Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Vilsmeier–Haack reagent mediated synthetic transformations with immobilized iridium complex photoredox catalyst

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Supplementary Informations

1. General procedures for oxime synthesis

To a solution of aldehyde/ketone (0.01 mol) in absolute ethanol (5 ml) was added a solution of hydroxylamine hydrochloride 0.6 g (0.008 mol) in water (1.2 ml). After heating under reflux for 5 minutes, a solution of sodium hydroxide (1 g) in water (2 ml) was added dropwise and reacted for 30 minutes to 2 hours, and the progress of the reaction was monitored by a thin layer chromatography plate. After completion of the reaction, it was cooled to room temperature, and 10-20 ml of a 25% sulfuric acid solution was added thereto, followed by extraction with 20 ml of ethyl acetate. The organic phase was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The product was isolated by column chromatography, and the yield was over 85%.

2. General procedures for synthesis of the immobilized iridium complex

The immobilized iridium complex was synthesized according to the method in our previous work. Briefly, 4-vinylpyridine (0.886g, 8.5mmol, Vpy), divinylbenzene (2.202 g, 17 mmol), azobisisobutyronitrile (AIBN, 0.01 g) and 20 ml ethyl acetate were mixed and stirred for 2 h at room temperature to form the homogeneous solution. Then, the solution was transferred to an stainless-steel autoclave and heated at 100 °C for 24 h in an oven to form the white organic gel. The gel was dried at room temperature overnight and ground to powder. The obtained powder was washed with hot acetone. The copolymer was obtained after drying at 80 °C in an oven for 12 h with the yield over 95%.

Tetrakis-(2-phenylpyridine)-bis-(μ-chloro)-diiridium(III) (0.14mmol, 0.152 g) and copolymer (4mmol, 0.234g, calculated with the molar amount of pyridine, the content of pyridyl moiety in the copolymers was determined by elemental analysis) were mixed in 10 mL glycol. The mixture was stirred at **150** °C for 2 h under Ar atmosphere. Then, after cooling to room temperature, the celadon powder was filtered, washed and dried in a vacuum oven at 50 °C for 24 h to afford the supported catalyst 0.331g (85%).

3. Gram scale reactions

Synthesis of amides:

To a solution of diphenylmethanone oxime (1.48 g, 7.5 mmol, 1.0 euqiv), CBr_4 (4.97 g, 15.0 mmol) and DMF (1.5 mmol) in acetonitrile (150 mL) $Ir(ppy)_2$(PDVB-ppy) (0.4 mol%) was added. The flask was sealed and the reaction mixture sparged with Argon for 30min. The reaction vessel was stirred 4cm away from a 20 W blue LEDs and irradiated for 12h. Centrifugal removal of catalyst, quenched with saturated aqueous sodium bicarbonate (200 mL) and extracted with ethyl acetate. The organic phase was dried over anhydrous magnesium sulfate and evaporated to give crude product. The crude mixture was purified by silica gel column chromatography gave product **2a**, yield 90% (1.33 g).

Synthesis of nitriles:

In a flask was charged with 4-biphenyl carboxaldehyde oxime (1.48 g, 7.5 mmol, 1.0 euqiv), CBr_4 (6.22 g, 18.8 mmol), $Ir(ppy)_2$(PDVB-ppy) (0.8 mol%), DMF (1.5 mmol) in acetonitrile (150 mL). The flask was sealed and the reaction mixture sparged with Argon for 10min, and irradiated with a 20 W blue LEDs for 12 h. Centrifugal removal of catalyst, quenched with saturated aqueous sodium bicarbonate (200 mL) and extracted with ethyl acetate. The organic phase was dried over anhydrous magnesium sulfate and evaporated to give crude product. The crude mixture was purified by silica gel column chromatography gave product **4i**, yield 86% (1.15 g).

Synthesis of anhydrides:

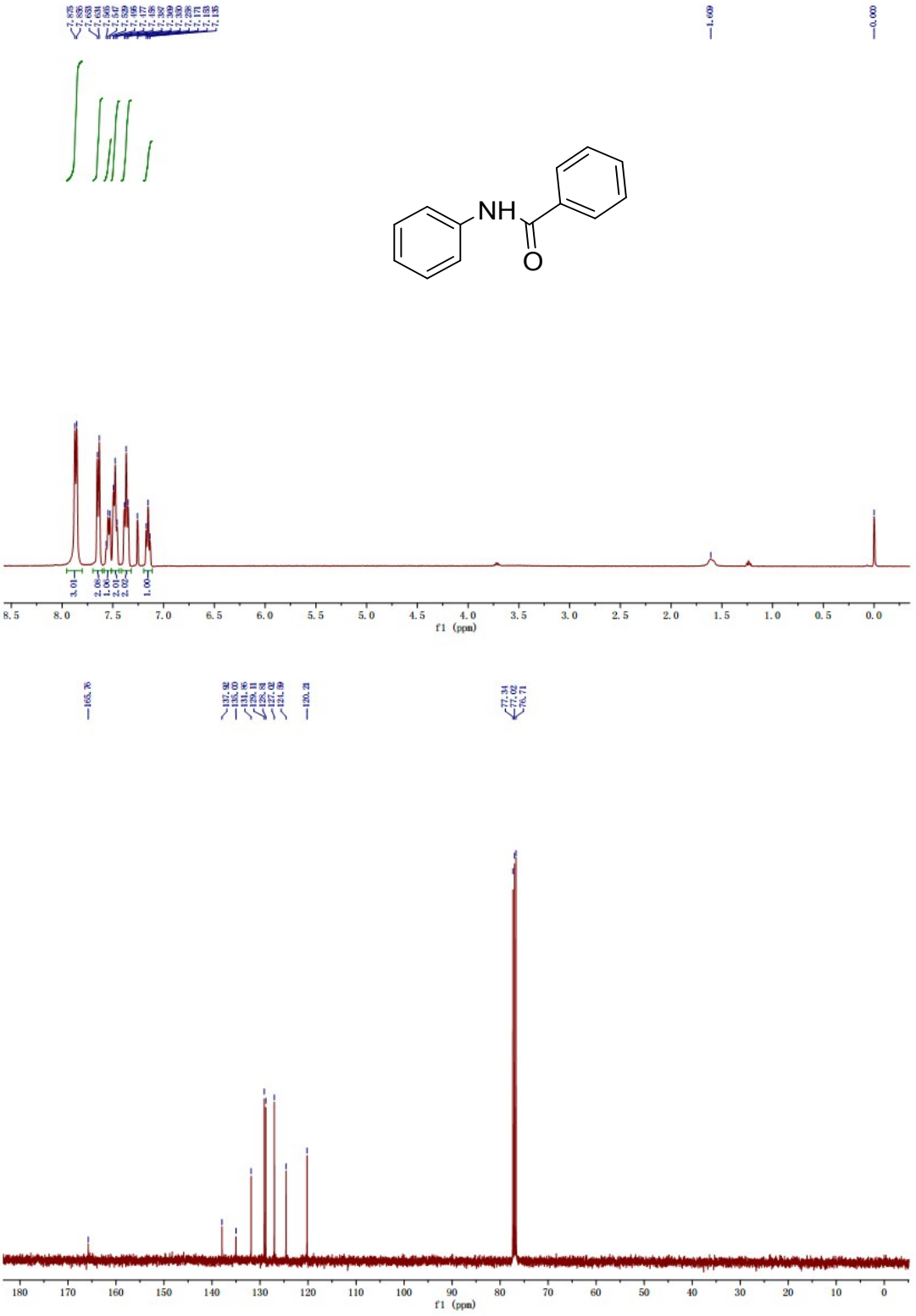
In a falsk was charged with 4-methylbenzoic acid (1.36 g, 10.0 mmol, 1.0 euqiv), CBr_4 (6.63 g, 20.0 mmol), $Ir(ppy)_2$(PDVB-ppy) (0.4 mol%), DMF (2.0 mmol), 2,6-dimethylpyridine (2.14 g, 20.0 mmol) in acetonitrile (200 mL). The flask was irradiated with a 20 W blue LEDs for 18h. Centrifugal removal of catalyst, quenched with water and extracted with ethyl acetate. The organic solvent is washed with saturated aqueous sodium bicarbonate (150 ml) and NaCl solution (150 ml), dried over anhydrous magnesium sulfate and evaporated to give crude product. The crude mixture was purified by column chromatography gave product **7b**, yield 84% (1.07 g).

4. Photoreaction setup for scale-up reactions

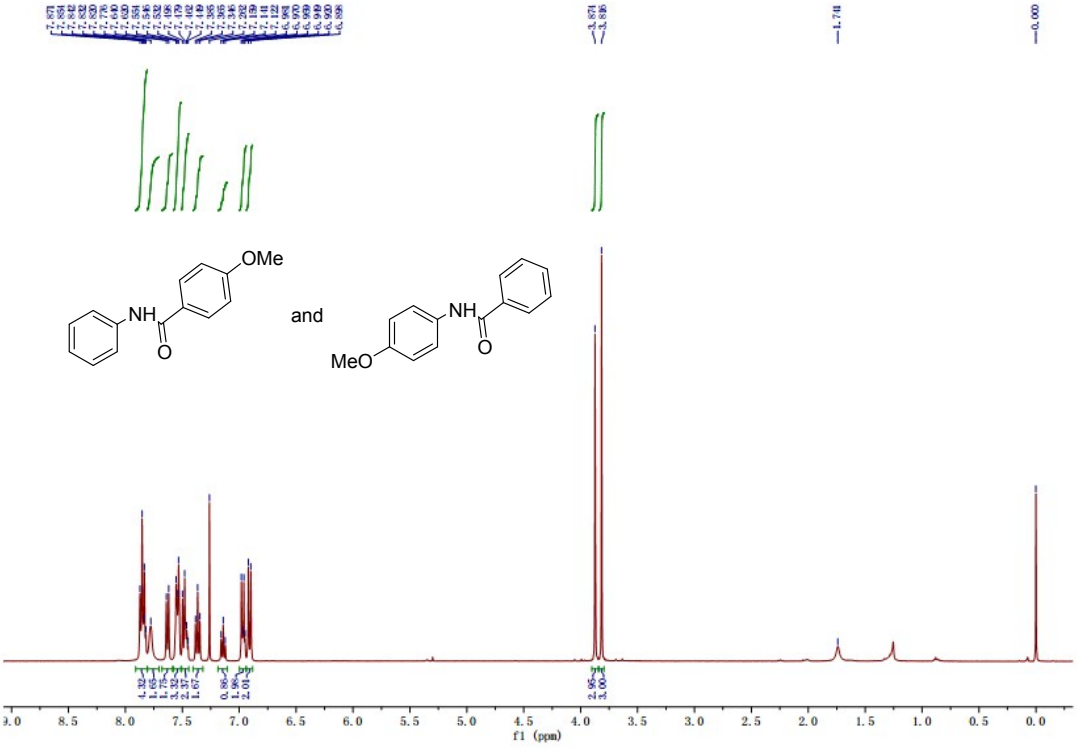
Figure 1s Photoreaction setup for scale-up reaction under 20W blue LED irradiation.

