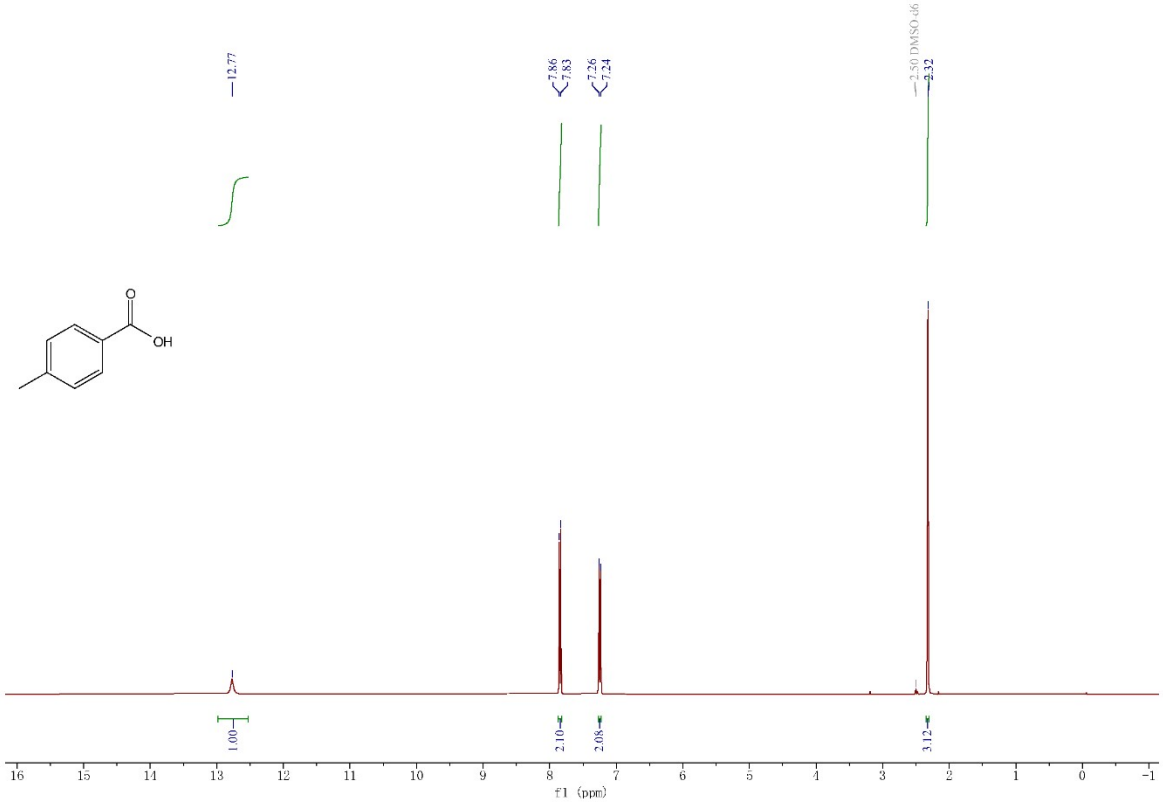


Fig.3 **3b** ^{1}H NMR

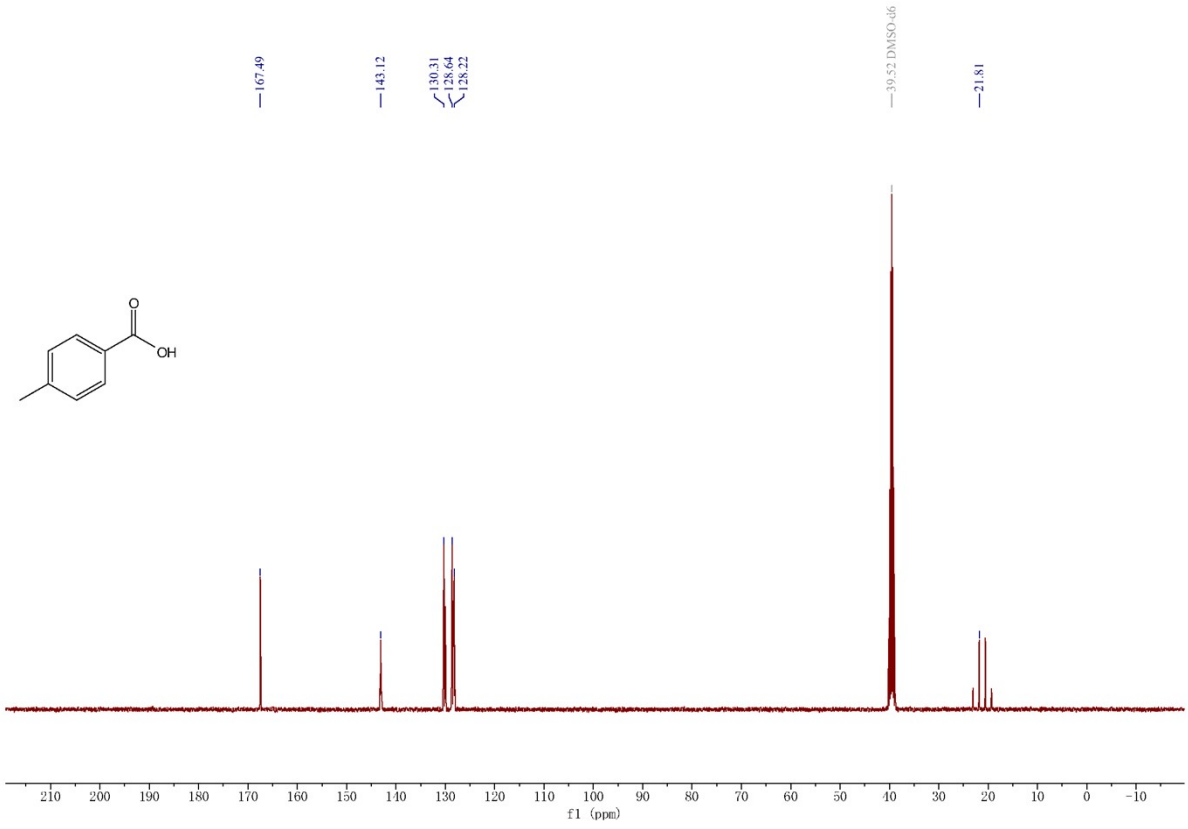


Fig.4 **3b** ^{13}C NMR

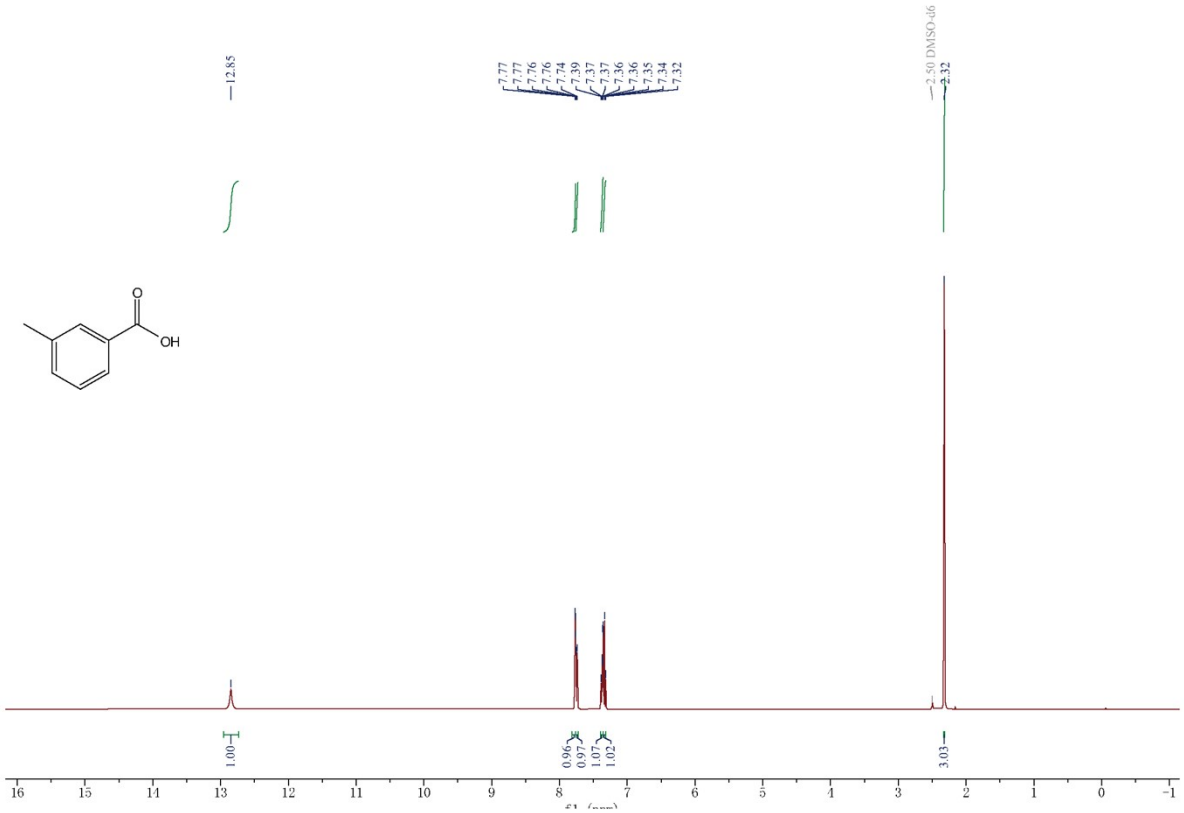


Fig.5 **3c** ^{1}H NMR

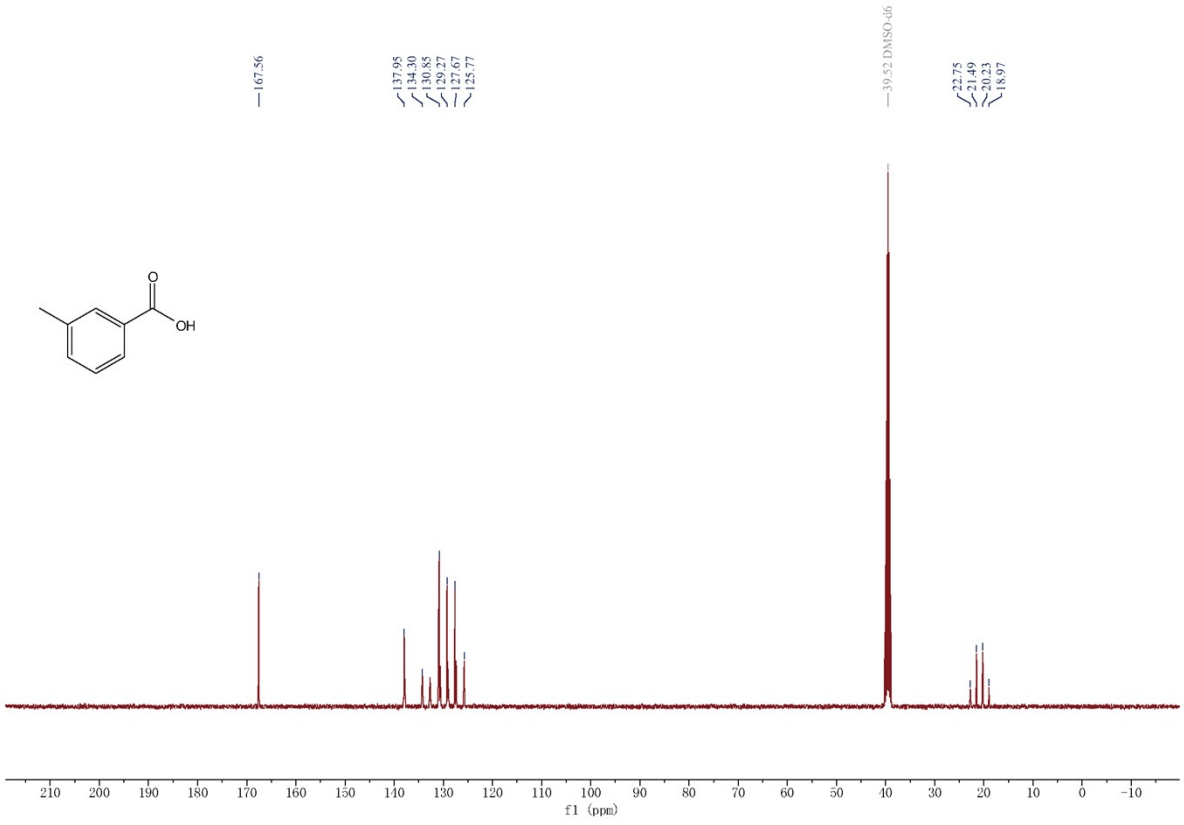


Fig.6 **3c** ^{13}C NMR

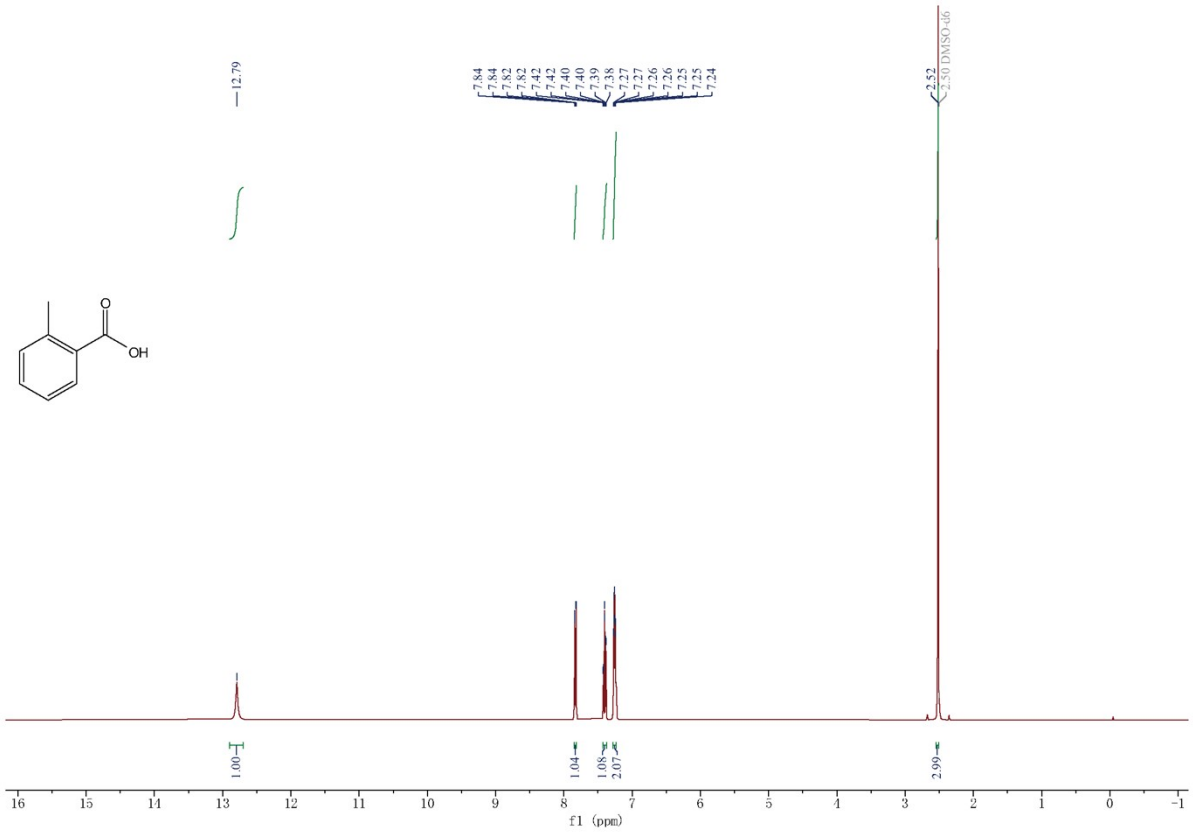


Fig.7 **3d** ^{1}H NMR

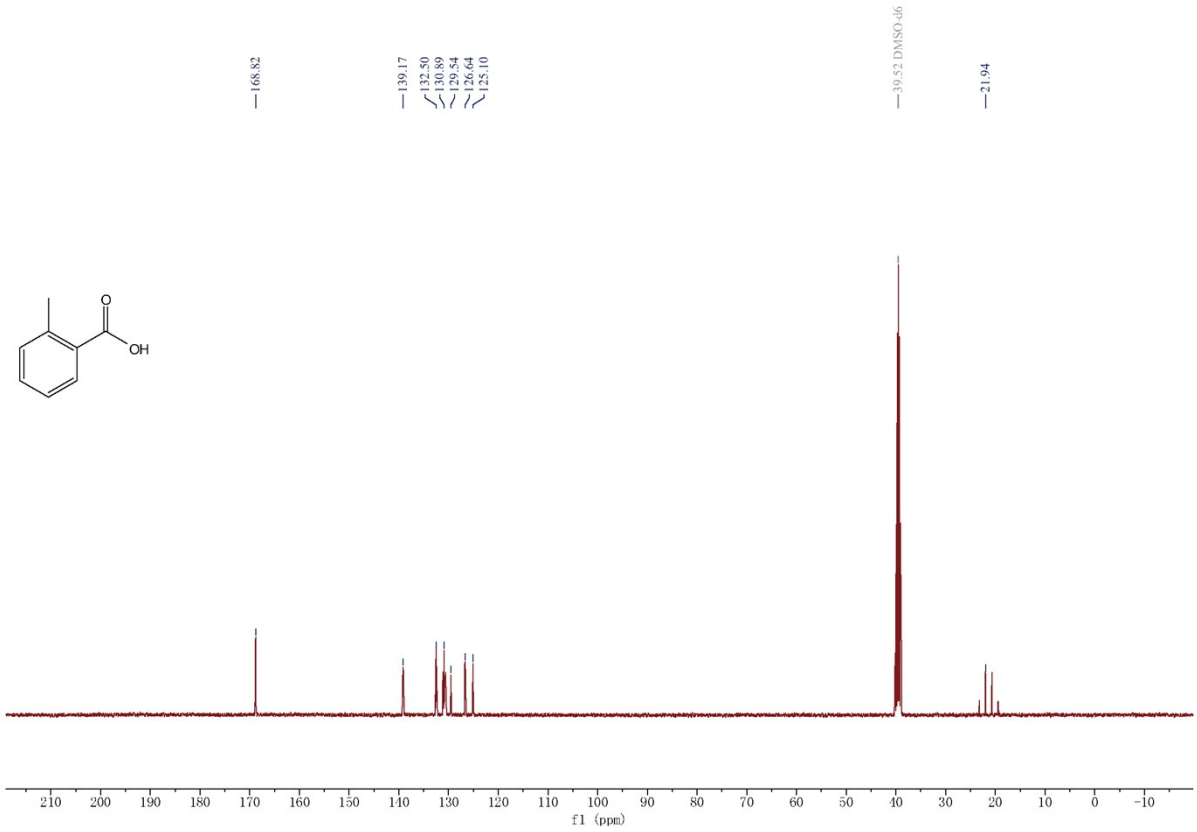


Fig.8 **3d** ^{13}C NMR

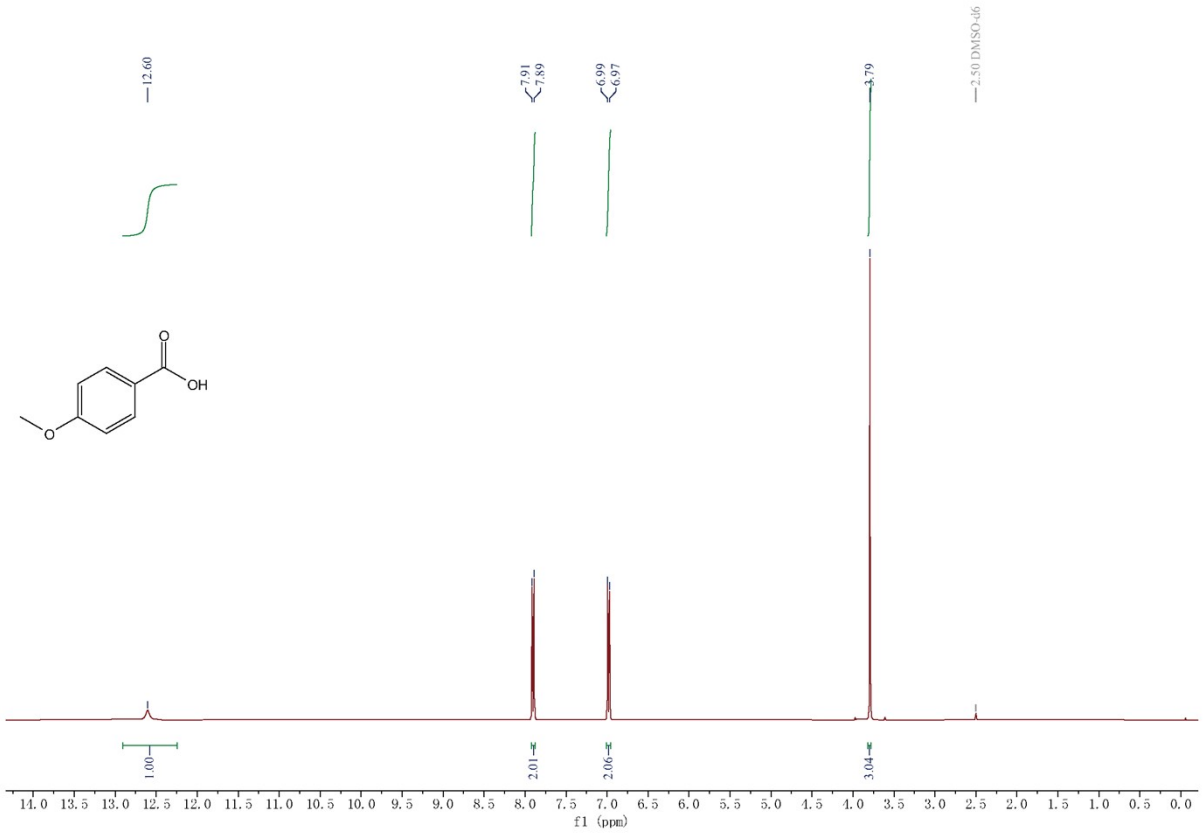


Fig.9 **3e** ^{1}H NMR

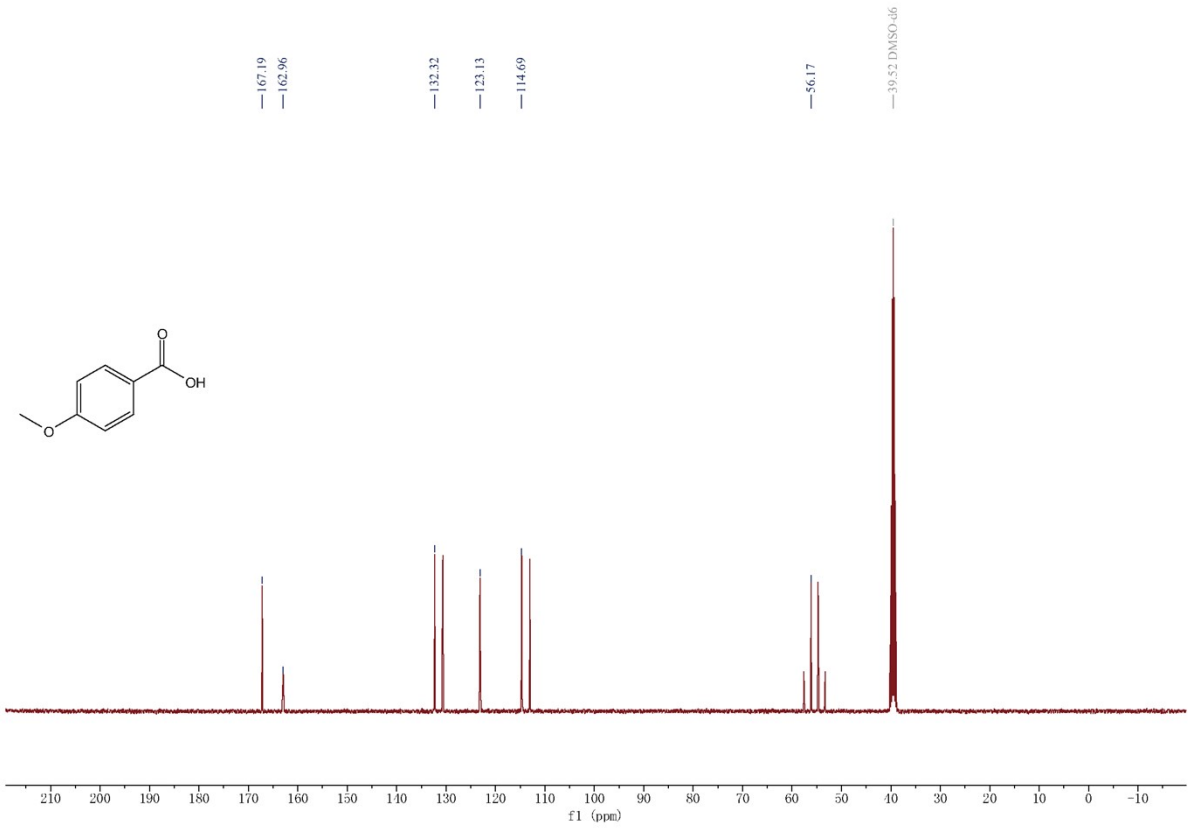


