

## Supporting Information

### **C<sub>3</sub>N<sub>4</sub>-photocatalyzed Aerobic Oxidative Cleavage of C≡C Bonds in Alkynes with Diazonium Salts Leading to Two Different Aldehydes or Esters in One Pot**

Jingjing Wang<sup>a</sup>, Bangqin Ni<sup>a</sup>, Tengfei Niu\*<sup>a</sup>, Fei Ji\*<sup>a</sup>

<sup>a</sup> School of Chemical and Material Engineering, Jiangnan University, Wuxi

<sup>b</sup> China Pharmaceutical University, Department of Pharmaceutical Engineering, Nanjing, P.R. China

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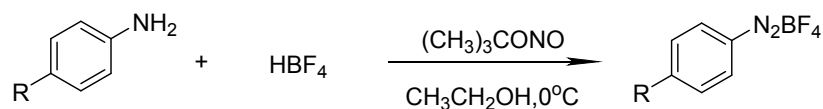
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## General Methods

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.  $^1\text{H}$  NMR spectra were recorded on a Bruker DRX (400 MHz) and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DRX (100 MHz) spectrometer, using  $\text{CDCl}_3$  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.

## Experimental Section

### 1、 Preparation of aryl diazonium tetrafluoroborate:



In a 50 mL circular flask bottom with a magnetic stirring, adding 3 ~10 mL anhydrous ethanol to dissolve the 10mmol aromatic amine, and 2.5 mL HBF<sub>4</sub> solution (50 wt%, 20 mmol) was injected into the flask and placed in an ice bath. Finally, add 2.7 mL *tert*-butyl nitrite (20 mmol) into the flask slowly at 0°C. After dropping, the flask was removed from the ice bath and stirred for 1 hour at room temperature.

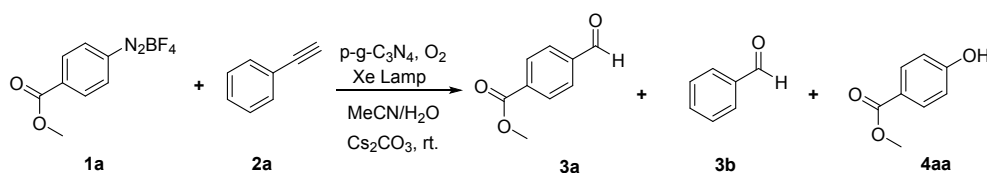
The aryl tetrafluoroborate diazo salt is better precipitated and then filtered, and the filter cake is washed three times with 10 mL ether to ensure that the product is not lost. The filter cake was then poured into the beaker and dried in a vacuum oven at 40°C for 10 minutes. The powder solid was the corresponding aryl tetrafluoroborate diazoium salt.

### 2、 Synthesis of p-g-C<sub>3</sub>N<sub>4</sub>

Typically, porous graphite phase carbon nitride (p-g-C<sub>3</sub>N<sub>4</sub>) was synthesized by

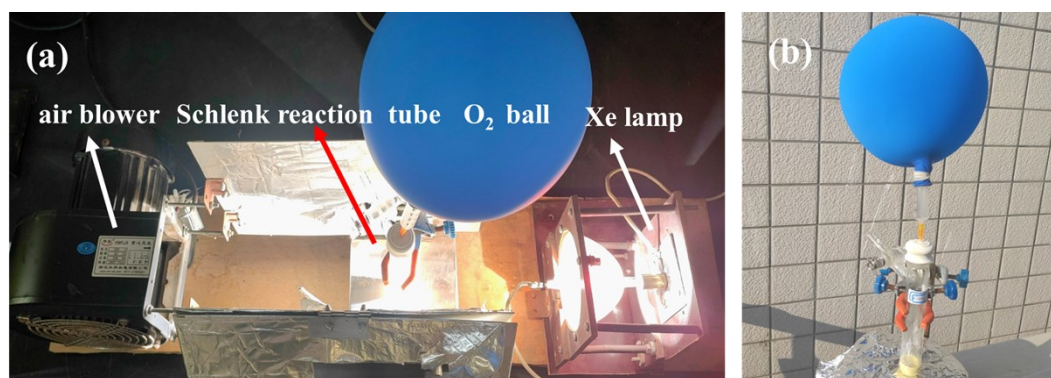
melamine (10 g). It was dissolved in hot distilled water. After cooling down, adding slowly an appropriate amount of hydrochloric acid (37%w, 6.82 mL) into the above melamine solution under magnetic stirring. After 30 min the solution was transferred to an oven to evaporate water thoroughly at 80 °C to obtain melamine hydrochloride without further purification. Then, melamine hydrochloride was contained in a covered crucible and then heated to 500 °C in a muffle furnace for 2 h with a heating rate of 20 °C min<sup>-1</sup>, followed by a further heat treatment at 520 °C for 2 h to get desired yellow powder solid p-g-C<sub>3</sub>N<sub>4</sub> (4.42g).

### 3、 Preparation of methyl *p*-formylbenzoate (**3aa**) and benzaldehyde (**3'aa**):



A 25 mL clean and dry Schlenk reaction tube with a magnetic stirring rotor was equipped with diazonium salt **1a** (0.5 mmol), phenylacetylene **2a** (0.6 mmol), p-g-C<sub>3</sub>N<sub>4</sub> (20 mg), Cs<sub>2</sub>CO<sub>3</sub> (0.2 equiv.), CH<sub>3</sub>CN (1.8 mL) and H<sub>2</sub>O (0.2 mL). The mixture was irradiated with a Xe lamp (250 W) and cooled by a air blower with an oxygen ball for 4 h. The temperature of the reaction mixture is about 33 °C and the distance of the reaction vial from the light is about 10 centimeters (Figure S1).

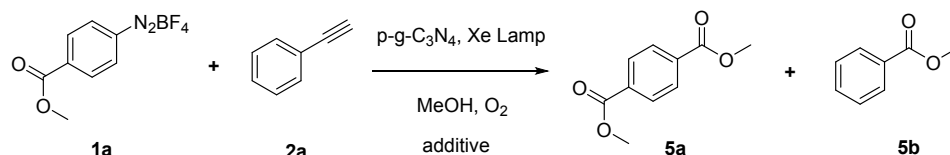
After the reaction, the solvent was removed under reduced pressure. Purification of the crude product was achieved by flash column chromatography using petrol n-hexane /ethyl acetate (4:1~6:1) as eluent, and the collected product was evaporated and concentrated in the oven (50 °C) for further drying and weighing.



**Figure S1.** The photochemical set (a) Xe lamp and (b) Sunlight

### 4、 Optimization of the Esterification reaction conditions

**Table S1** Optimization of the Esterification reaction conditions

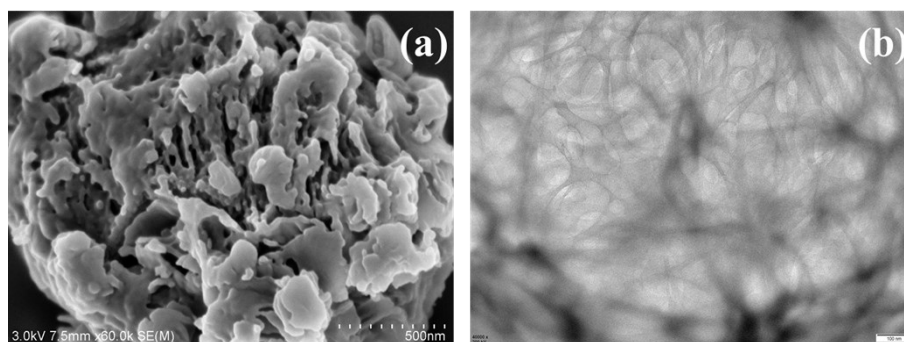


Entry	Cat.	Solvent <sup>b</sup>	additive	Yield/% <sup>c</sup>	
				5a	5b
1	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH	-	trace	trace
2	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH	Na <sub>2</sub> CO <sub>3</sub>	NR	NR
3	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH	Cs <sub>2</sub> CO <sub>3</sub>	NR	NR
4	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH	<i>t</i> BuOK	NR	NR
5	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH	DBU	30	19
6	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH	H <sub>2</sub> SO <sub>4</sub>	20	25
7	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH	HCl	45	39
8	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH	HNO <sub>3</sub>	25	20
9	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH	HClO <sub>4</sub>	70	75
10	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH	H <sub>3</sub> PO <sub>4</sub>	24	32
11	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH	H <sub>3</sub> O <sub>40</sub> PW <sub>12</sub>	NR	NR
12 <sup>d</sup>	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH/H <sub>2</sub> O	HClO <sub>4</sub>	23	25
13 <sup>e</sup>	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH/MeCN	HClO <sub>4</sub>	70	75
14	CN620 (20mg)	MeOH	HClO <sub>4</sub>	62	60
15 <sup>f</sup>	-	MeOH	HClO <sub>4</sub>	NR	NR
16 <sup>g</sup>	p-g-C <sub>3</sub> N <sub>4</sub> (20mg)	MeOH	HClO <sub>4</sub>	NR	NR

<sup>a</sup> Reaction conditions: at room temperature, under a 250W Xenon short arc lamp, light distance 10 cm, substrate **1a** (0.5 mmol), **2a** (0.6 mmol), 20mg p-g-C<sub>3</sub>N<sub>4</sub> as catalyst, 0.5mL HClO<sub>4</sub>, O<sub>2</sub> atmosphere, reaction for 4 hours. <sup>b</sup> solvent (3 mL). <sup>c</sup> Isolated yield. <sup>d</sup> MeOH/H<sub>2</sub>O=5:1 <sup>e</sup> MeOH/MeCN=1:2. <sup>f</sup> No photocatalyst. <sup>g</sup> Without light.

## 5、Characterization of p-g-C<sub>3</sub>N<sub>4</sub>

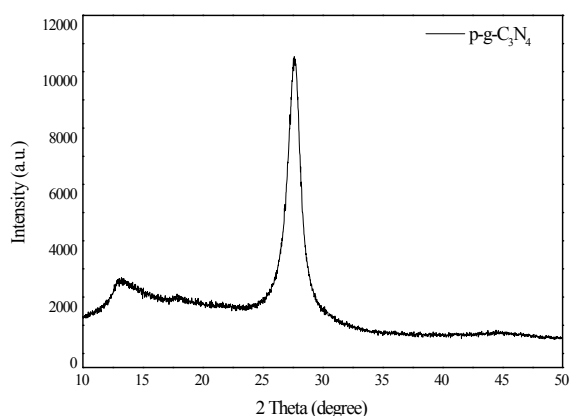
The morphology of the sample was observed by SEM and TEM. The morphology of the synthesized sample is porous thin plate, indicating that we successfully synthesized porous graphite phase carbon nitride through a simple non-template method.



**Figure S2.** (a) SEM and (b) TEM of p-g-C<sub>3</sub>N<sub>4</sub>

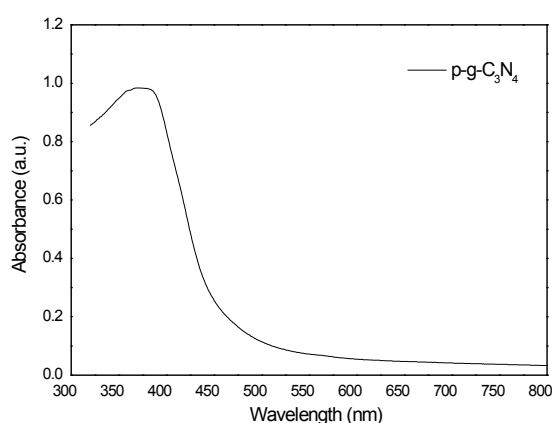
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The X-ray diffraction (XRD) patterns, obtained on an X-ray diffractometer (Bruker D8 Advance) using Cu K $\alpha$  radiation, were used to characterize the crystalline phase of the sample p-g-C<sub>3</sub>N<sub>4</sub>. XRD patterns (Figure S3) was determined to provide the phase structures information for p-g-C<sub>3</sub>N<sub>4</sub>. It had distinct diffraction peaks at 13.0° and 27.4° which can be indexed to graphitic materials as the (100) and (002) crystal plane of g-C<sub>3</sub>N<sub>4</sub>. And the peak intensity of 27.4° is very strong, which is produced by stacking each layer of carbon nitride on each other.



**Figure S3.** XRD of p-g-C<sub>3</sub>N<sub>4</sub>

The UV-vis diffuse reflectance spectroscopy (UV-vis DRS) of the samples were measured using a UV-3600 plus spectrometer (Shimadzu, Japan) and the spectra were collected at 300–800nm using BaSO<sub>4</sub> as a reference. Obviously, the p-g-C<sub>3</sub>N<sub>4</sub> had an absorption edge of 400 nm (Figure S4).



**Figure S4.** Diffuse reflectance UV-vis spectra of p-g-C<sub>3</sub>N<sub>4</sub>

The nitrogen (N<sub>2</sub>) adsorption–desorption isotherms were measured and analyzed to characterize the textural properties of the samples (Figure S5) using a Micromeritics ASAP-2020MP instrument. The samples outgassed at 200 °C for 3 h under vacuum

prior to the experiments. The p-g-C<sub>3</sub>N<sub>4</sub> showed III adsorption-desorption isotherms with H<sub>3</sub> hysteresis loop, indicating the formation of fissure like pore.

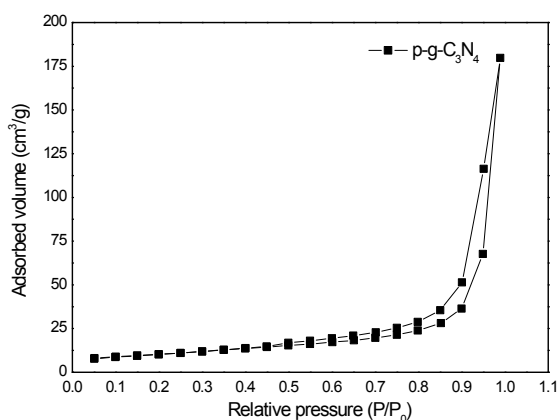
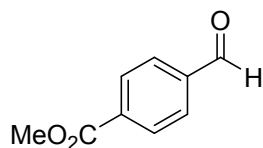
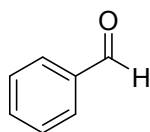


Figure S5. Nitrogen adsorption-desorption isotherms of p-g-C<sub>3</sub>N<sub>4</sub>

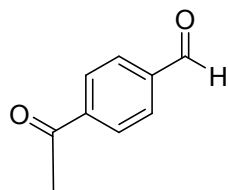
## Characterization data



methyl 4-formylbenzoate (**3a**). Yellow solid (61.8mg, 75%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.10 (s, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 3.96 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 191.6, 166.0, 139.2, 135.1, 130.2, 129.5, 52.5. ESI-MS: *m/z* = 165[M+1]<sup>+</sup>.



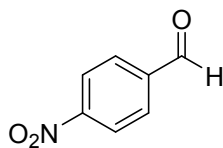
Benzaldehyde (**3b**). White liquid (38.5mg, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.03 (s, 1H), 8.00–7.82 (m, 1H), 7.68–7.47 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 192.4, 136.4, 134.5, 129.8, 129.0. ESI-MS: *m/z* = 107[M+1]<sup>+</sup>.



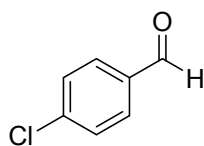
4-acetylbenzaldehyde (**3c**). Yellow solid. (56.5mg, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.12 (s, 1H), 8.11 (d, *J* = 8.2 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 2H), 2.67 (s,

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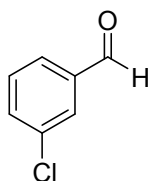
3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.39, 191.57, 141.25, 139.08, 129.82, 128.82, 26.95. ESI-MS:  $m/z = 149[\text{M}+1]^+$ .



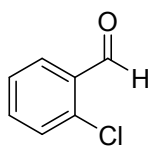
4-nitrobenzaldehyde (**3d**). White solid. (57.0mg, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.18 (s, 1H), 8.45–8.34 (m, 1H), 8.13 – 8.03 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.3, 151.1, 140.1, 130.5, 124.3. ESI-MS:  $m/z = 152[\text{M}+1]^+$ .



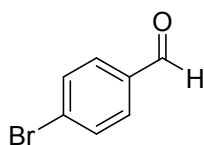
4-chlorobenzaldehyde (**3e**). White liquid (47.3mg, 67%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.00 (s, 1H), 7.87–7.82 (m, 1H), 7.57–7.50 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.3, 144.6, 140.1, 136.4, 134.6. ESI-MS:  $m/z = 141[\text{M}+1]^+$ .



3-chlorobenzaldehyde (**3f**). White liquid (44.1mg, 63%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.98 (s, 1H), 7.85 (t,  $J = 1.8$  Hz, 1H), 7.77 (dt,  $J = 7.6, 1.3$  Hz, 1H), 7.60 (ddd,  $J = 8.0, 2.2, 1.2$  Hz, 1H), 7.49 (t,  $J = 7.8$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.8, 137.8, 135.5, 134.4, 130.4, 129.3, 128.0. ESI-MS:  $m/z = 141[\text{M}+1]^+$ .

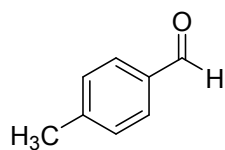


2-chlorobenzaldehyde (**3g**). White liquid (47.8mg, 54%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.48 (d,  $J = 0.8$  Hz, 1H), 7.92 (dd,  $J = 7.7, 1.8$  Hz, 1H), 7.53 (ddd,  $J = 8.1, 7.2, 1.8$  Hz, 1H), 7.47 – 7.43 (m, 1H), 7.41 – 7.36 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  189.7, 137.9, 135.1, 132.5, 130.6, 129.4, 127.3. ESI-MS:  $m/z = 141[\text{M}+1]^+$ .

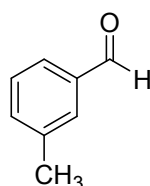


4-bromobenzaldehyde (**3h**). White liquid (59.8mg, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.00 (s, 1H), 7.79–7.75 (m, 1H), 7.73–7.68 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,

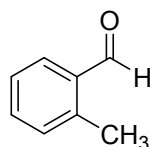
CDCl<sub>3</sub>)  $\delta$  191.0, 135.1, 132.4, 131.0, 129.8. ESI-MS:  $m/z = 184[M+1]^+$ .



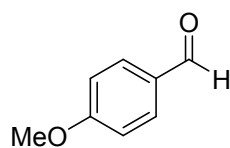
4-methylbenzaldehyde (**3i**). White liquid (42.6mg, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.96 (s, 1H), 7.78 (d,  $J = 8.1$  Hz, 1H), 7.37 – 7.30 (m, 1H), 2.44 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  192.0, 171.6, 145.6, 134.2, 130.2, 129.8, 129.7, 129.2, 21.83. ESI-MS:  $m/z = 121[M+1]^+$ .



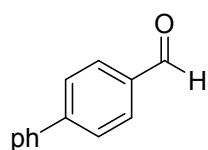
3-methylbenzaldehyde (**3j**). White liquid (41.1mg, 68%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.01 (s, 1H), 7.70 (dd,  $J = 6.9, 1.1$  Hz, 1H), 7.50 – 7.41 (m, 1H), 2.46 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  192.6, 138.9, 136.5, 135.3, 130.0, 128.9, 127.3, 21.2. ESI-MS:  $m/z = 121[M+1]^+$ .



2-methylbenzaldehyde (**3k**). White liquid (34.2mg, 57%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.27 (s, 1H), 7.80 (dd,  $J = 7.6, 1.2$  Hz, 1H), 7.48 (td,  $J = 7.5, 1.4$  Hz, 1H), 7.36 (t,  $J = 7.5$  Hz, 1H), 7.26 (d,  $J = 7.6$  Hz, 1H), 2.67 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  192.8, 140.6, 134.2, 133.7, 132.1, 131.8, 126.3, 19.6. ESI-MS:  $m/z = 121[M+1]^+$ .



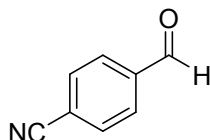
4-methoxybenzaldehyde (**3l**). White liquid (50.3mg, 74%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.89 (s, 1H), 7.93 – 7.79 (m, 1H), 7.06 – 6.94 (m, 1H), 3.89 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.8, 164.6, 132.0, 130.0, 114.3, 55.6. ESI-MS:  $m/z = 137[M+1]^+$ .



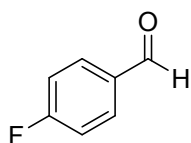
[1,1'-biphenyl]-4-carbaldehyde (**3m**). White solid (60.3mg, 66%). <sup>1</sup>H NMR (400



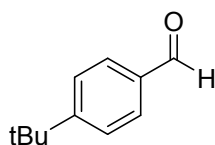
MHz, CDCl<sub>3</sub>)  $\delta$  10.08 (s, 1H), 8.02 – 7.95 (m, 1H), 7.78 (d,  $J$  = 8.2 Hz, 1H), 7.67 (dd,  $J$  = 7.0, 1.5 Hz, 1H), 7.55–7.48 (m, 1H), 7.48–7.42 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  191.9, 147.2, 139.7, 135.2, 130.3, 129.1, 128.5, 127.7, 127.4. ESI-MS:  $m/z$  =183[M+1]<sup>+</sup>.



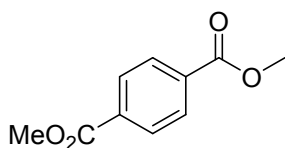
4-formylbenzonitrile (**3n**). Yellow solid (51.5mg, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.10 (s, 1H), 8.03–7.98 (m, 1H), 7.88–7.84 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.7, 138.8, 132.9, 129.9, 117.7, 117.6. ESI-MS:  $m/z$  =132[M+1]<sup>+</sup>.