Fig.10 **3e** ^{13}C NMR

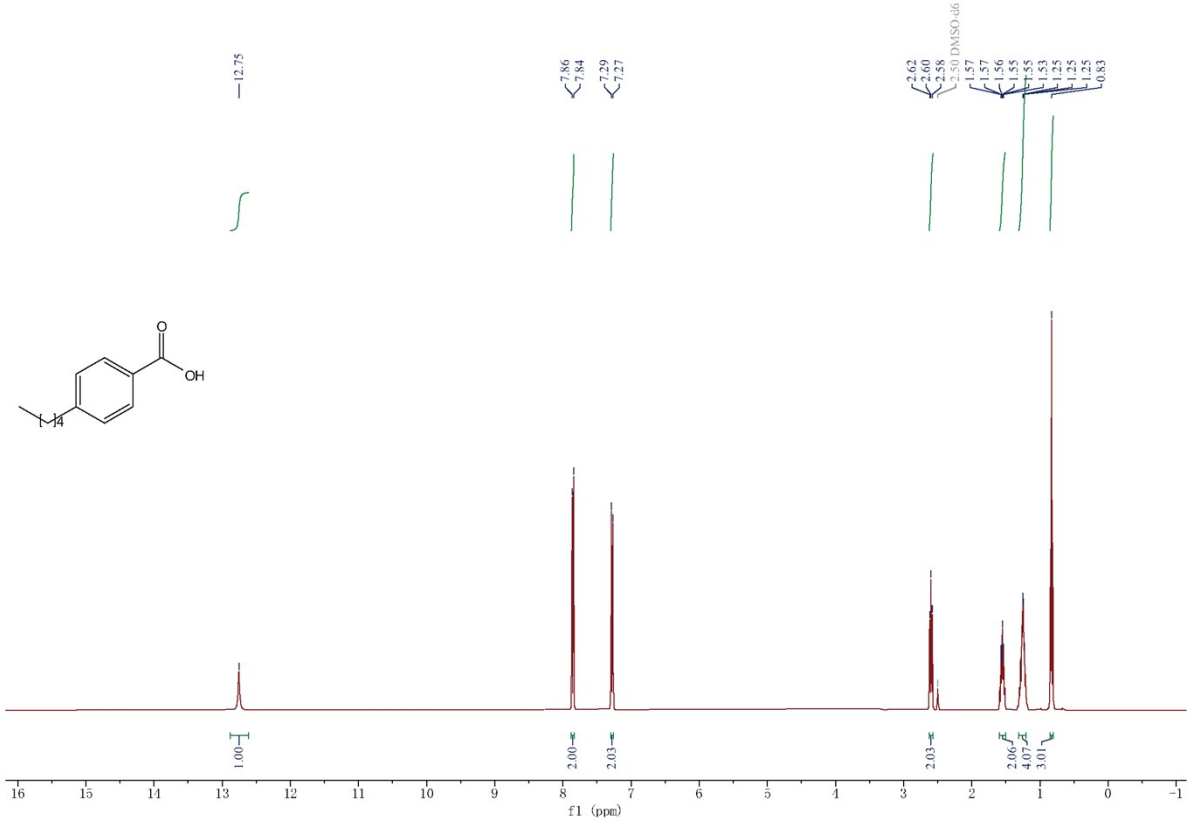


Fig.11 **3f** ^{1}H NMR

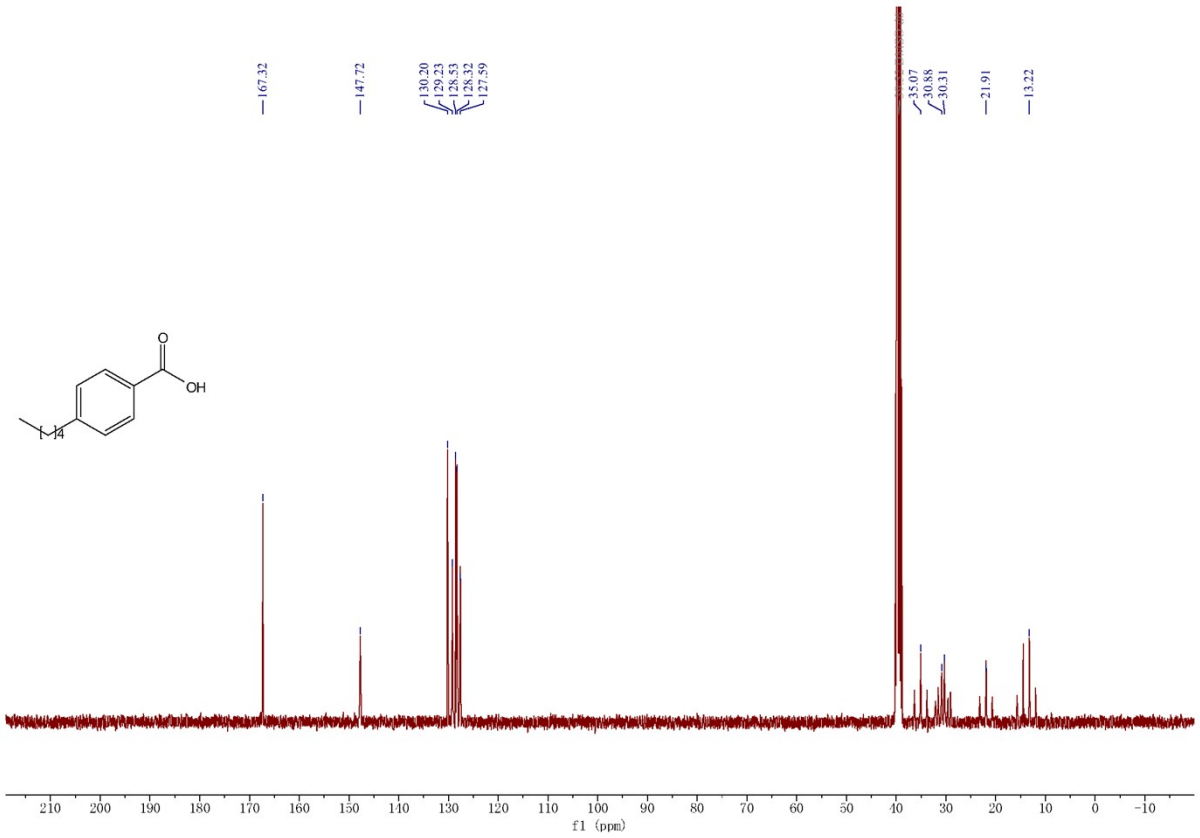


Fig.12 **3f** ^{13}C NMR

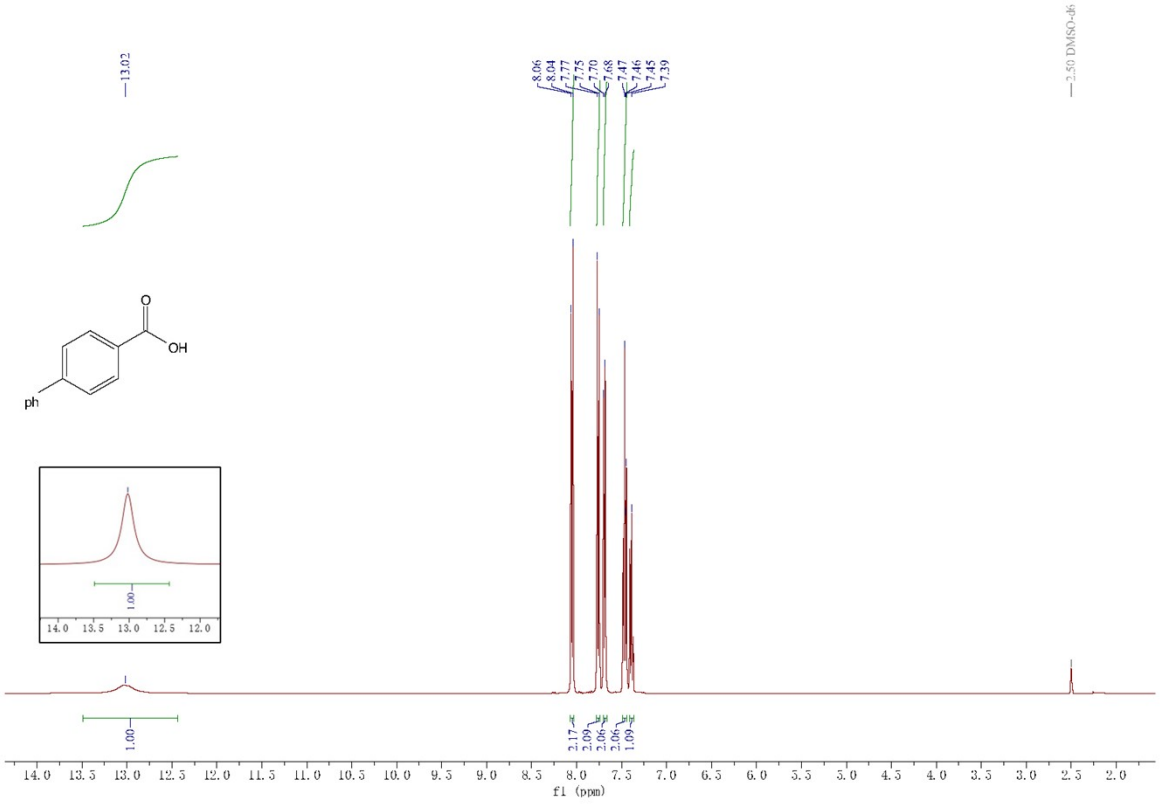


Fig.13 **3g** ^{1}H NMR

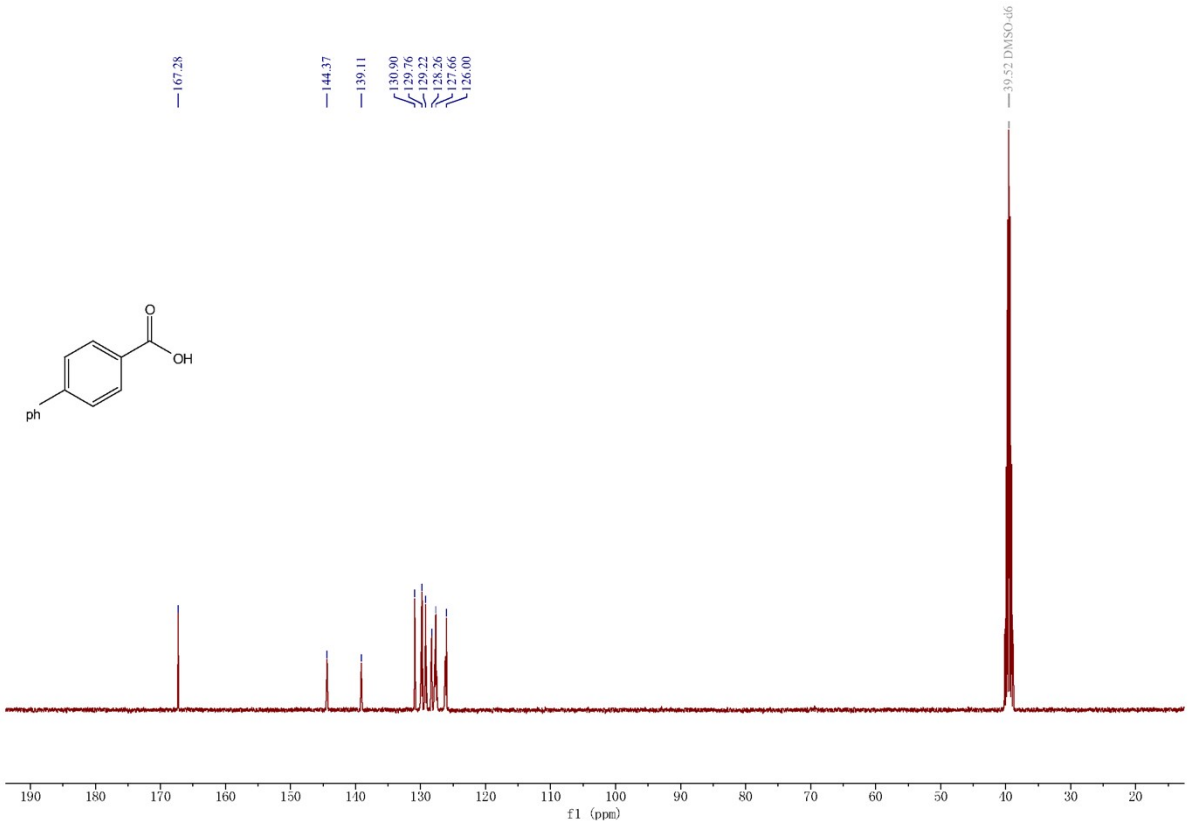


Fig.14 **3g** ^{13}C NMR

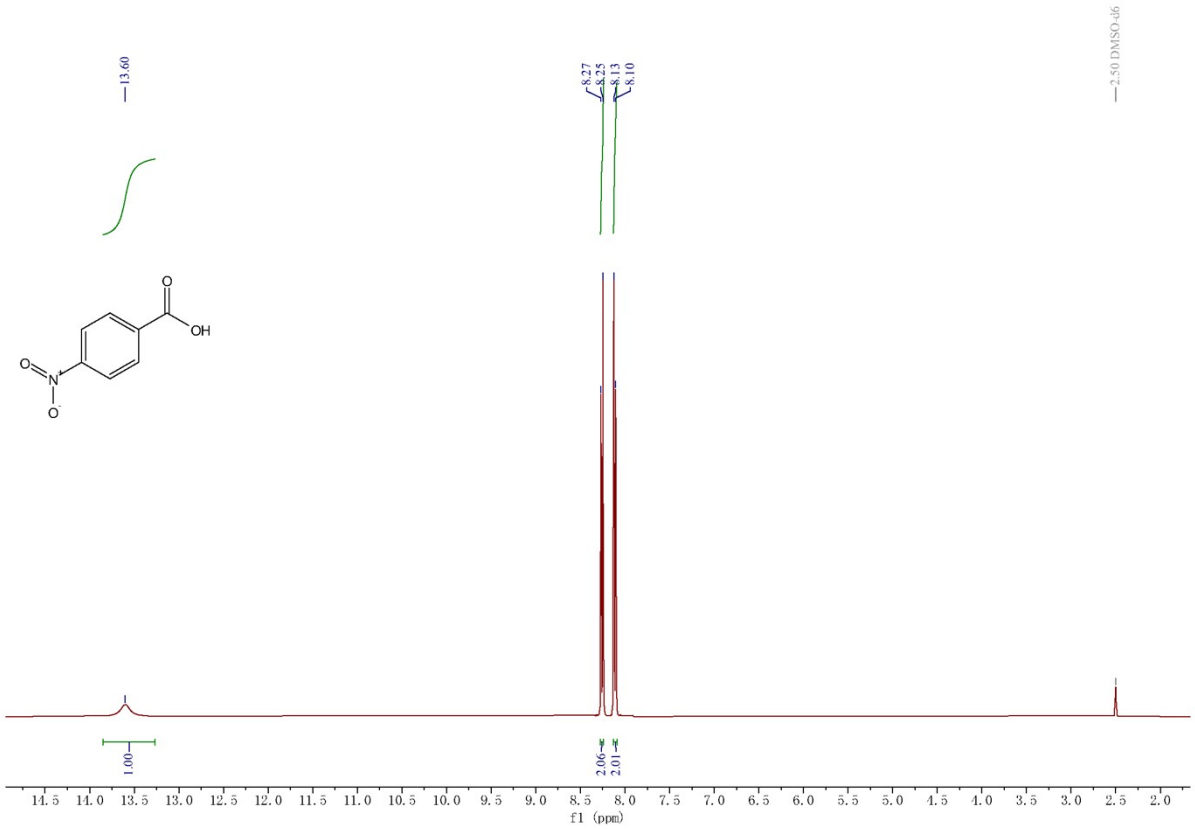


Fig.15 **3h** ^{1}H NMR

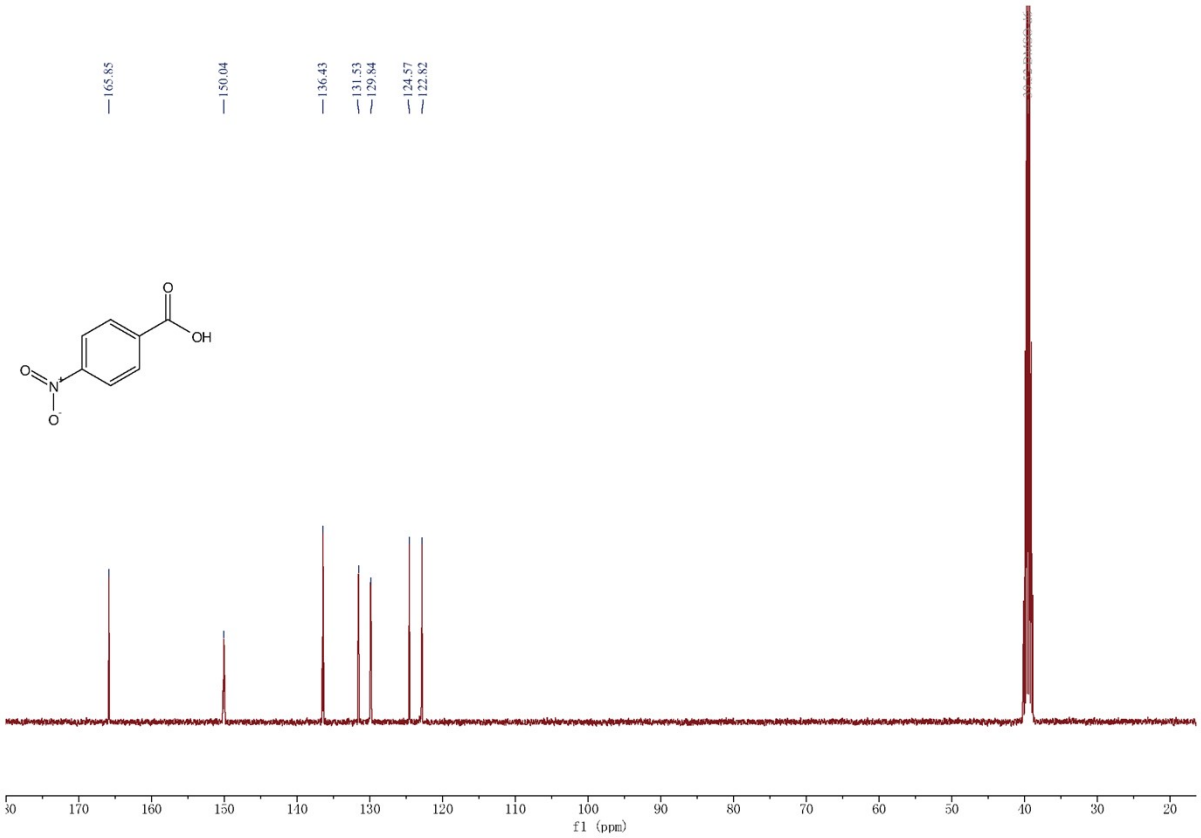


Fig.16 **3h** ^{13}C NMR

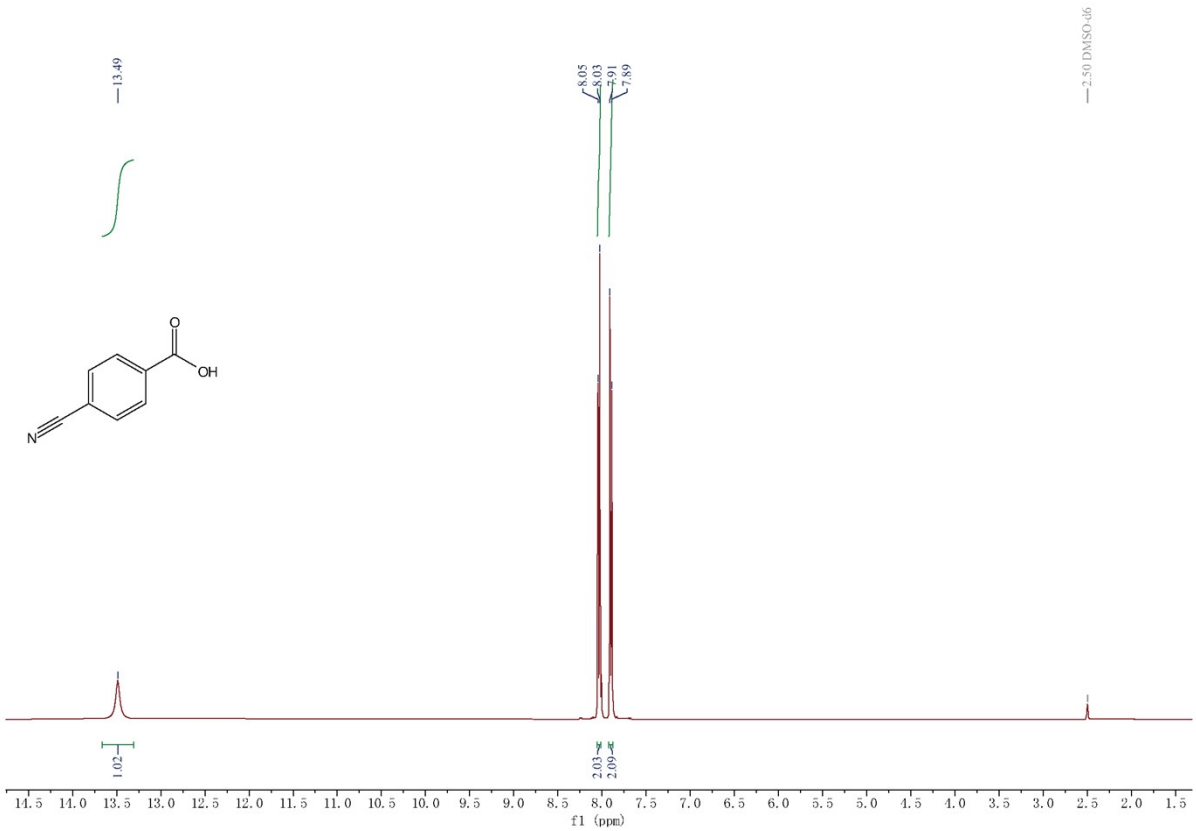