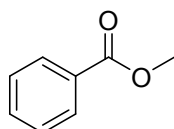
4-fluorobenzaldehyde (**3o**). Yellow liquid (36.2mg, 58%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.98 (s, 1H), 7.95–7.89 (m, 1H), 7.22 (dd,  $J$  = 11.9, 5.2 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  190.5, 167.8, 133.0, 133.0, 132.3, 132.2, 116.5, 116.2. ESI-MS:  $m/z$  =125[M+1]<sup>+</sup>.



4-(tert-butyl)benzaldehyde (**3p**). Yellow solid (47.8mg, 59%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.01 (s, 1H), 7.84 (d,  $J$  = 8.4 Hz, 1H), 7.58 (d,  $J$  = 8.3 Hz, 1H), 1.38 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  192.0, 158.5, 134.3, 129.7, 126.0, 35.5, 31.1. ESI-MS:  $m/z$  =163[M+1]<sup>+</sup>.



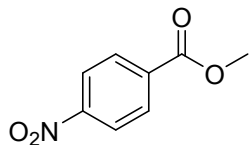
dimethyl terephthalate (**5a**). White solid (68mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (s, 4H), 3.93 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.3, 133.9, 129.6, 52.4. ESI-MS:  $m/z$  =195[M+1]<sup>+</sup>.



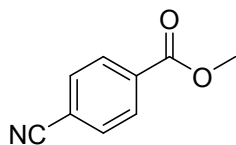
methyl benzoate (**5b**). Yellow liquid. (52mg, 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

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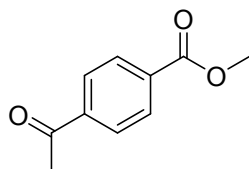
$\delta$  8.08 – 7.98 (m, 2H), 7.56 – 7.48 (m, 1H), 7.40 (t,  $J = 7.6$  Hz, 2H), 3.88 (d,  $J = 1.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 132.9, 130.2, 129.6, 128.3, 52.0. ESI-MS:  $m/z = 136[\text{M}+1]^+$ .



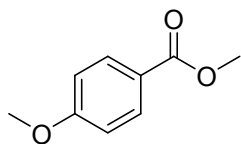
methyl 4-nitrobenzoate (**5c**). Yellow solid (63mg, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J = 8.8$  Hz, 2H), 8.18 (d,  $J = 8.8$  Hz, 2H), 3.96 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 150.6, 135.5, 130.7, 123.5, 52.8. ESI-MS:  $m/z = 182[\text{M}+1]^+$ .



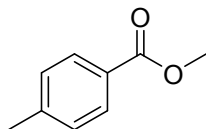
methyl 4-cyanobenzoate (**5d**). White solid (62mg, 76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d,  $J = 8.0$  Hz, 2H), 7.73 (d,  $J = 8.0$  Hz, 2H), 3.94 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 133.9, 132.2, 130.1, 118.0, 117.4, 52.7. ESI-MS:  $m/z = 162[\text{M}+1]^+$ .



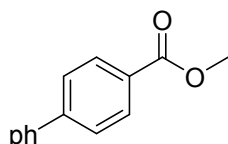
methyl 4-acetylbenzoate (**5e**). Yellow solid. (76mg, 85%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (t,  $J = 7.2$  Hz, 2H), 8.01 (d,  $J = 8.5$  Hz, 2H), 3.96 (s, 3H), 2.65 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.6, 166.2, 140.2, 133.9, 129.8, 128.2, 52.5, 26.9. ESI-MS:  $m/z = 179[\text{M}+1]^+$ .



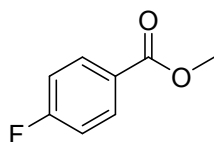
methyl 4-methoxybenzoate (**5f**). White solid. (69mg, 82%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 – 7.80 (m, 2H), 6.90 – 6.80 (m, 2H), 3.78 (s, 3H), 2.47 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.7, 163.5, 130.5, 130.2, 113.6, 55.4, 26.2. ESI-MS:  $m/z = 167[\text{M}+1]^+$ .



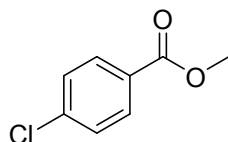
methyl 4-methylbenzoate (**5g**). Yellow liquid (52mg, 69%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 7.8$  Hz, 2H), 7.18 (d,  $J = 7.4$  Hz, 2H), 3.85 (s, 3H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 143.5, 129.6, 129.0, 127.4, 51.8, 21.5. ESI-MS:  $m/z = 152[\text{M}+1]^+$ .



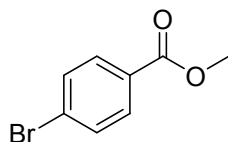
methyl [1,1'-biphenyl]-4-carboxylate (**5h**). White solid. (58mg, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d,  $J = 8.5$  Hz, 2H), 7.65 (dd,  $J = 15.1, 8.1$  Hz, 4H), 7.43 (dt,  $J = 29.1, 7.2$  Hz, 3H), 3.94 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 145.7, 140.0, 130.1, 129.0, 128.9, 128.2, 127.3, 127.1, 52.2. ESI-MS:  $m/z = 213[\text{M}+1]^+$ .



methyl 4-fluorobenzoate (**5i**). White solid (48mg, 62%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 – 7.97 (m, 2H), 7.08 (dd,  $J = 12.1, 5.3$  Hz, 2H), 3.88 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 166.1, 164.5, 132.1, 132.1, 126.4, 126.4, 115.6, 115.4, 52.2. ESI-MS:  $m/z = 155[\text{M}+1]^+$ .



methyl 4-chlorobenzoate (**5j**). White solid (57mg, 67%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 8.5$  Hz, 2H), 7.40 (d,  $J = 8.5$  Hz, 2H), 3.91 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 139.4, 130.9, 128.7, 128.6, 52.3. ESI-MS:  $m/z = 171[\text{M}+1]^+$ .



methyl 4-bromobenzoate (**5k**). White solid (64mg, 60%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 8.6$  Hz, 2H), 7.57 (d,  $J = 8.6$  Hz, 2H), 3.90 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 131.7, 131.1, 129.0, 128.1, 52.3. ESI-MS:  $m/z$

=214[M+1]<sup>+</sup>.

## NMR Spectra

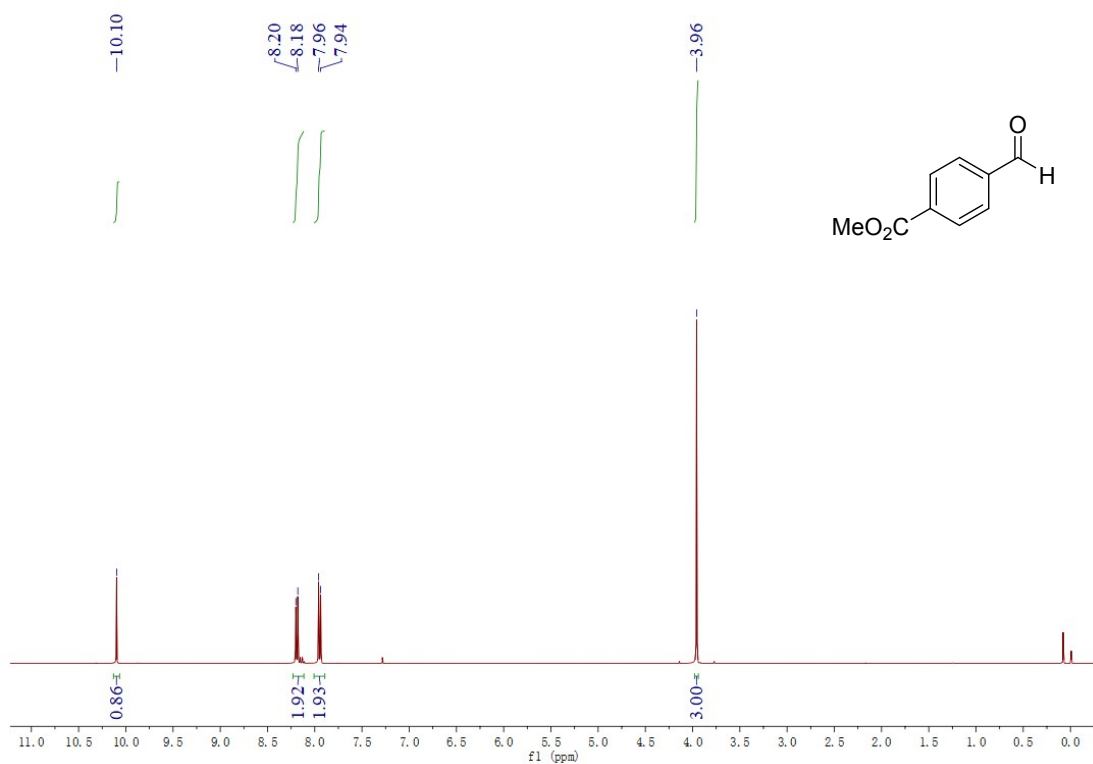


Fig.1 **3a** <sup>1</sup>H NMR

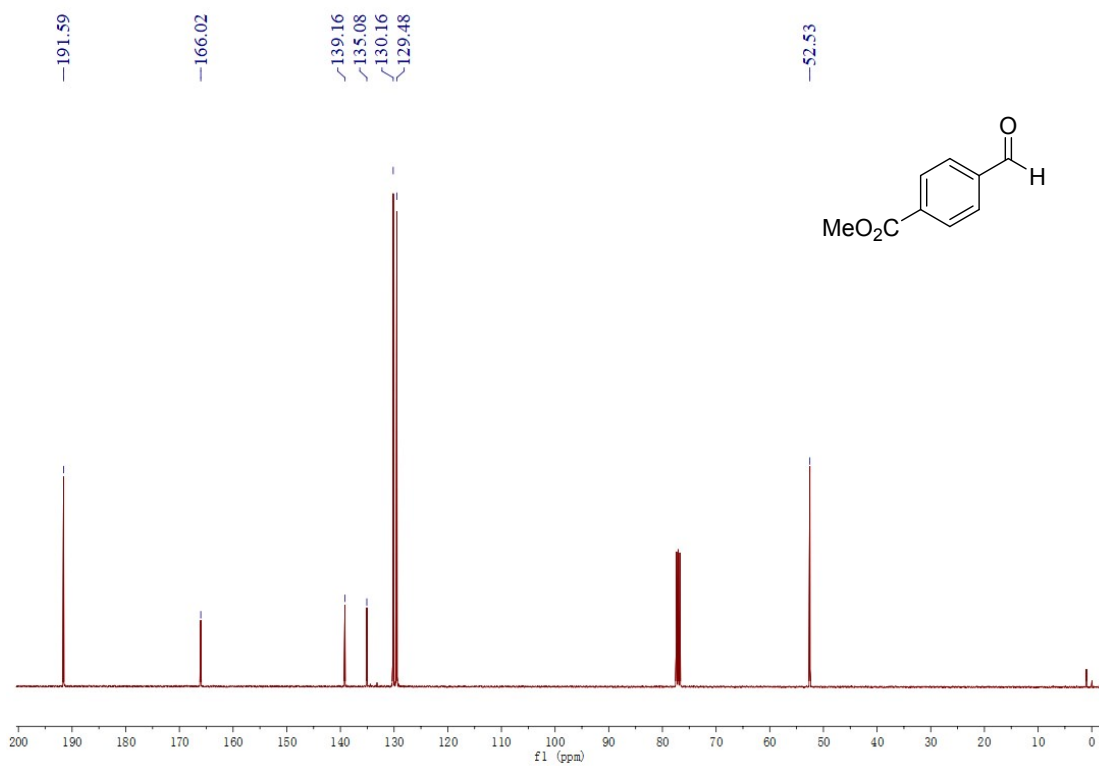


Fig.2 **3a** <sup>13</sup>C NMR

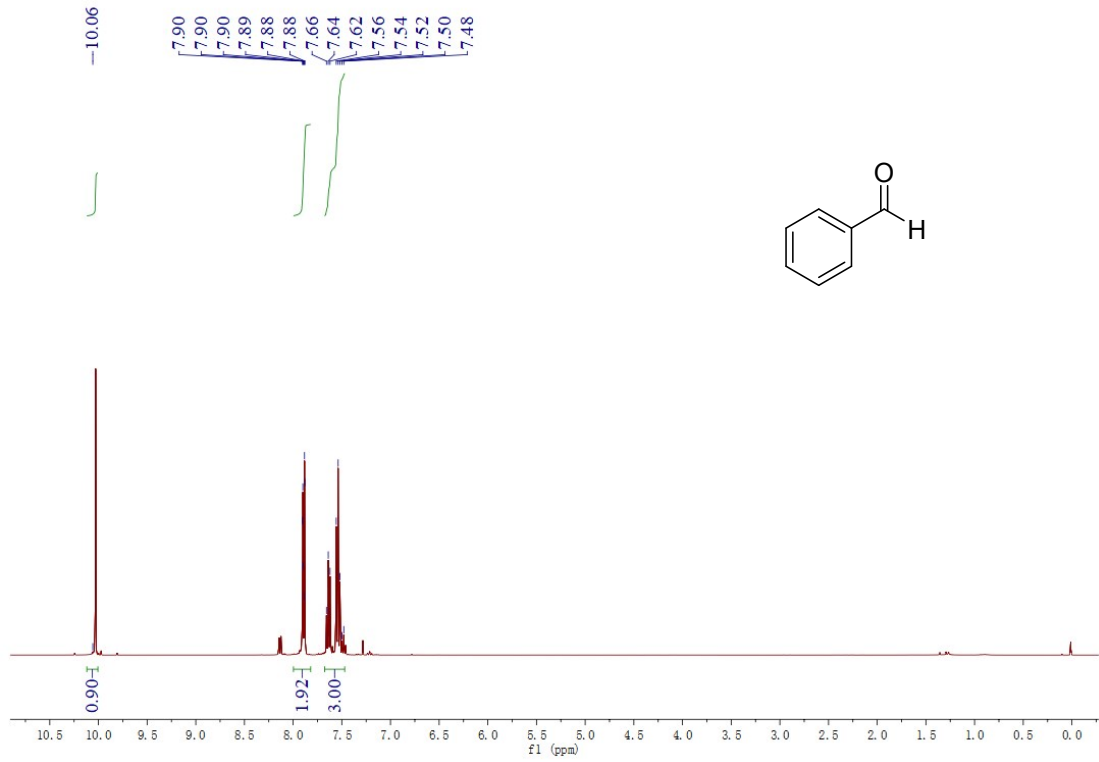


Fig.3 **3b**  $^1\text{H}$  NMR

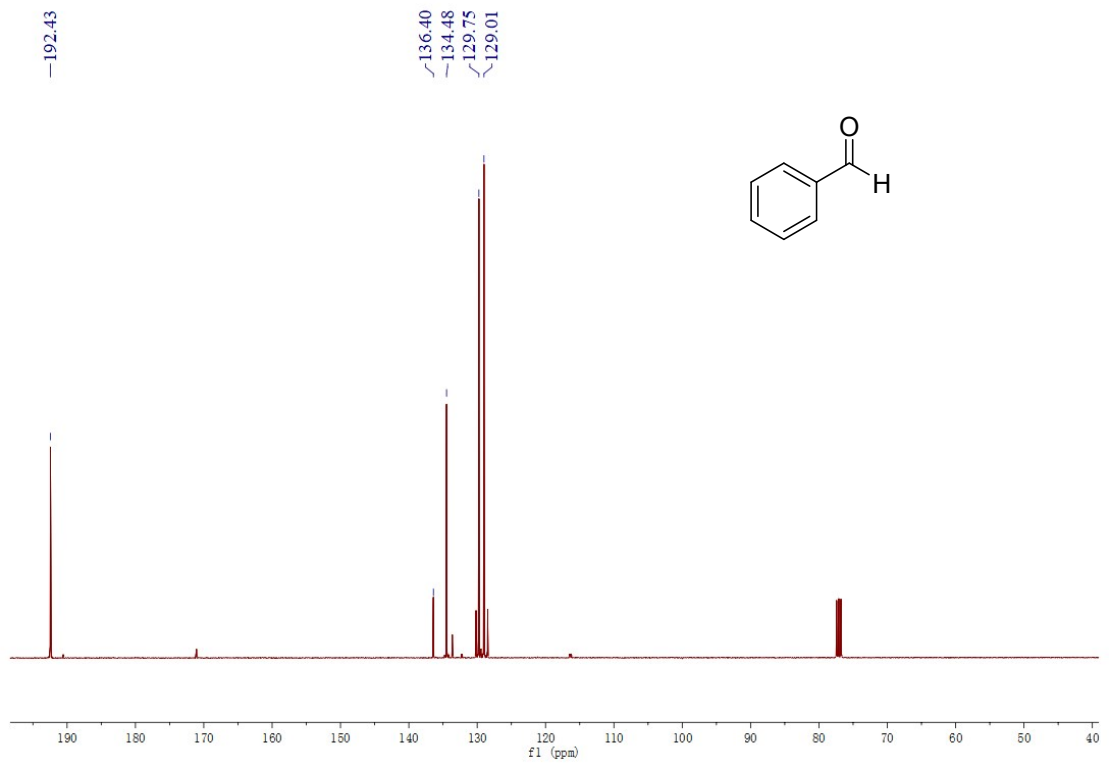


Fig.4 **3b**  $^{13}\text{C}$  NMR

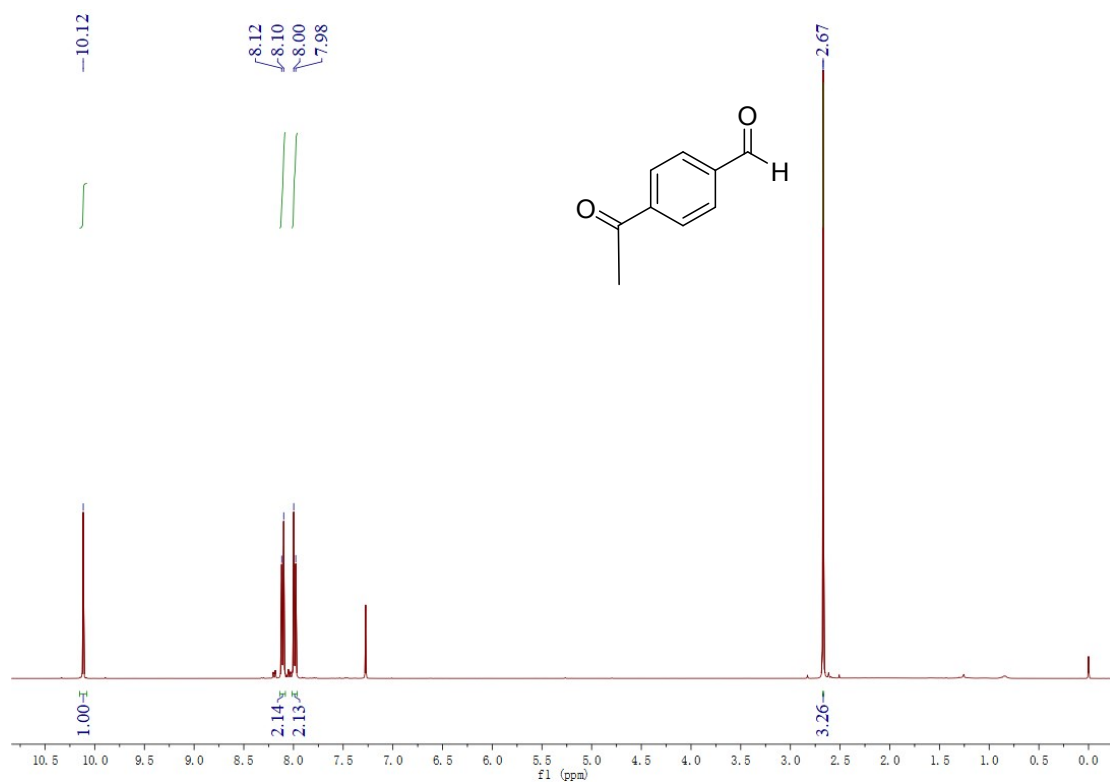


Fig.5 **3c**  $^1\text{H}$  NMR

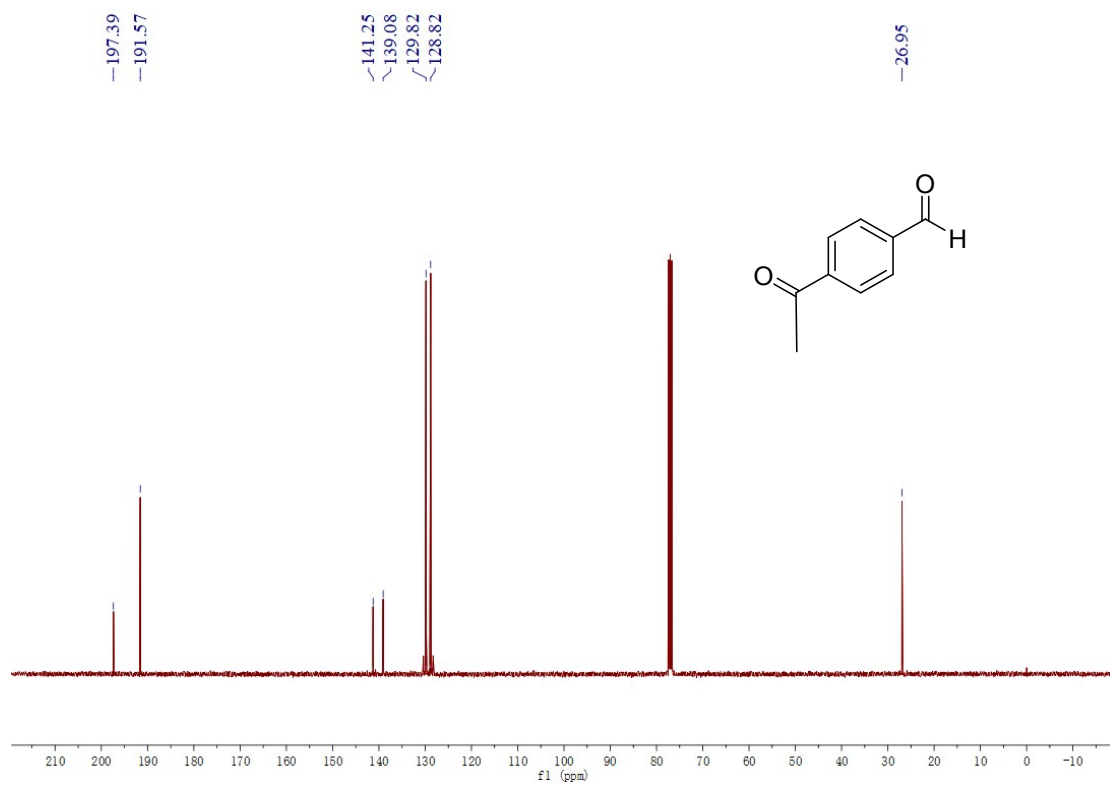


Fig.6 **3c**  $^{13}\text{C}$  NMR

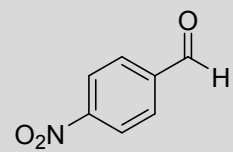


Fig.7 **3d** <sup>1</sup>H NMR

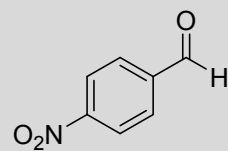


Fig.8 **3d** <sup>13</sup>C NMR

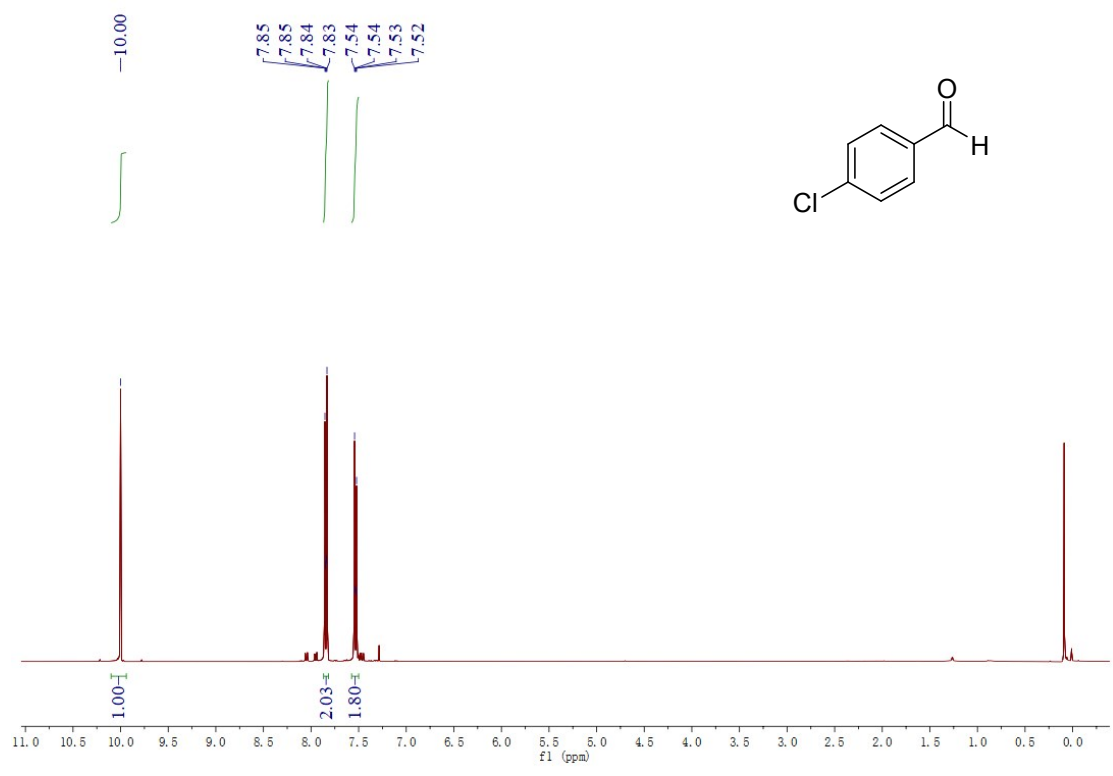


Fig.9 3e <sup>1</sup>H NMR