Fig.17 **3i** ^{1}H NMR

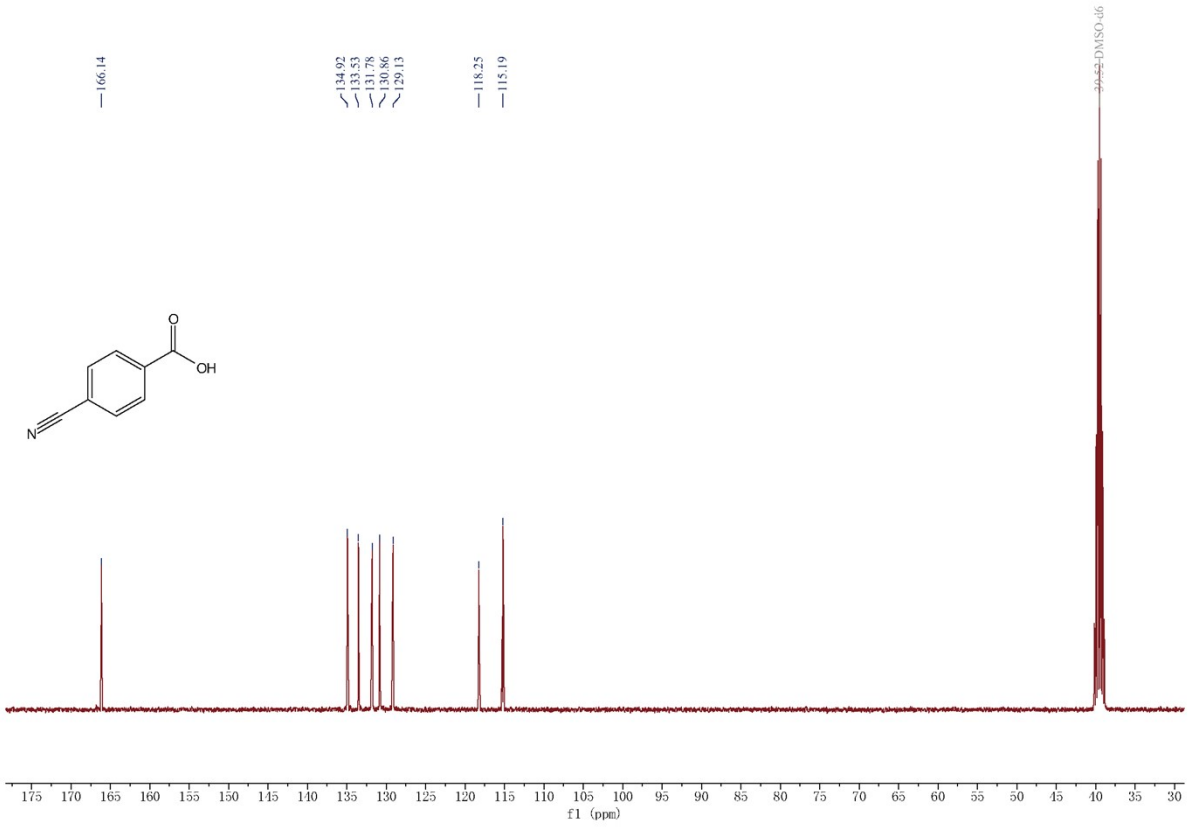


Fig.18 **3i** ^{13}C NMR

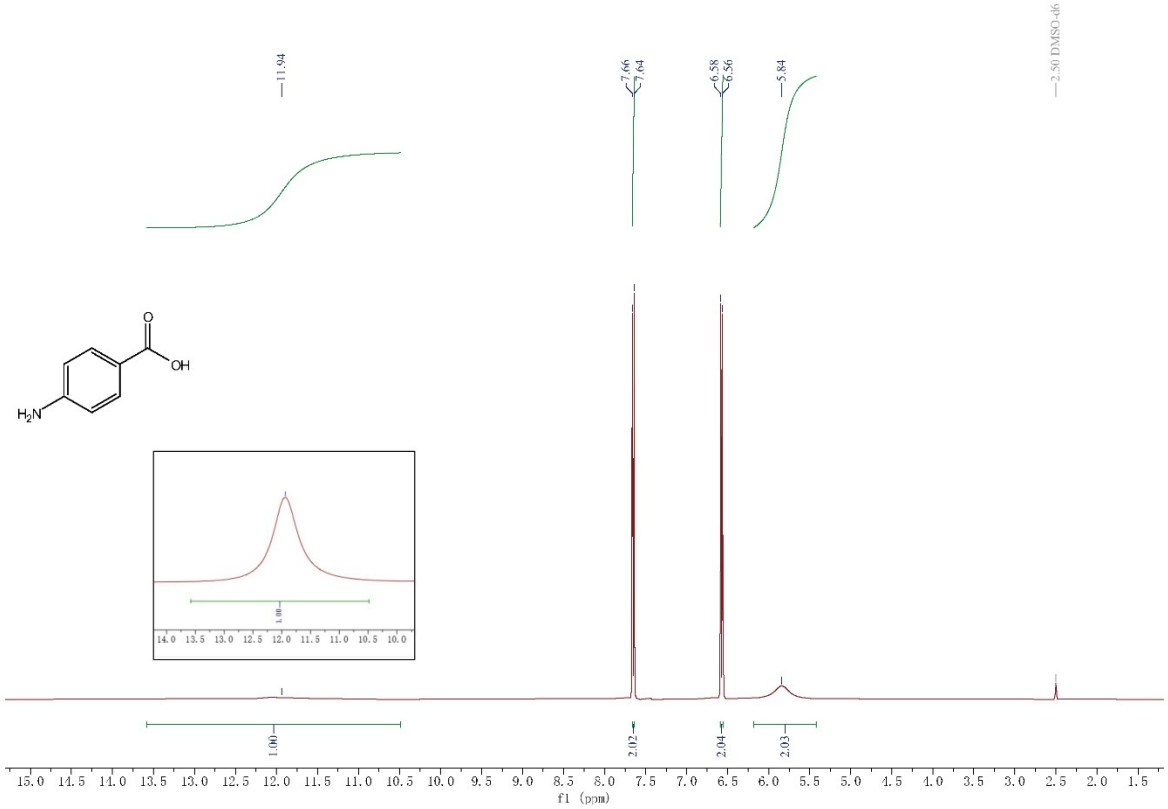


Fig.19 **3j** ^{1}H NMR

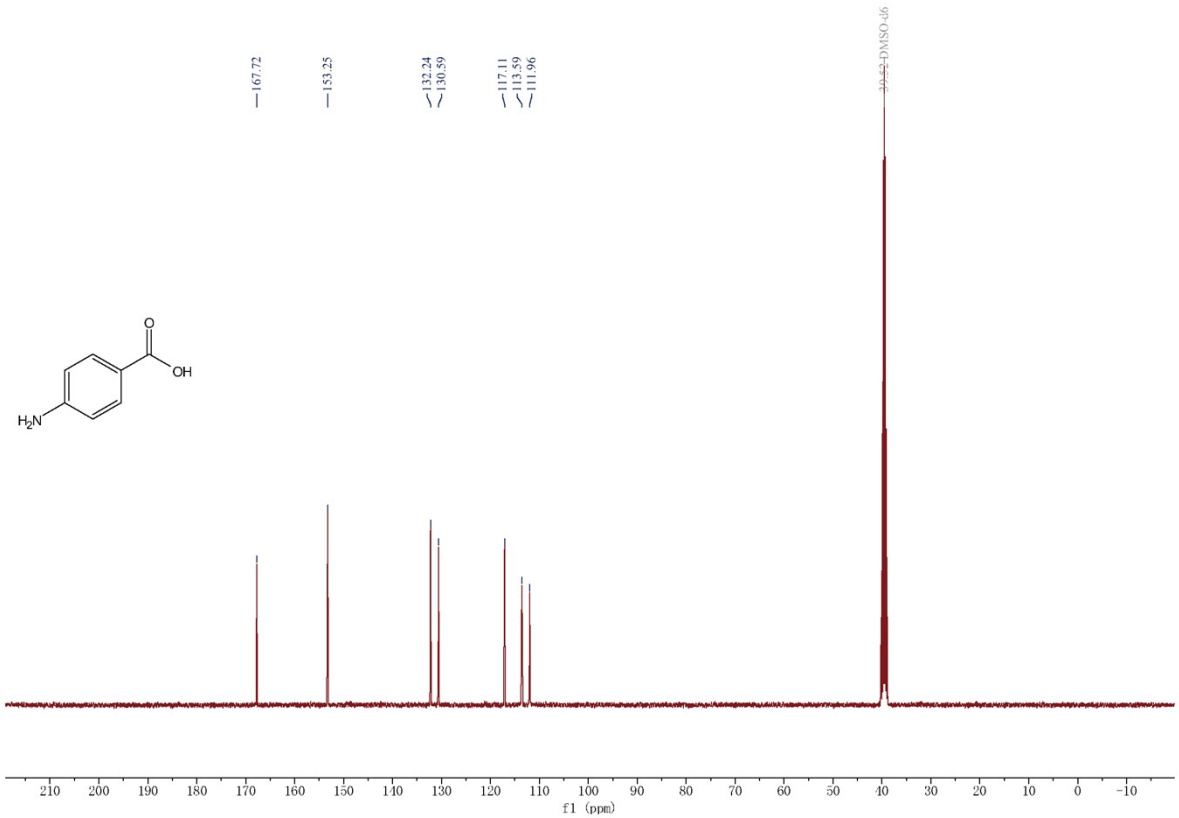


Fig.20 **3j** ^{13}C NMR

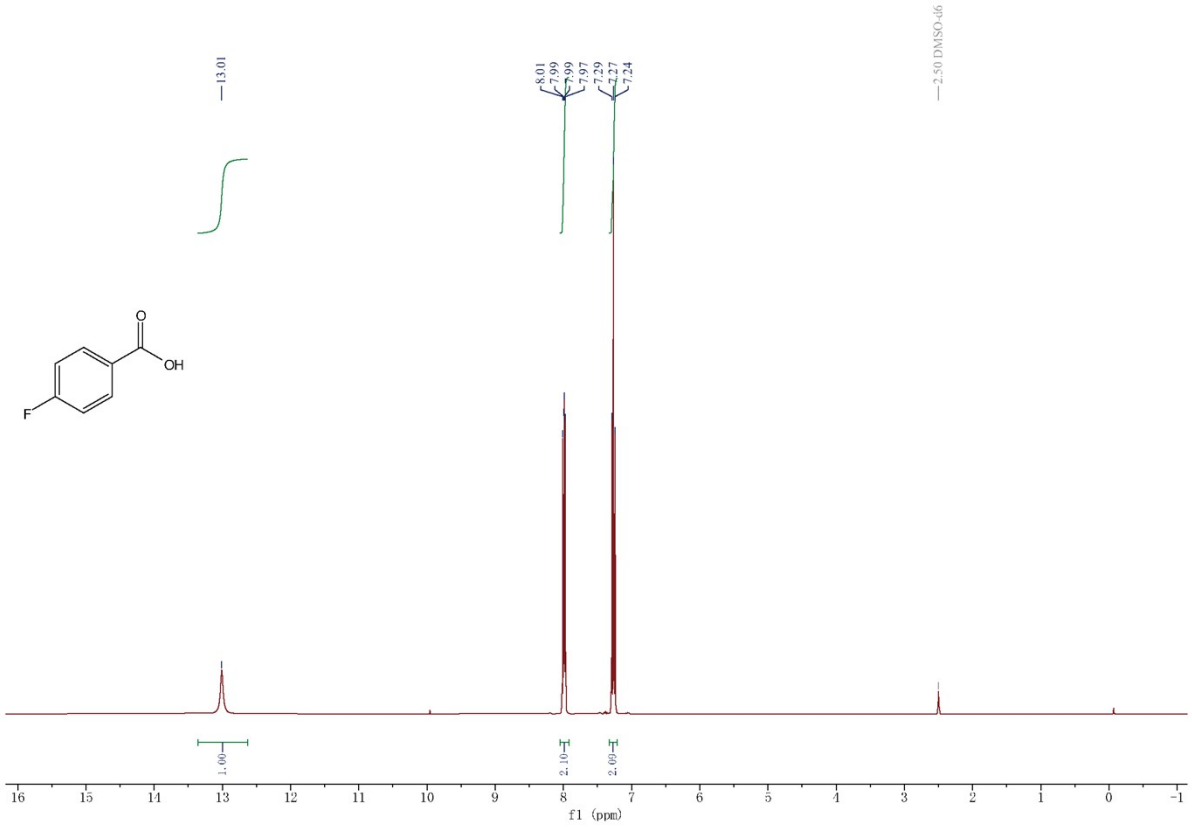


Fig.21 **3k** ^{1}H NMR

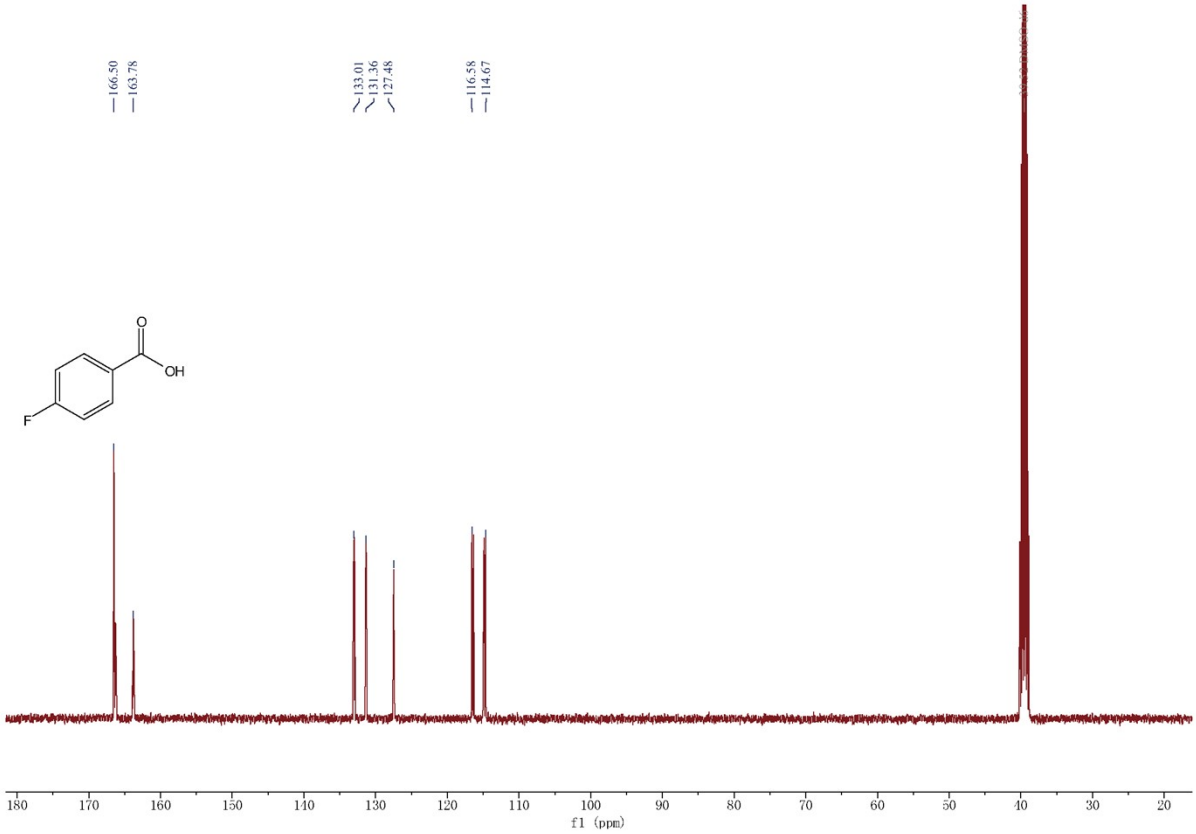


Fig.22 **3k** ^{13}C NMR

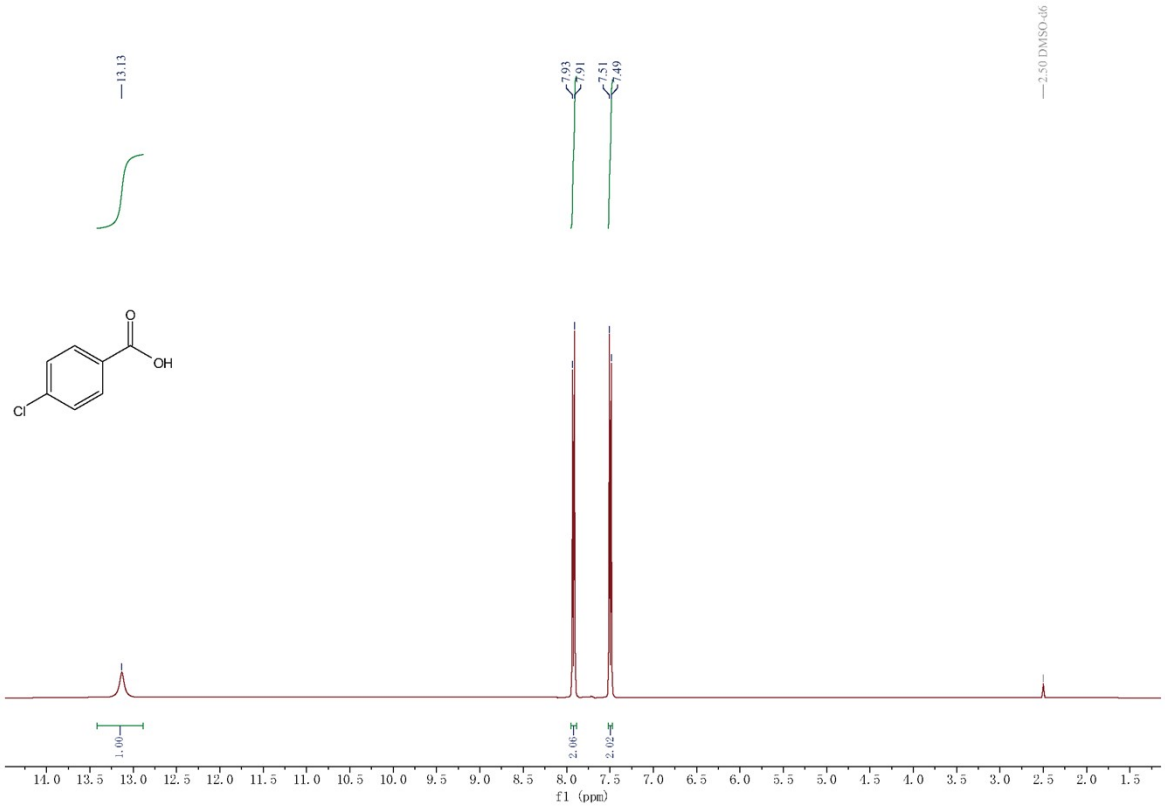


Fig.23 **3l** ^{1}H NMR

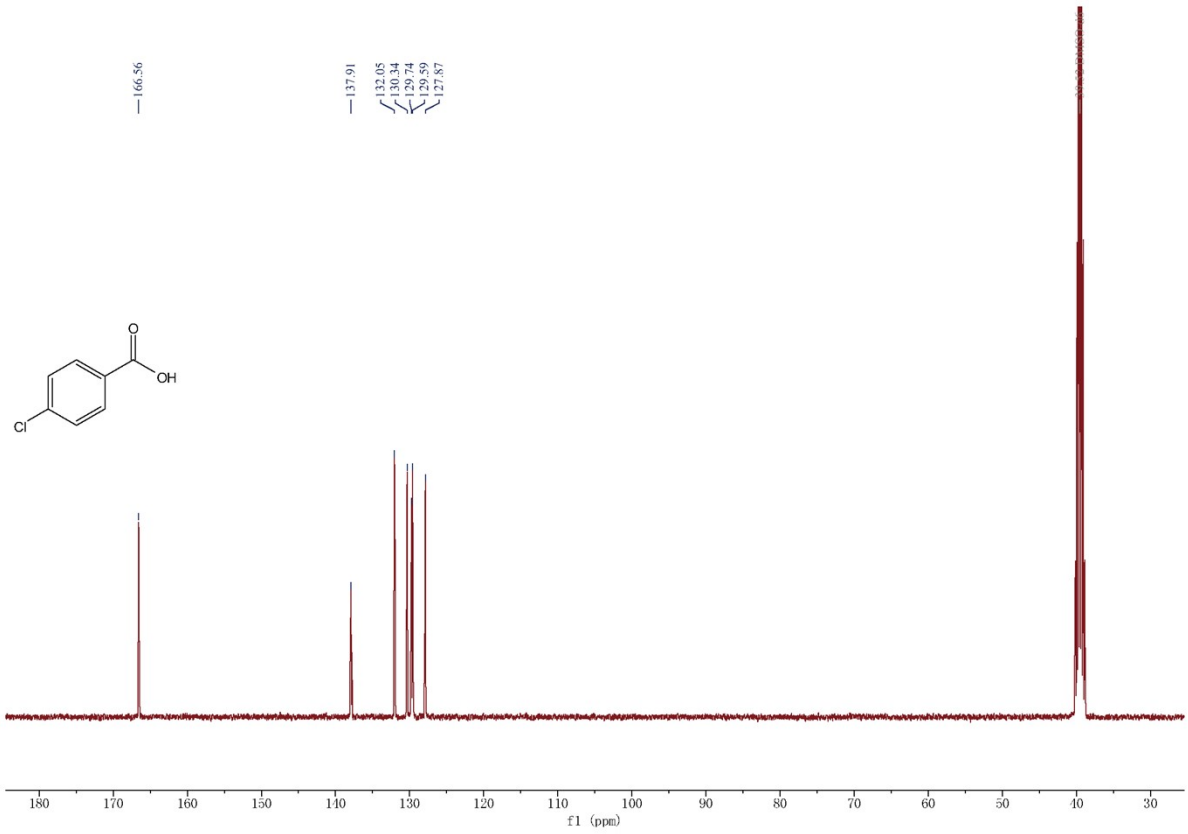


Fig.24 **3l** ^{13}C NMR

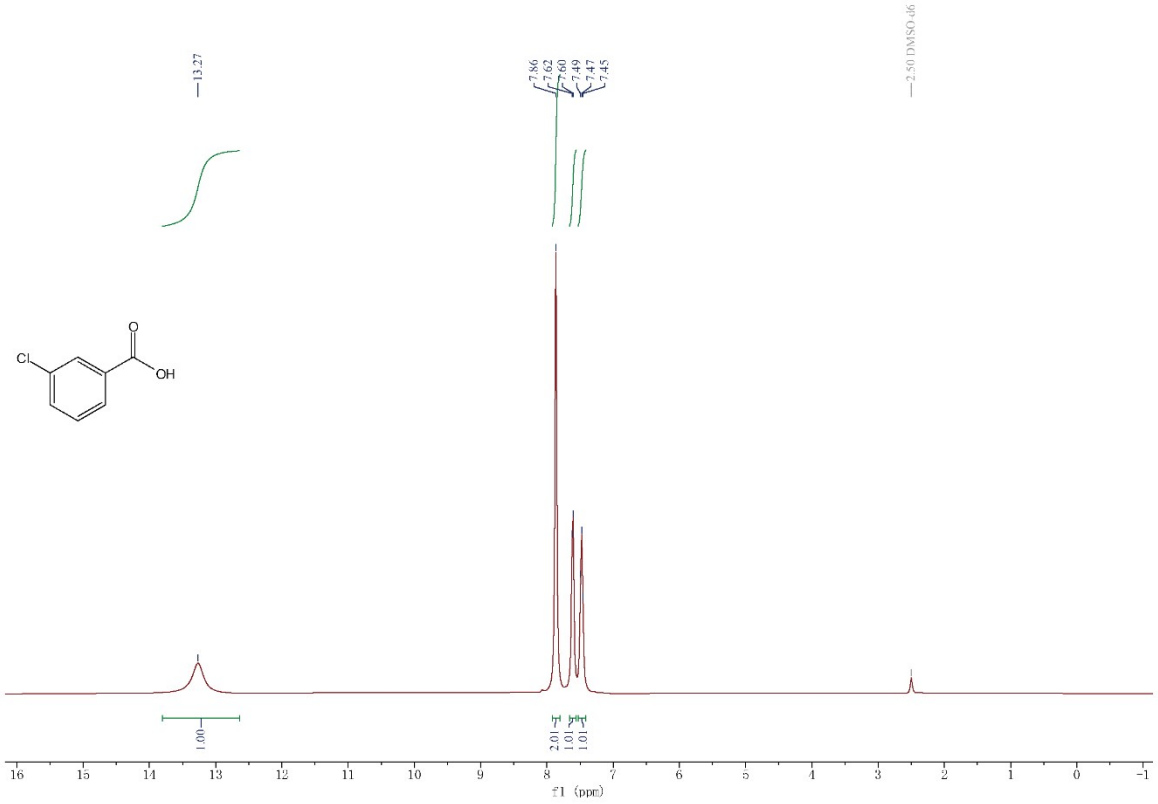


Fig.25 **3m** ^{1}H NMR

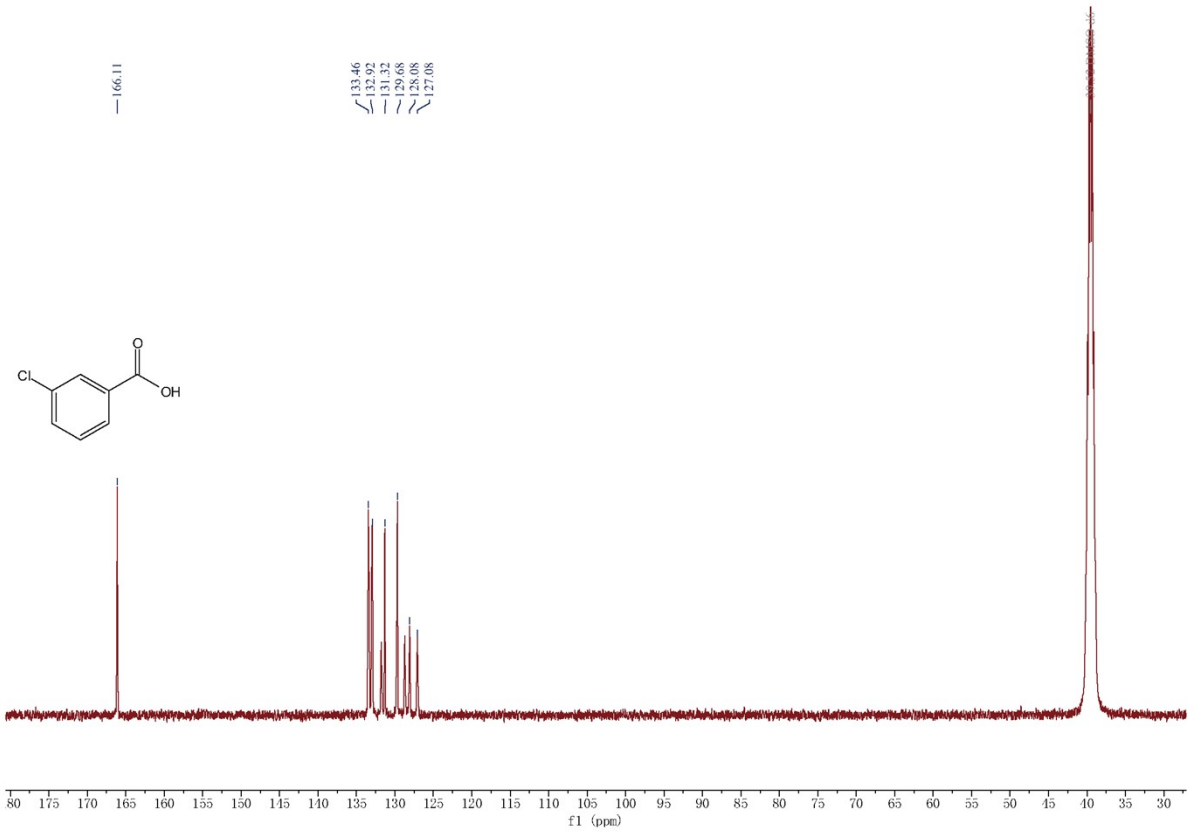


Fig.26 **3m** ^{13}C NMR

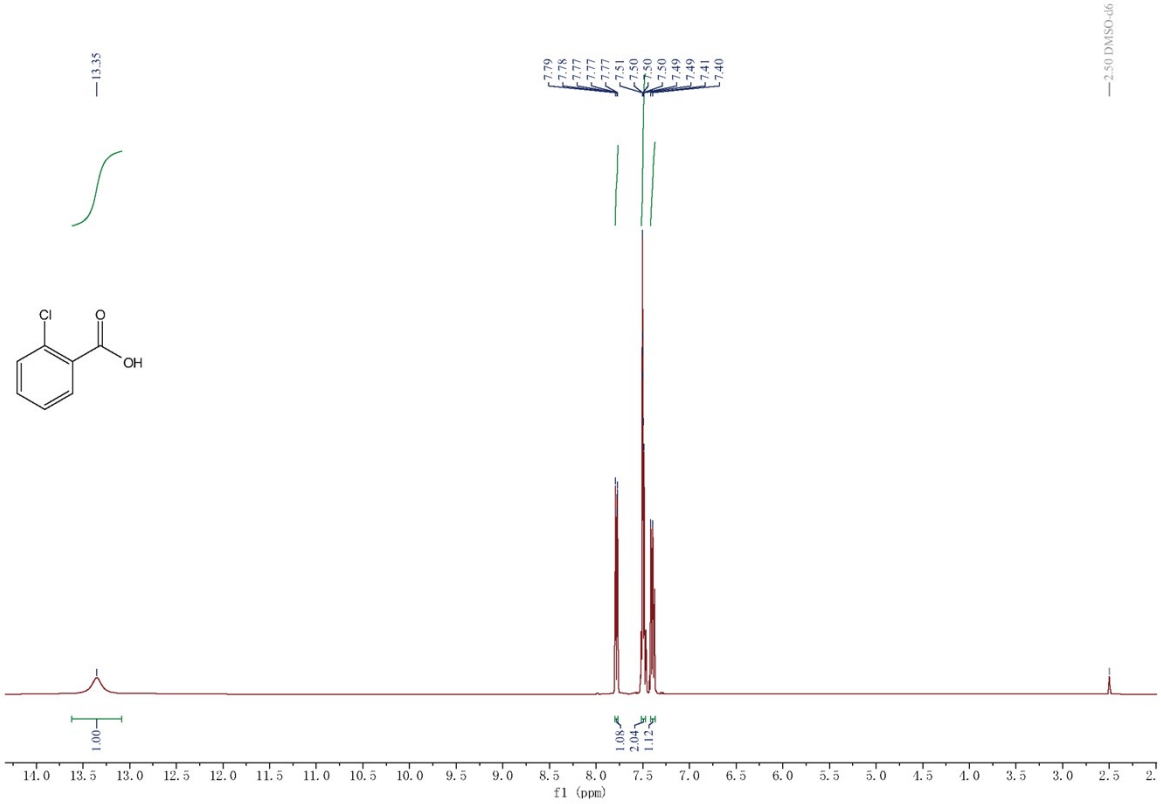


Fig.27 **3n** ^{1}H NMR

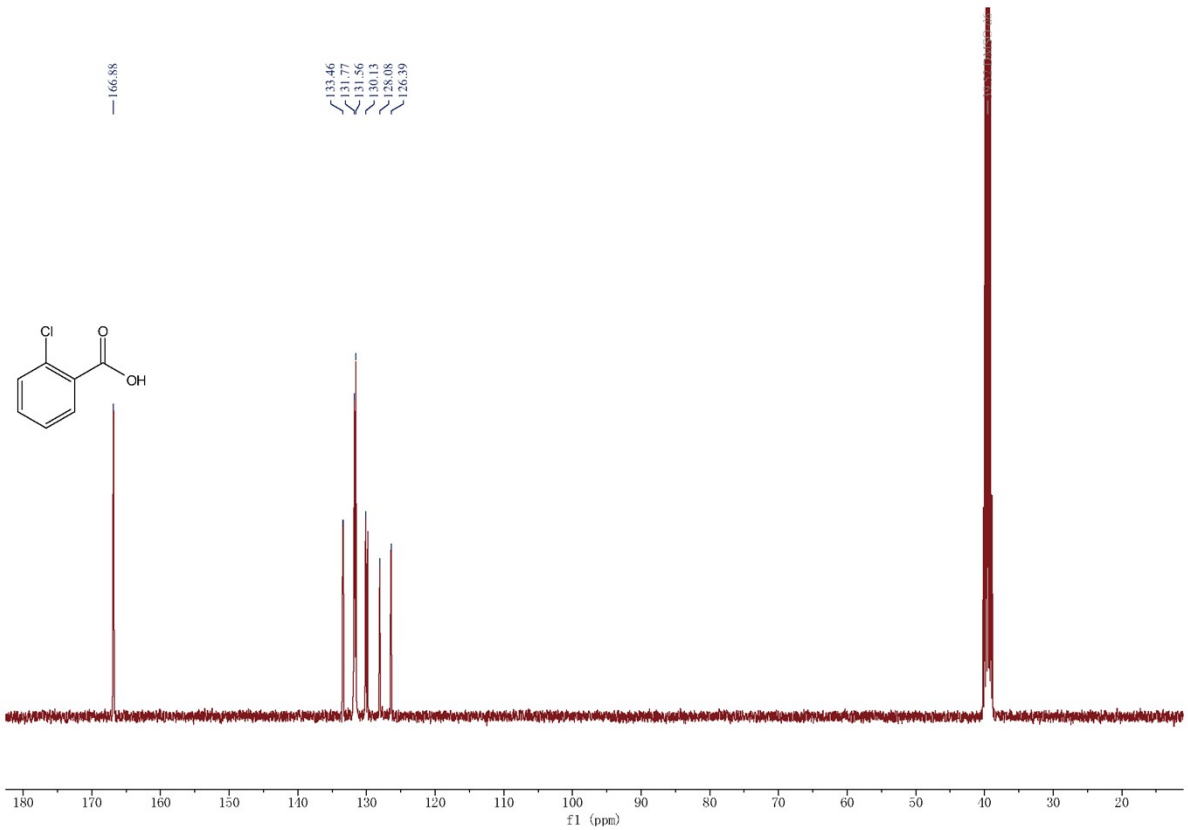


Fig.28 **3n** ^{13}C NMR

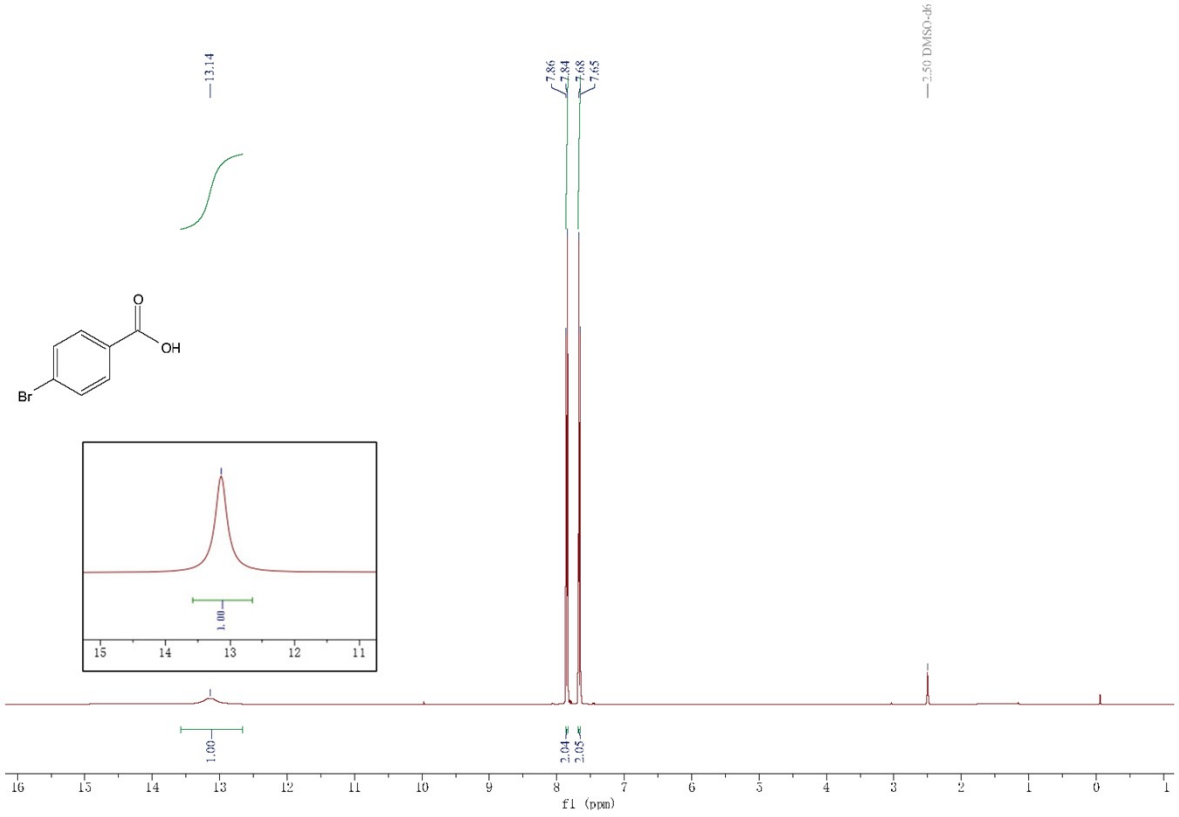


Fig.29 **3o** ^{1}H NMR

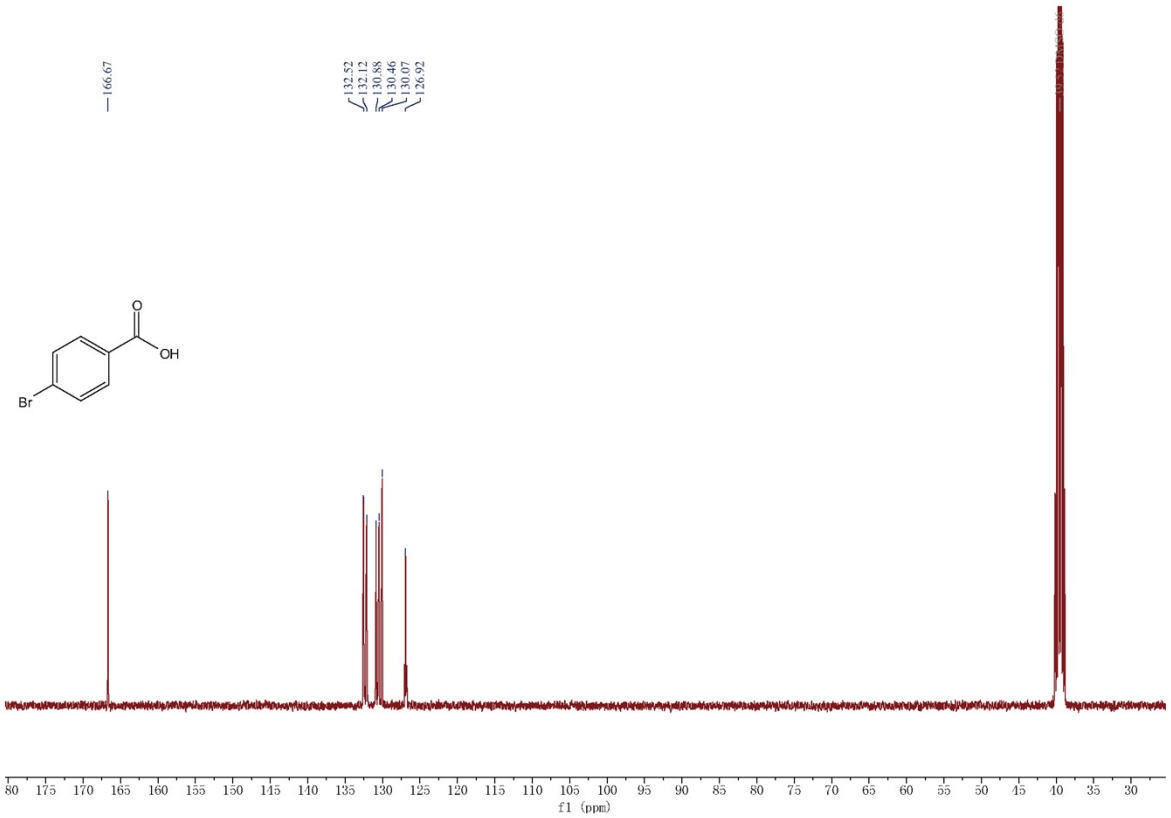


Fig.30 **3o** ^{13}C NMR

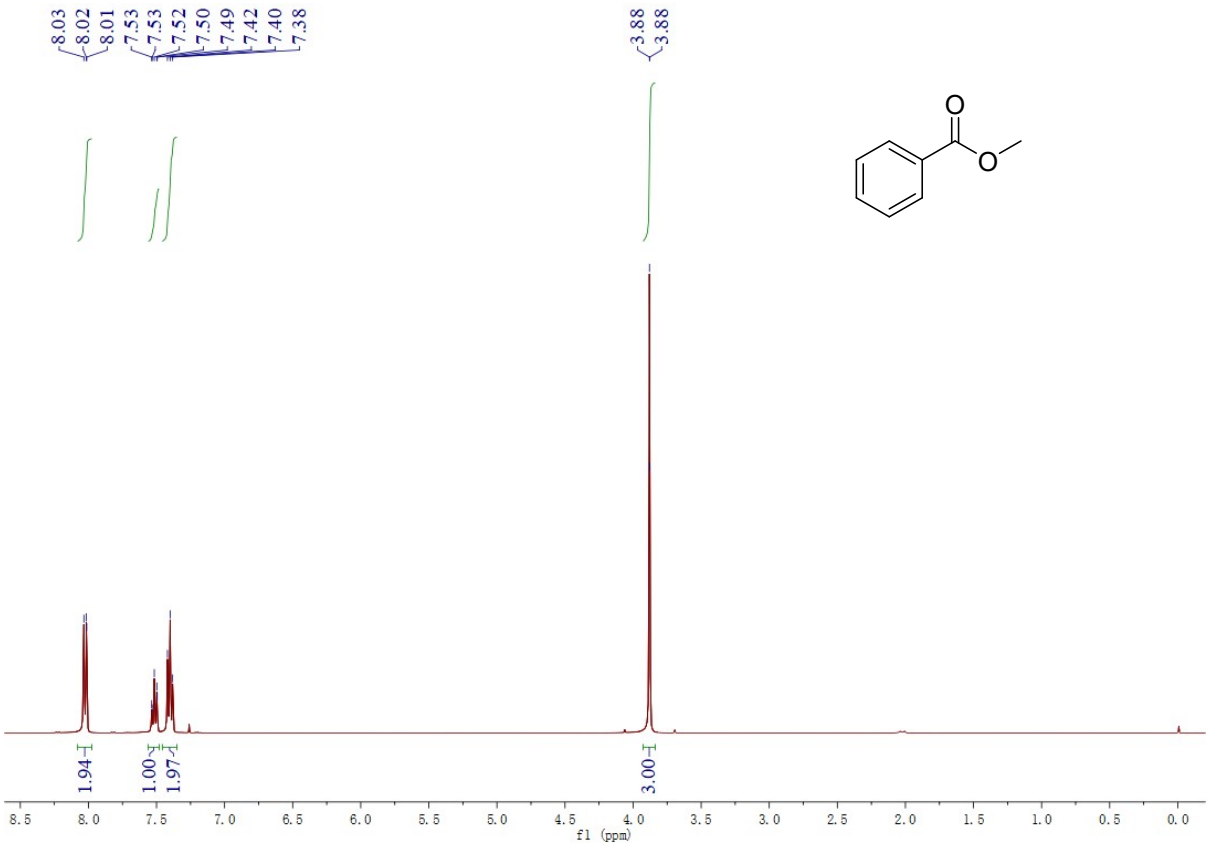


Fig.31 **4a** ^{1}H NMR