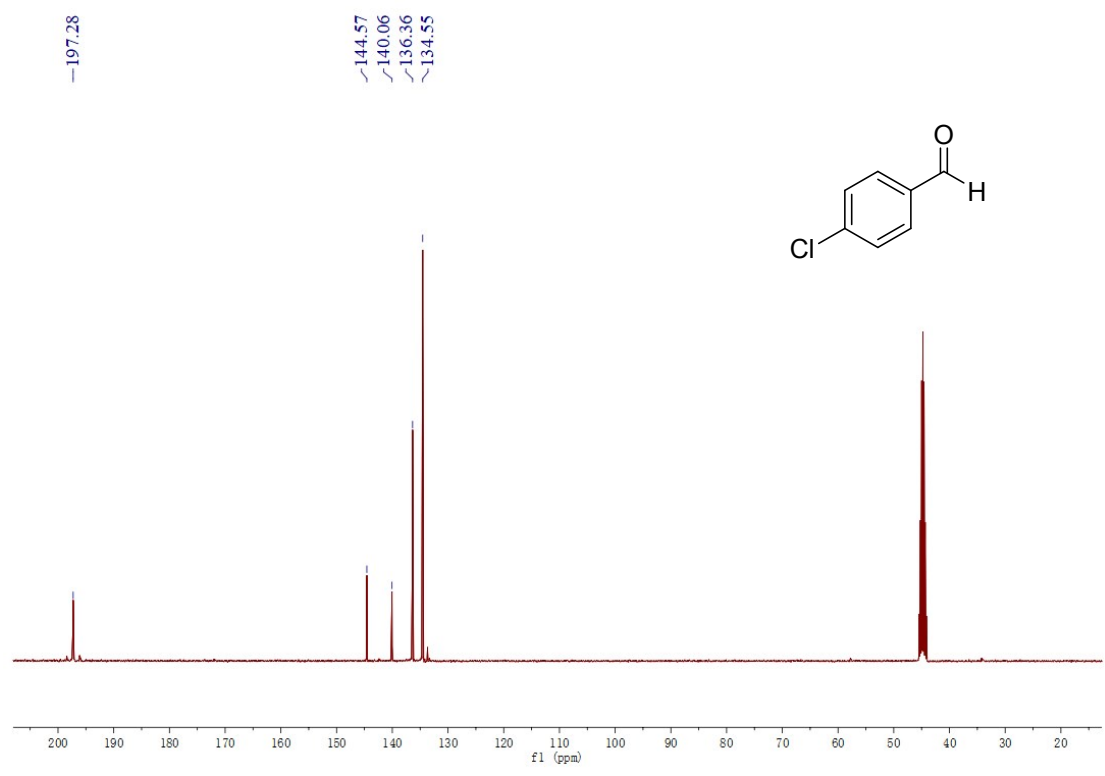


Fig.10 3e <sup>13</sup>C NMR



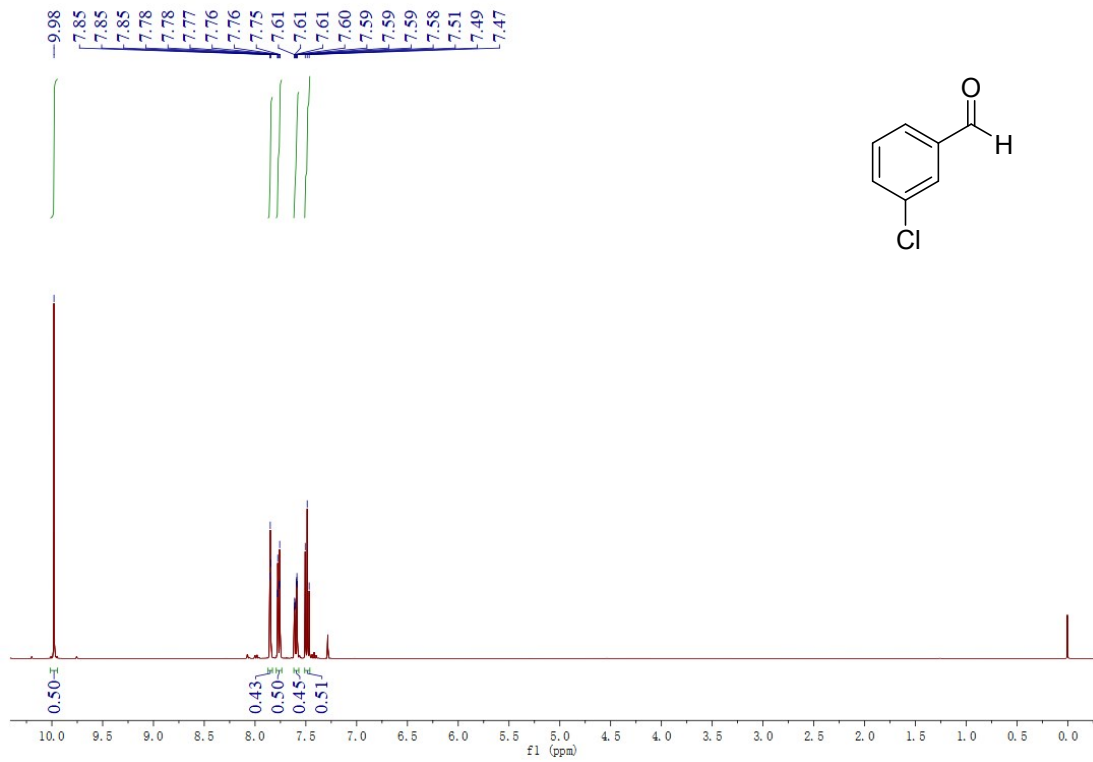


Fig.11 **3f** <sup>1</sup>H NMR

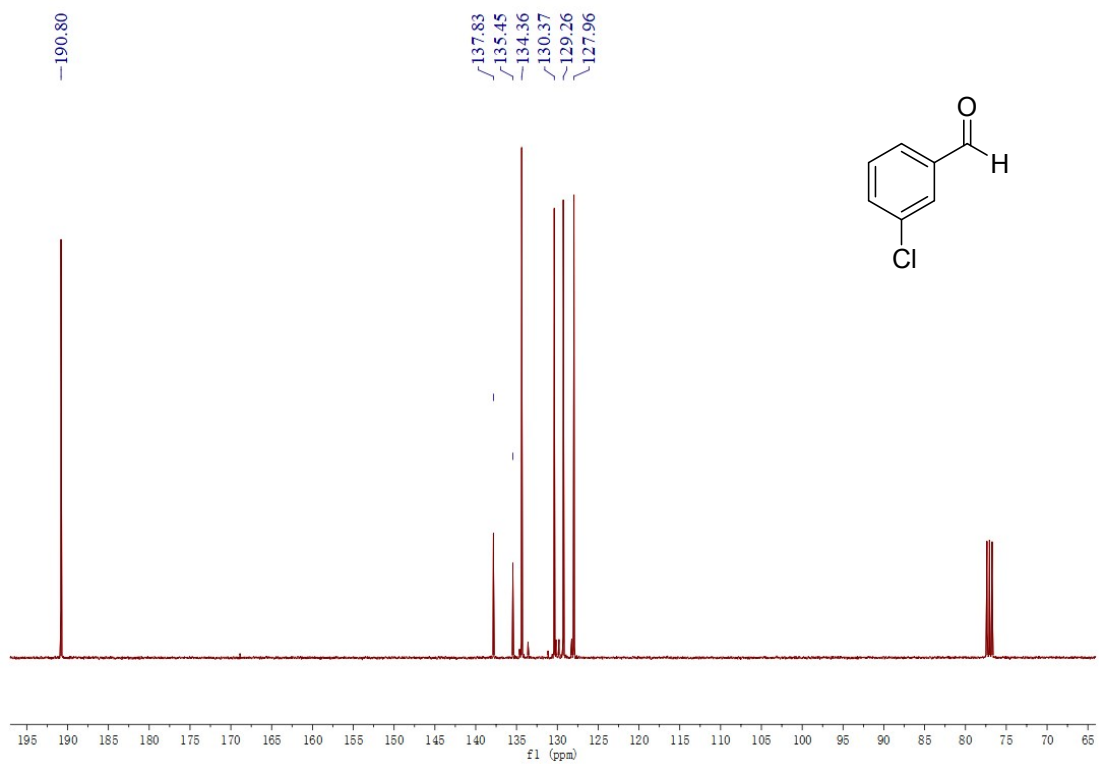


Fig.12 **3f** <sup>13</sup>C NMR

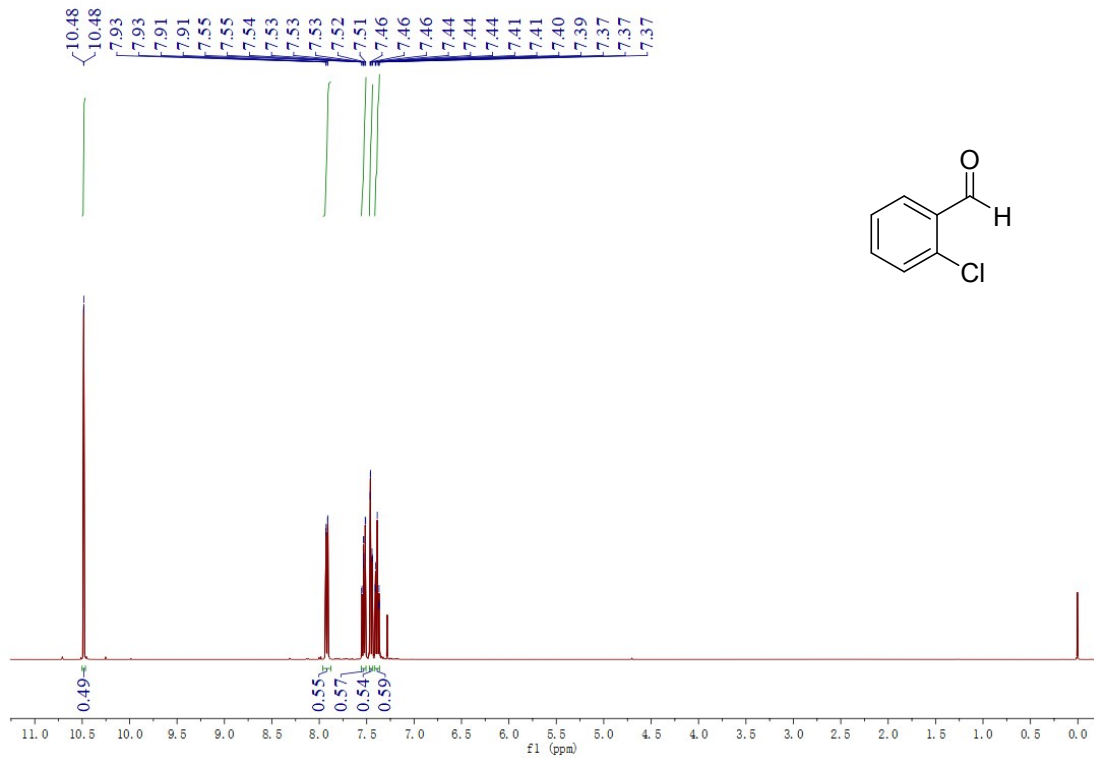


Fig.13 **3g**  $^1\text{H}$  NMR

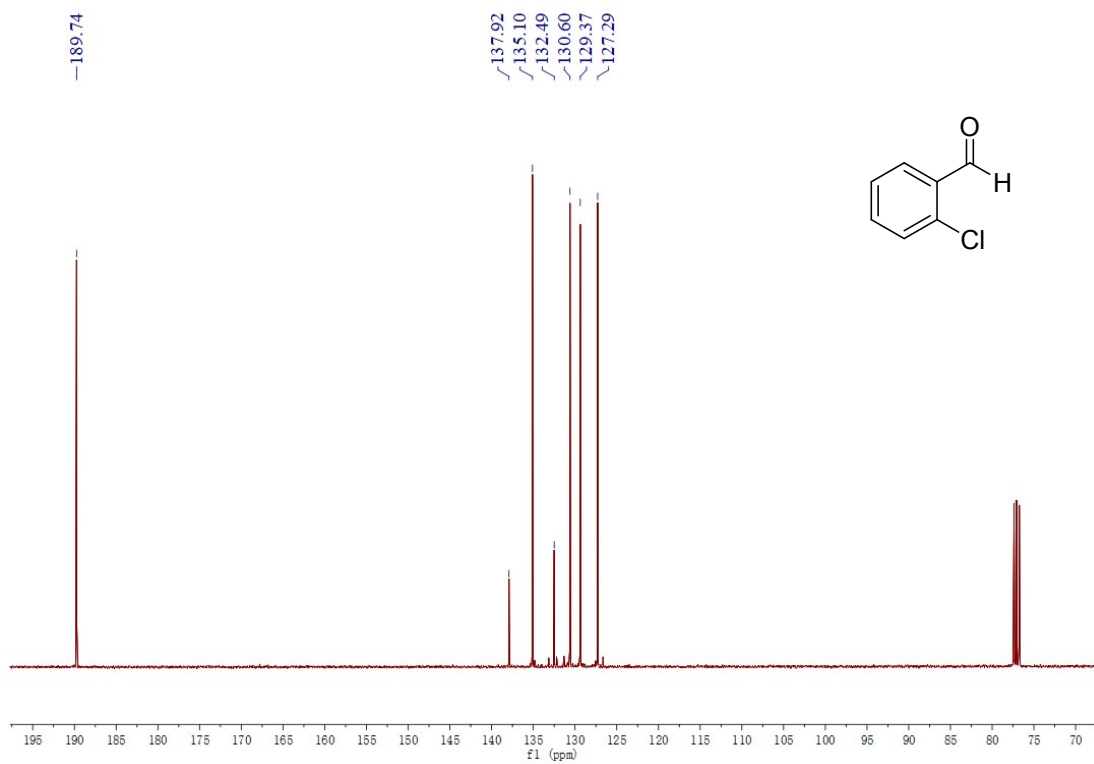


Fig.14 **3g**  $^{13}\text{C}$  NMR

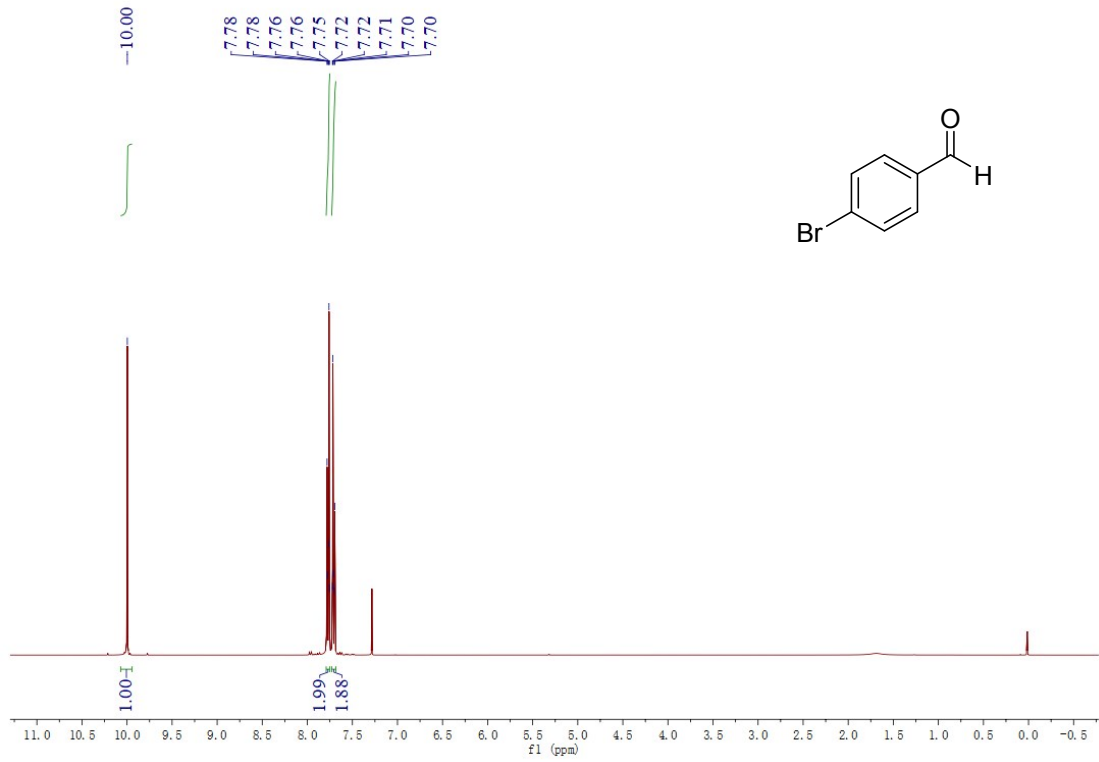


Fig.15 **3h**  $^1\text{H}$  NMR

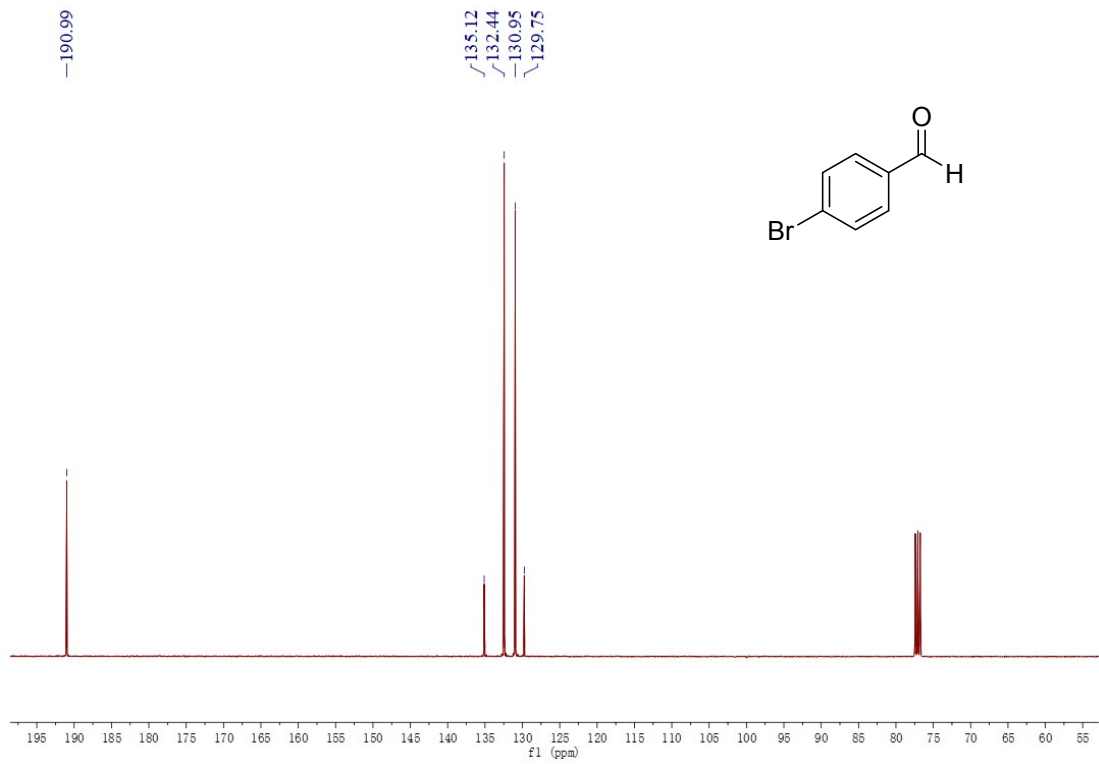


Fig.16 **3h**  $^{13}\text{C}$  NMR

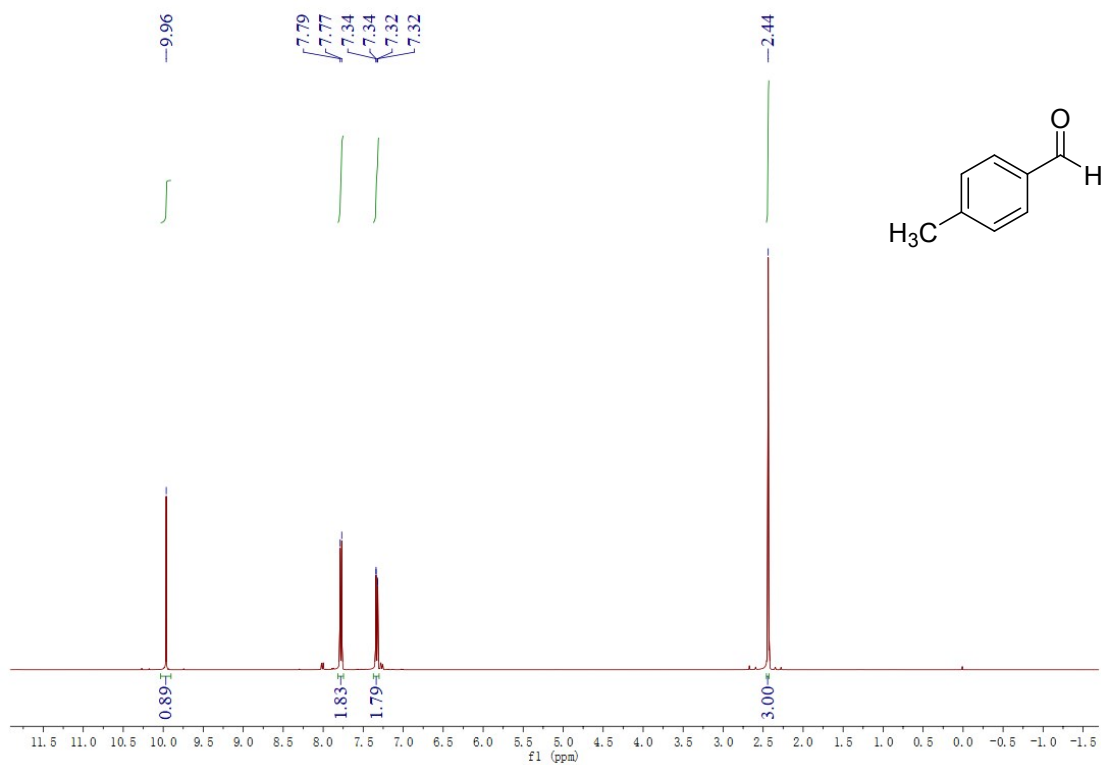


Fig.17 **3i**  $^1\text{H}$  NMR

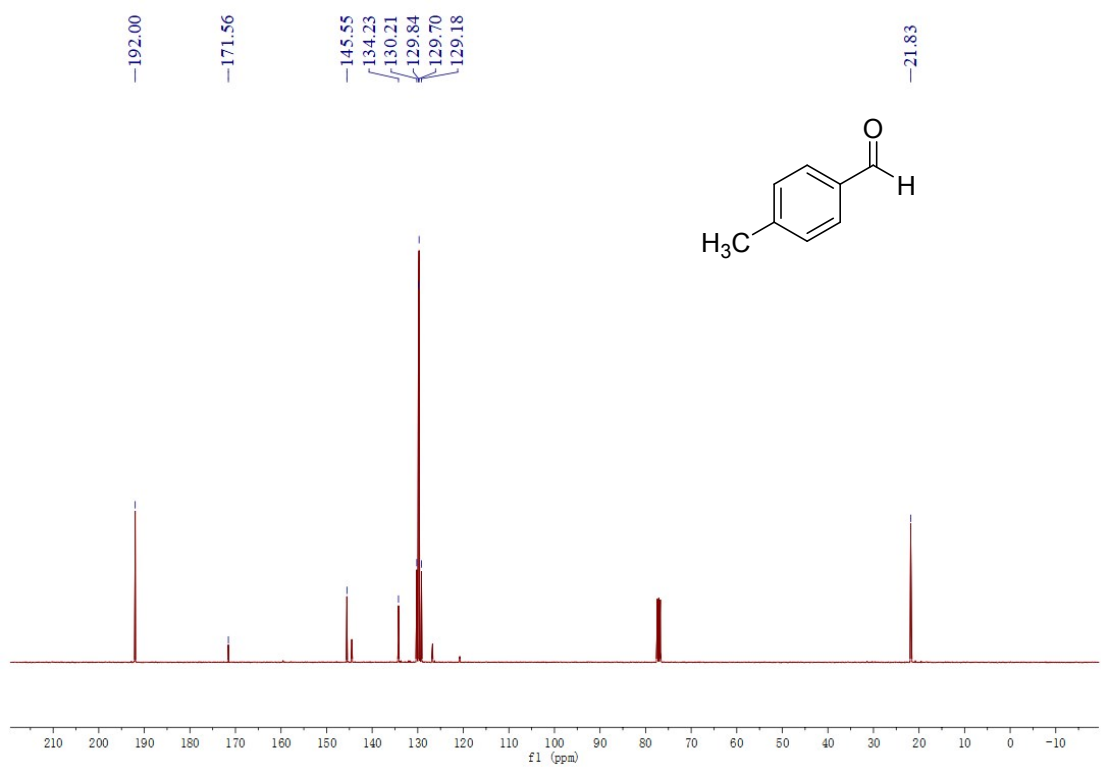


Fig.18 **3i**  $^{13}\text{C}$  NMR