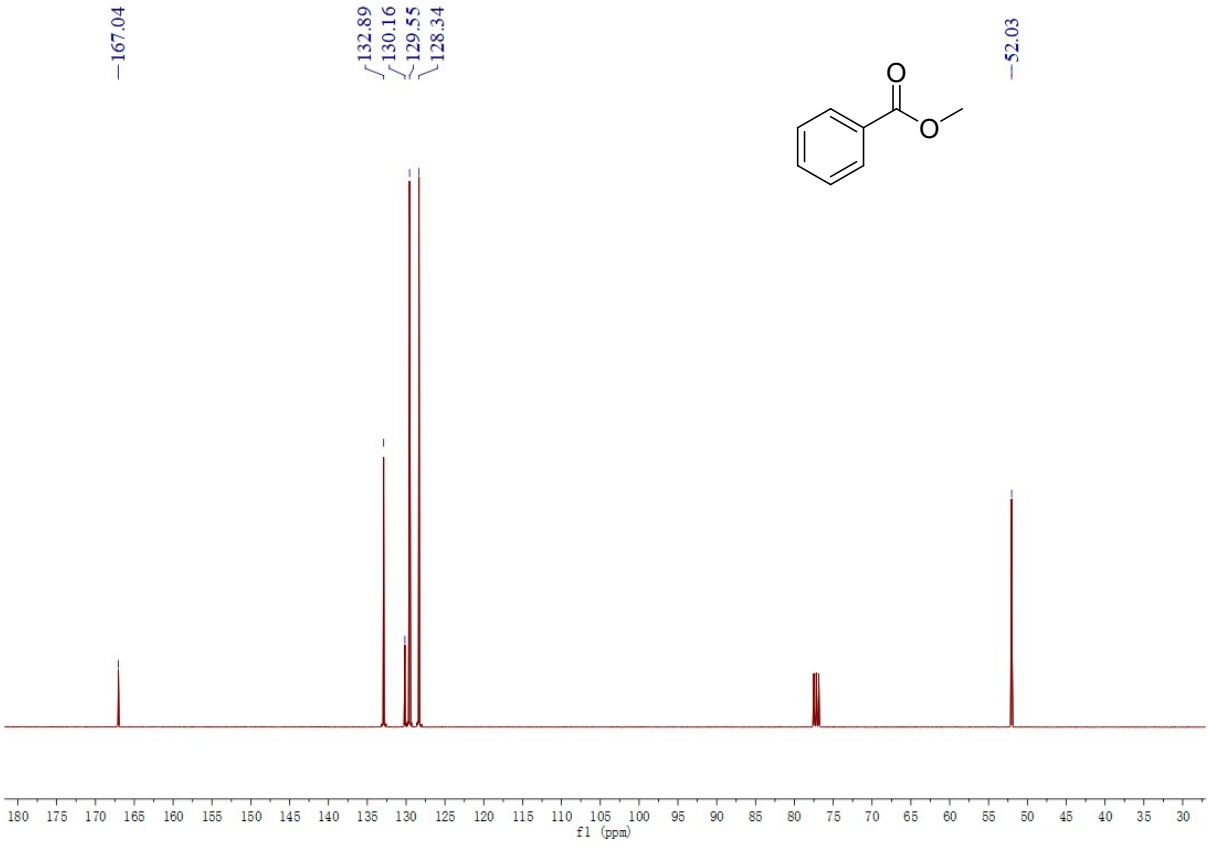


Fig.32 **4a** ^{13}C NMR

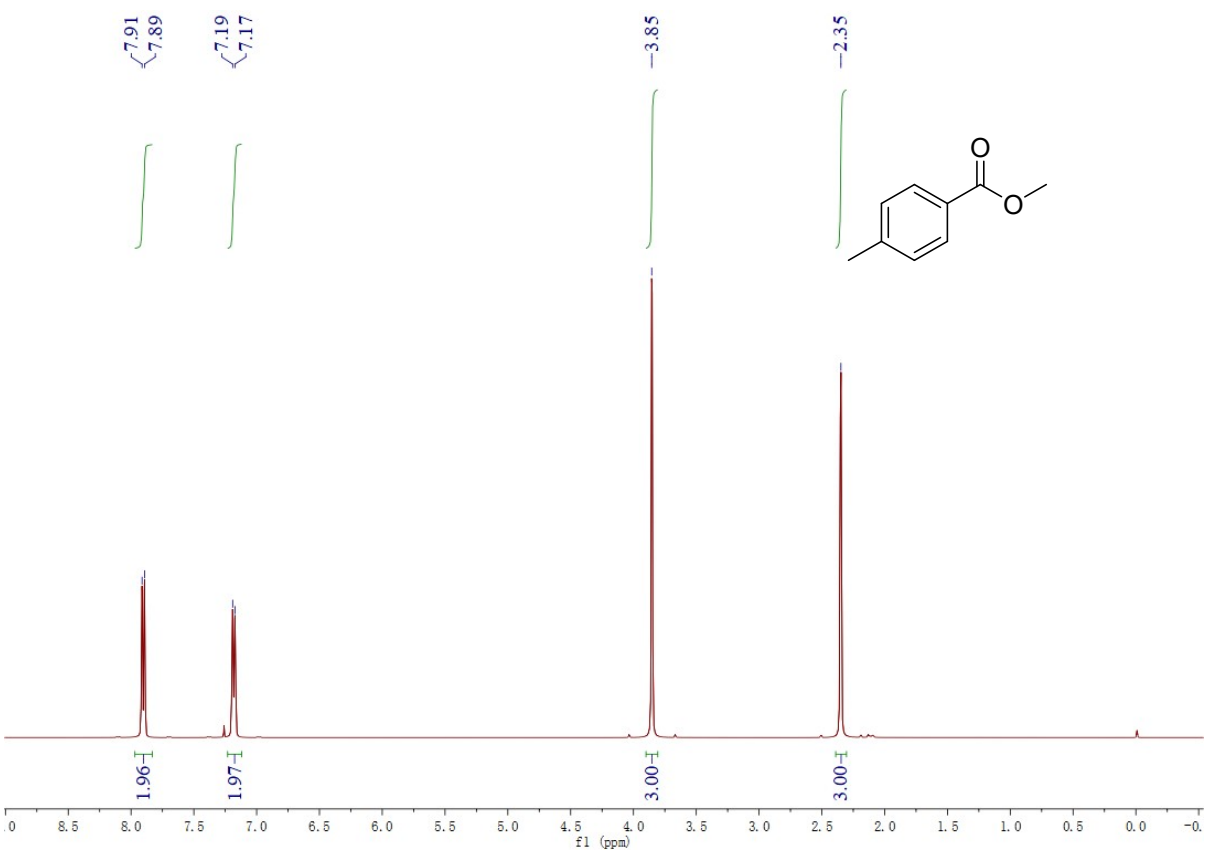


Fig.33 **4b** ^{1}H NMR

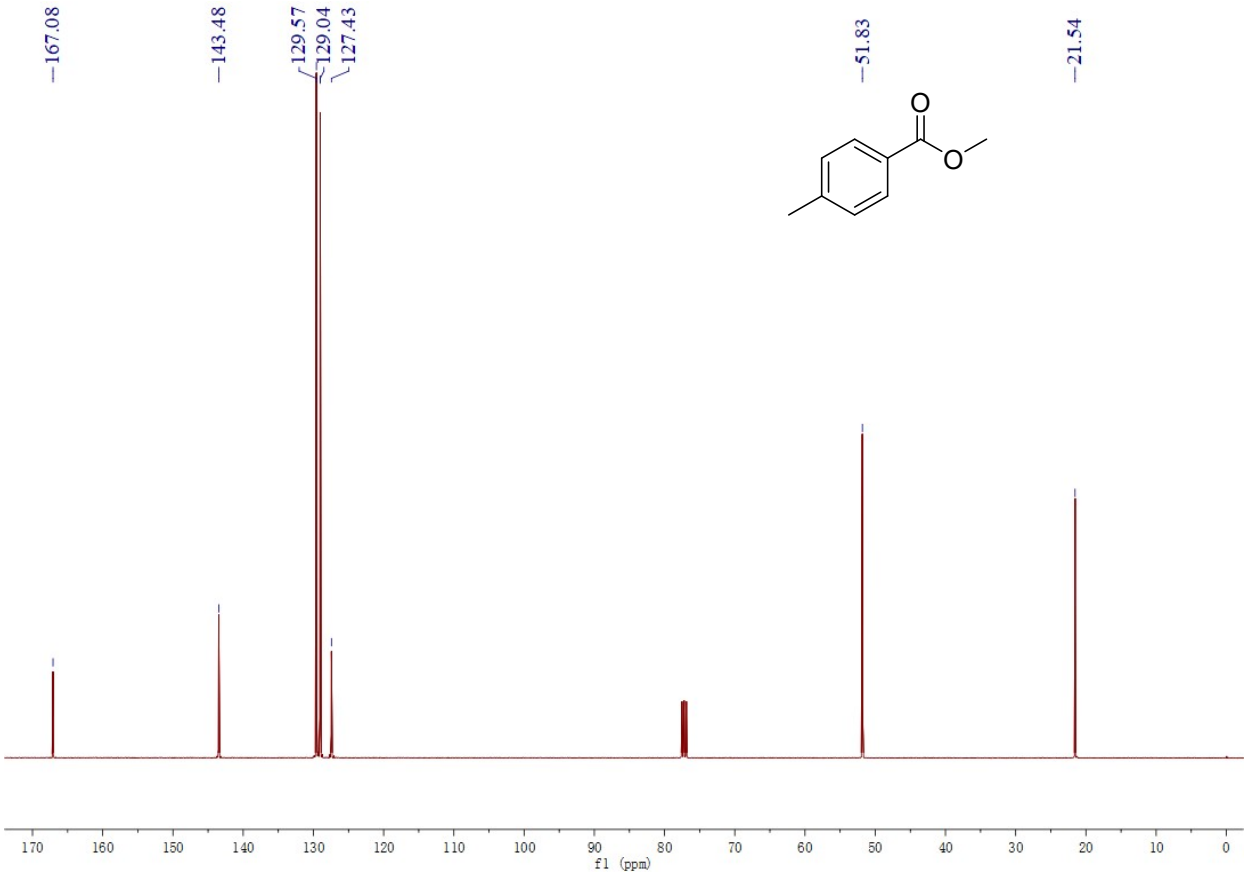


Fig.34 **4b** ^{13}C NMR

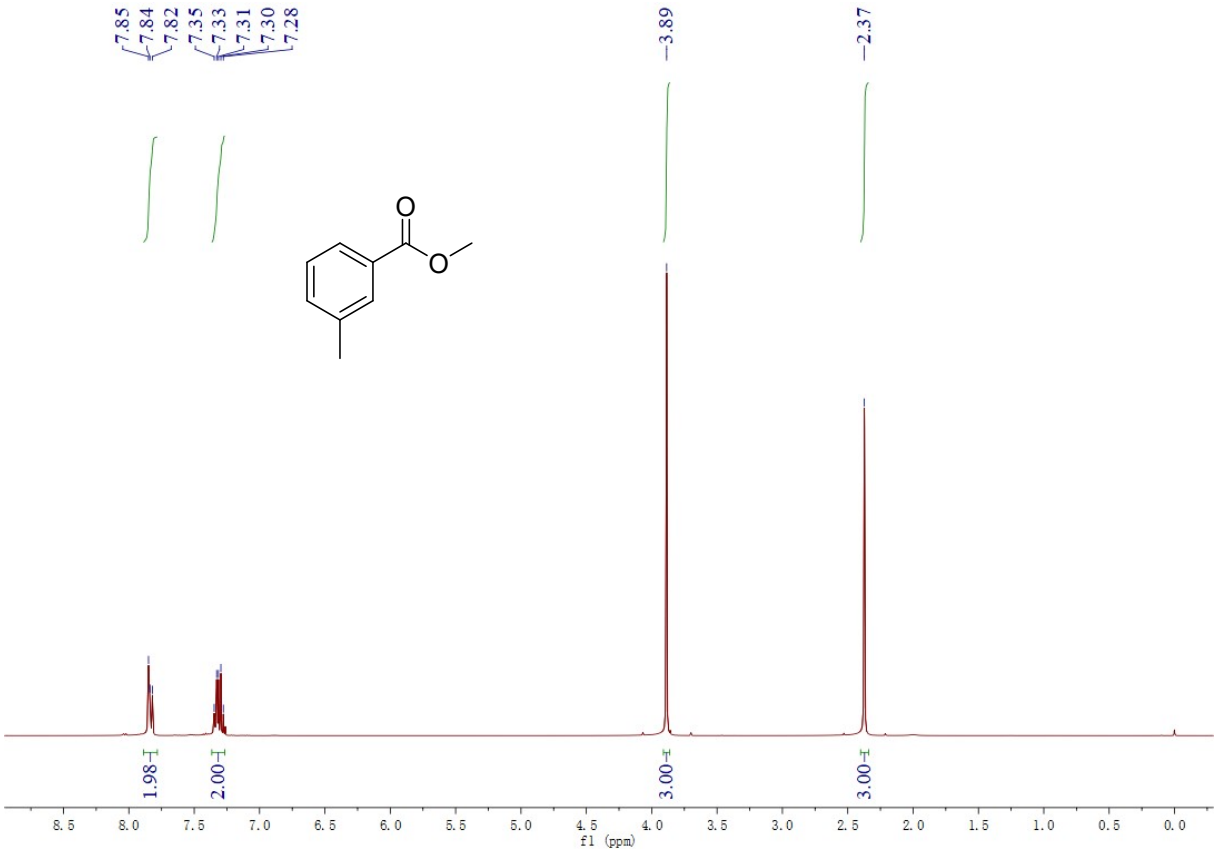


Fig.35 **4c** ^{1}H NMR

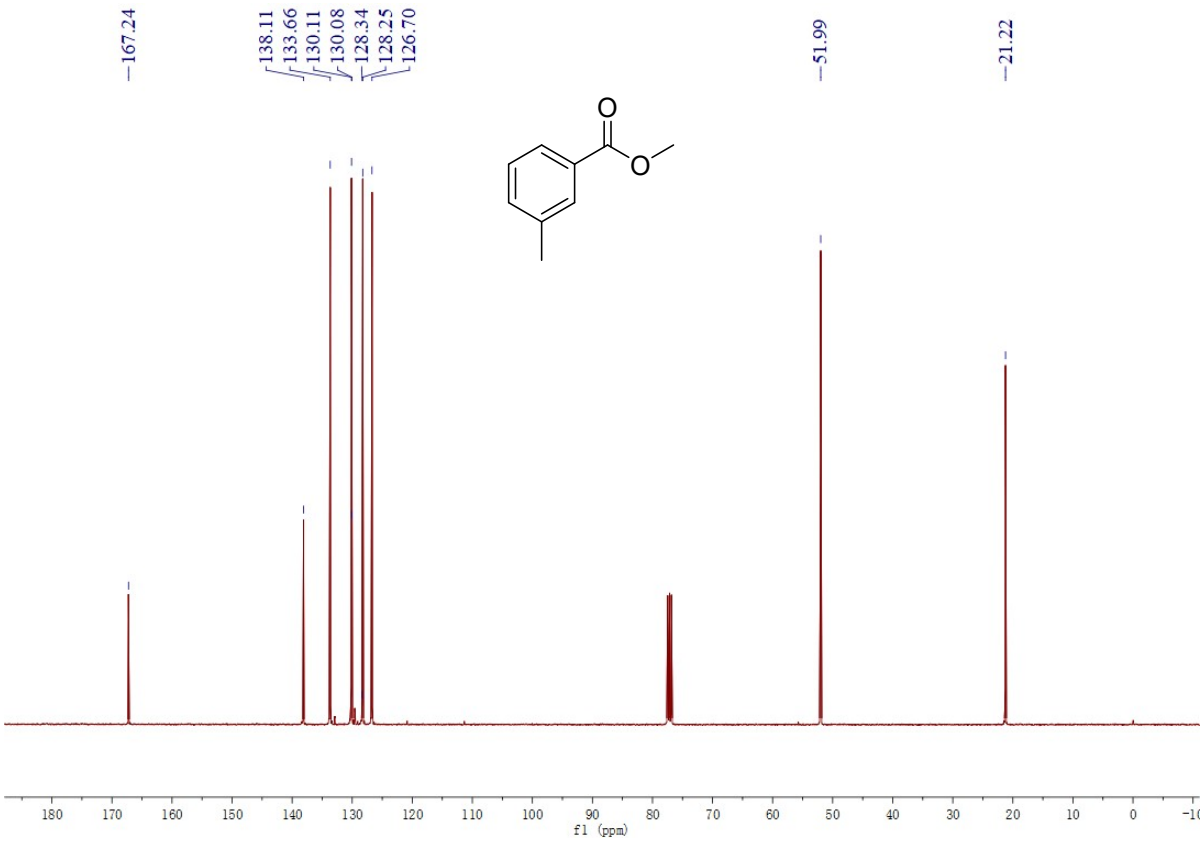


Fig.36 **4c** ^{13}C NMR

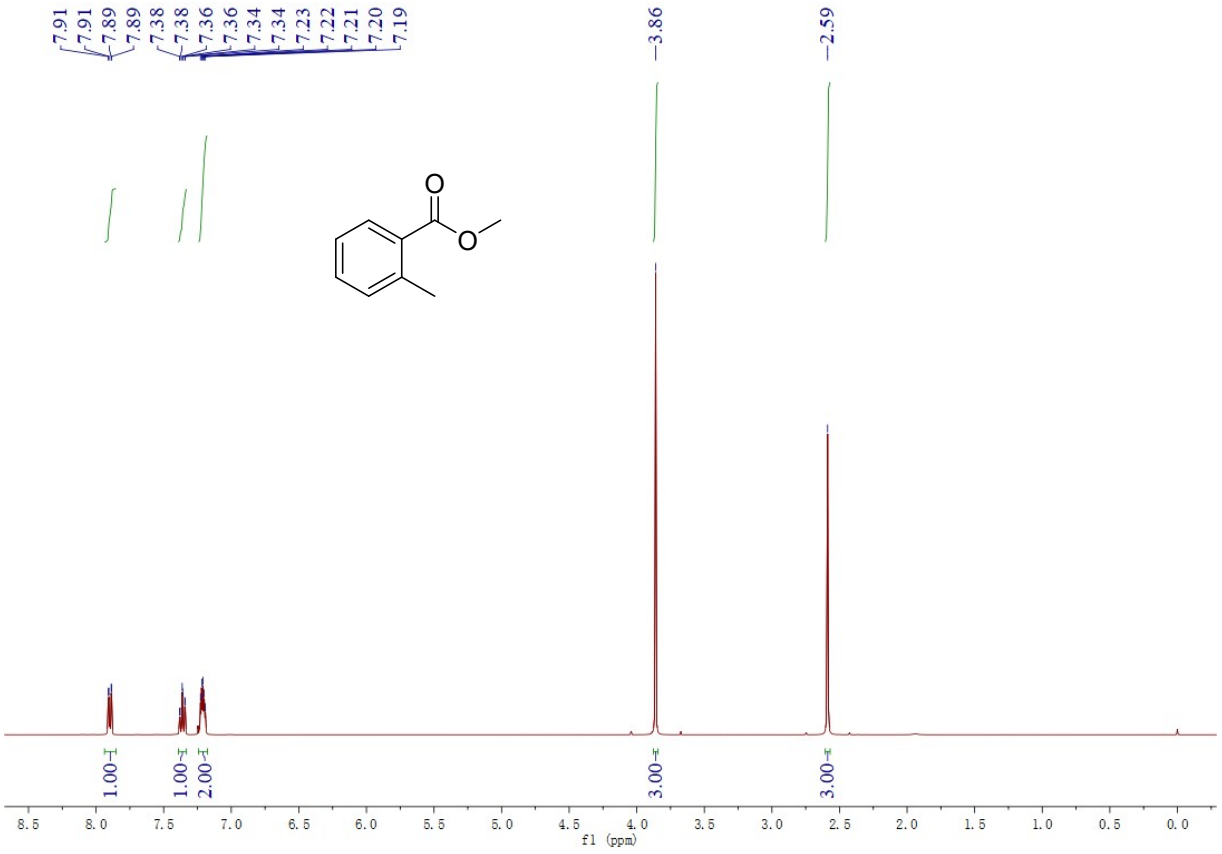


Fig.37 **4d** ^{1}H NMR

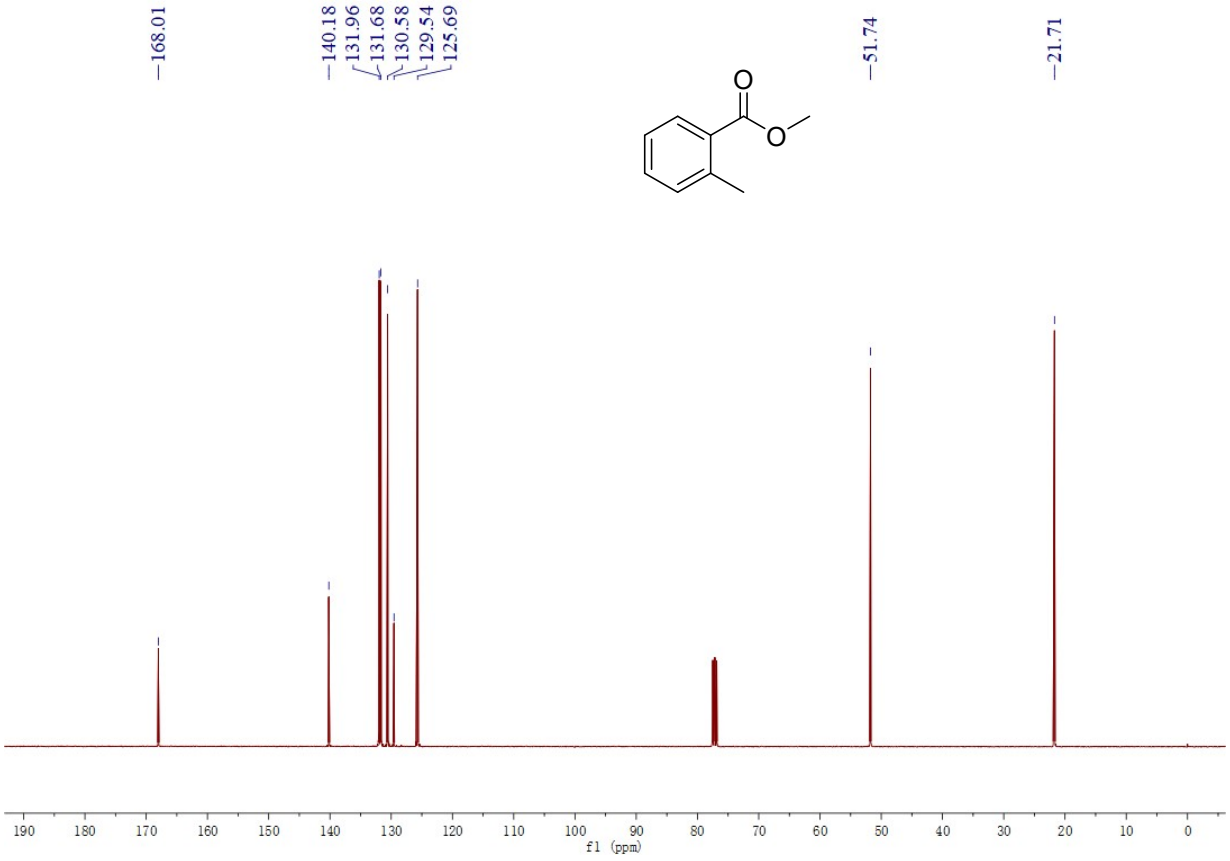


Fig.38 **4d** ^{13}C NMR