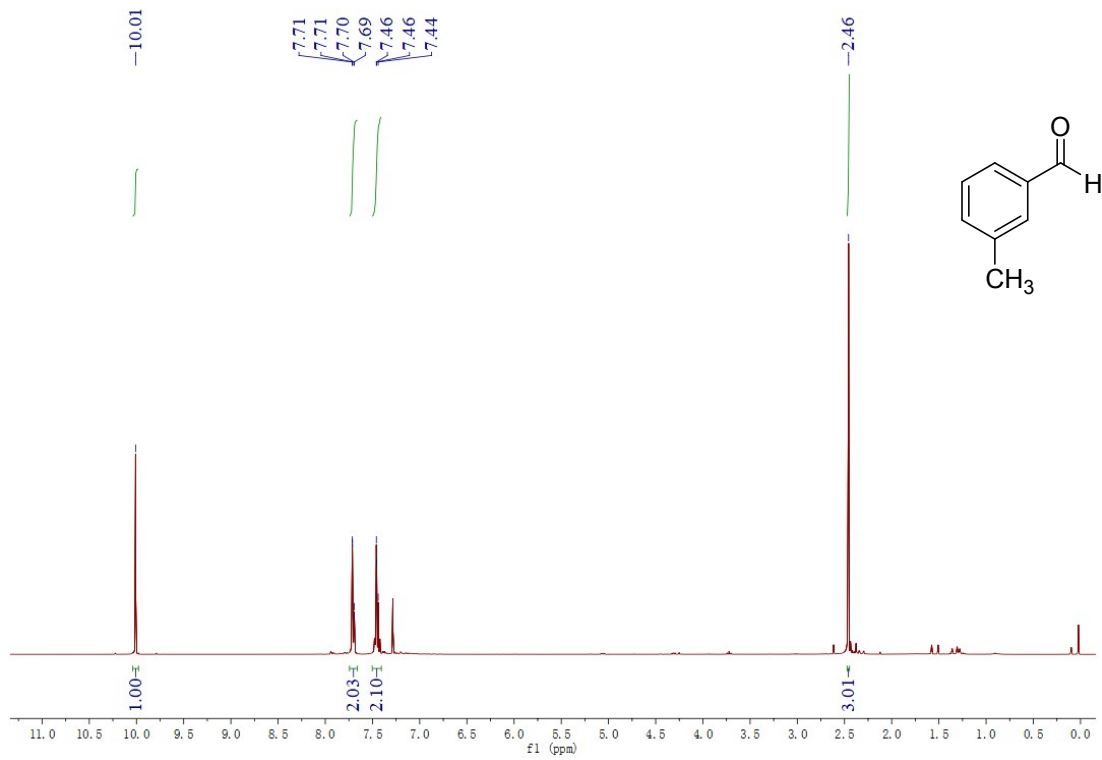


Fig.19 **3j**  $^1\text{H}$  NMR

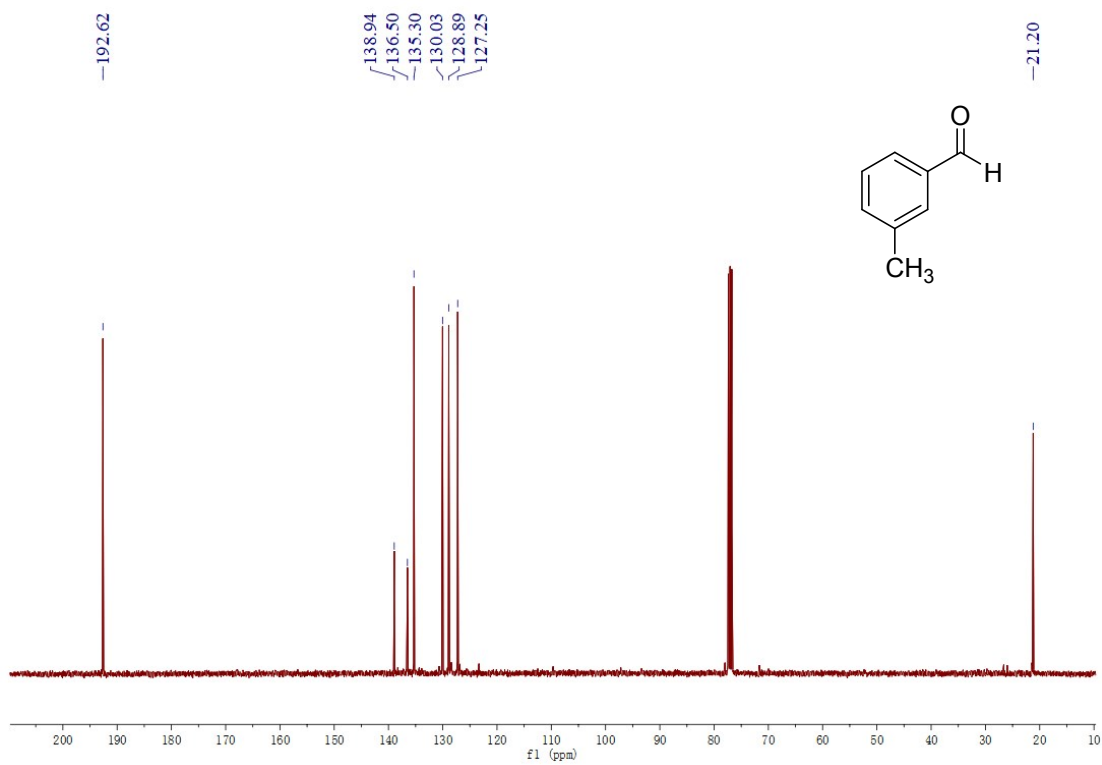


Fig.20 **3j**  $^{13}\text{C}$  NMR

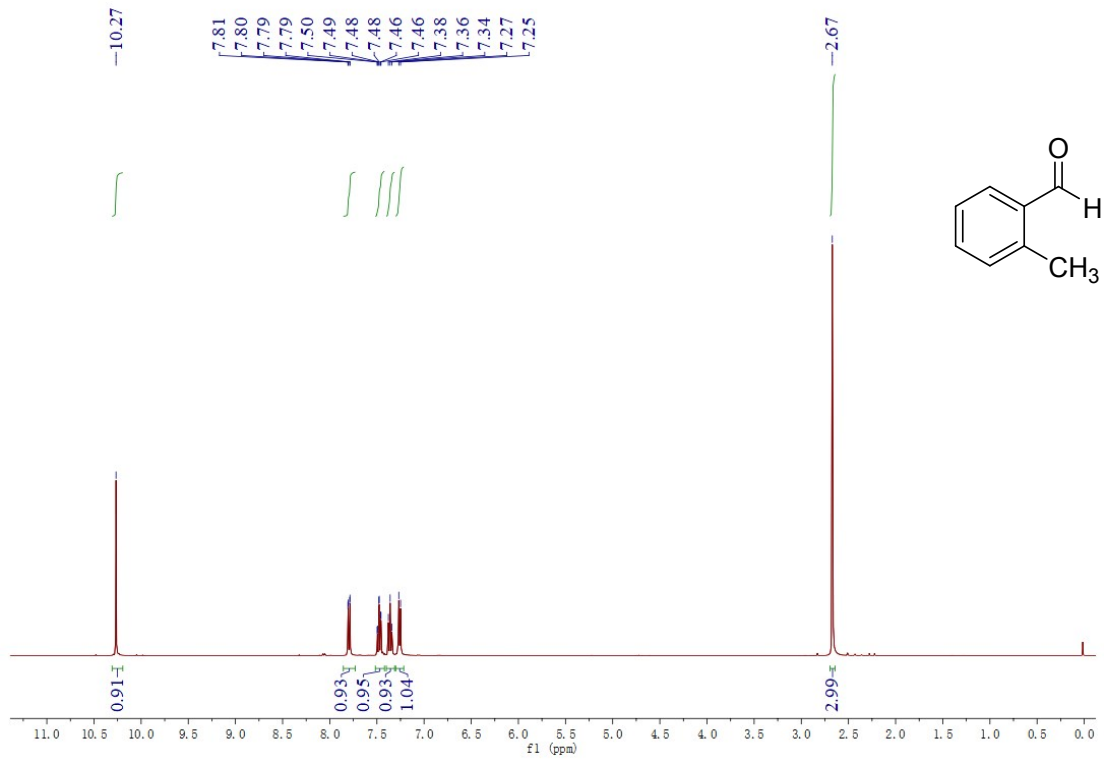


Fig.21 **3k**  $^1\text{H}$  NMR

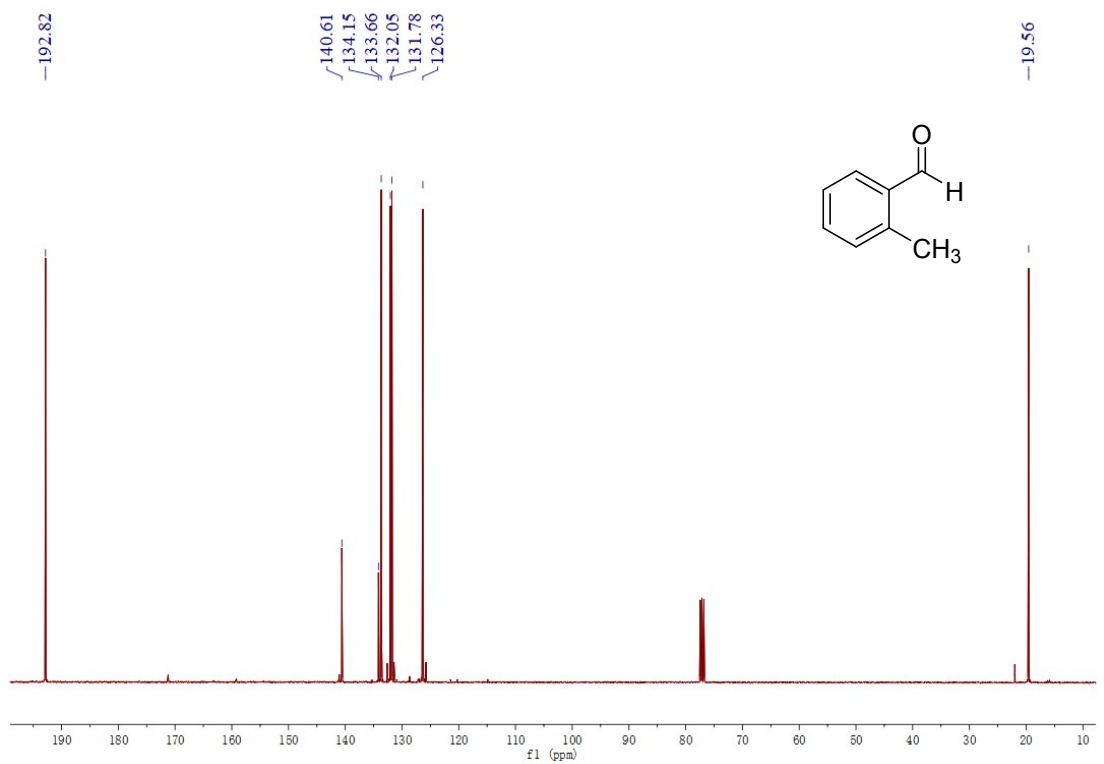


Fig.22 **3k**  $^{13}\text{C}$  NMR

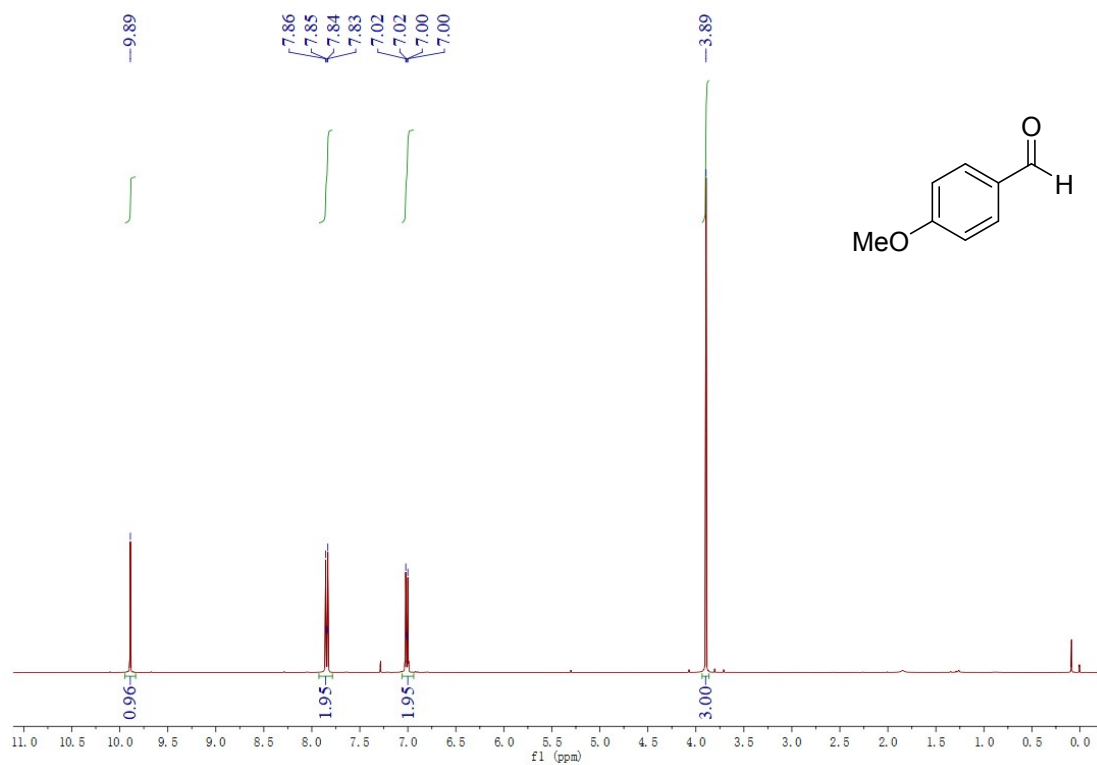


Fig.23 **31**  $^1\text{H}$  NMR

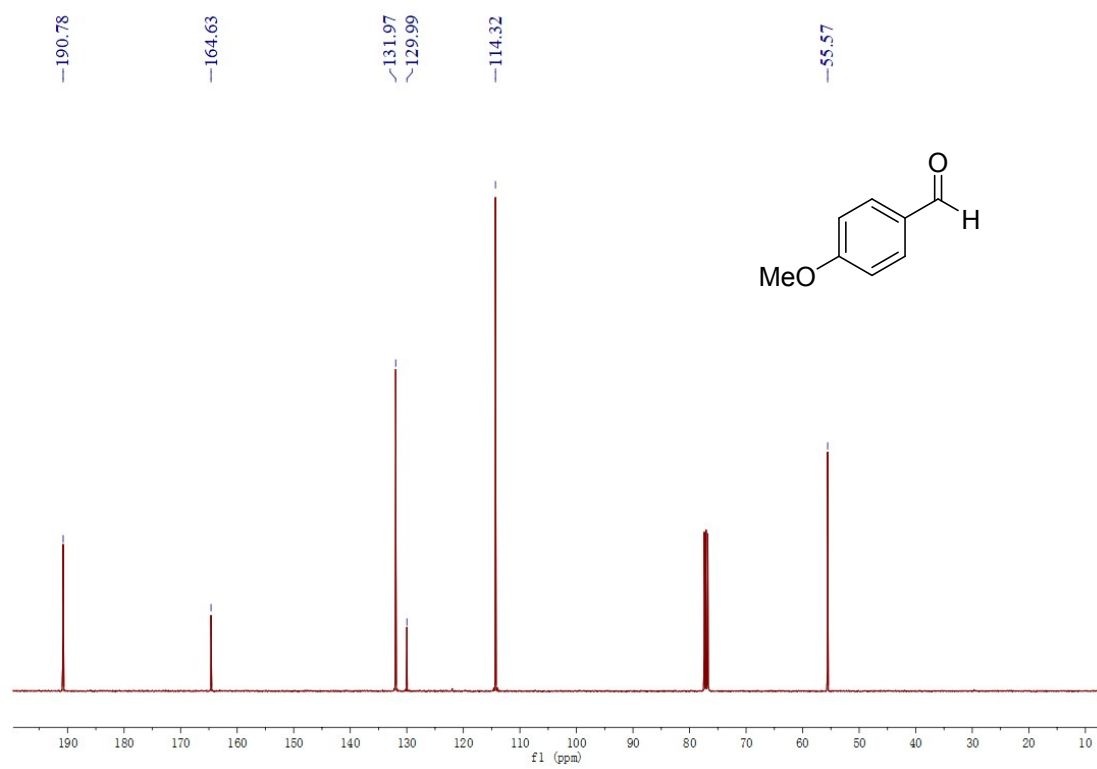


Fig.24 **31**  $^{13}\text{C}$  NMR

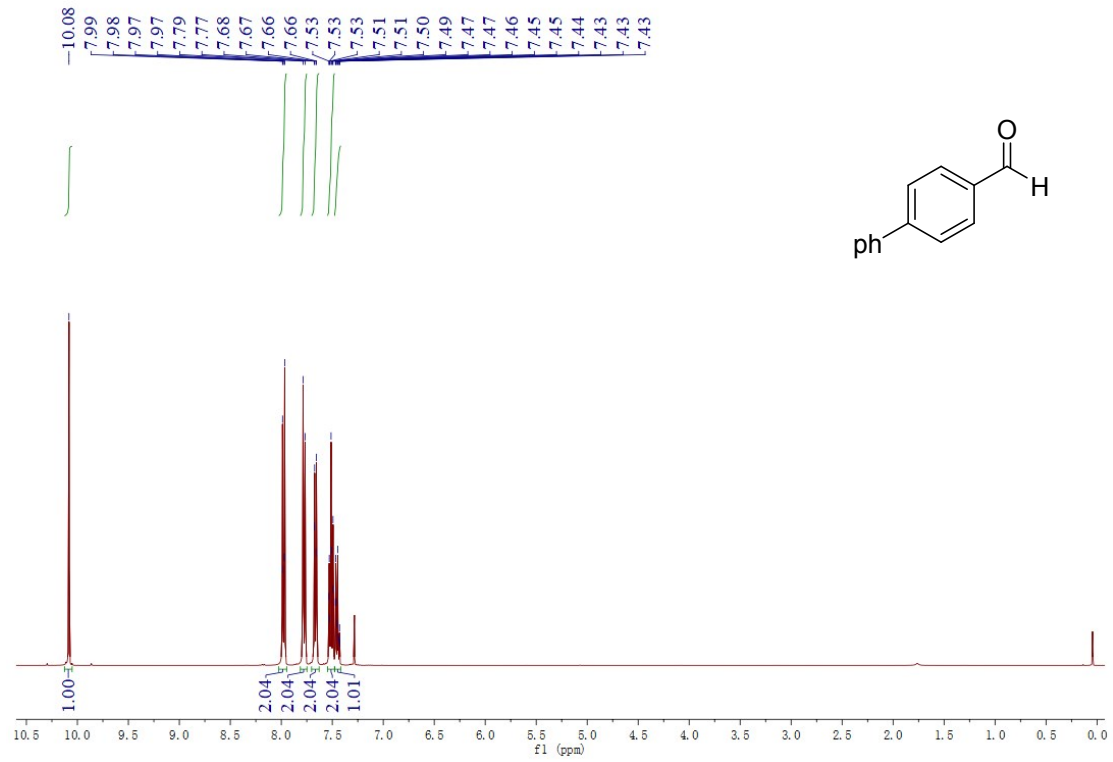


Fig.25 **3m**  $^1\text{H}$  NMR

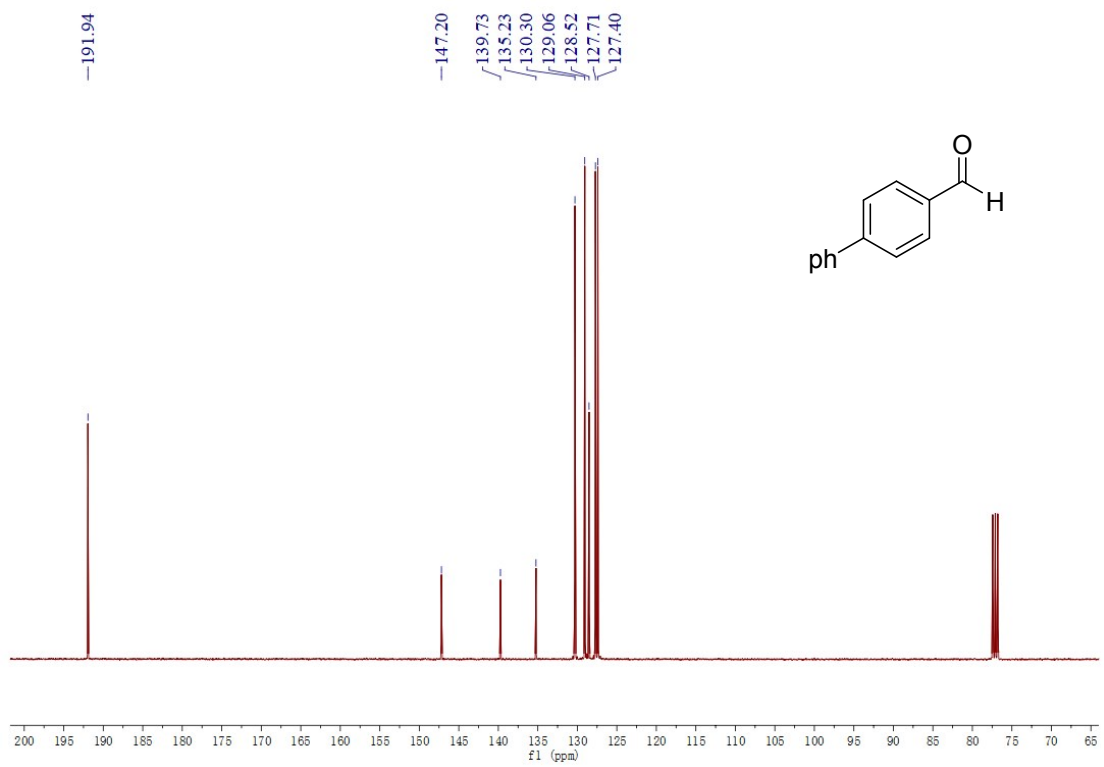


Fig.26 **3m**  $^{13}\text{C}$  NMR



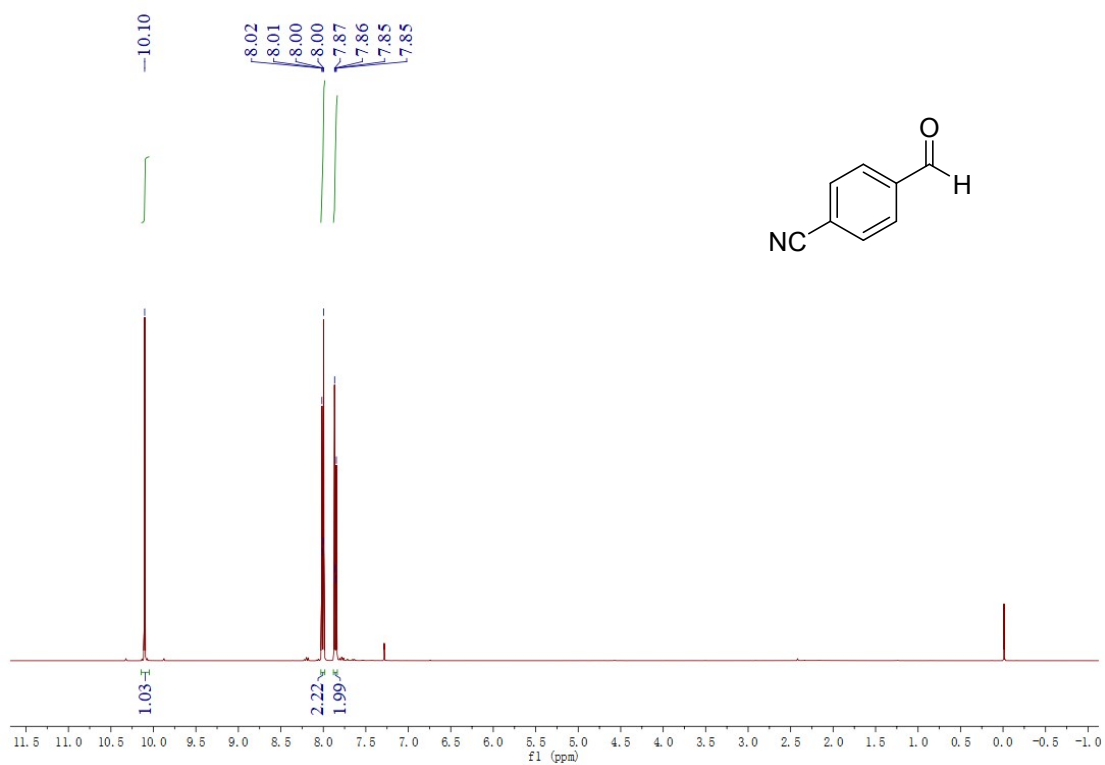


Fig.27 **3n** <sup>1</sup>H NMR