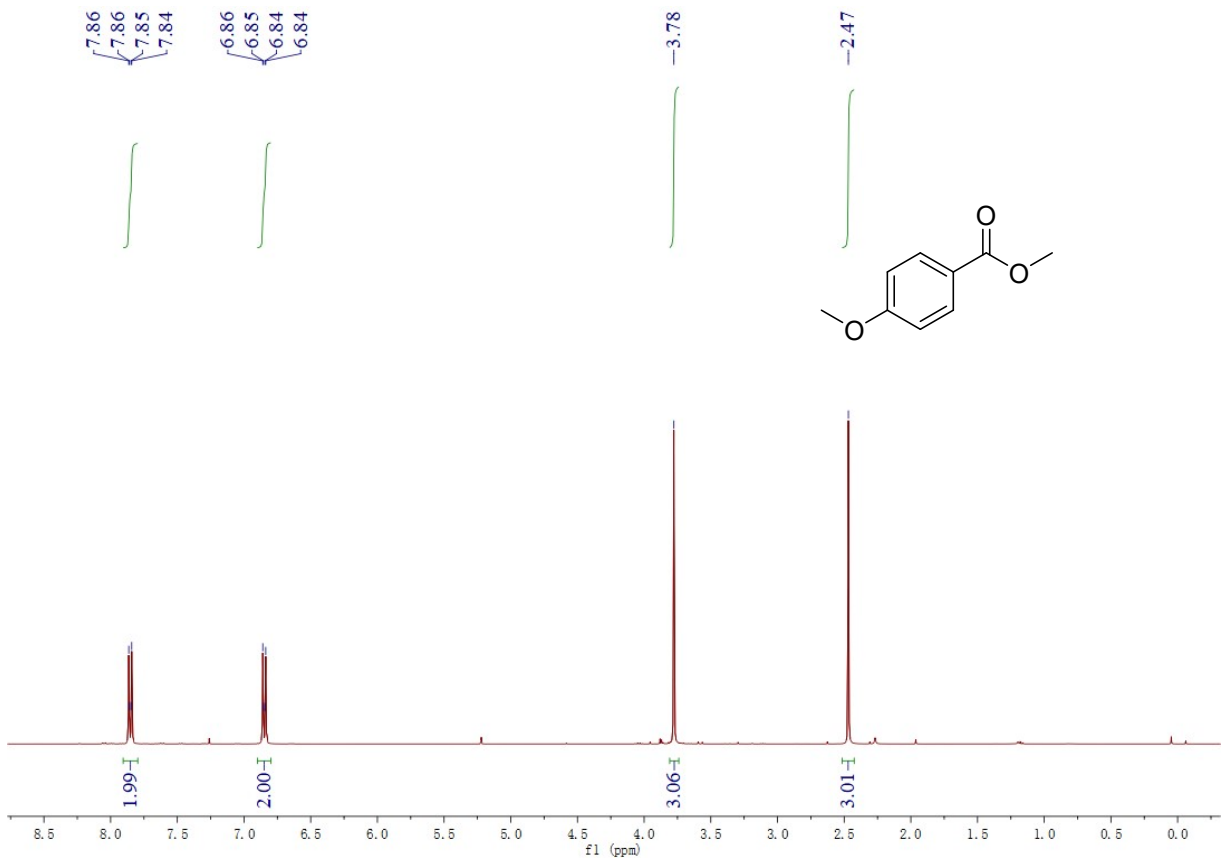


Fig.39 **4e** ^{1}H NMR

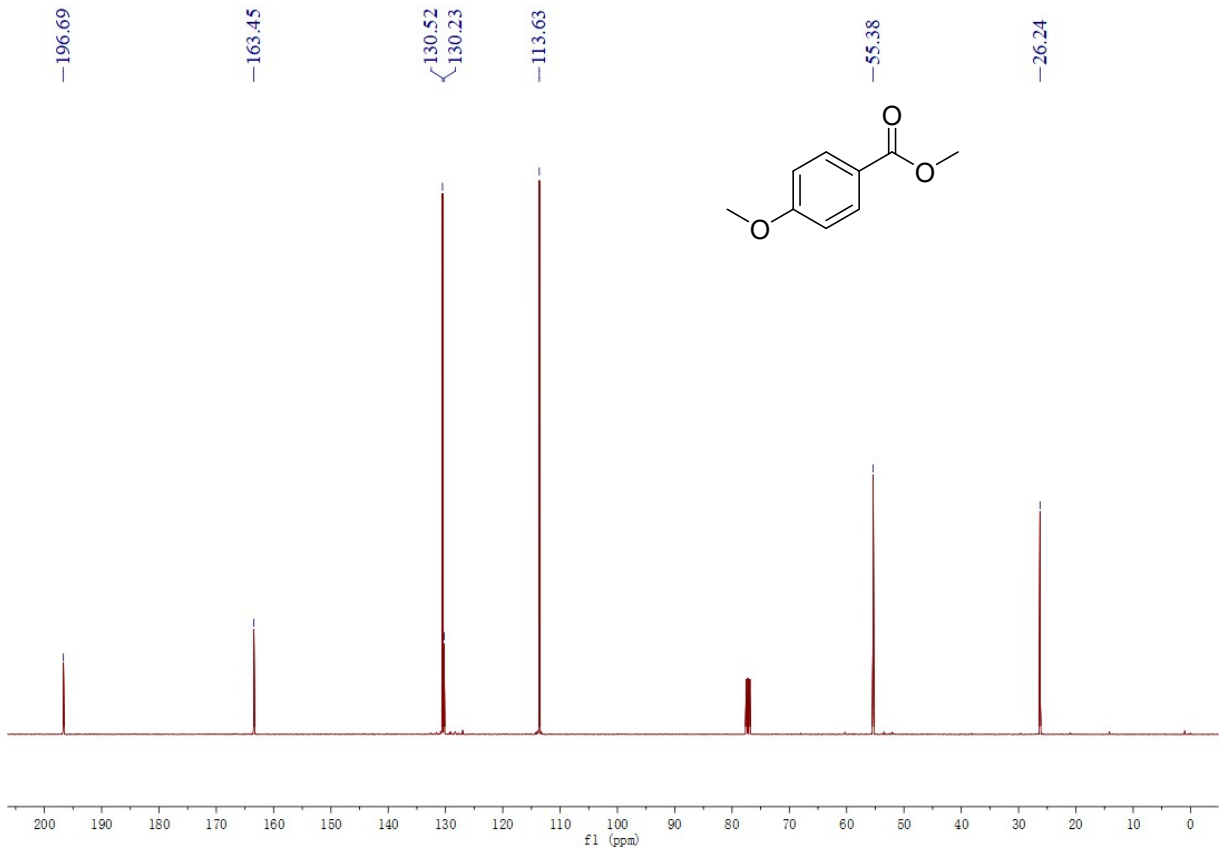


Fig.40 **4e** ^{13}C NMR

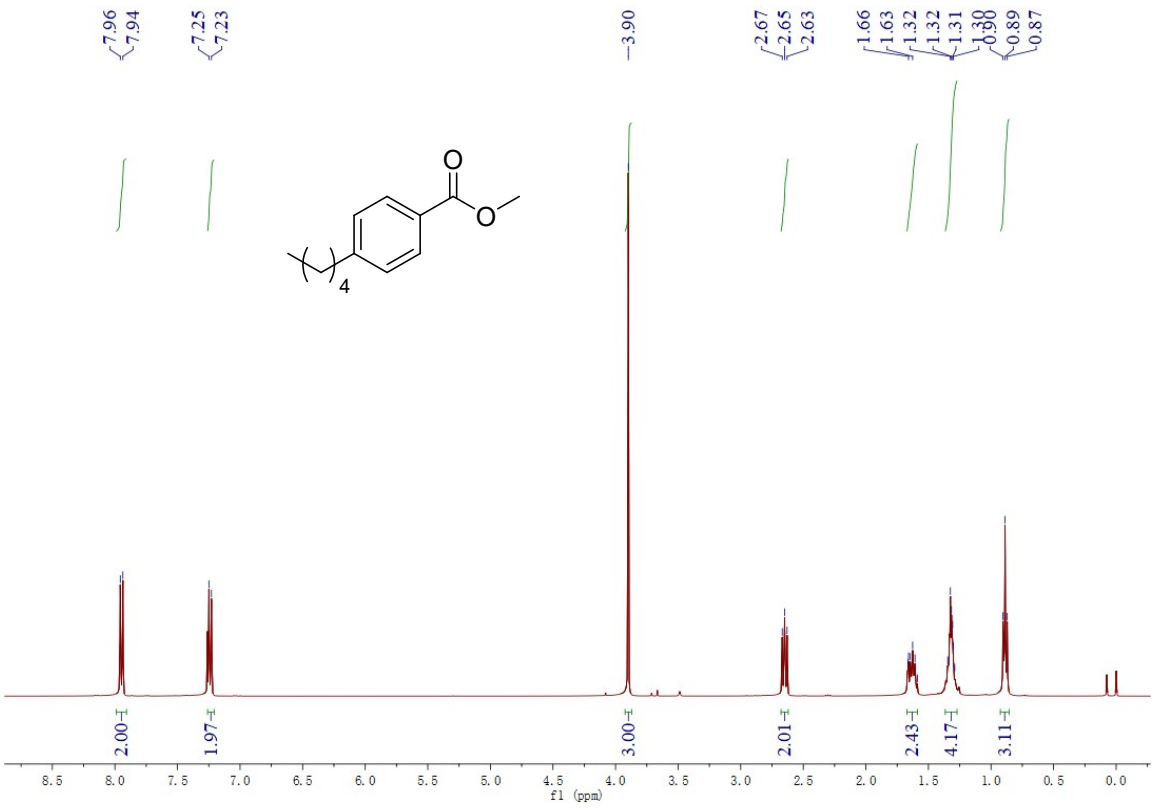


Fig.41 **4f** ^{1}H NMR

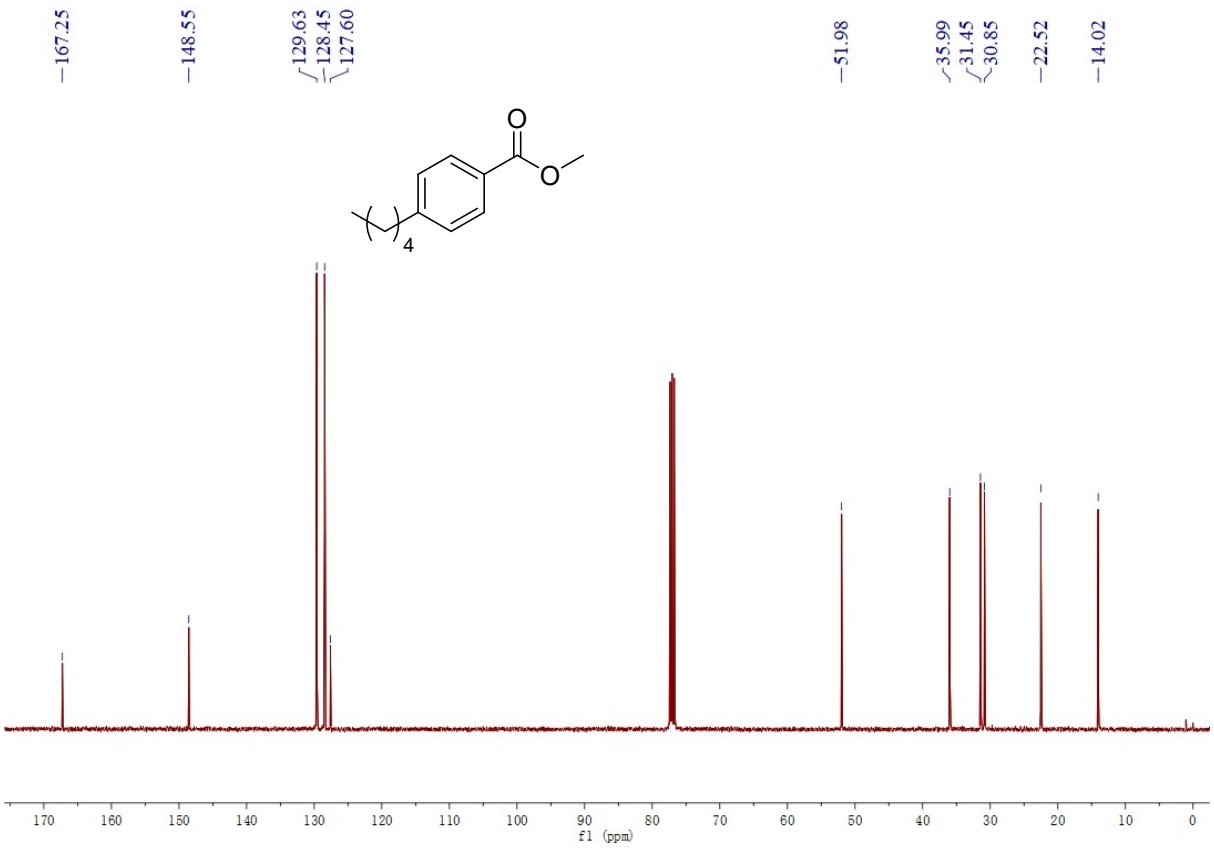


Fig.42 **4f** ^{13}C NMR

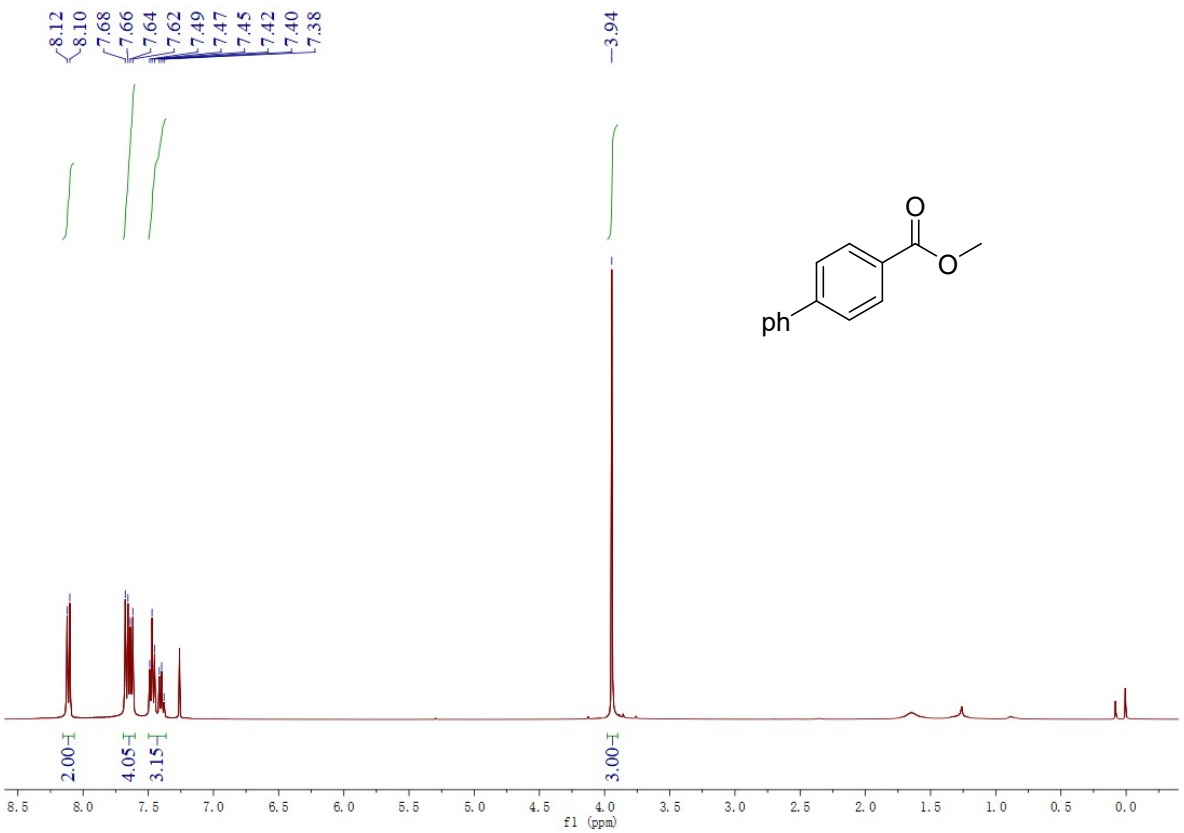


Fig.43 **4g** ^{1}H NMR

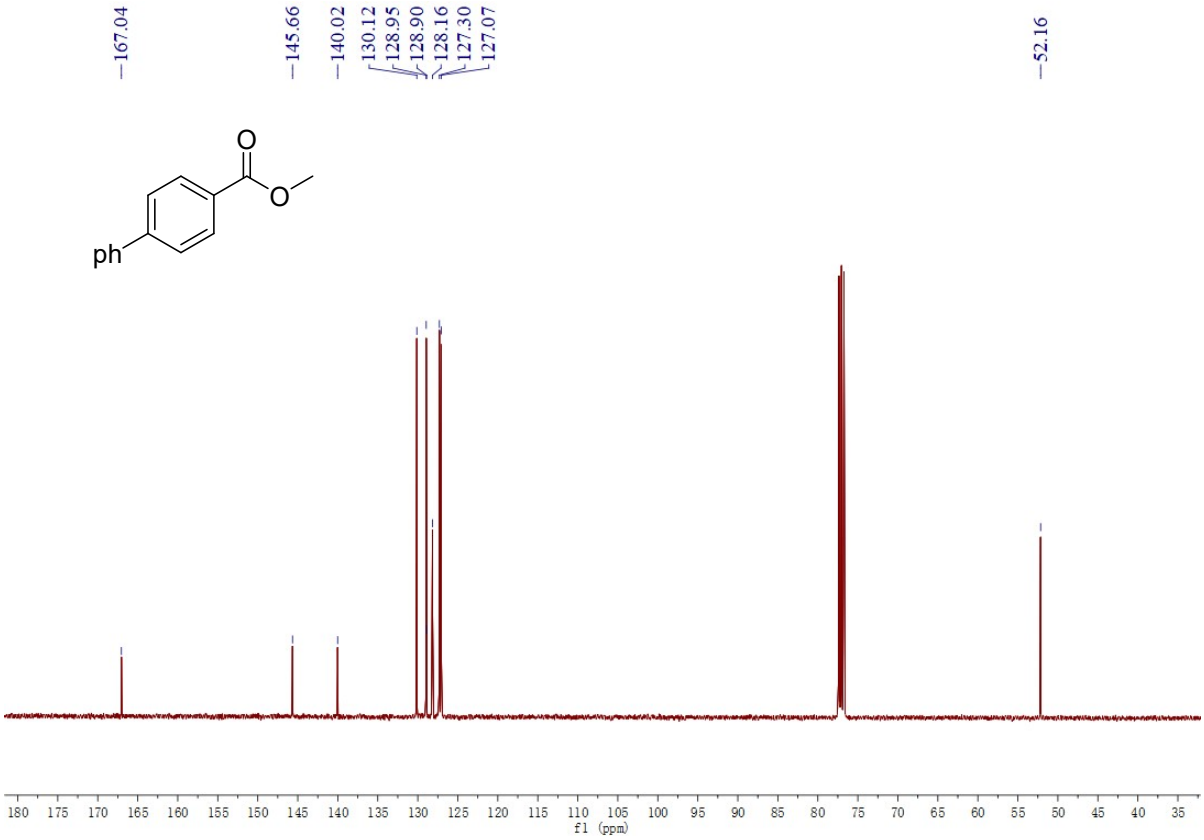


Fig.44 4**g** ^{13}C NMR

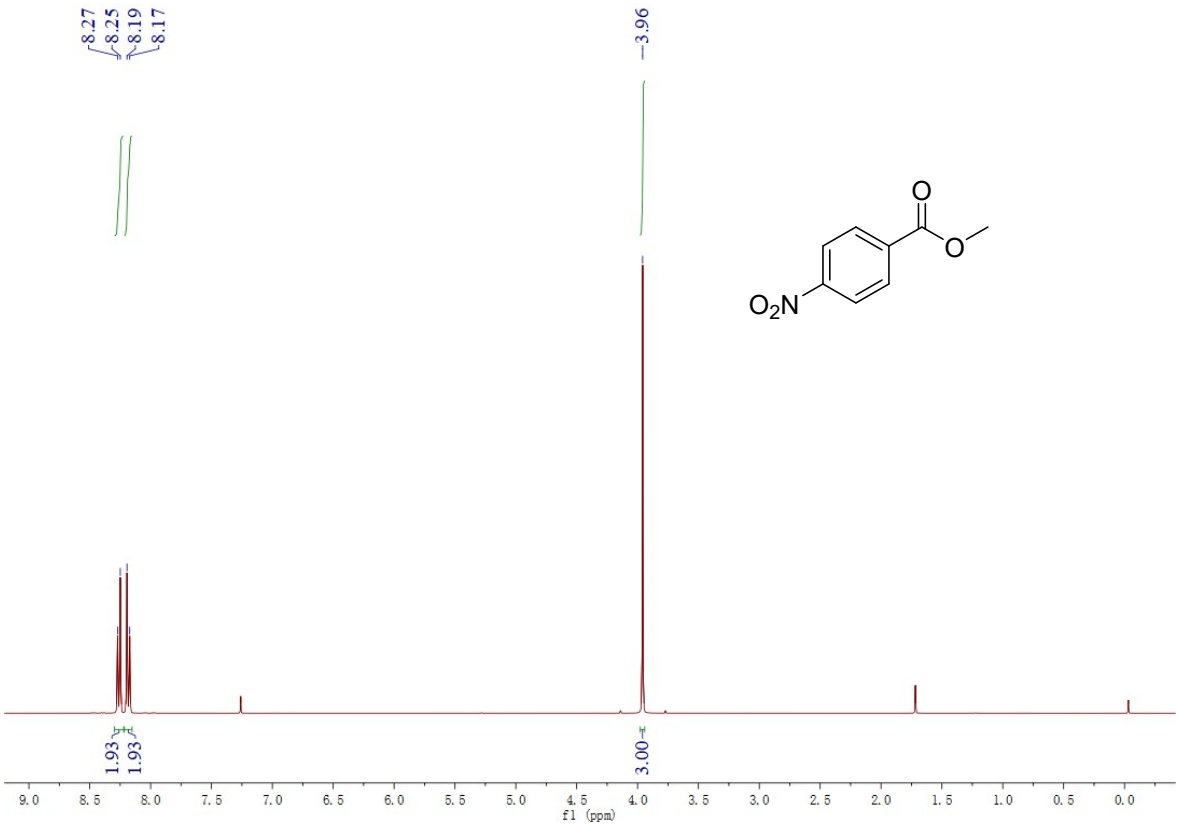


Fig.45 **4h** ^{1}H NMR

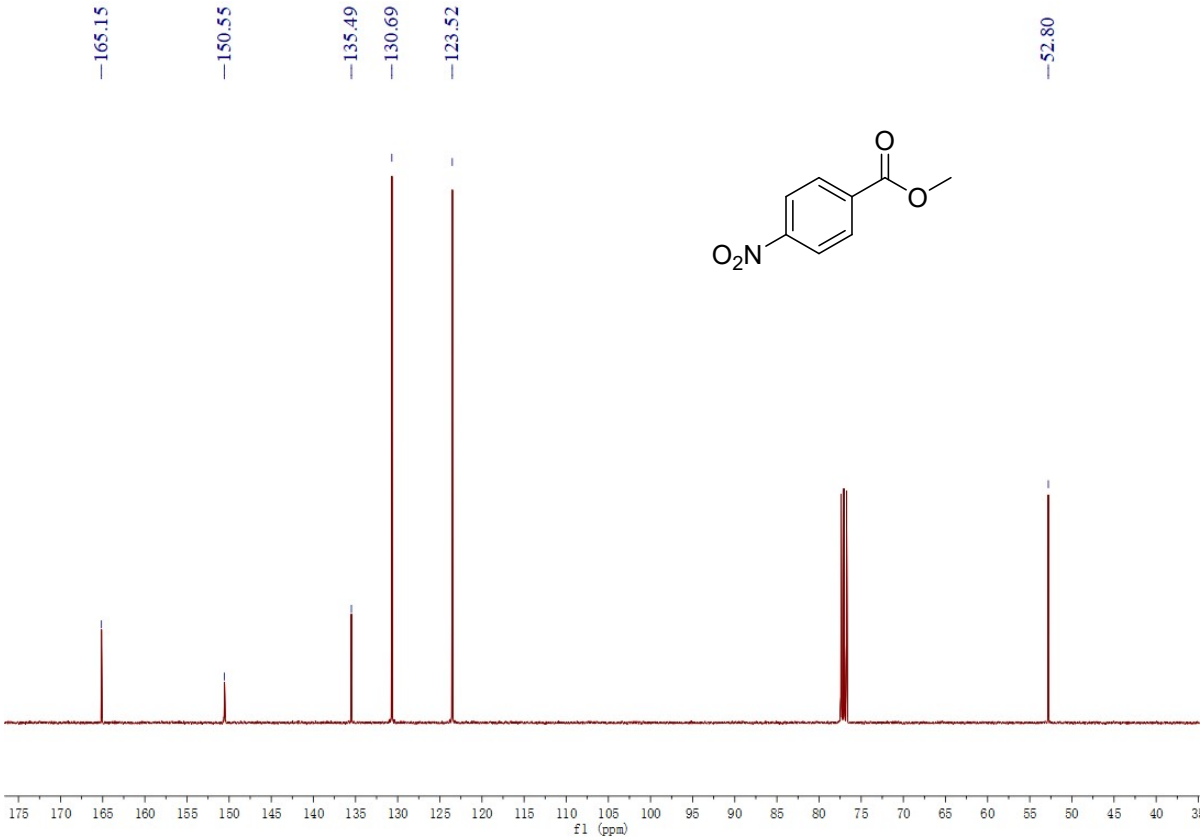