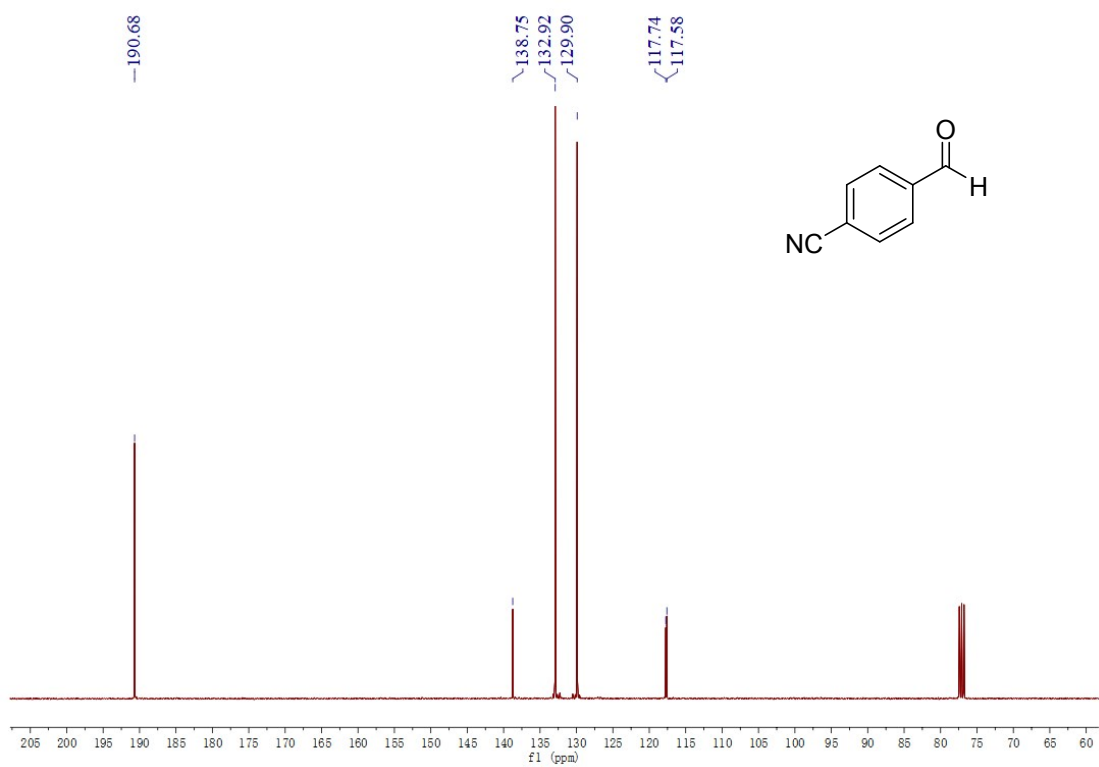


Fig.28 **3n** <sup>13</sup>C NMR

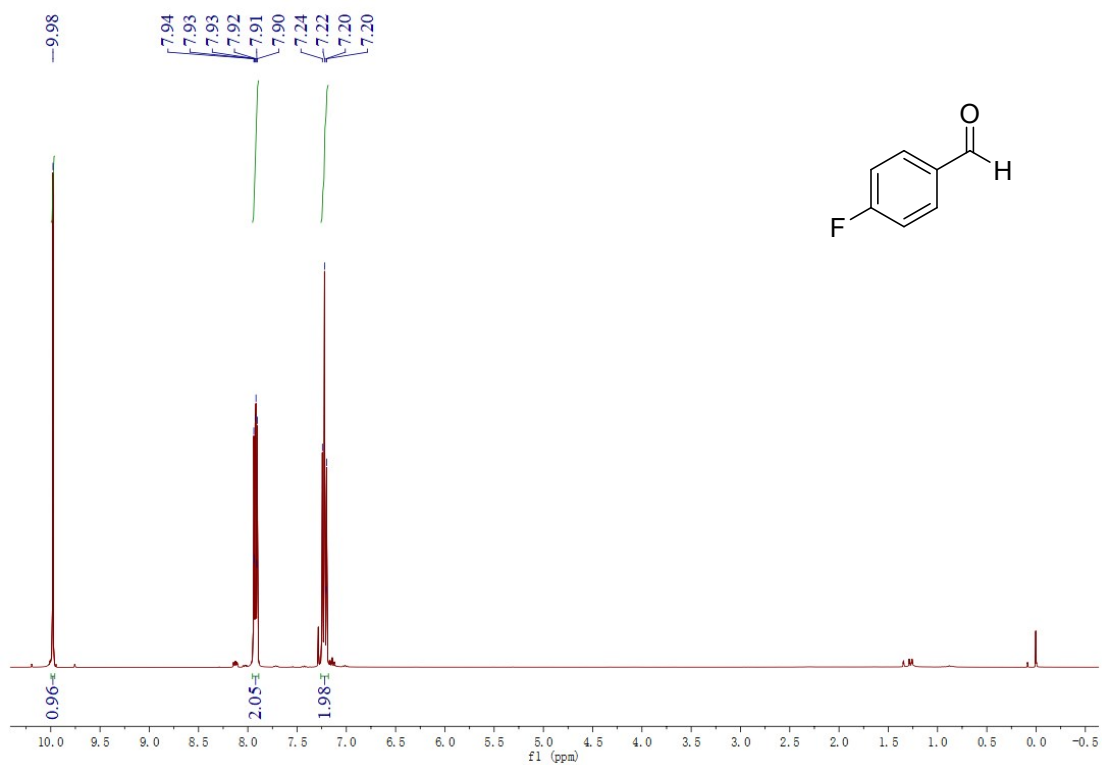


Fig.29 **3o**  $^1\text{H}$  NMR

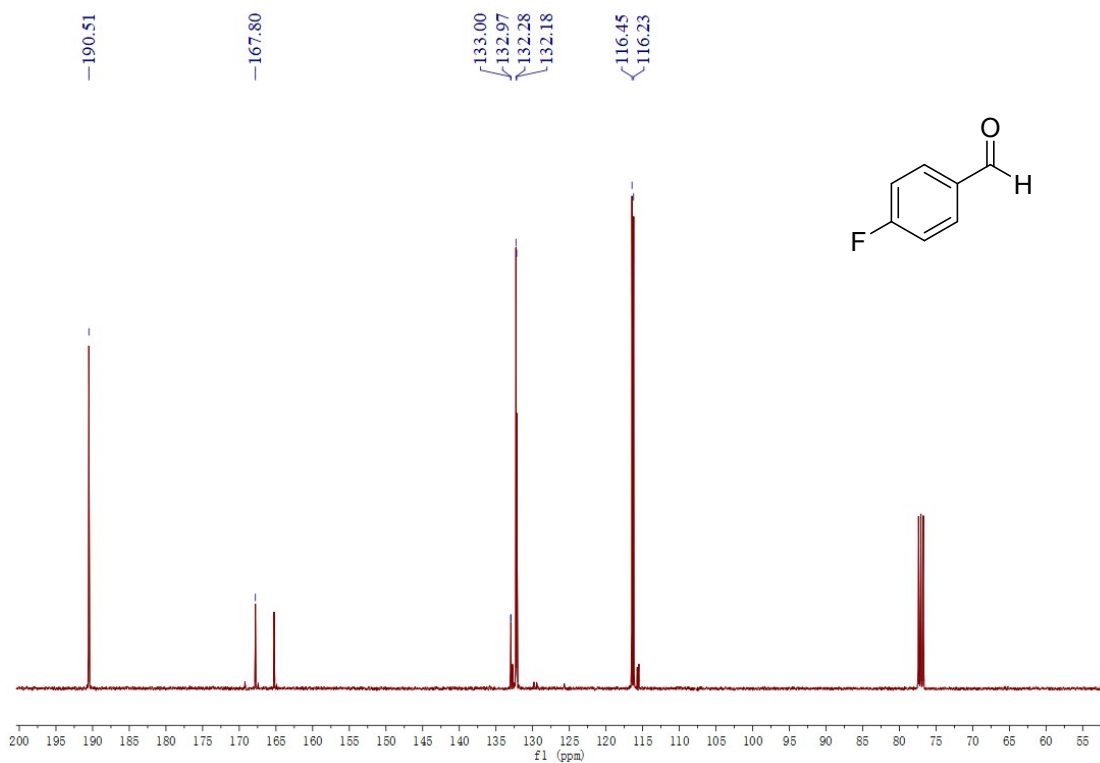


Fig.30 **3o**  $^{13}\text{C}$  NMR

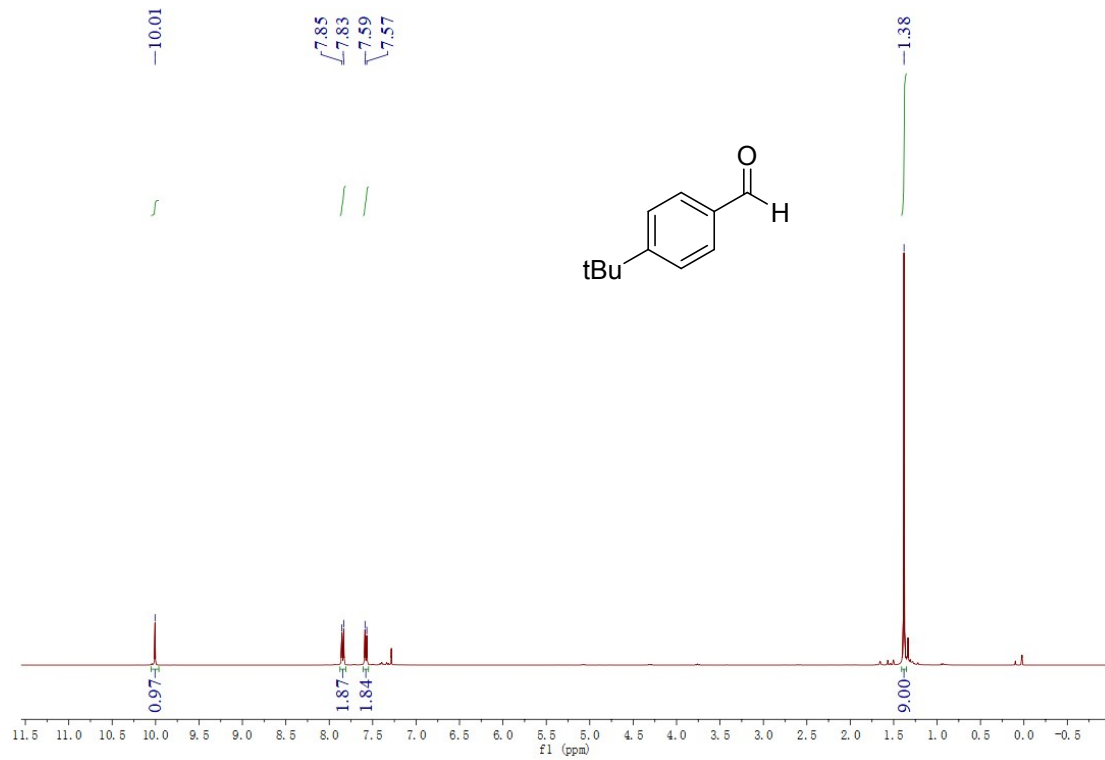


Fig.31 **3p**  $^1\text{H}$  NMR

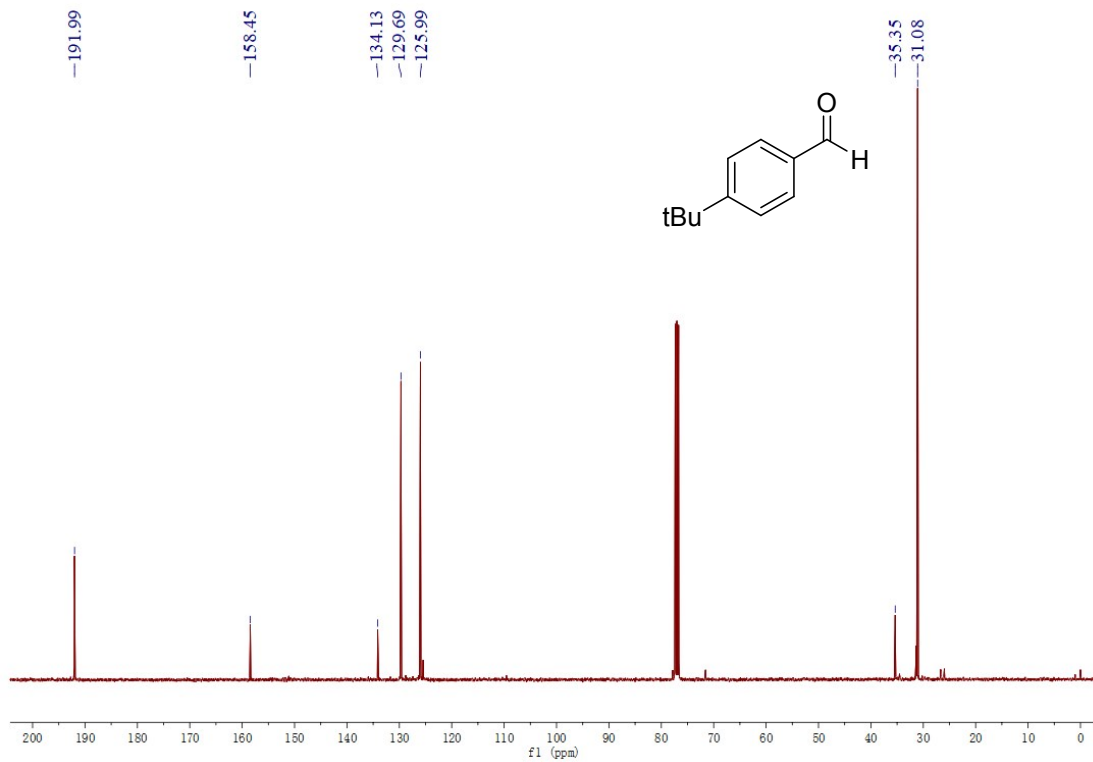


Fig.32 **3p**  $^{13}\text{C}$  NMR

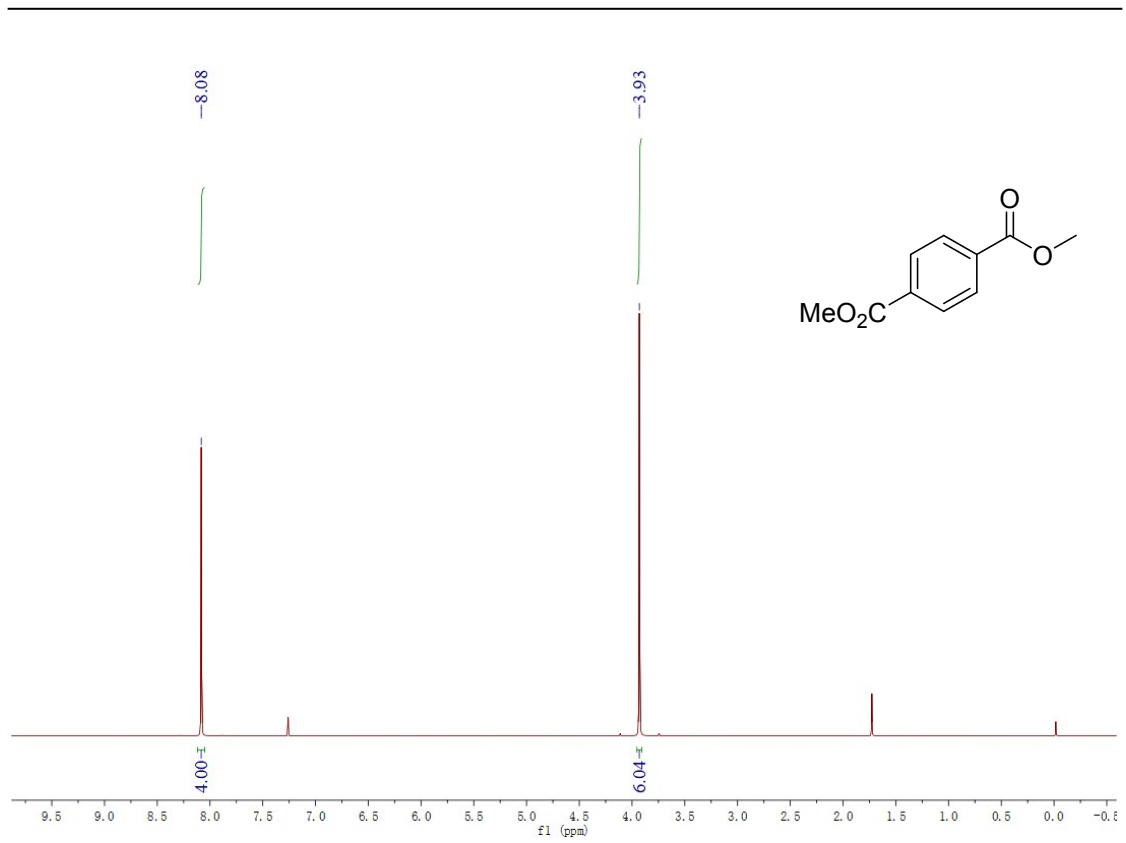


Fig.33 **5a**  $^1\text{H}$  NMR

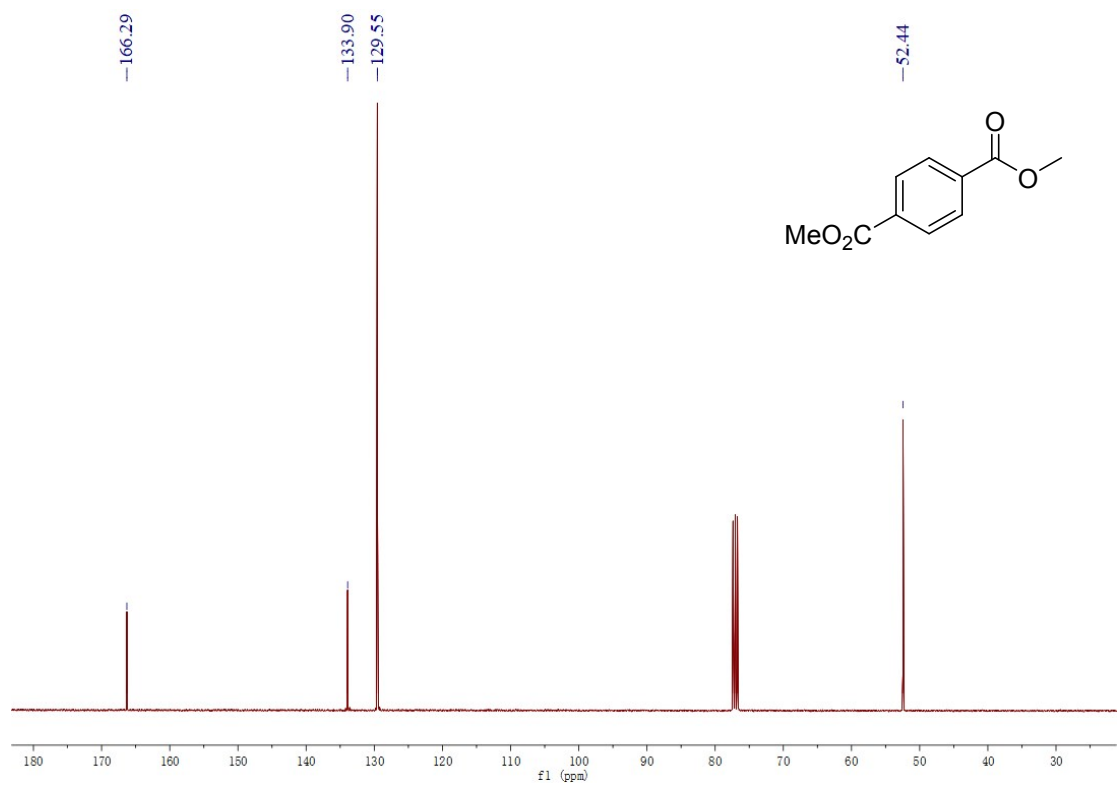


Fig.34 **5a**  $^{13}\text{C}$  NMR

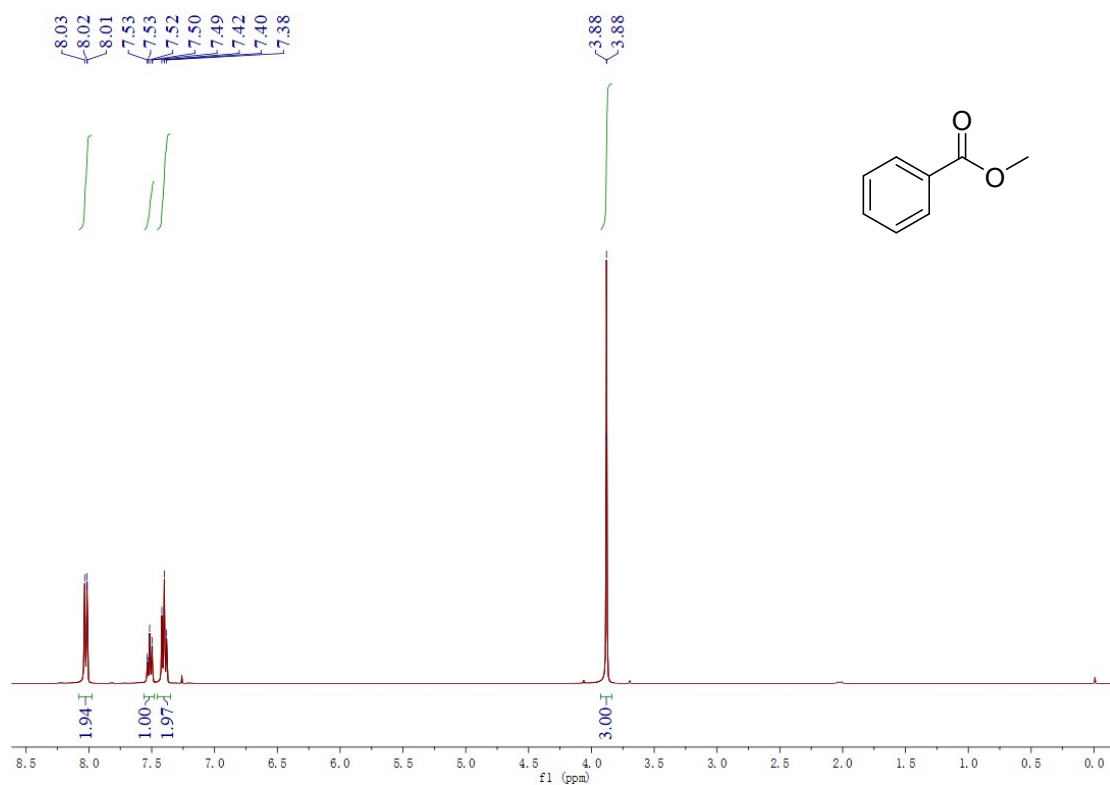


Fig.35 **5b**  $^1\text{H}$  NMR

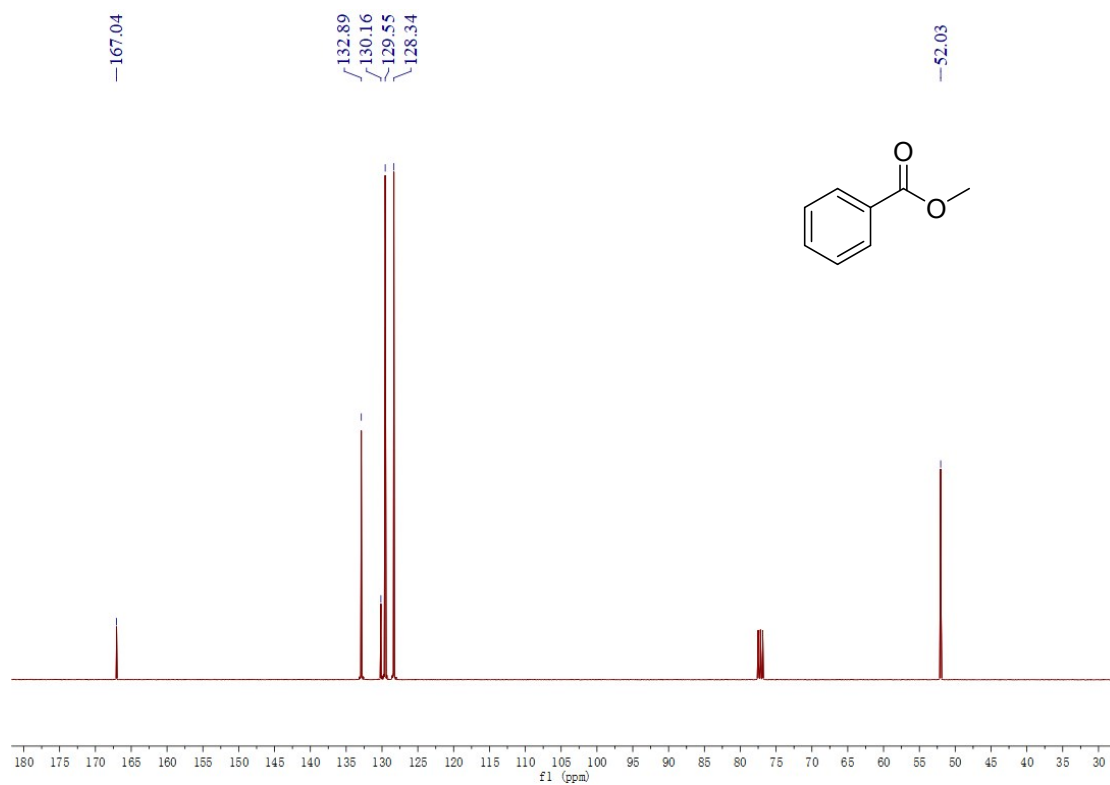


Fig.36 **5b**  $^{13}\text{C}$  NMR