Fig.46 **4h** ^{13}C NMR

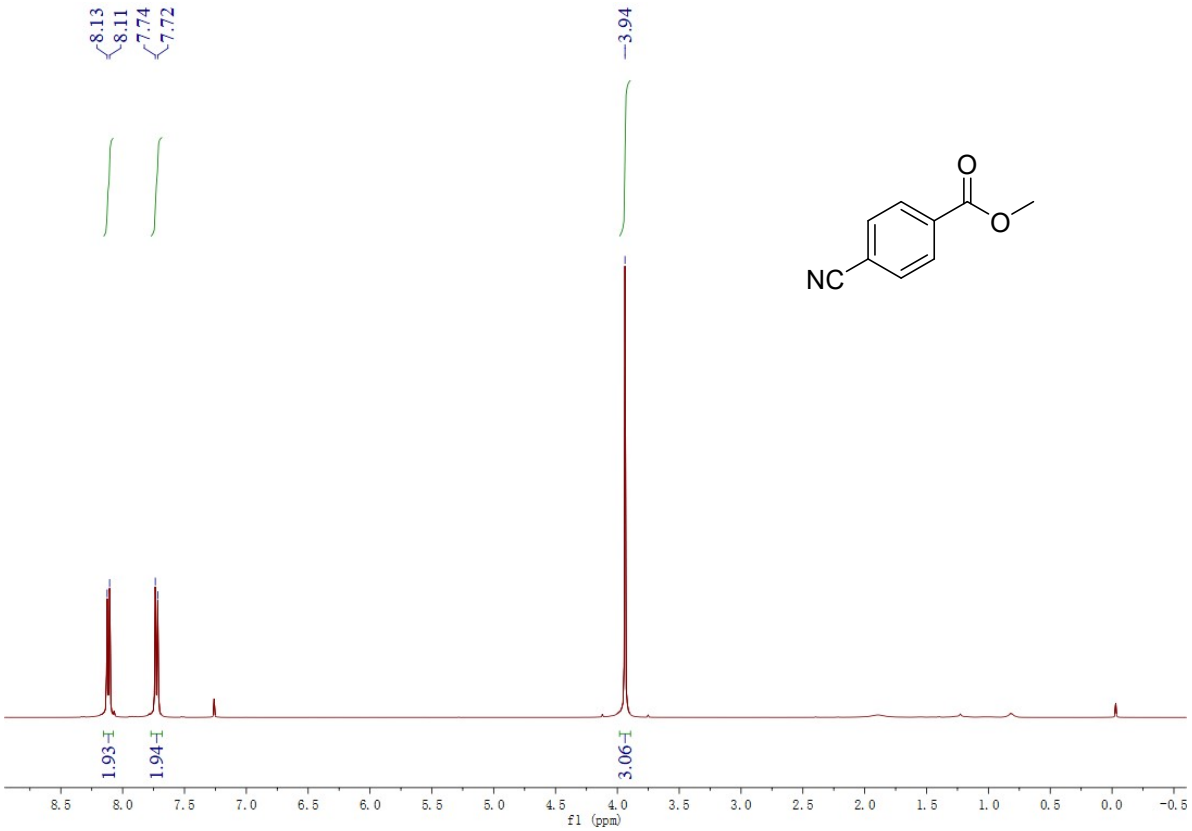


Fig.47 **4i** ^{1}H NMR

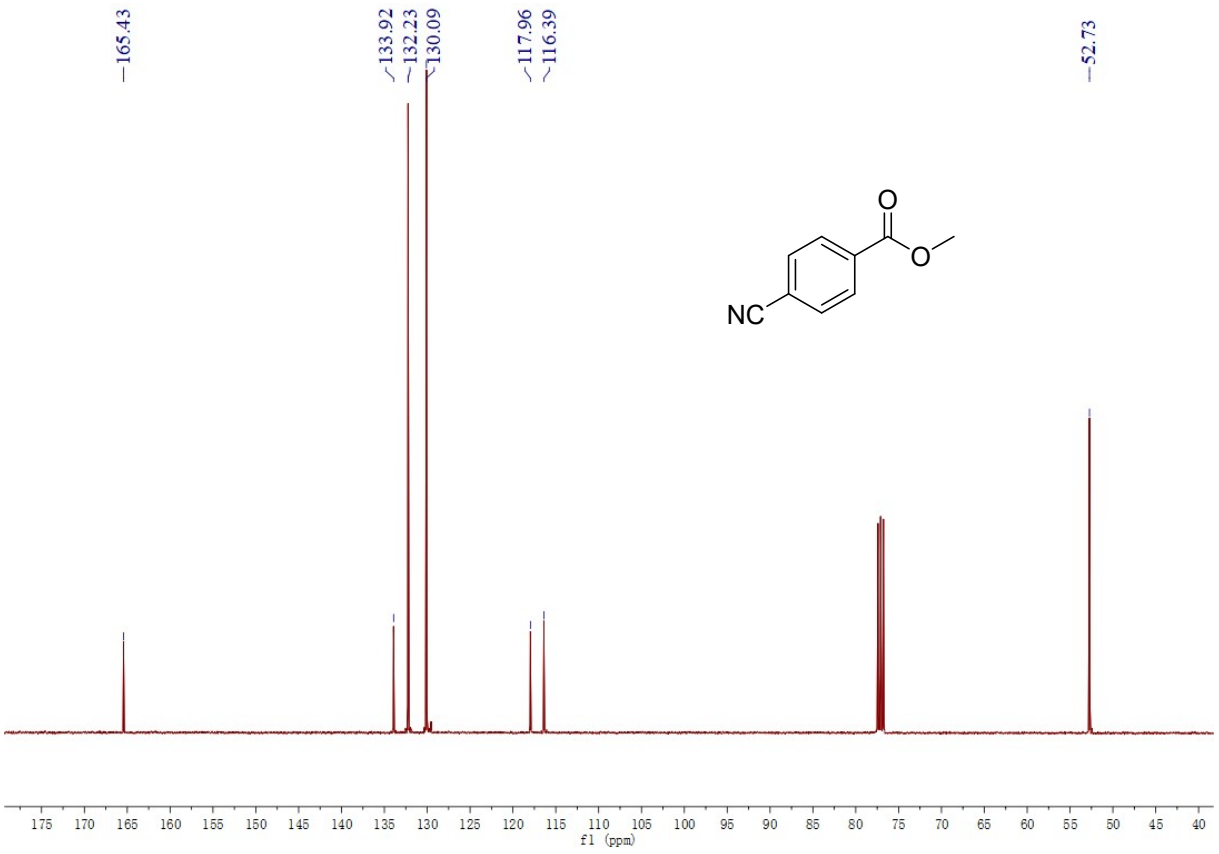


Fig.48 **4i** ^{13}C NMR

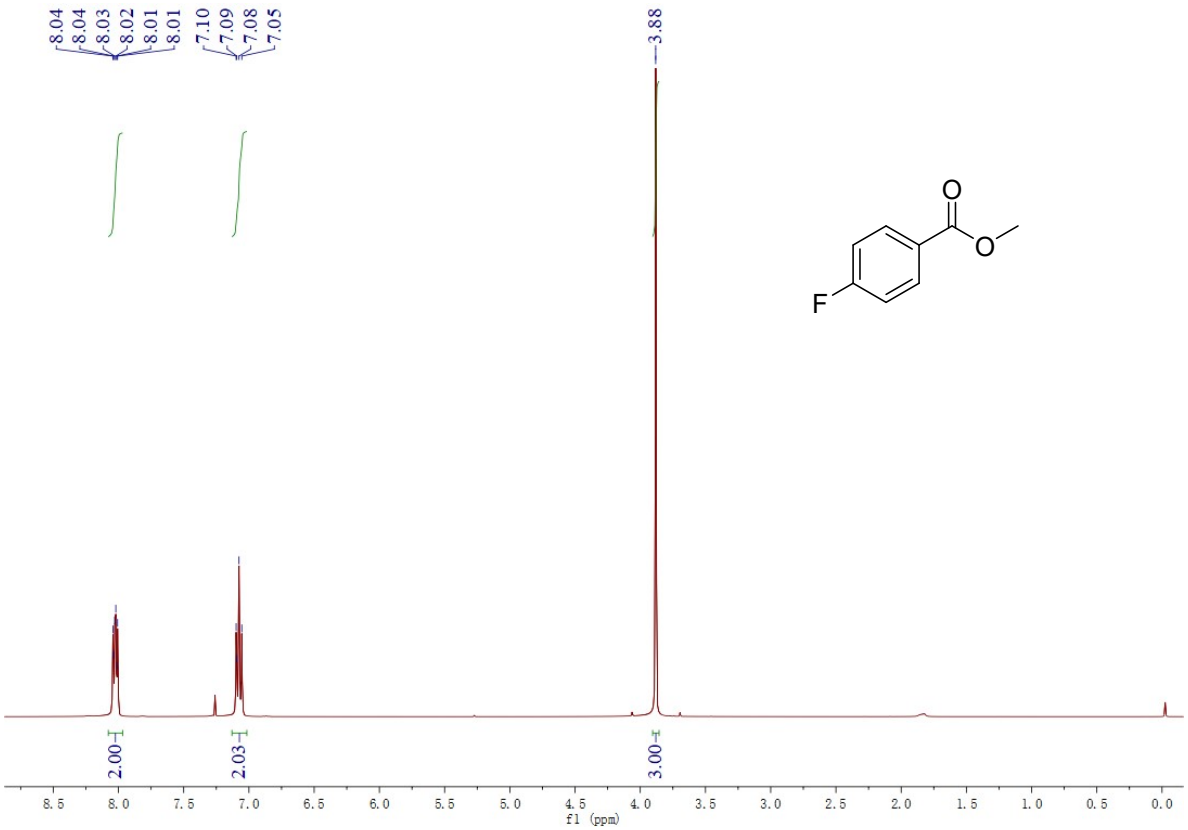


Fig.49 **4k** ^{1}H NMR

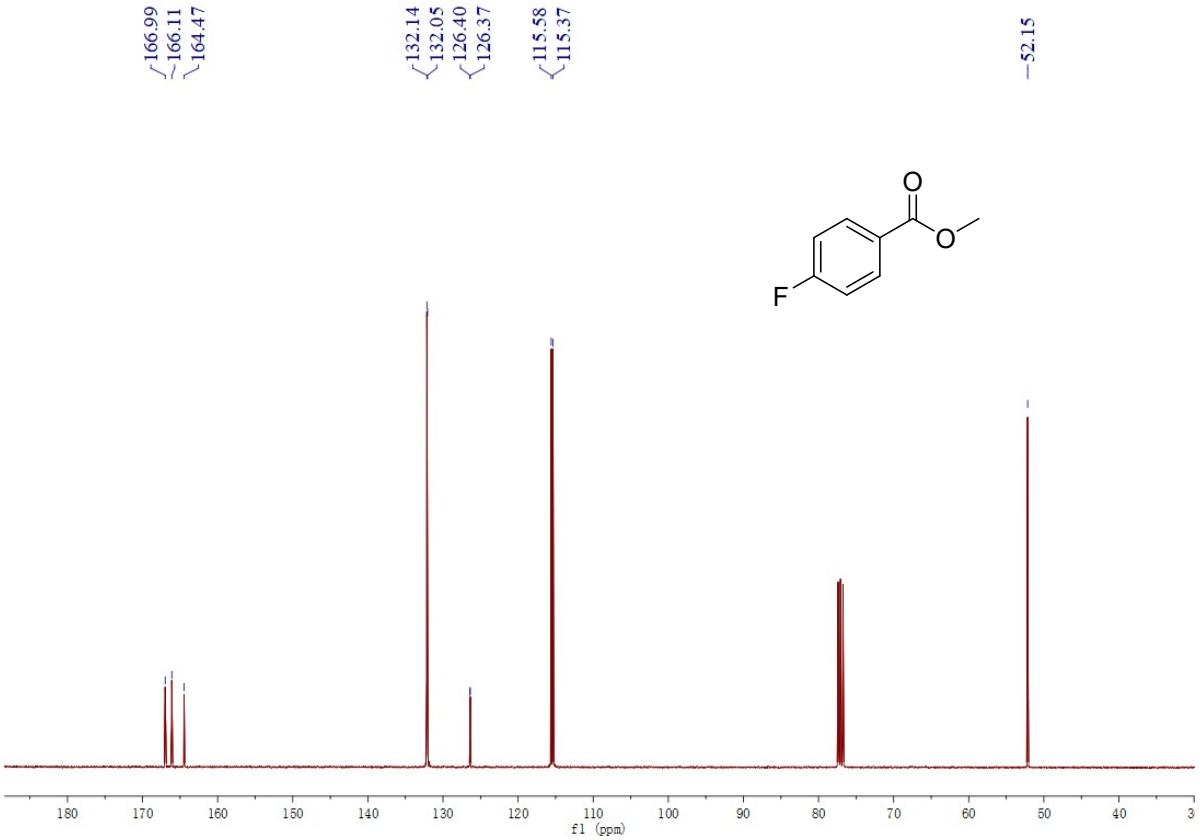


Fig.50 **4k** ^{13}C NMR

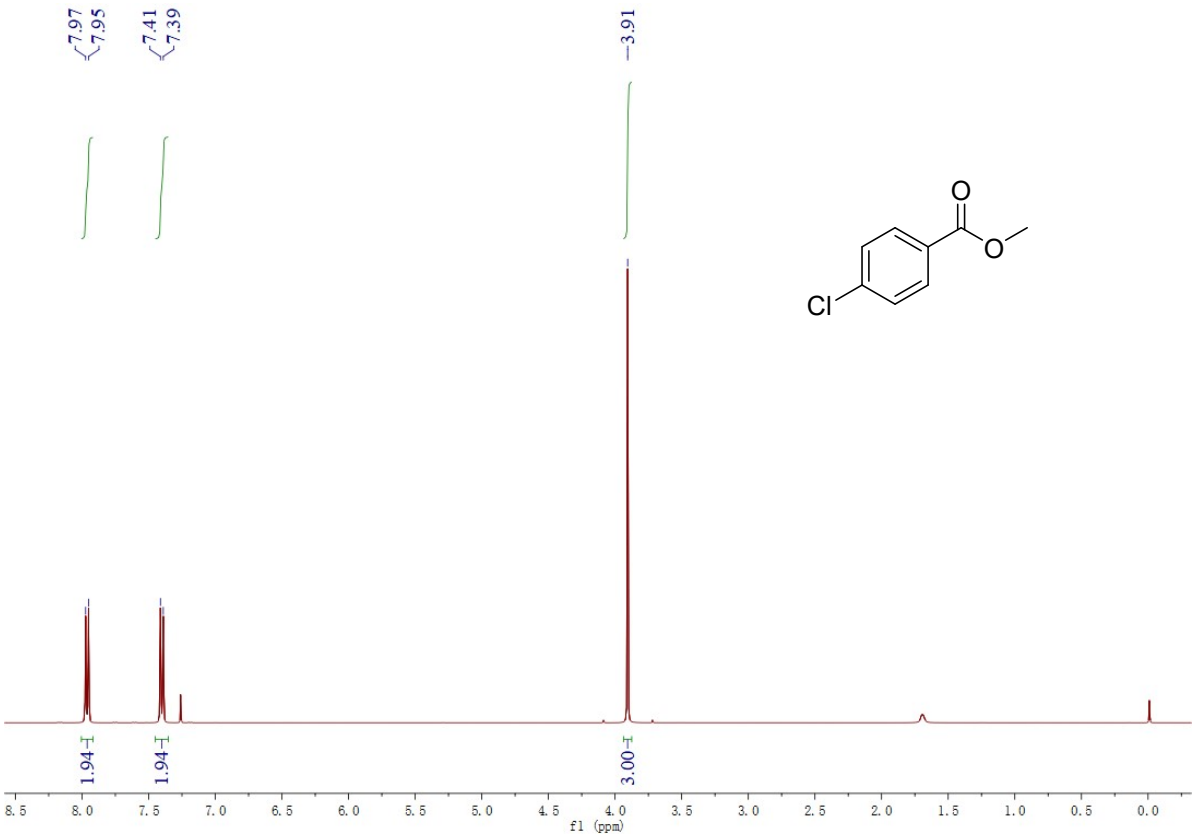


Fig.51 **4l** ^{1}H NMR

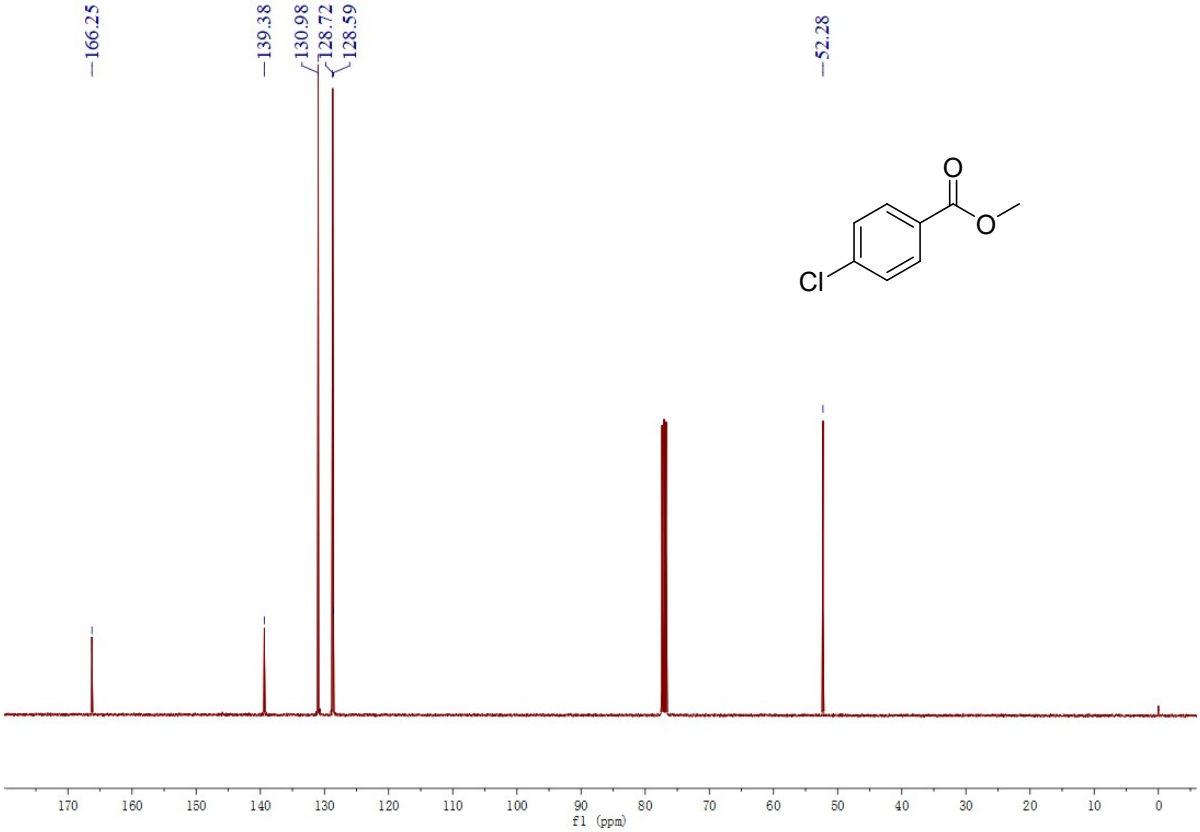


Fig.52 **4l** ^{13}C NMR

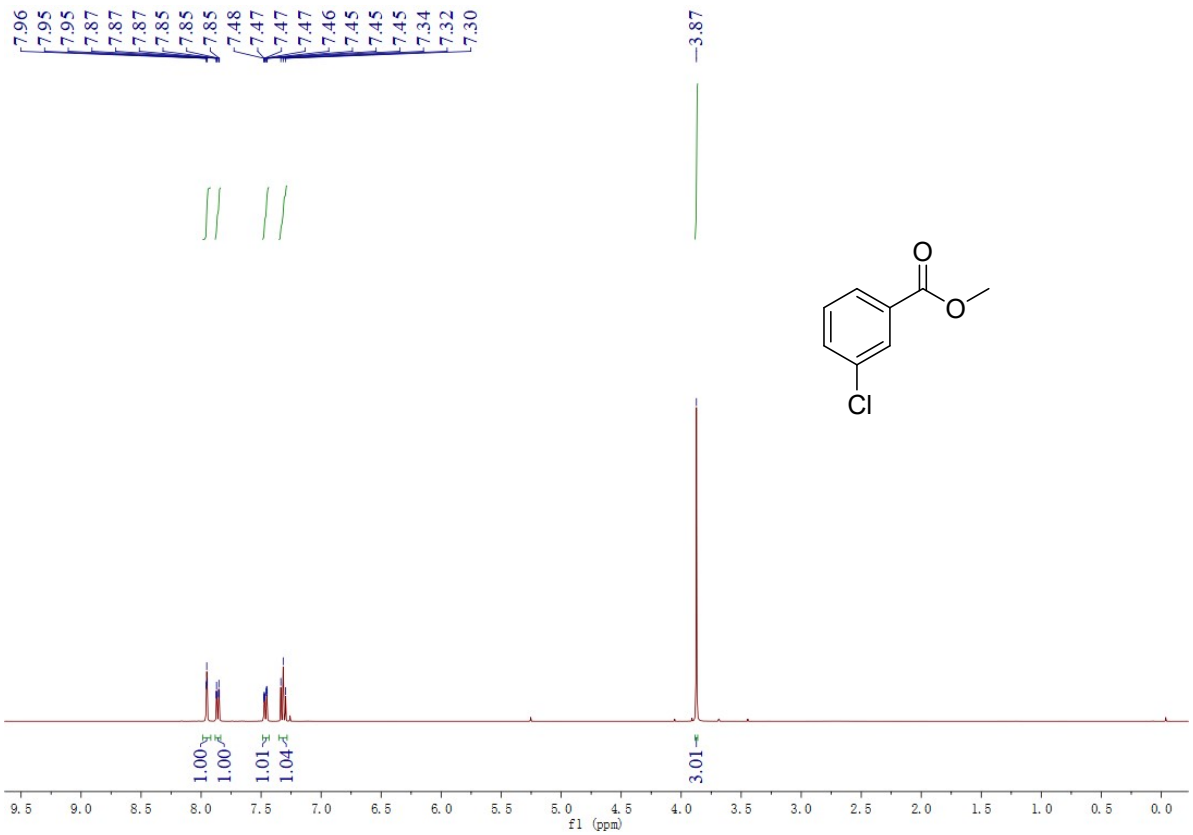