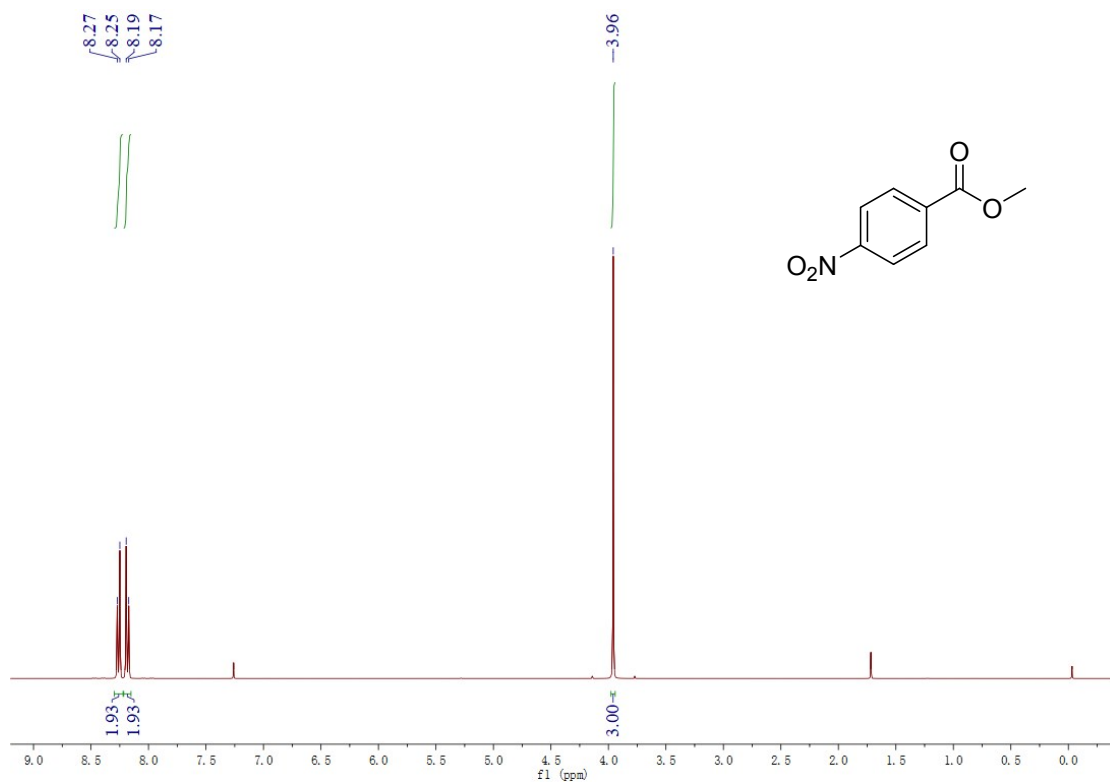


Fig.37 **5c**  $^1\text{H}$  NMR

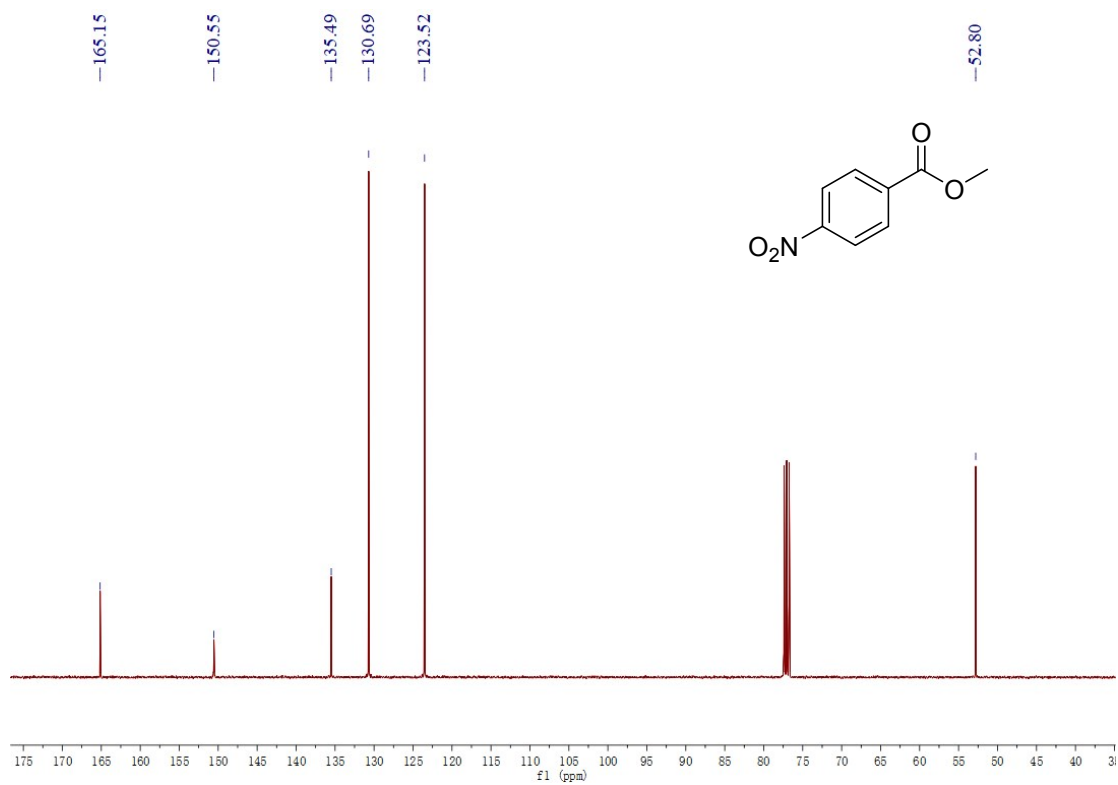


Fig.38 **5c**  $^{13}\text{C}$  NMR

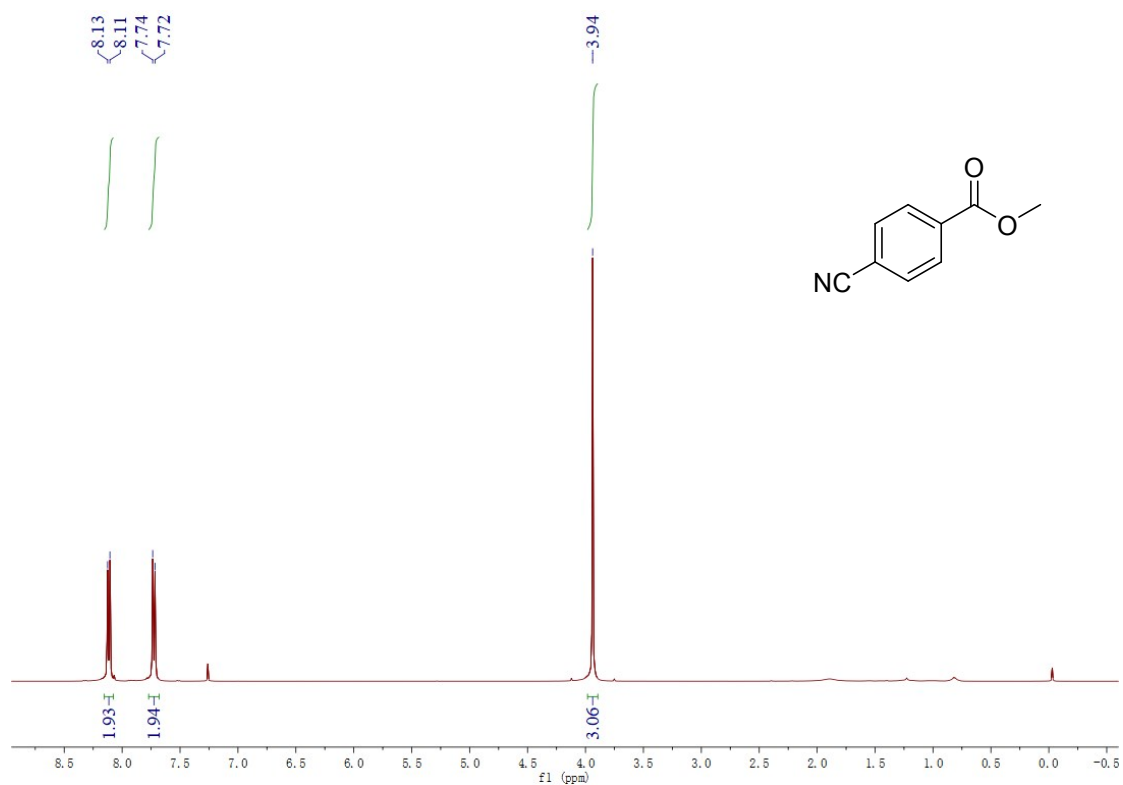


Fig.39 **5d**  $^1\text{H}$  NMR

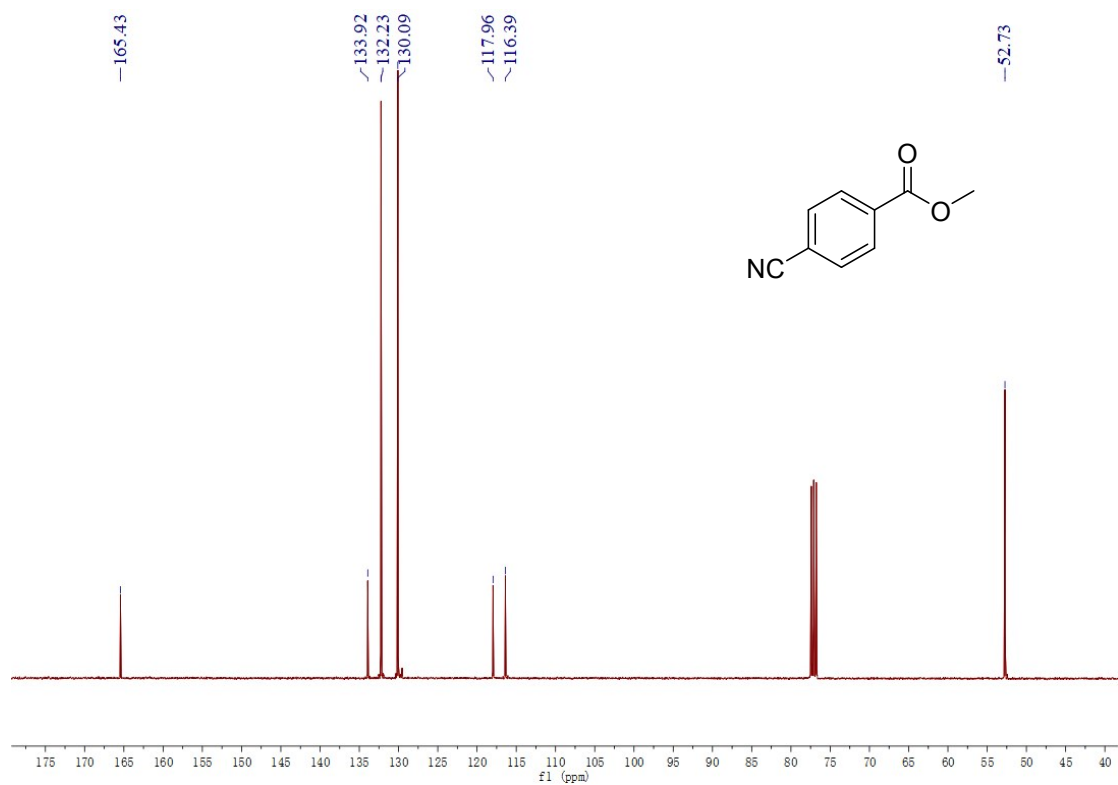


Fig.40 **5d**  $^{13}\text{C}$  NMR

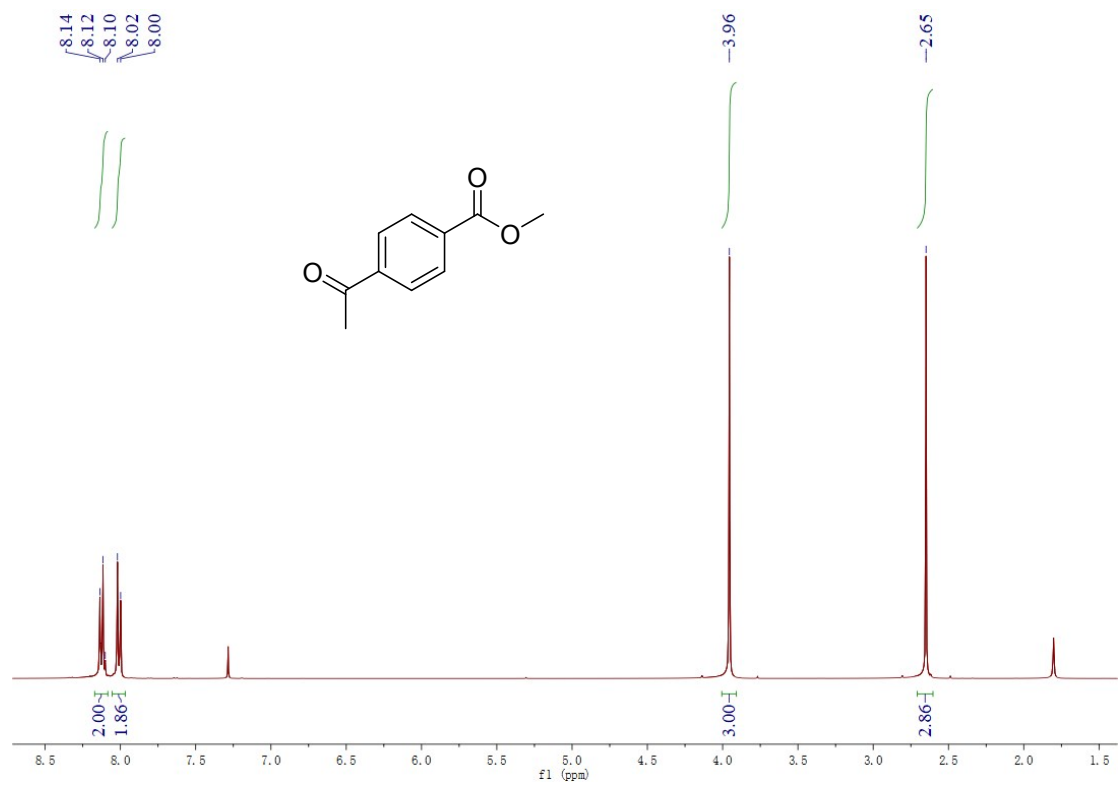


Fig.41 5e <sup>1</sup>H NMR

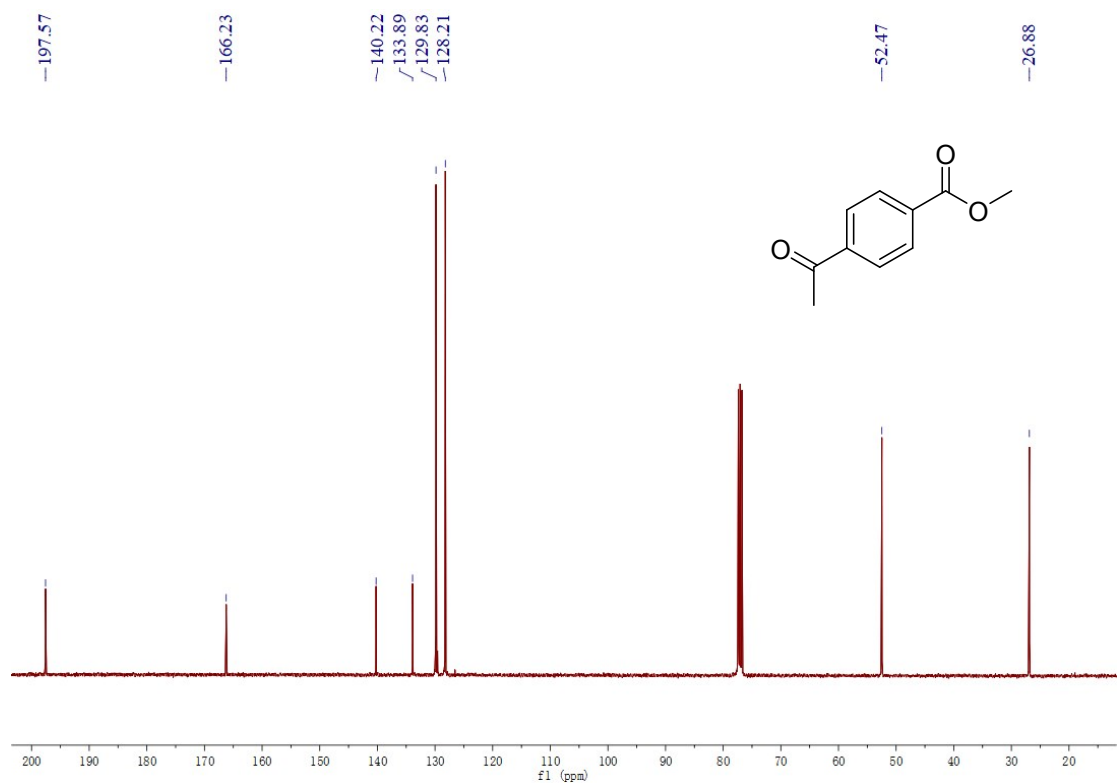


Fig.42 5e <sup>13</sup>C NMR



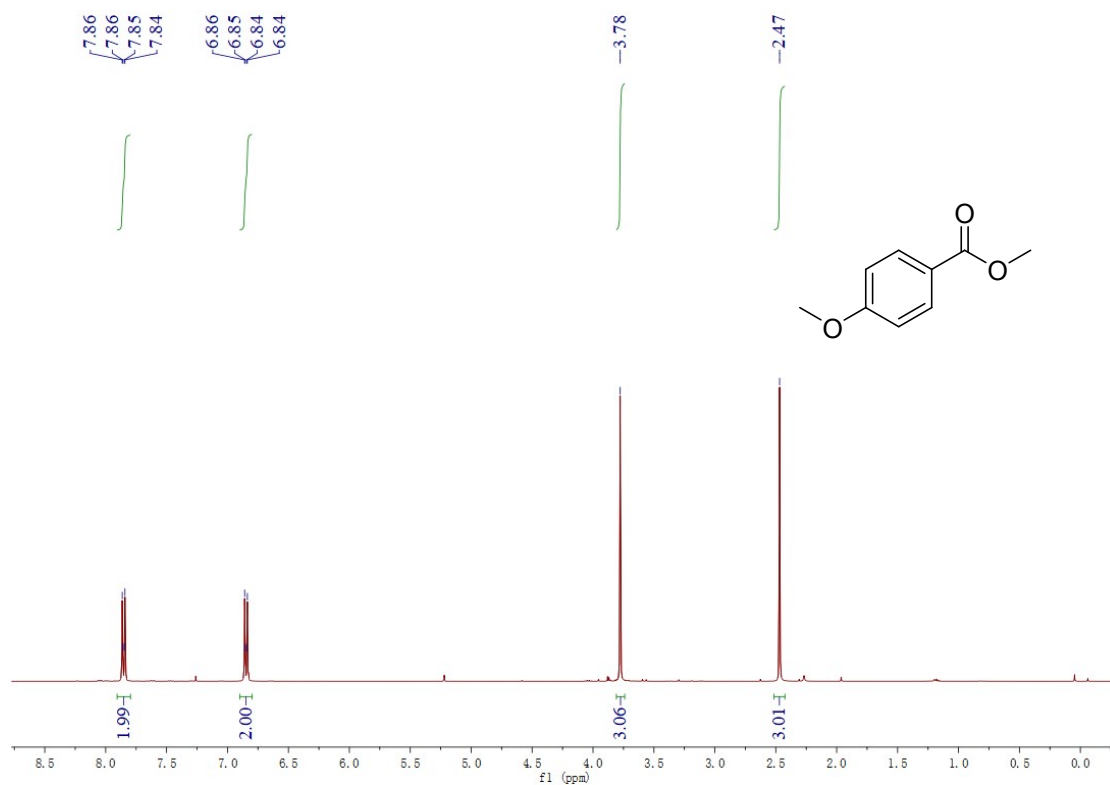


Fig.43 **5f**  $^1\text{H}$  NMR

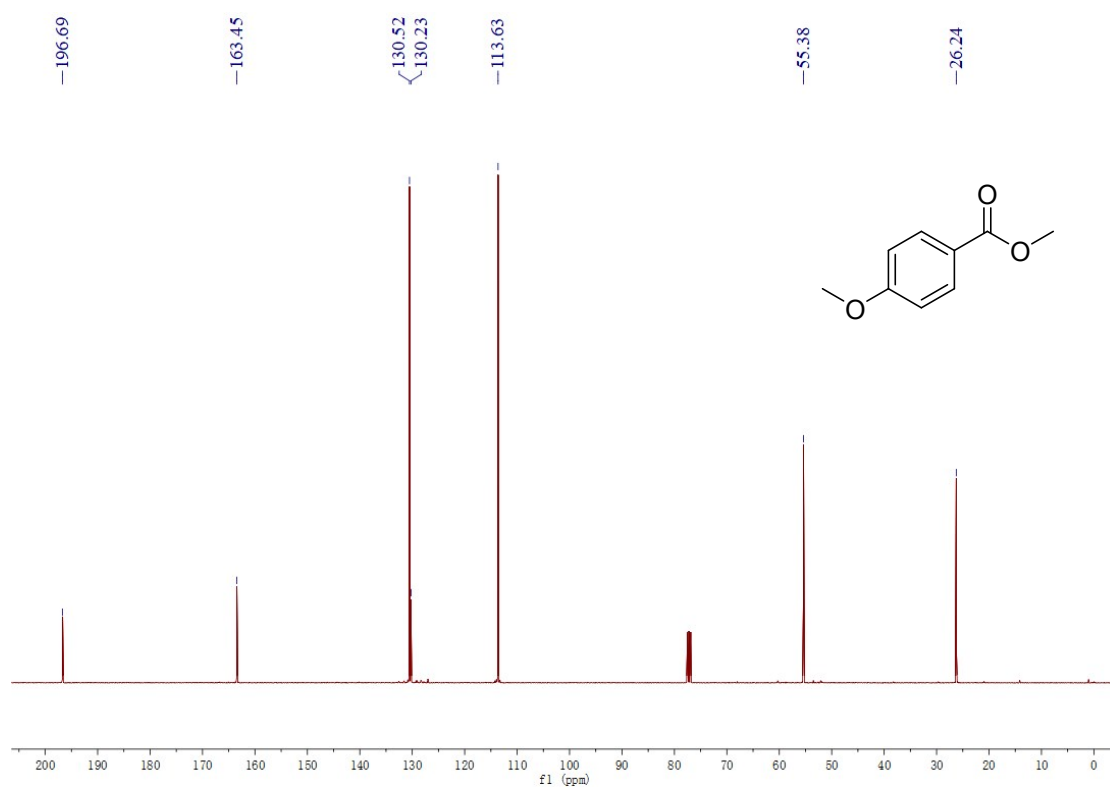


Fig.44 **5f**  $^{13}\text{C}$  NMR

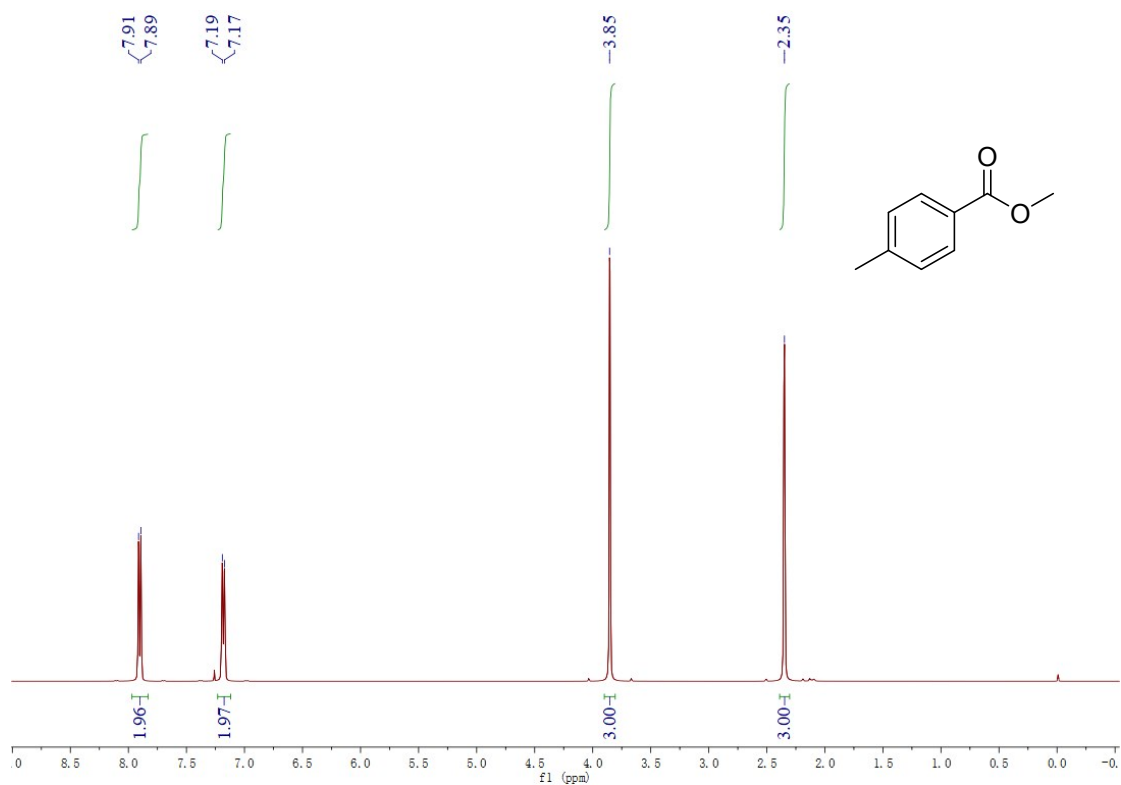


Fig.45 **5g**  $^1\text{H}$  NMR