Fig.53 **4m** ^{1}H NMR

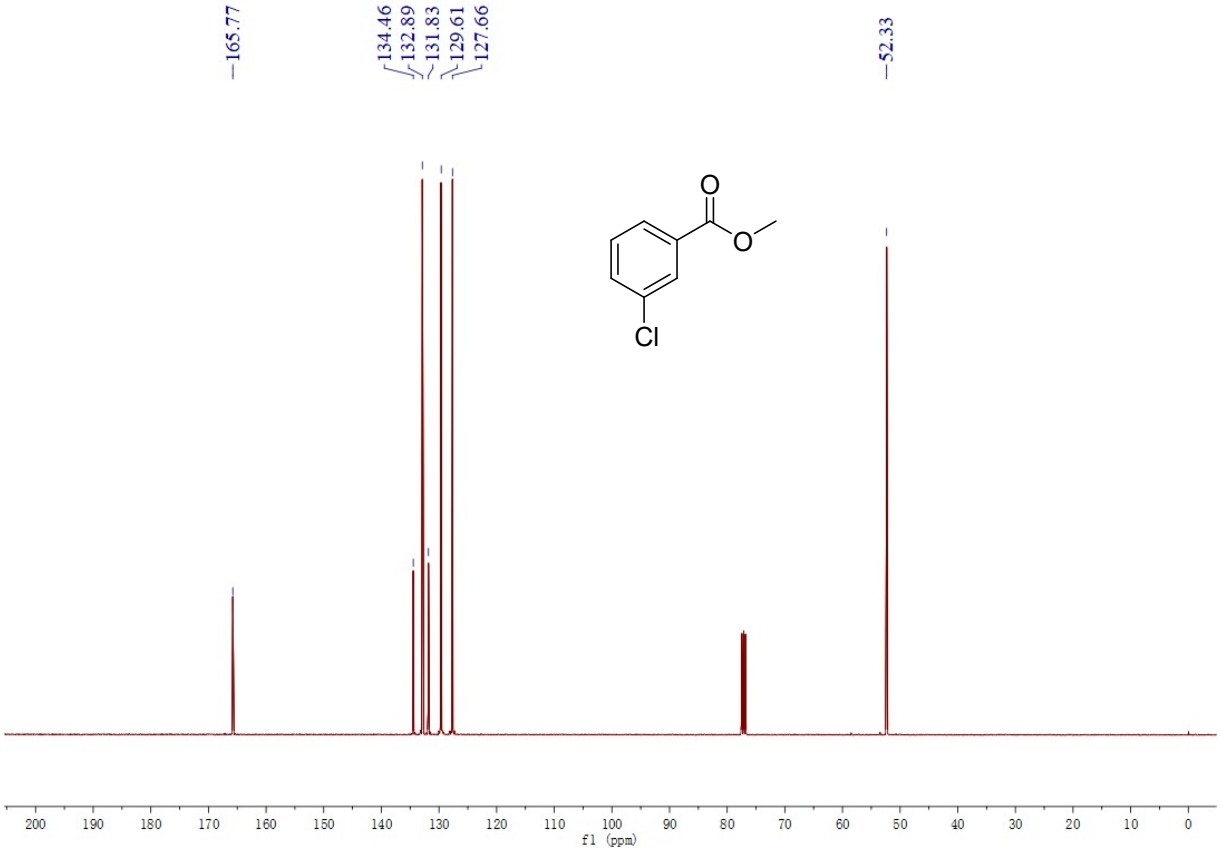


Fig.54 **4m** ^{13}C NMR

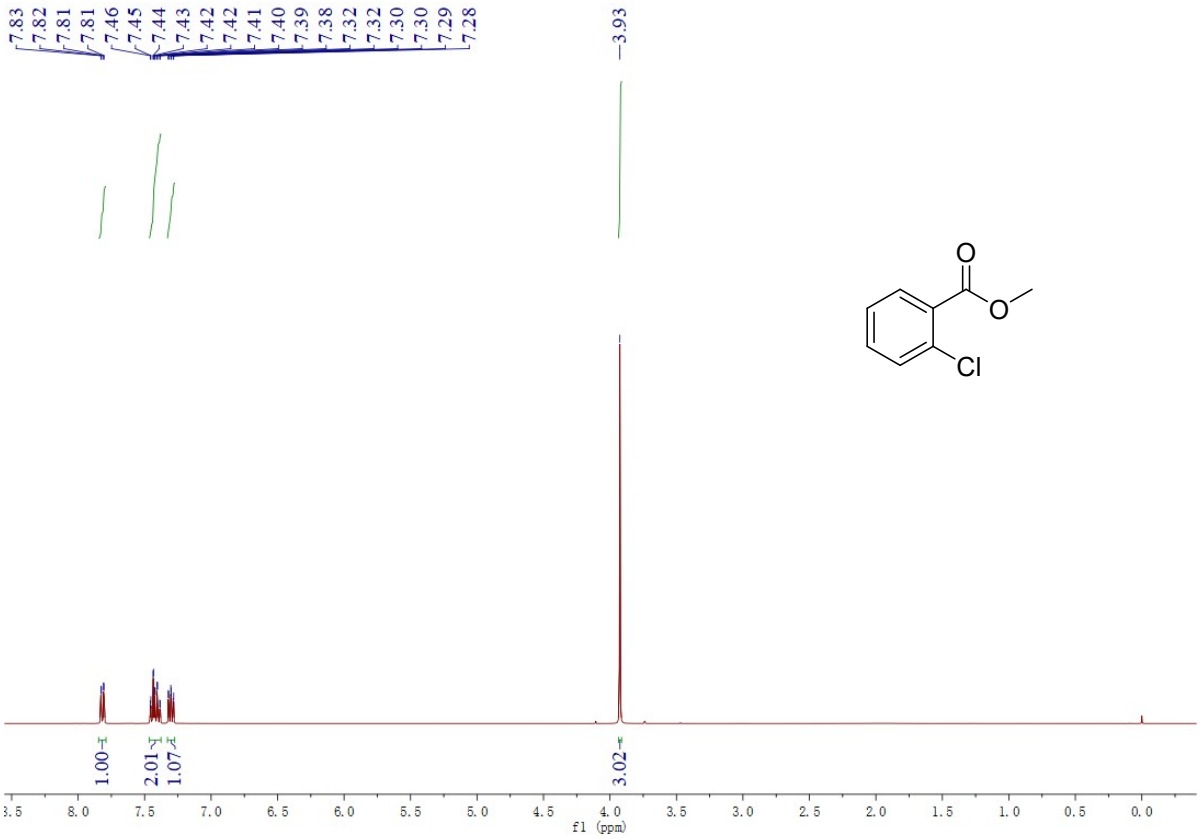


Fig.55 **4n** ^{1}H NMR

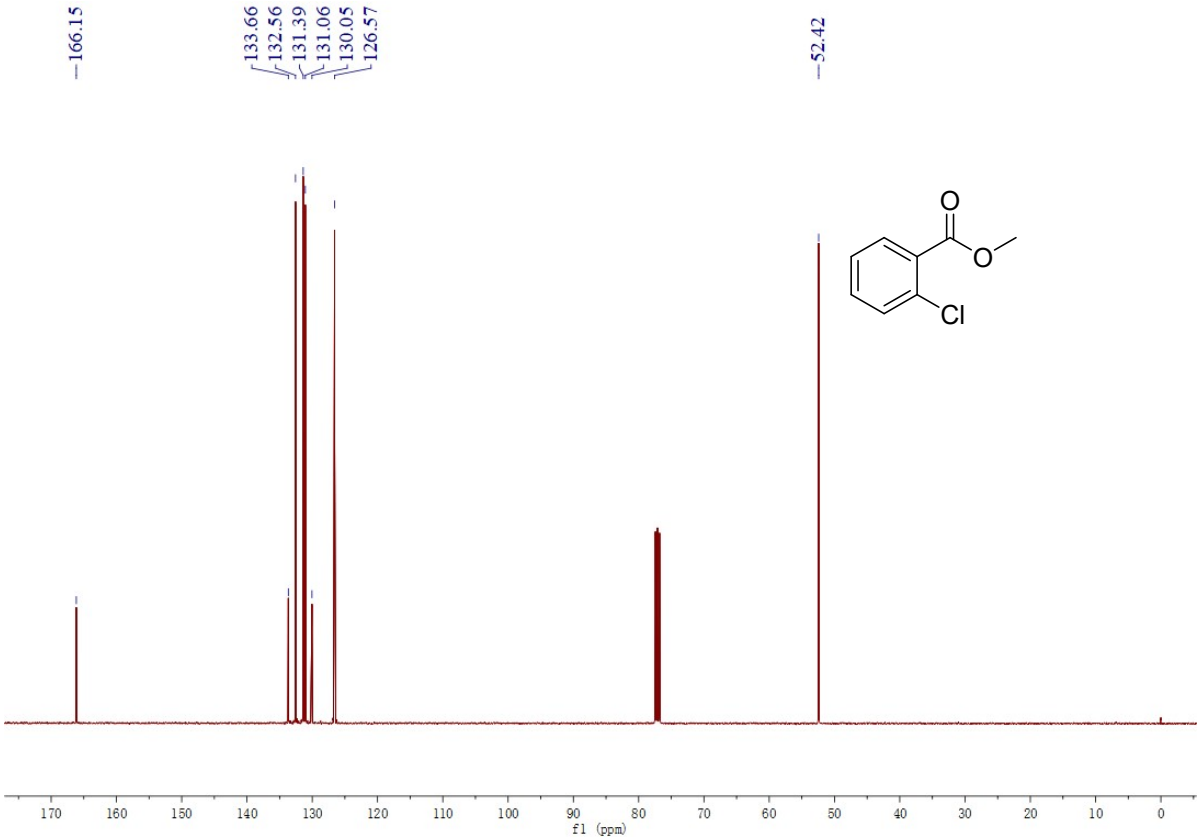


Fig.56 **4n** ^{13}C NMR

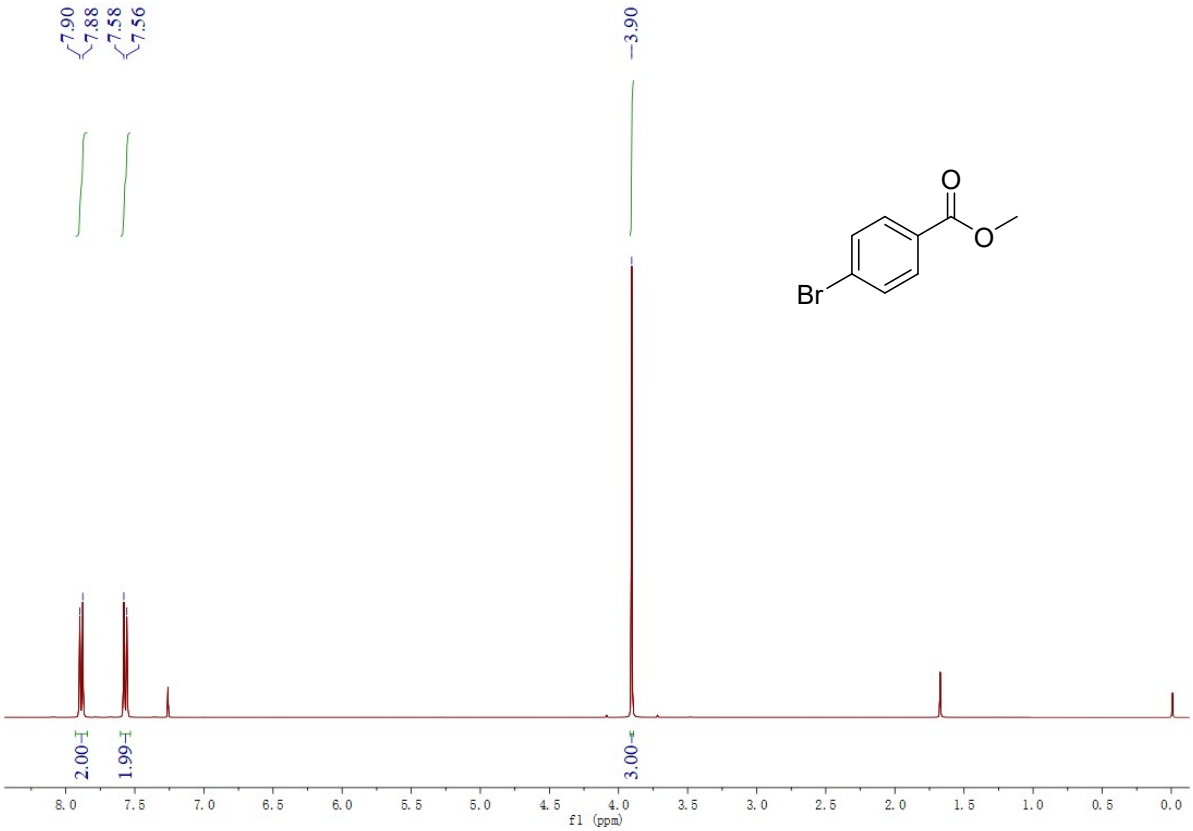


Fig.57 **4o** ^{1}H NMR

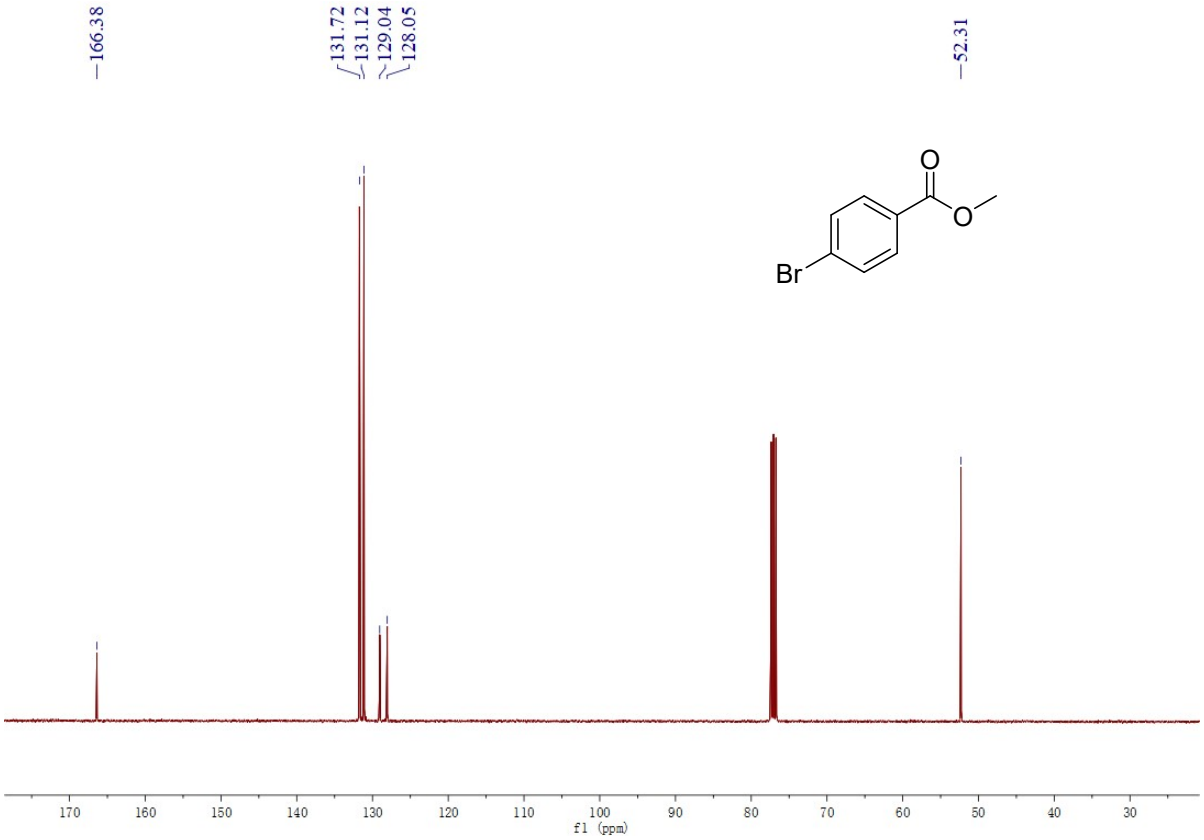


Fig.58 **4o** ^{13}C NMR

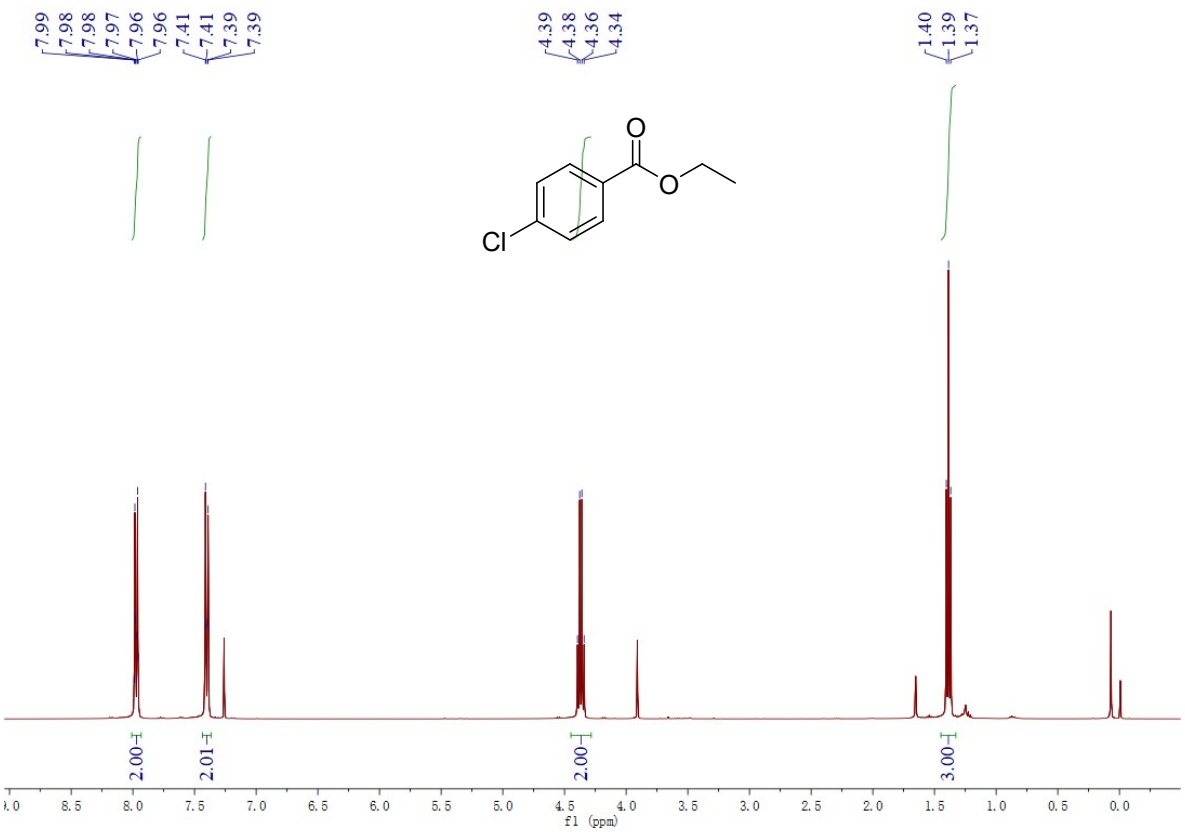


Fig.59 **5l** ^{1}H NMR

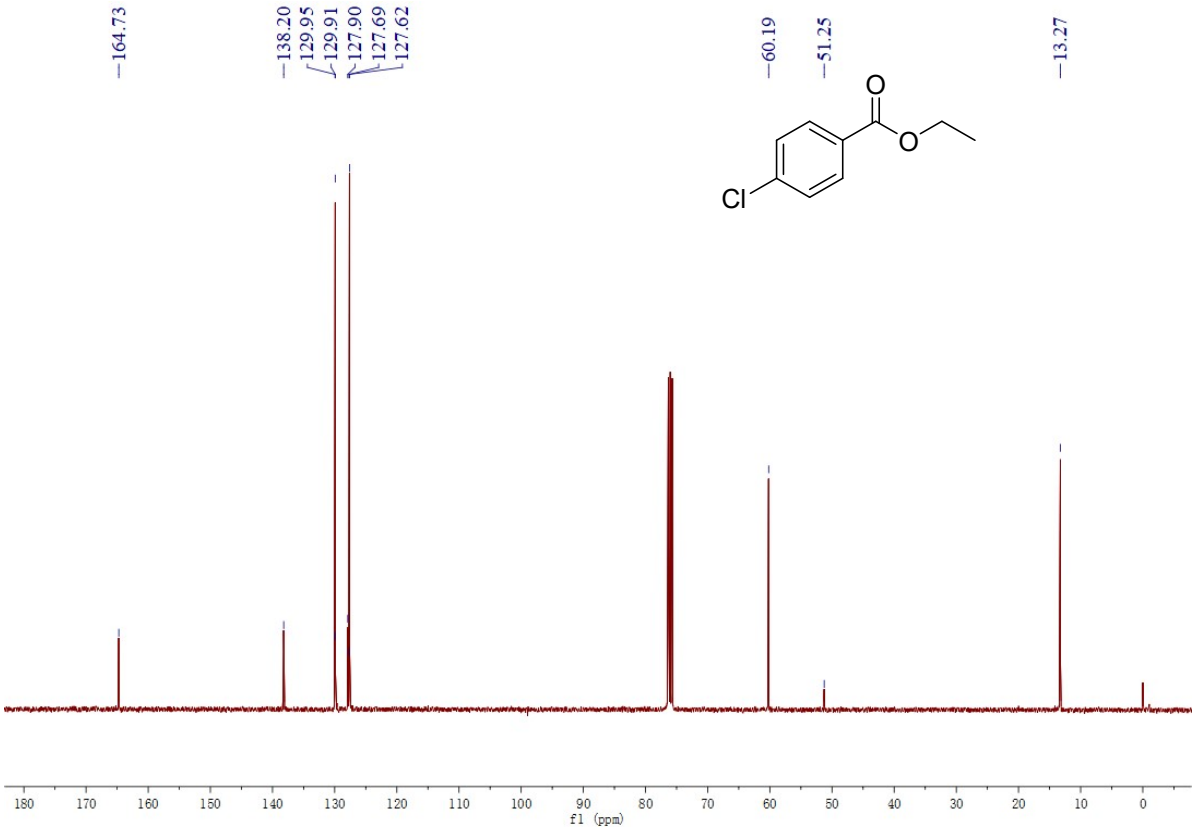


Fig.60 **5l** ^{13}C NMR