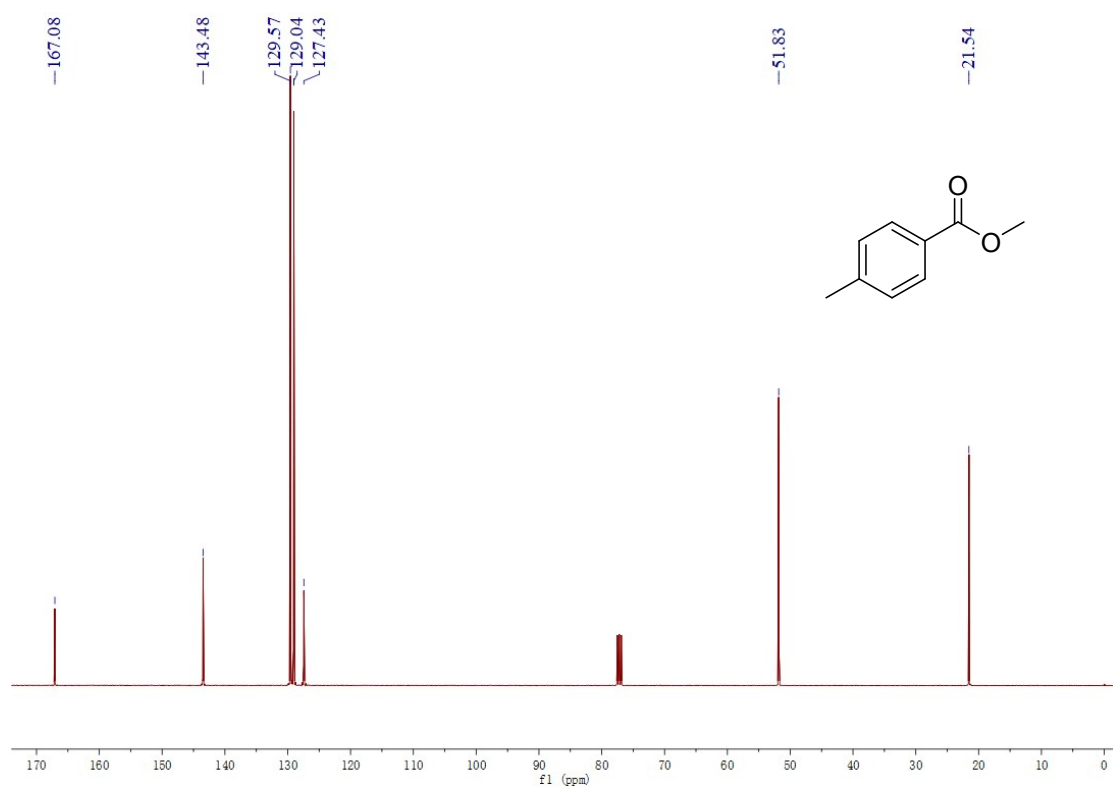


Fig.46 **5g**  $^{13}\text{C}$  NMR

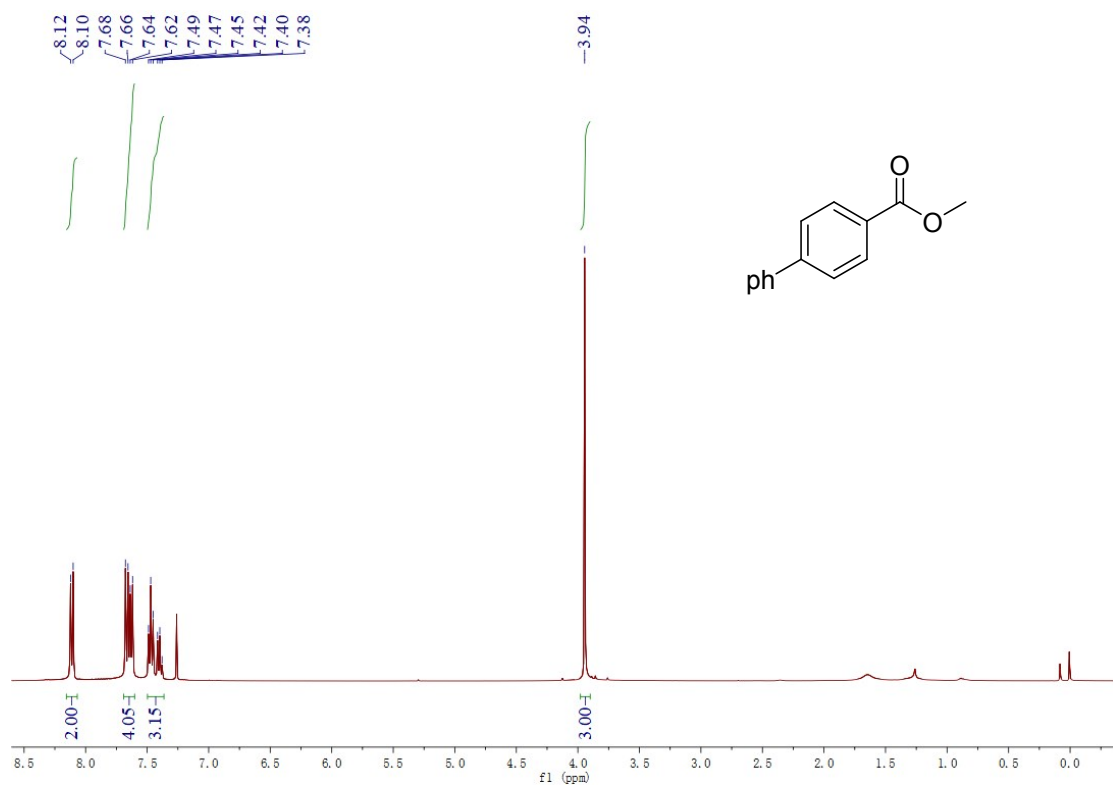


Fig.47 **5h**  $^1\text{H}$  NMR

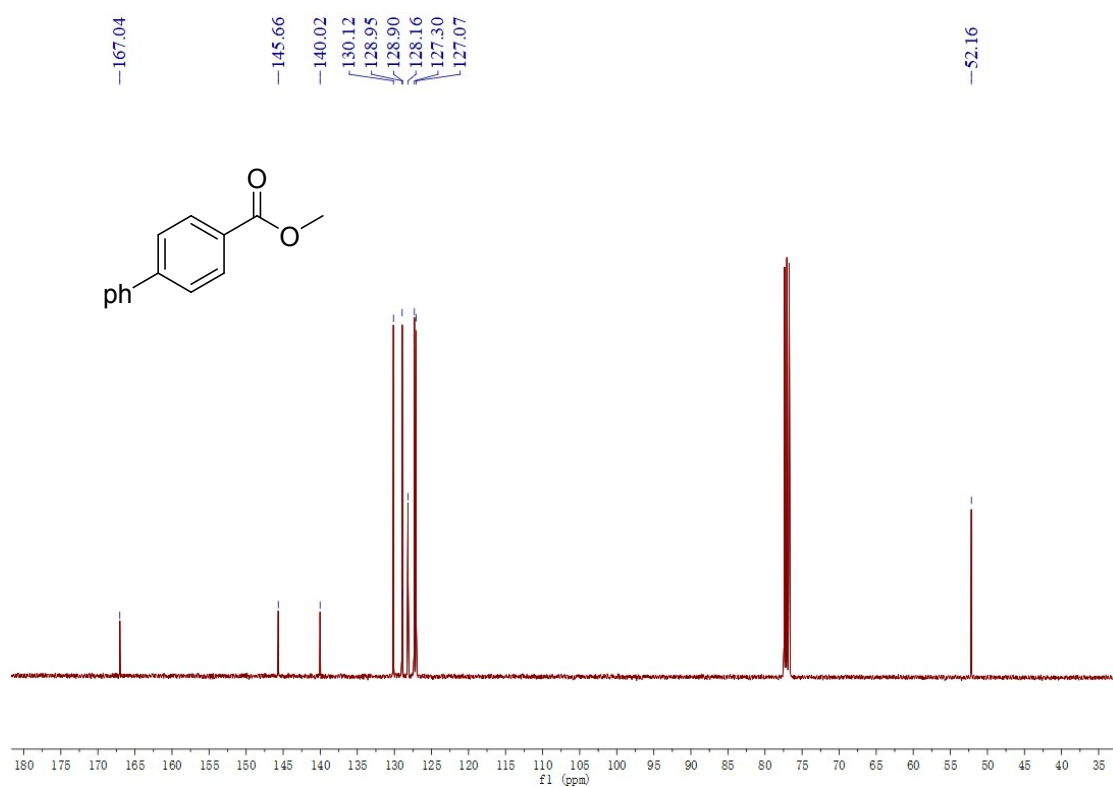


Fig.48 **5h**  $^{13}\text{C}$  NMR

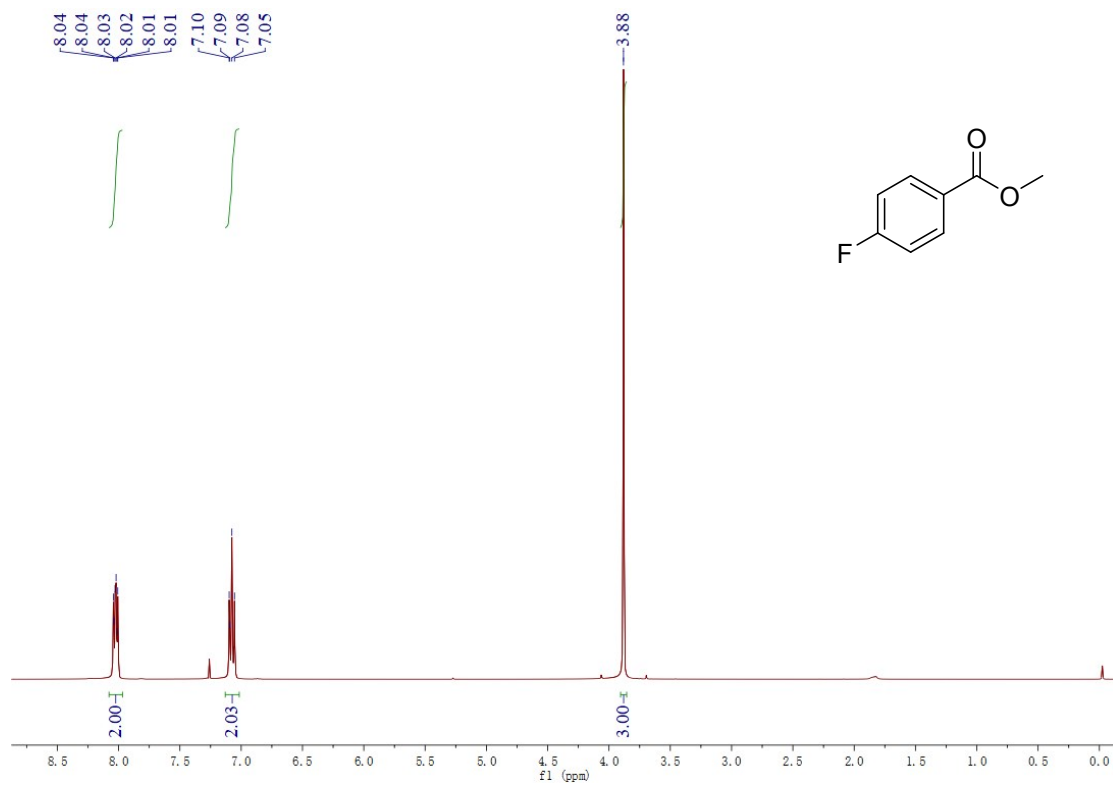


Fig.49 5i <sup>1</sup>H NMR

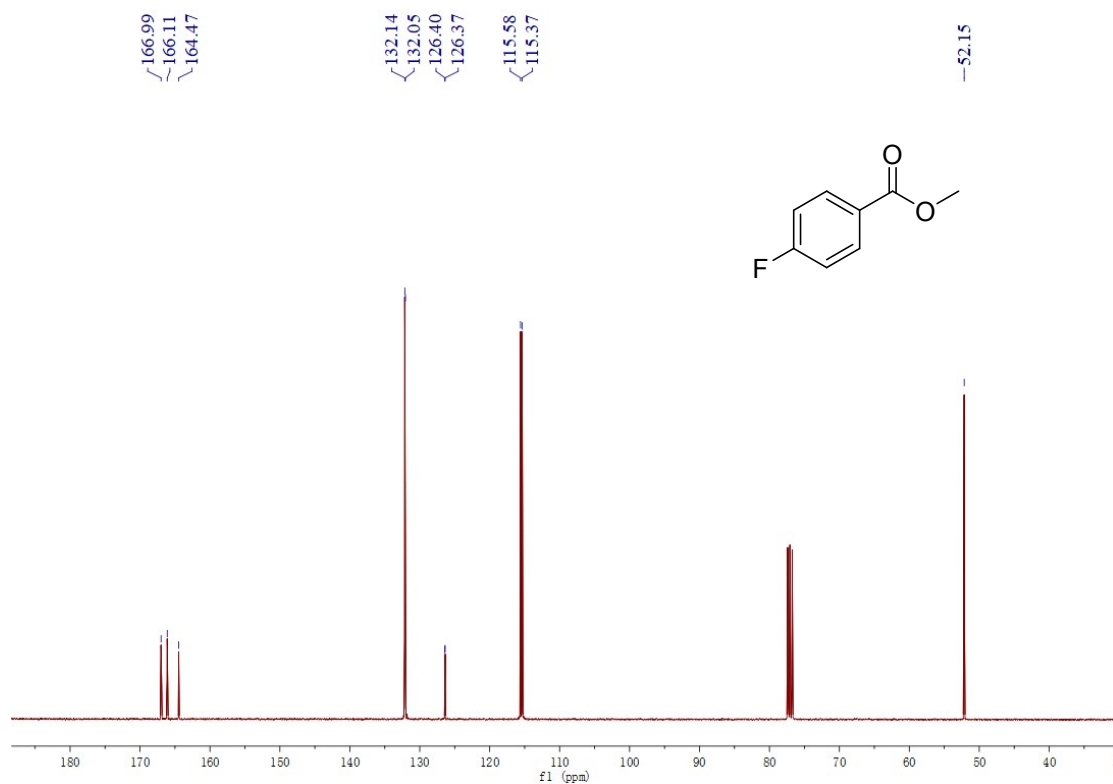


Fig.50 5i <sup>13</sup>C NMR

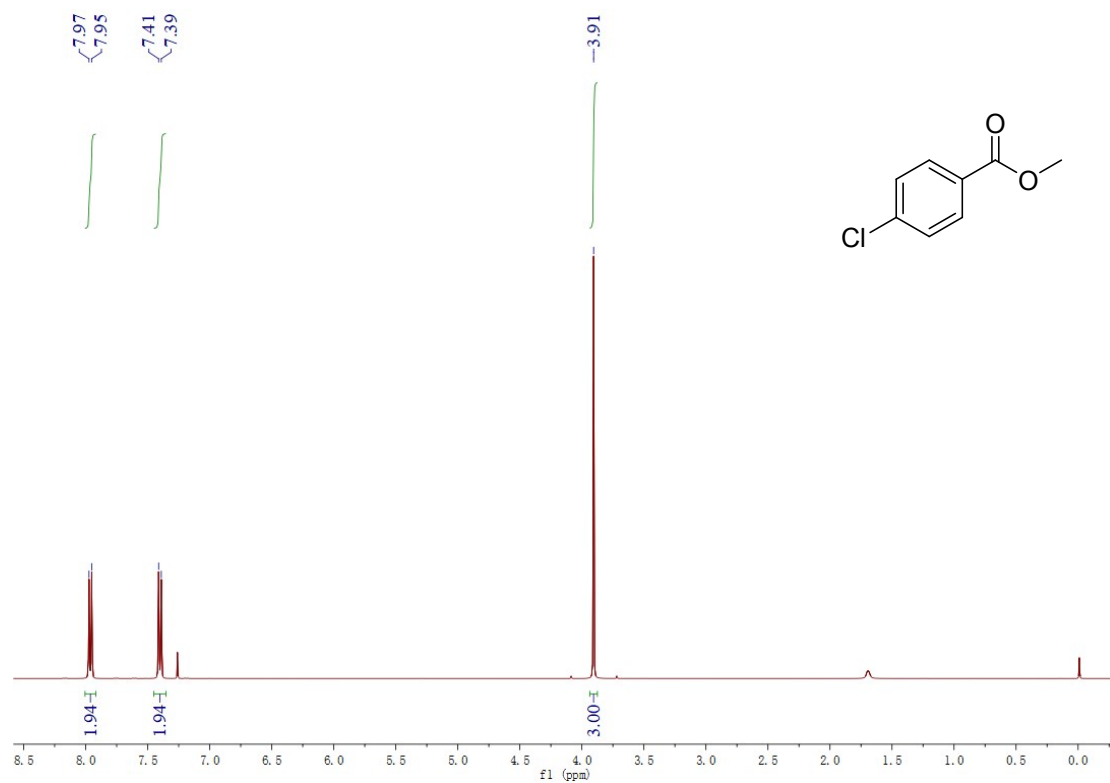


Fig.51 5j  $^1\text{H}$  NMR

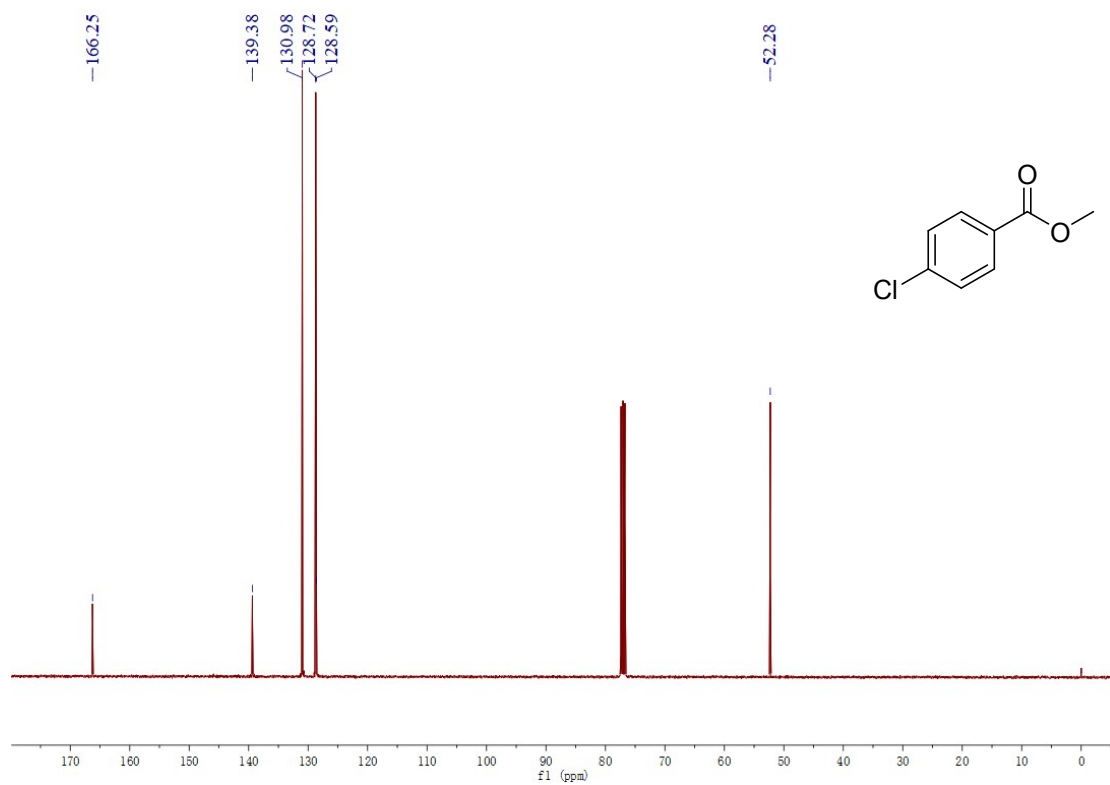


Fig.52 5j  $^{13}\text{C}$  NMR

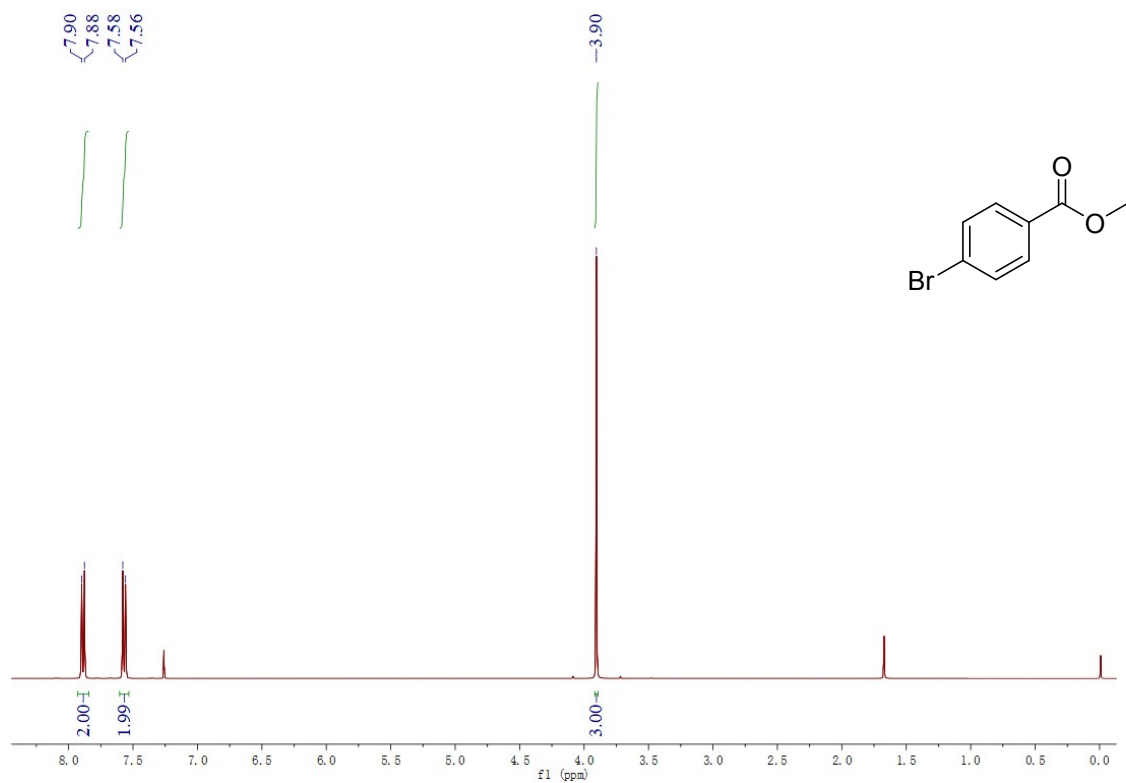


Fig.53 **5k**  $^1\text{H}$  NMR

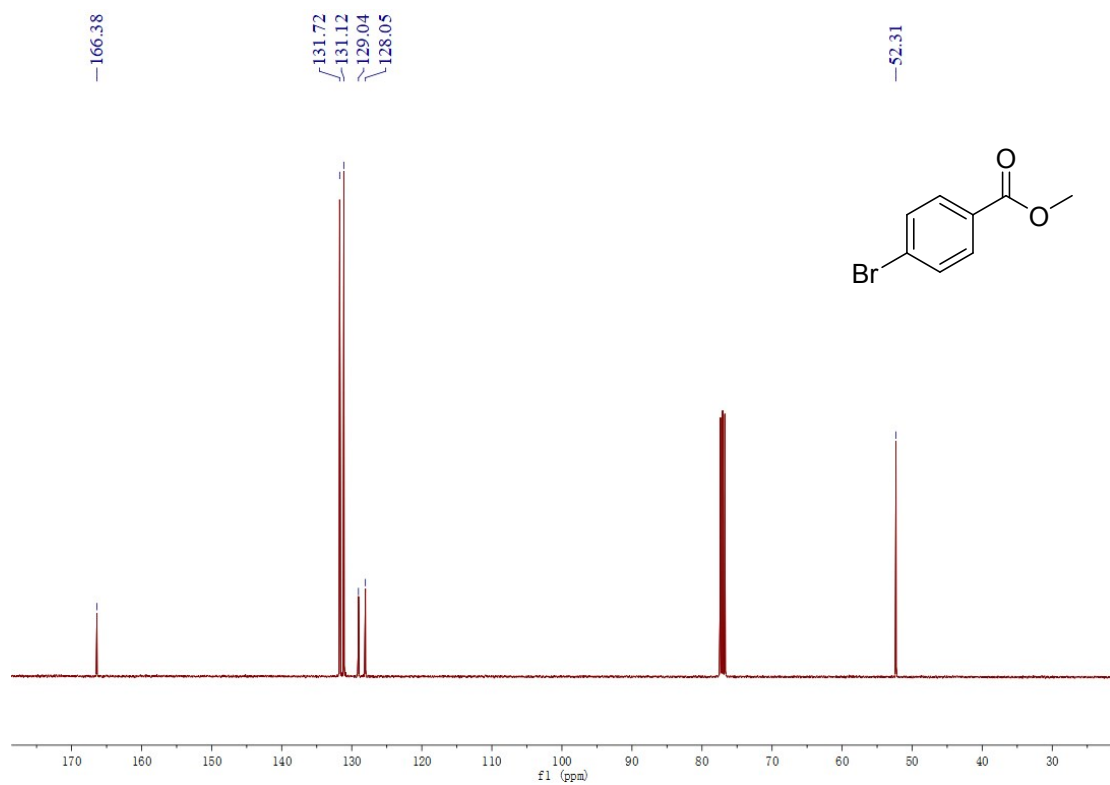


Fig.54 **5k**  $^{13}\text{C}$  NMR