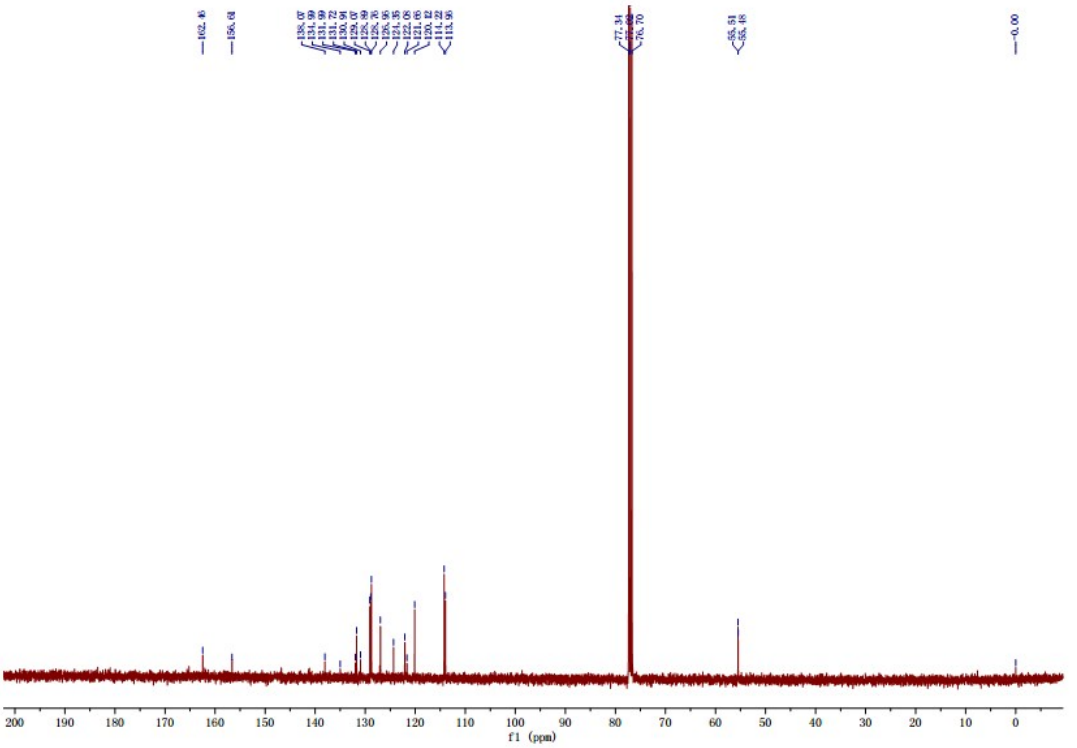
5. ^{1}H NMR and ^{13}C NMR spectra of compounds 2-7.

N-phenylbenzamide:

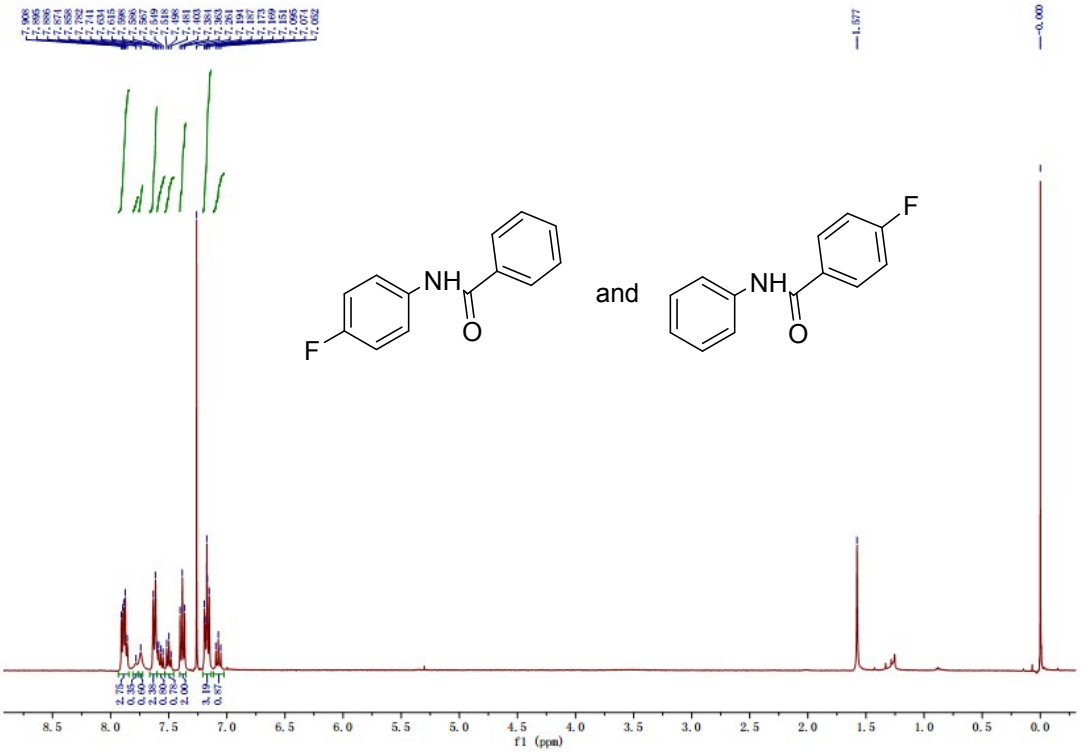


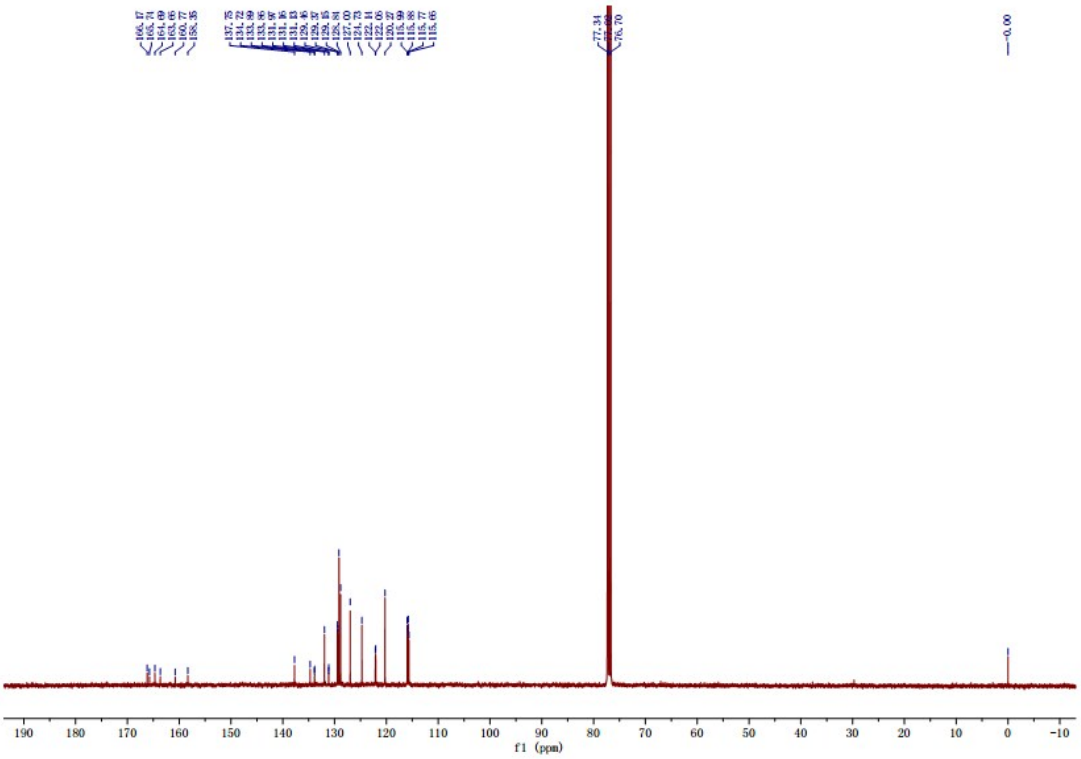
4-methoxy-N-phenylbenzamide and N-(4-methoxyphenyl)benzamide:



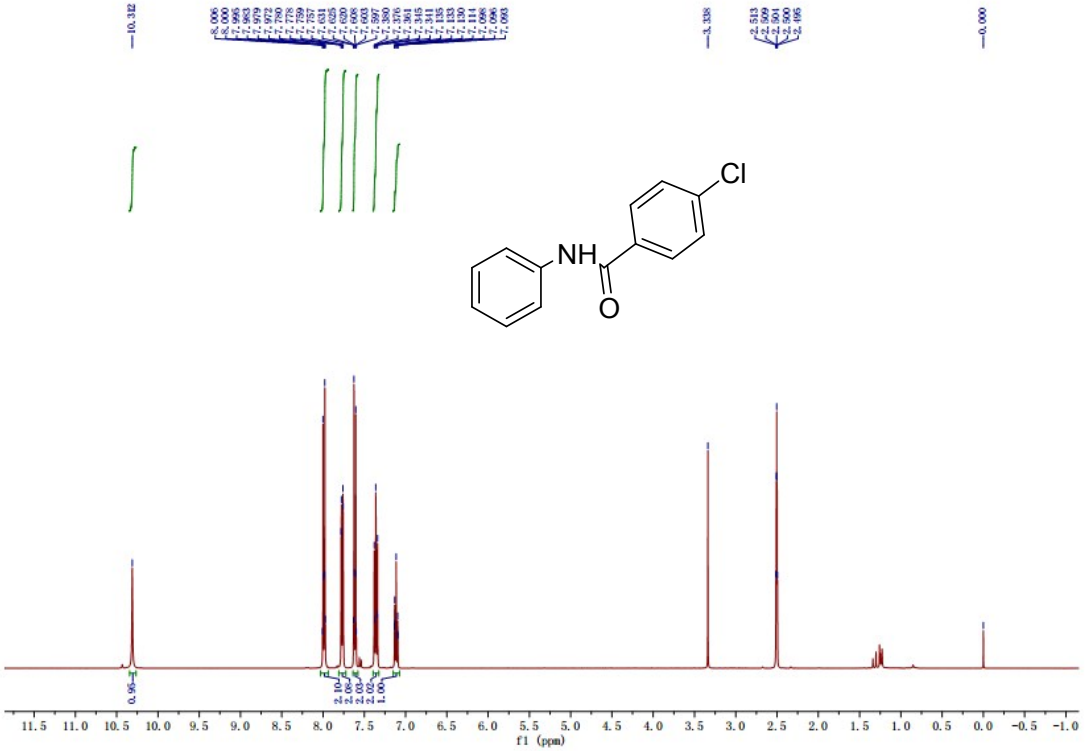


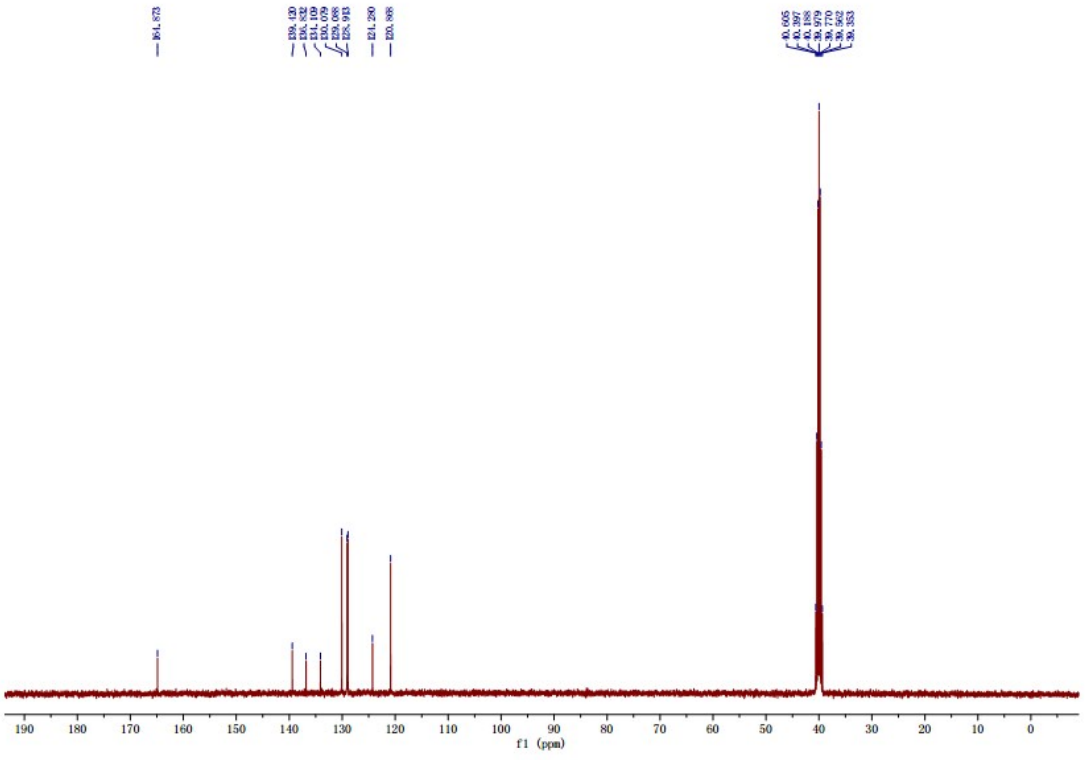
4-fluoro-N-phenylbenzamide and N-(4-fluorophenyl)benzamide:



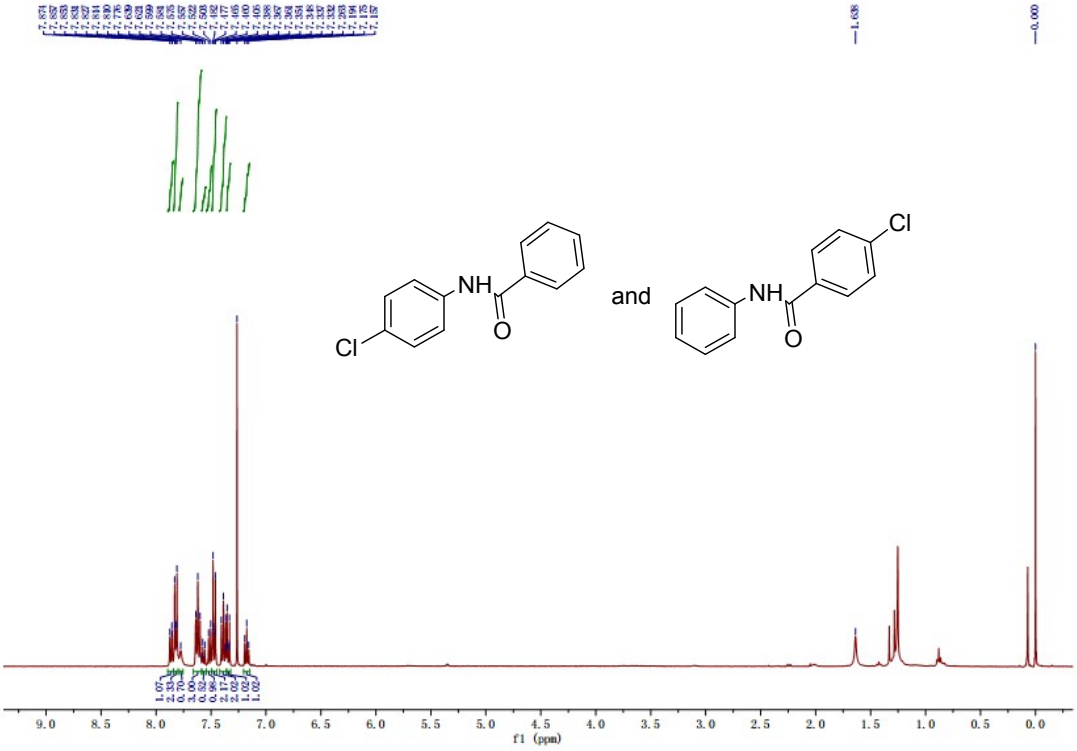


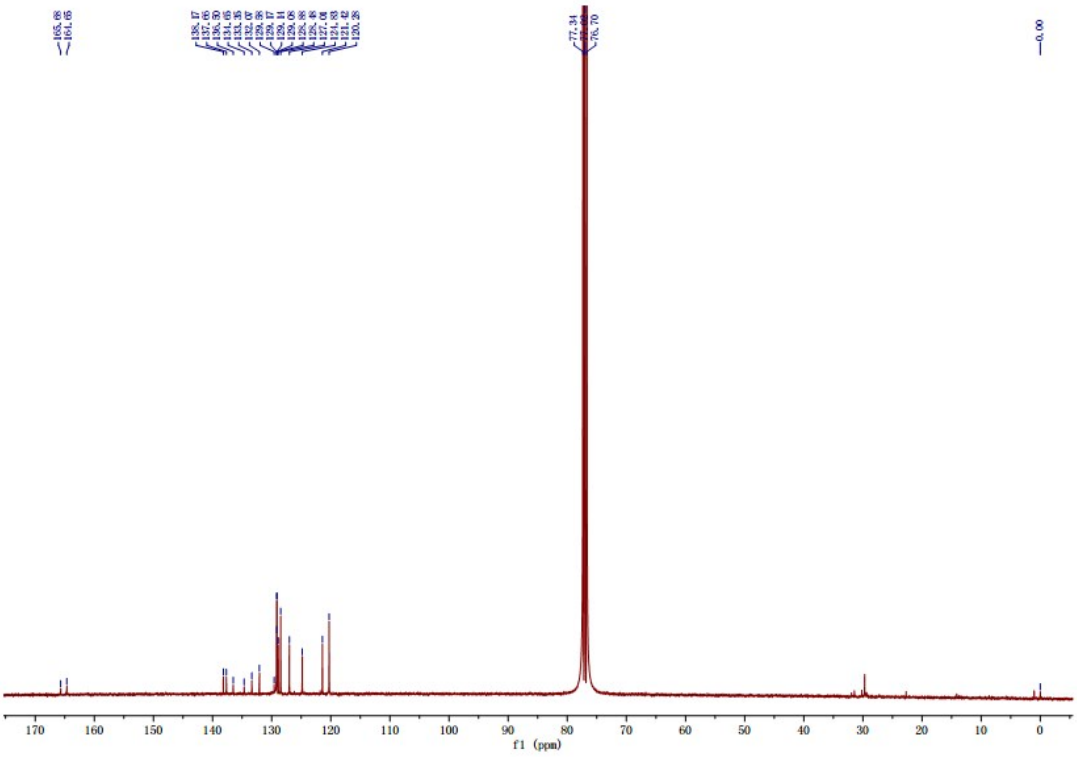
4-chloro-N-phenylbenzamide:



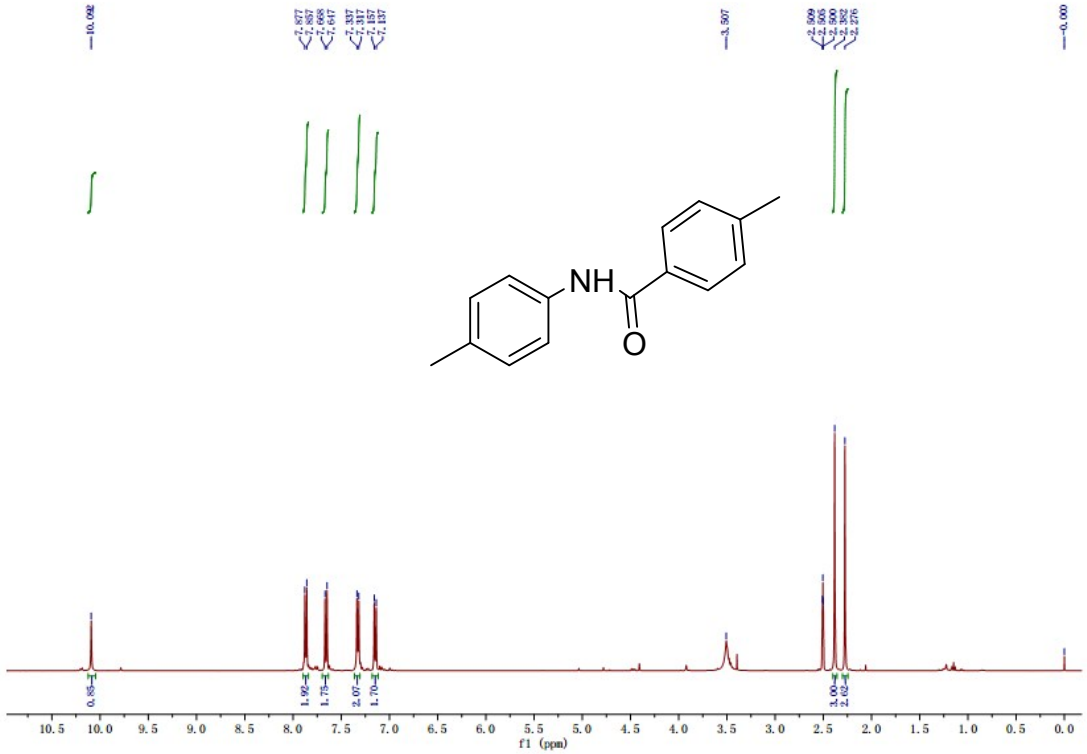


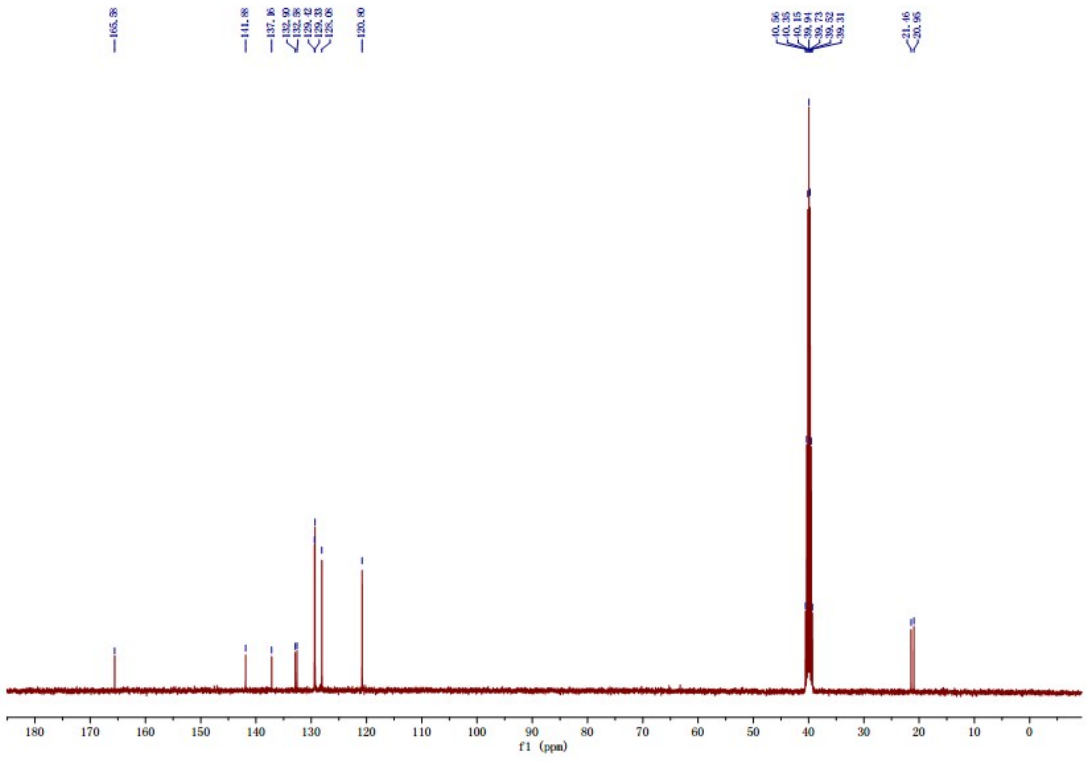
N-(4-chlorophenyl)benzamide and 4-chloro-N-phenylbenzamide:



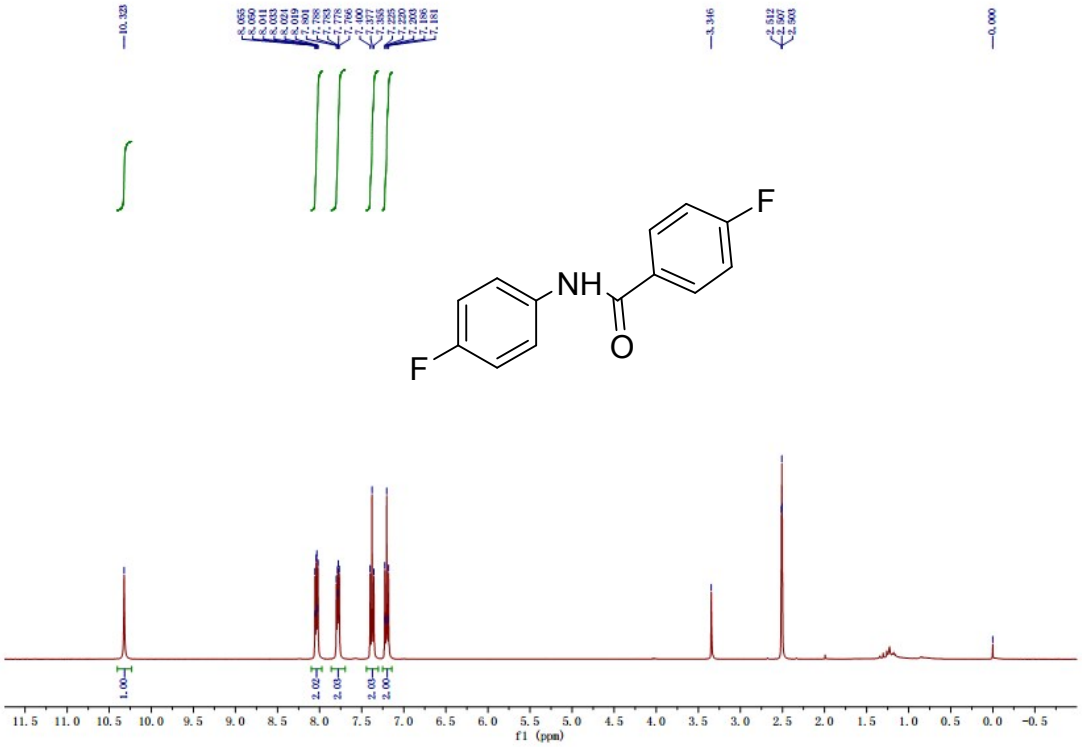


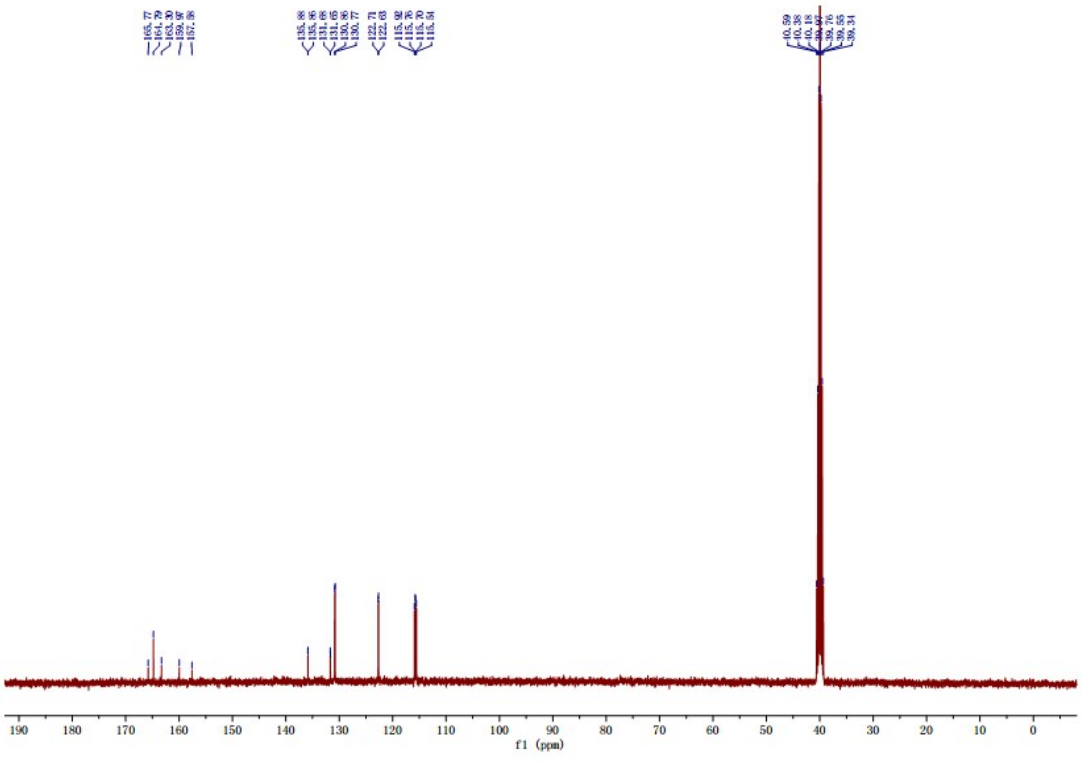
4-methyl-N-(p-tolyl)benzamide:



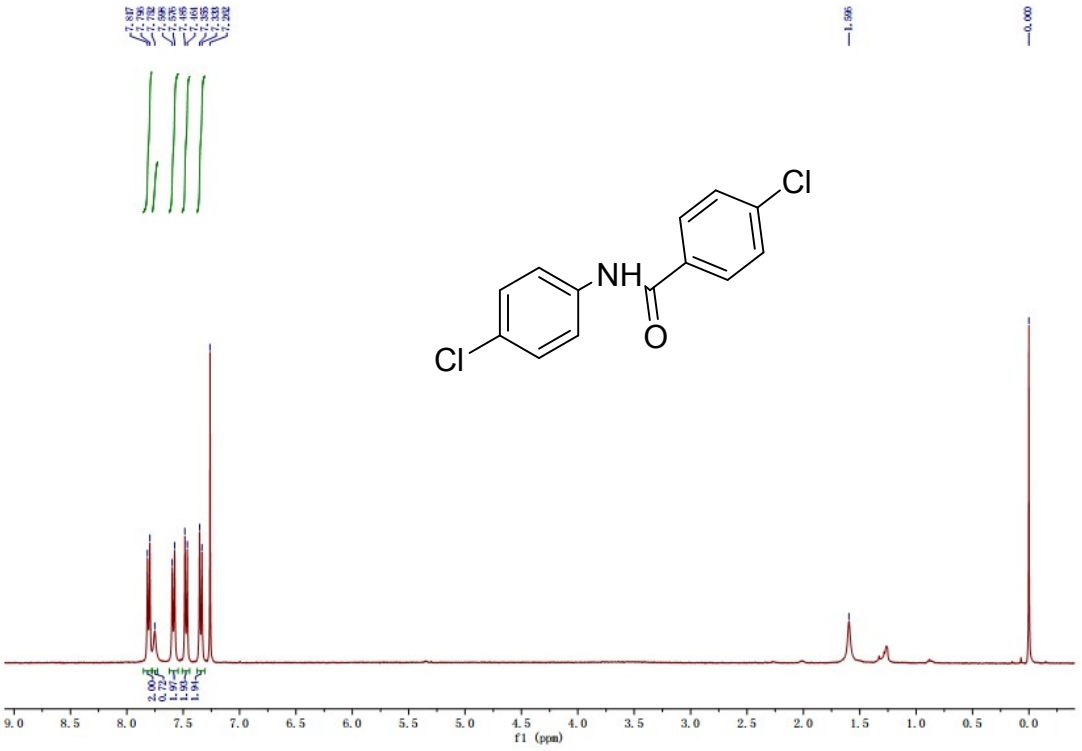


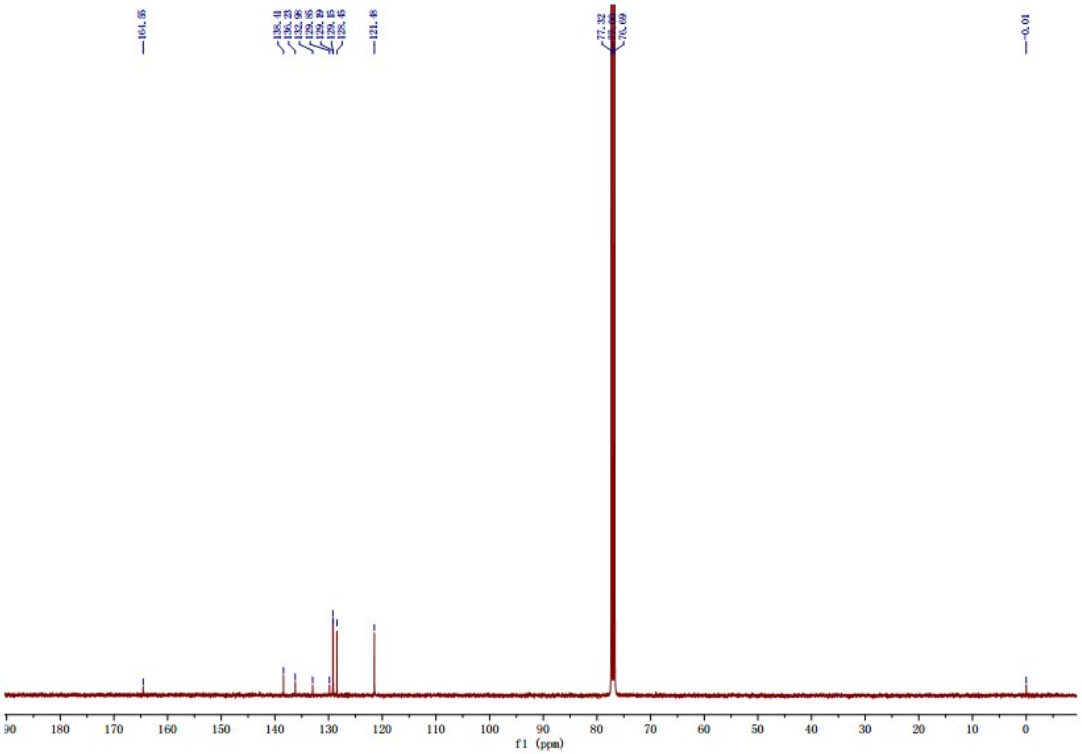
4-fluoro-N-(4-fluorophenyl)benzamide:



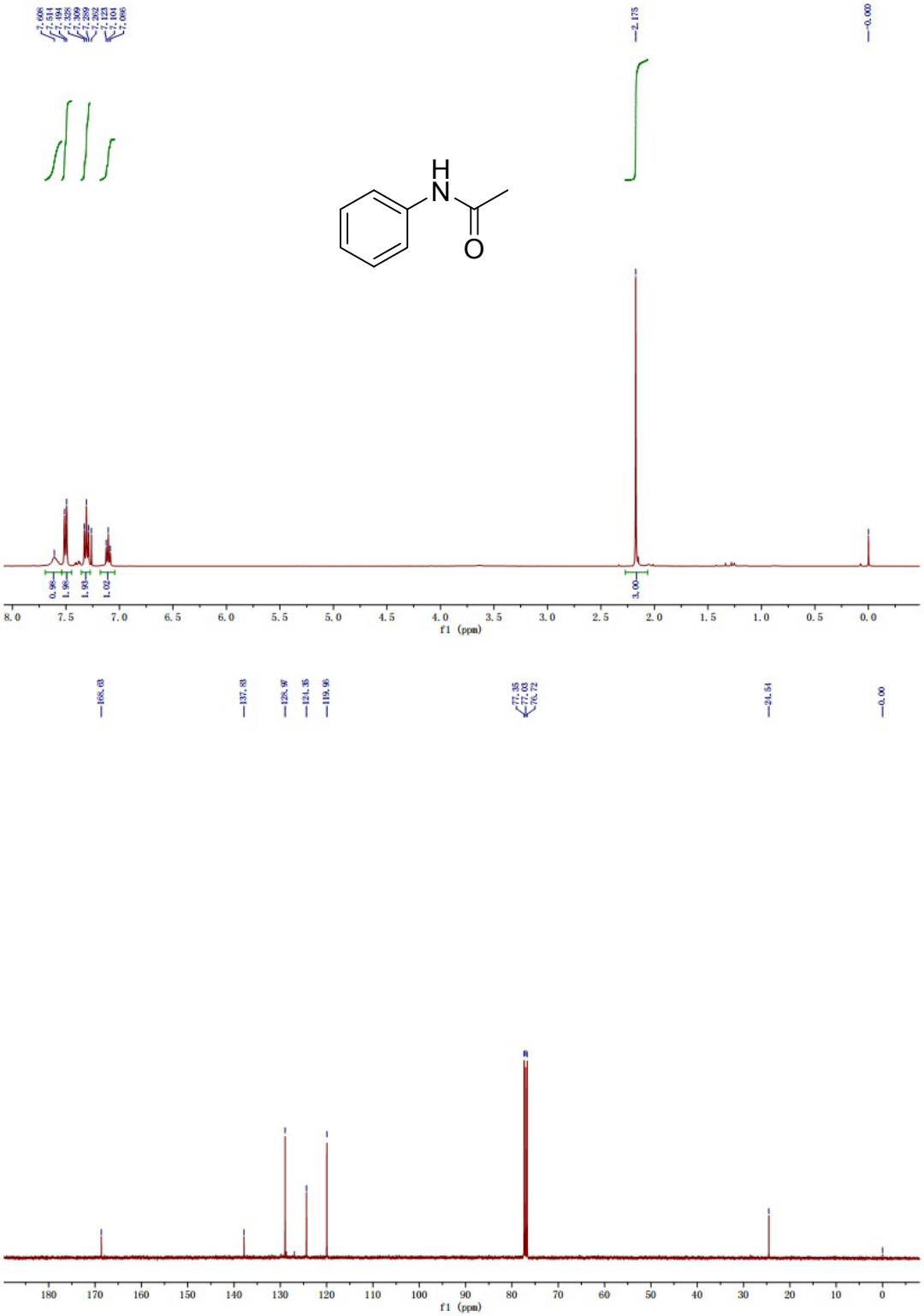


4-chloro-N-(4-chlorophenyl)benzamide:

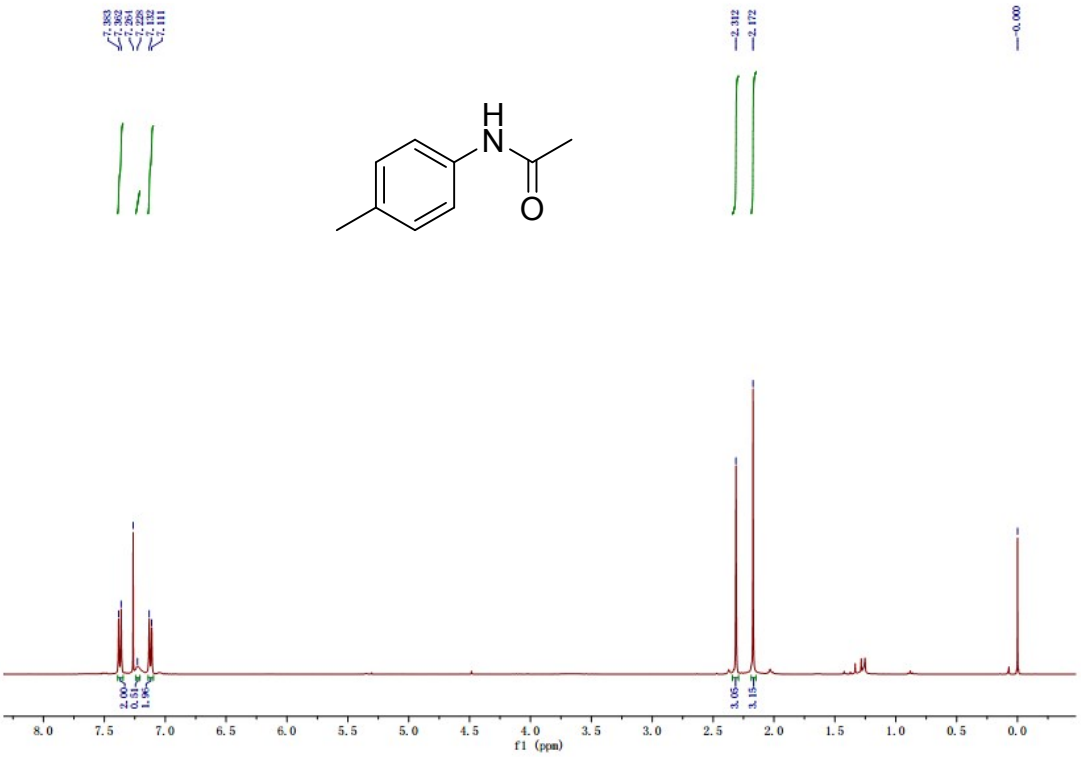


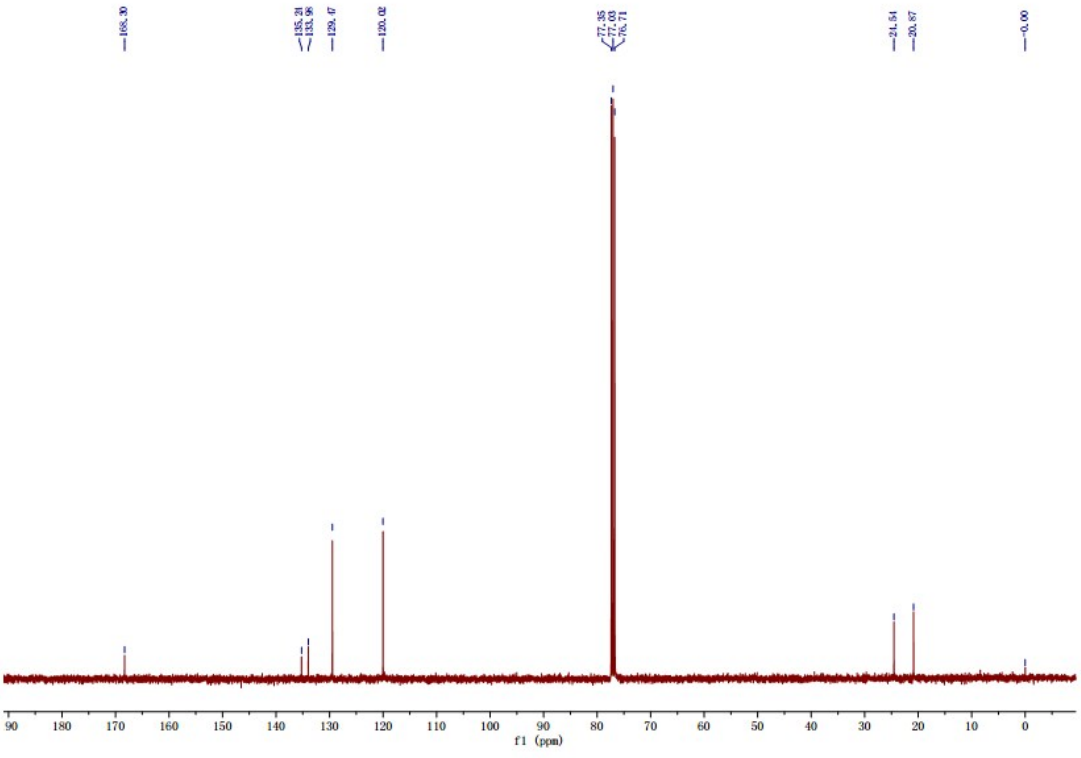


N-phenylacetamide:

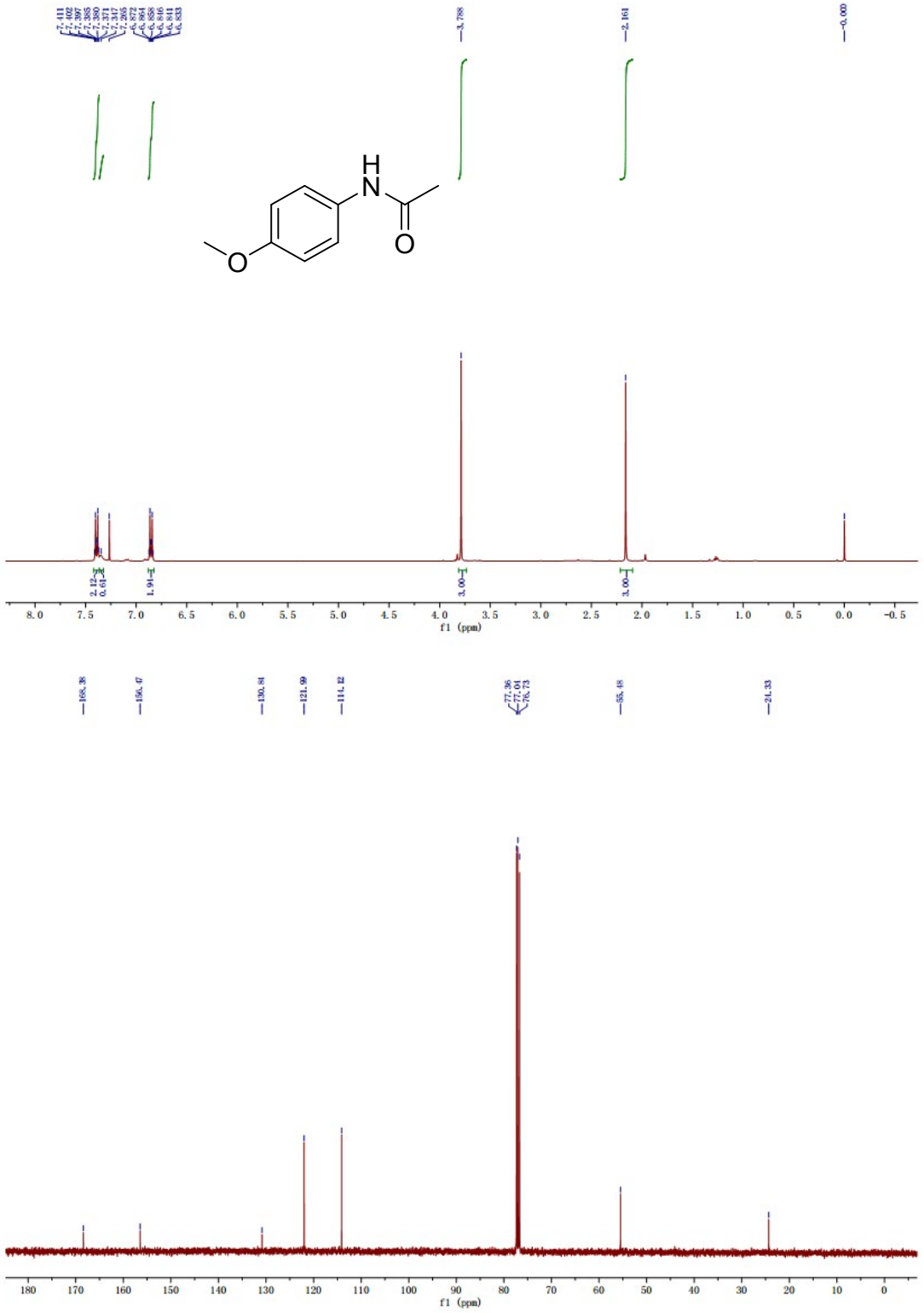


N-(p-tolyl)acetamide:

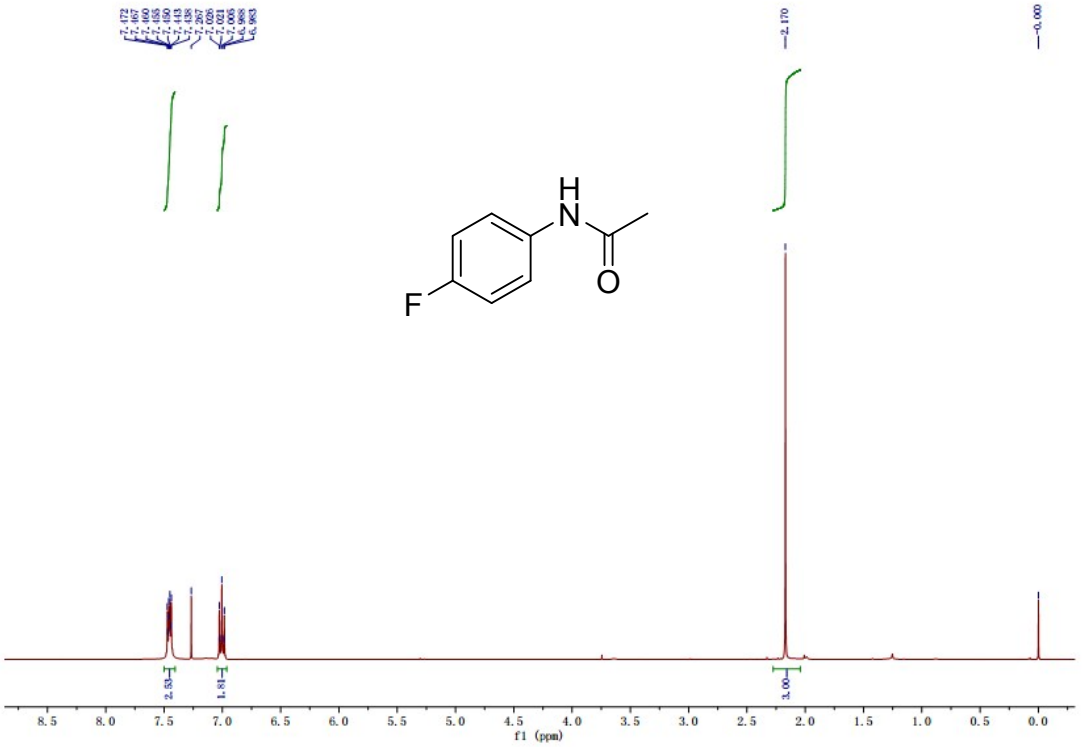


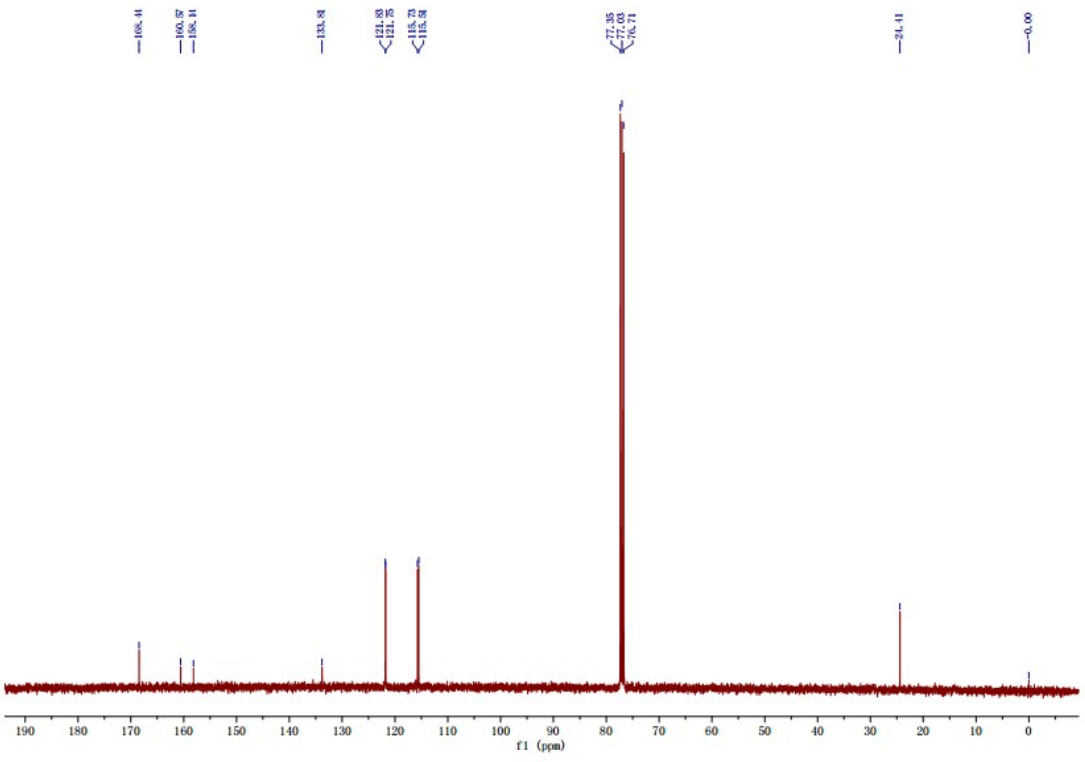


N-(4-methoxyphenyl)acetamide:

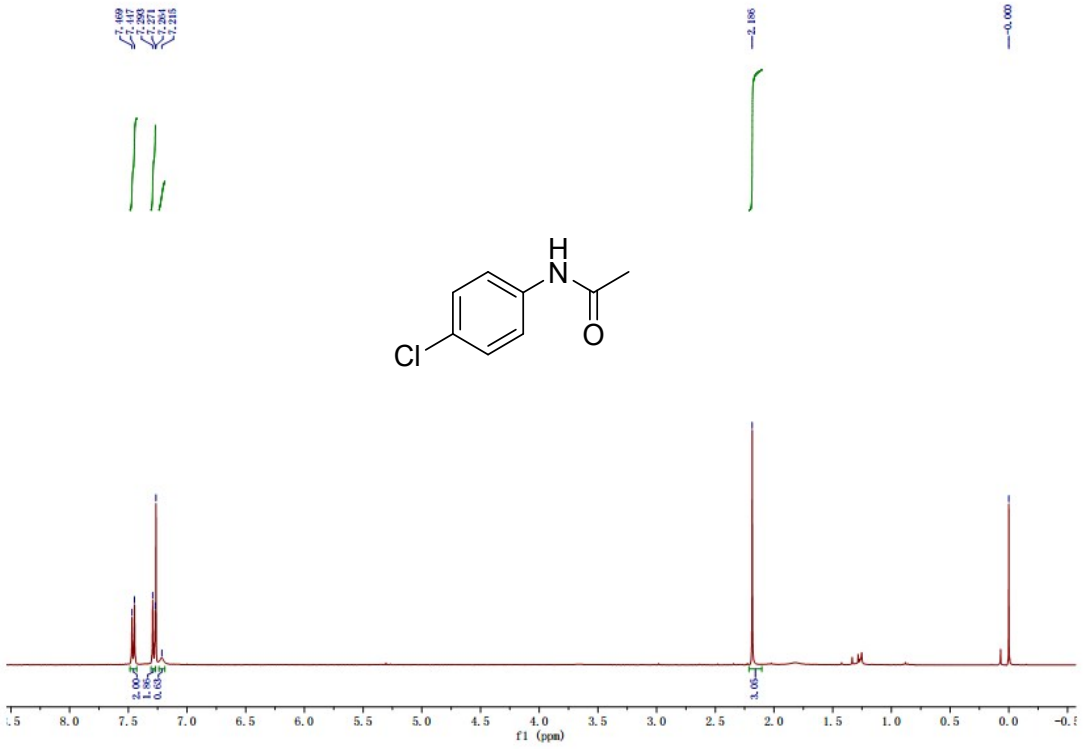


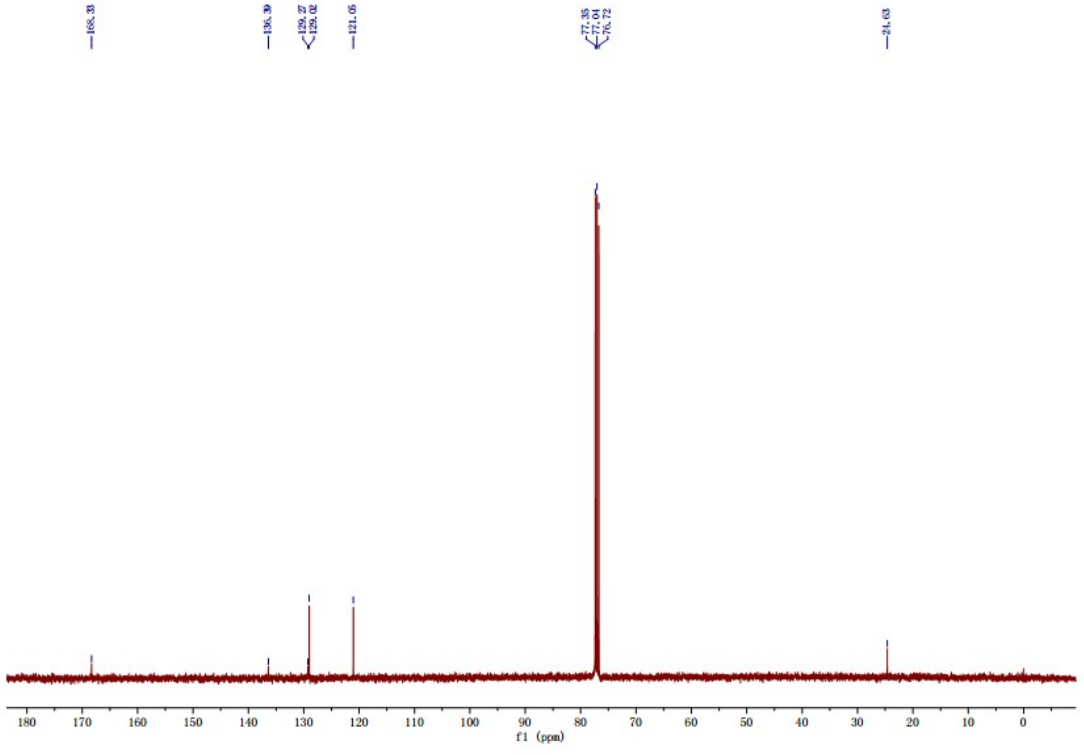
N-(4-fluorophenyl)acetamide:



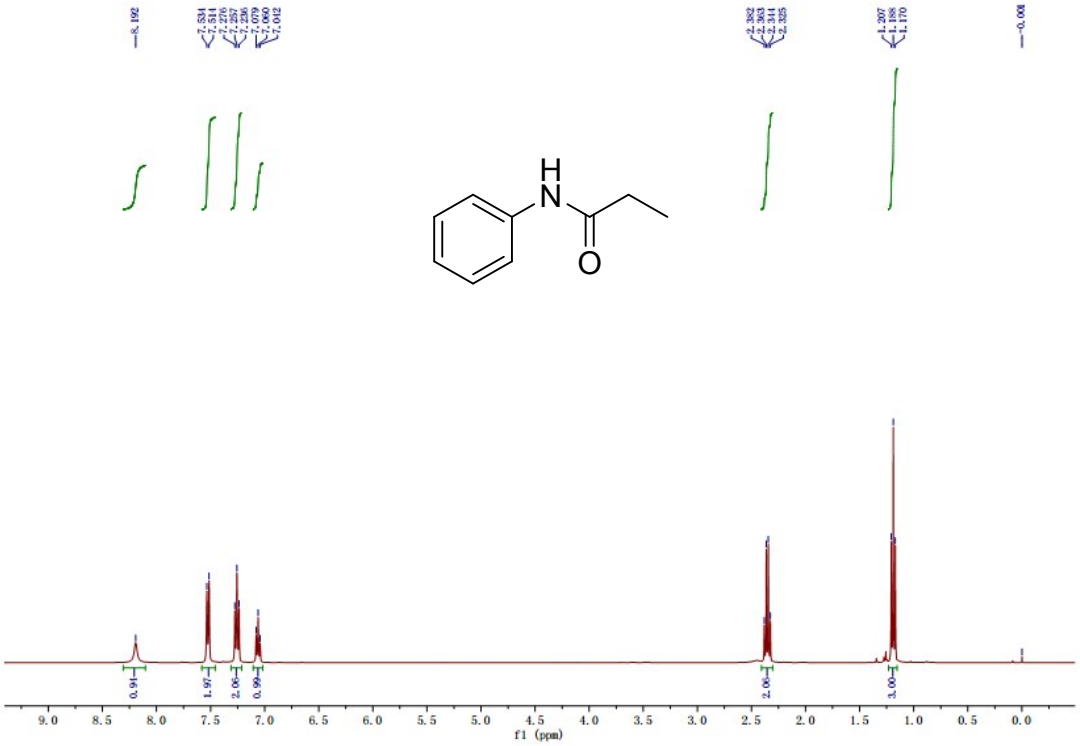


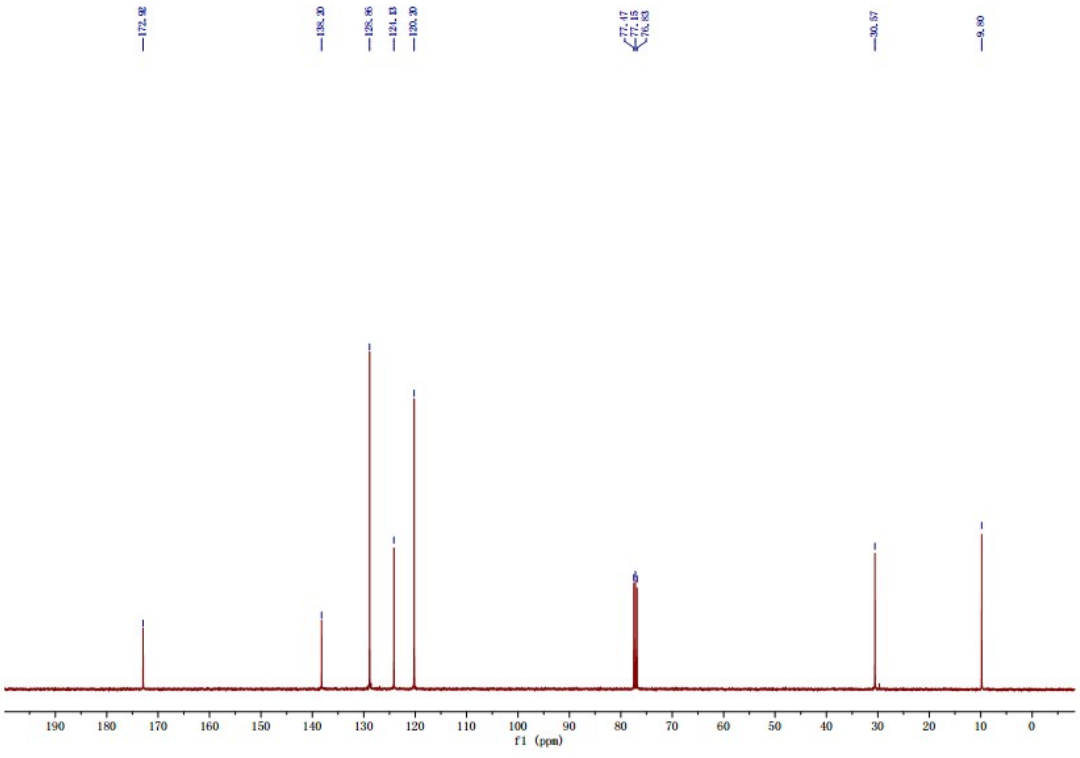
N-(4-chlorophenyl)acetamide:



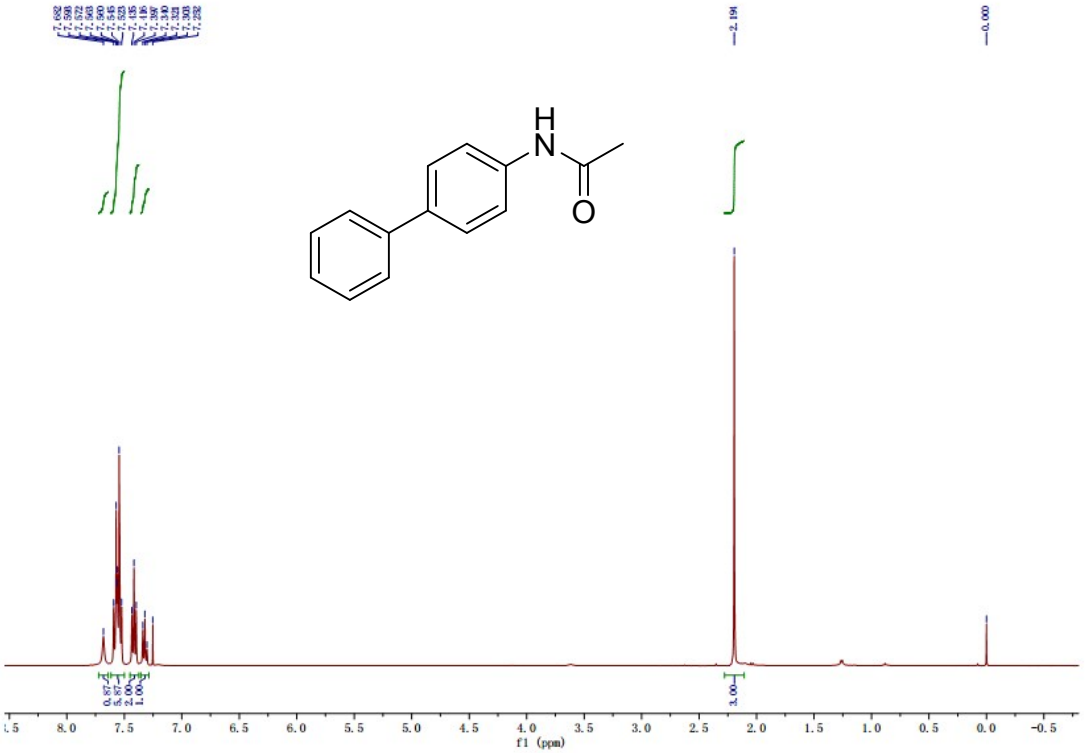


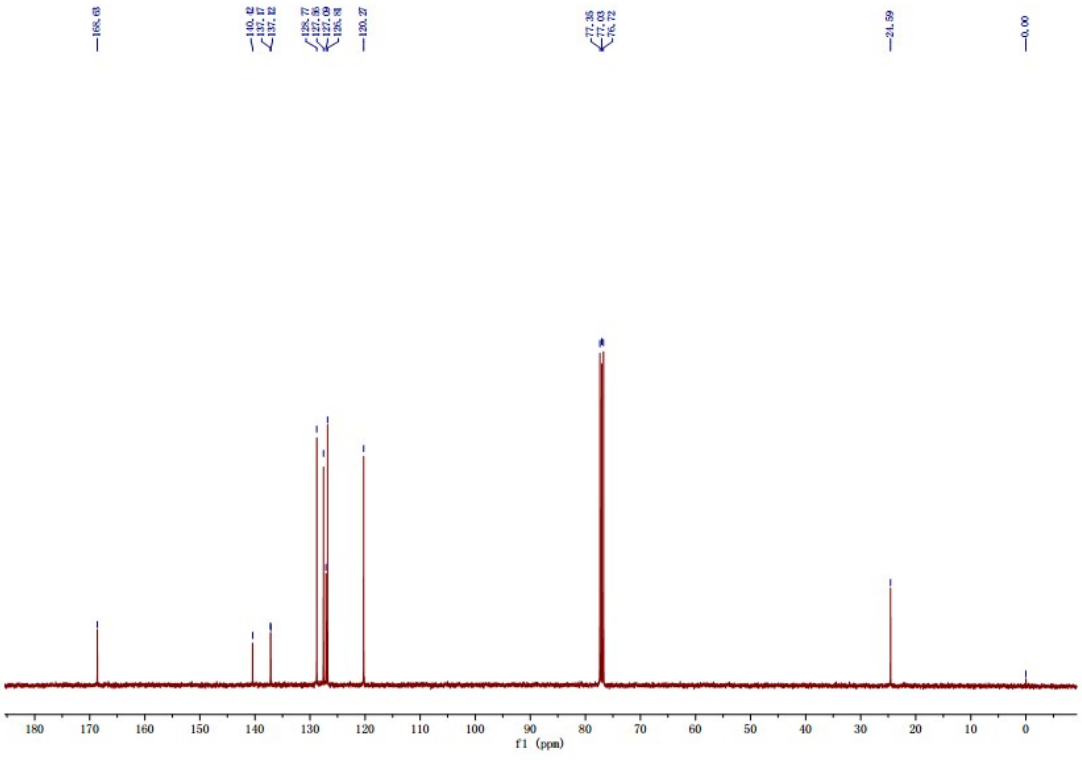
N-benzylacetamide:



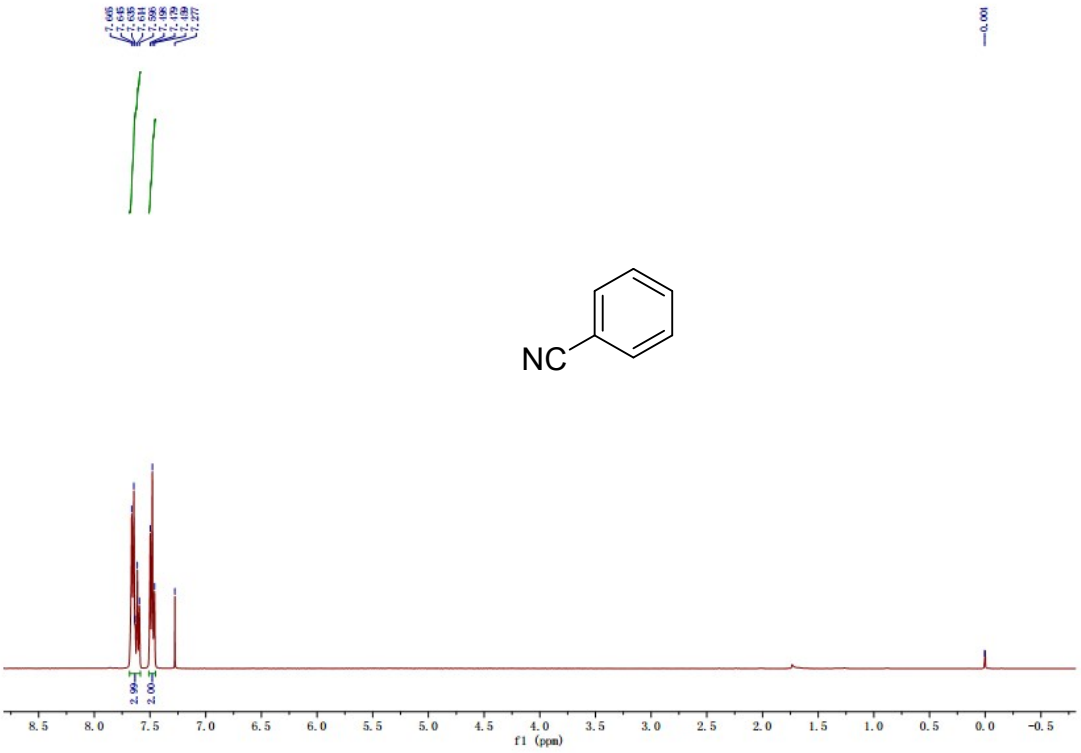


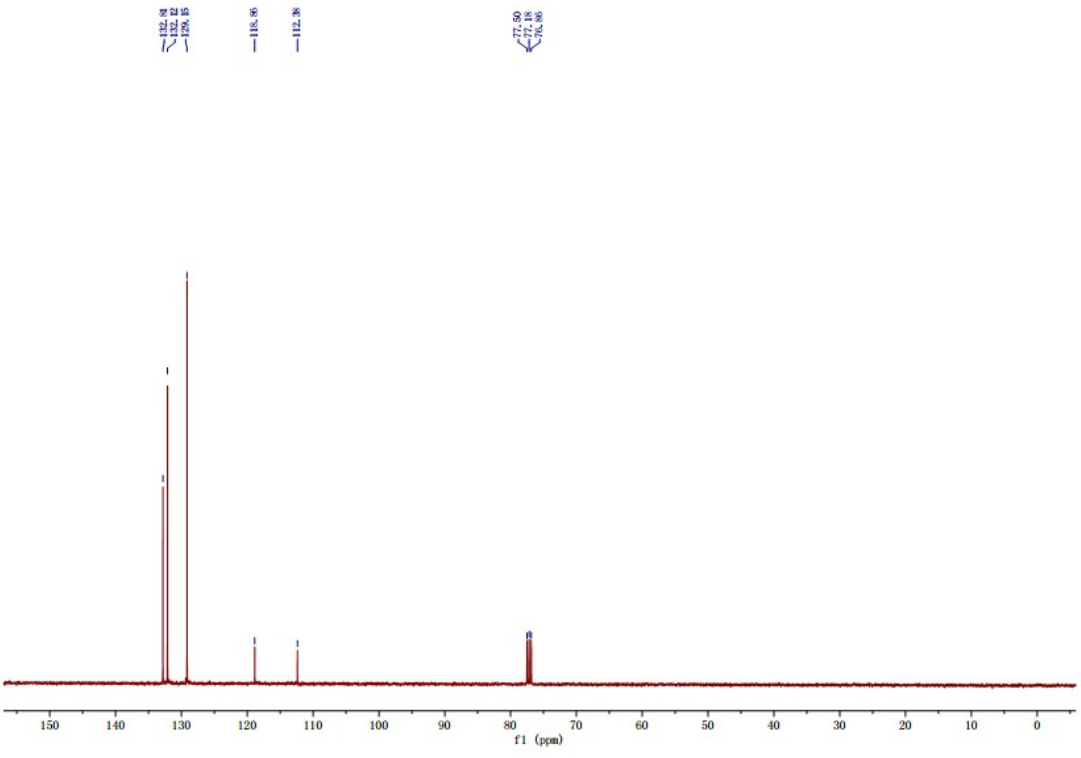
N-([1,1'-biphenyl]-4-yl)acetamide:



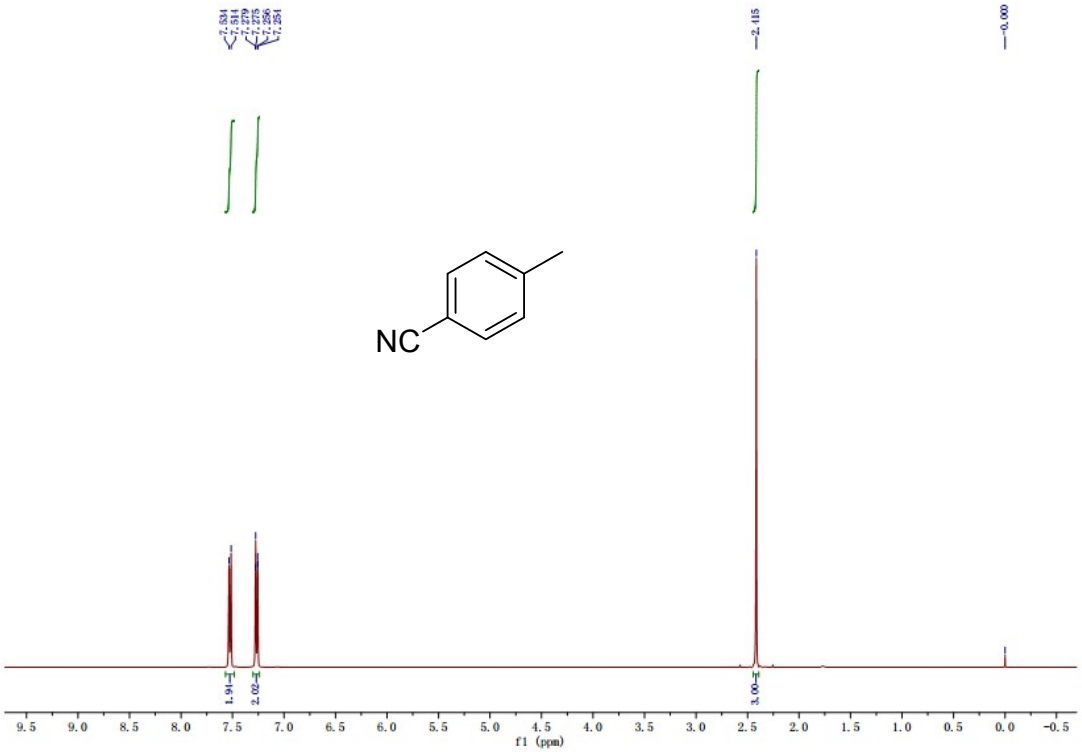


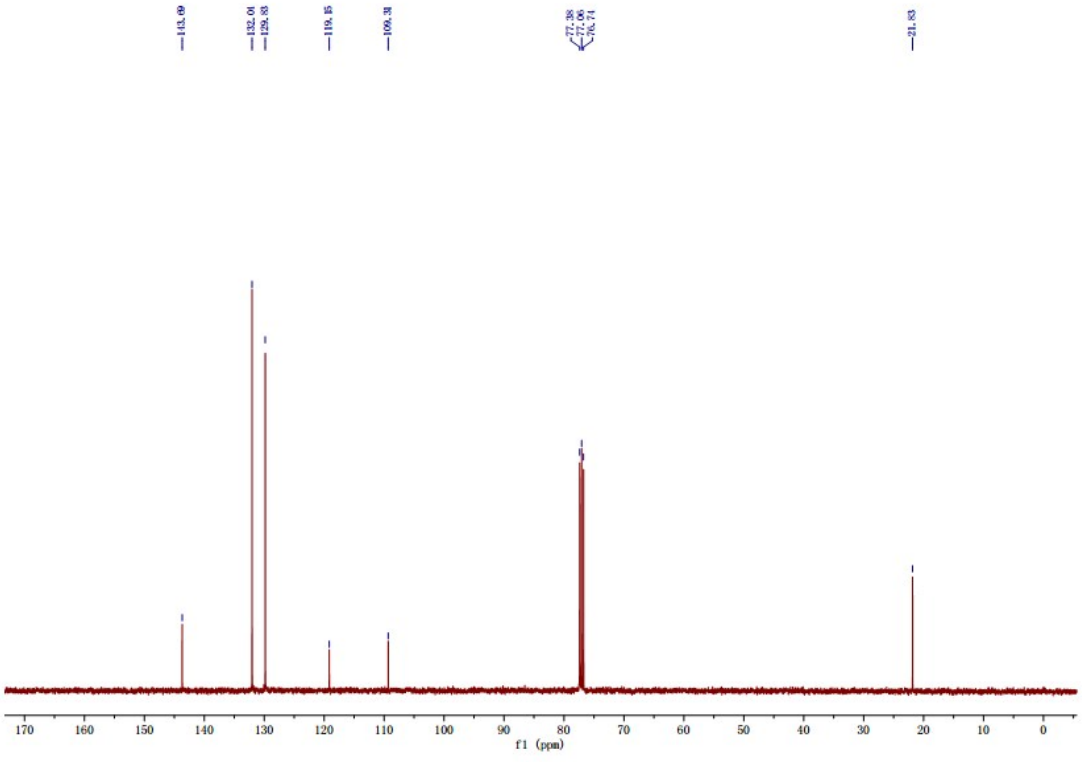
benzonitrile:



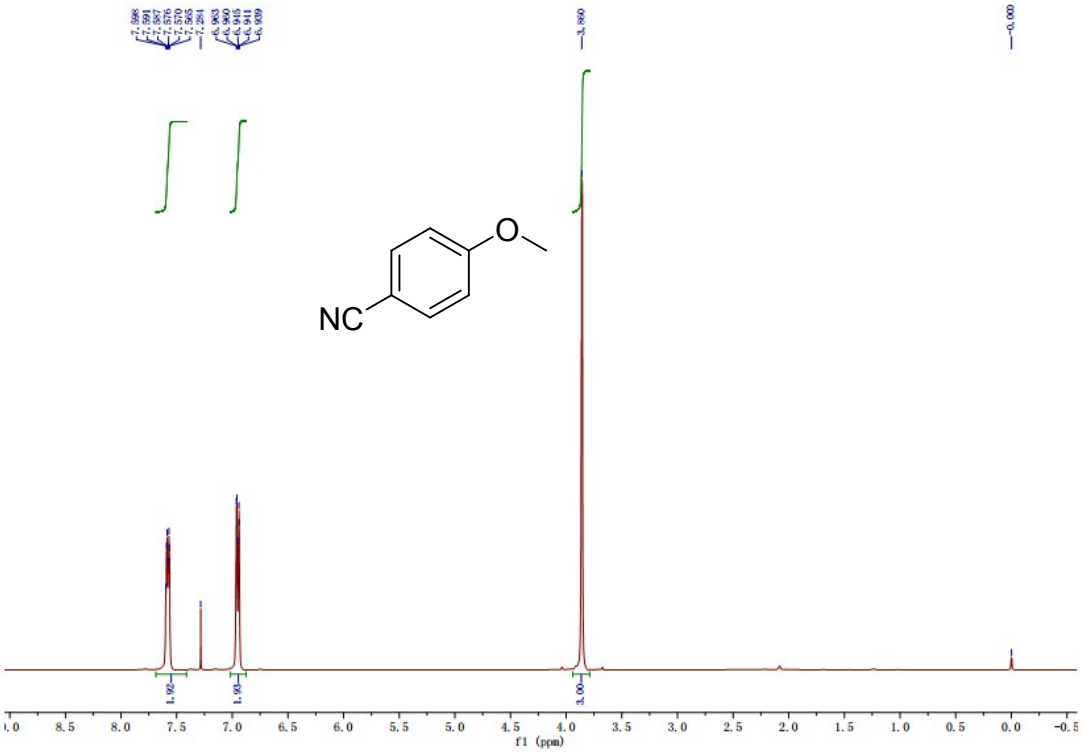


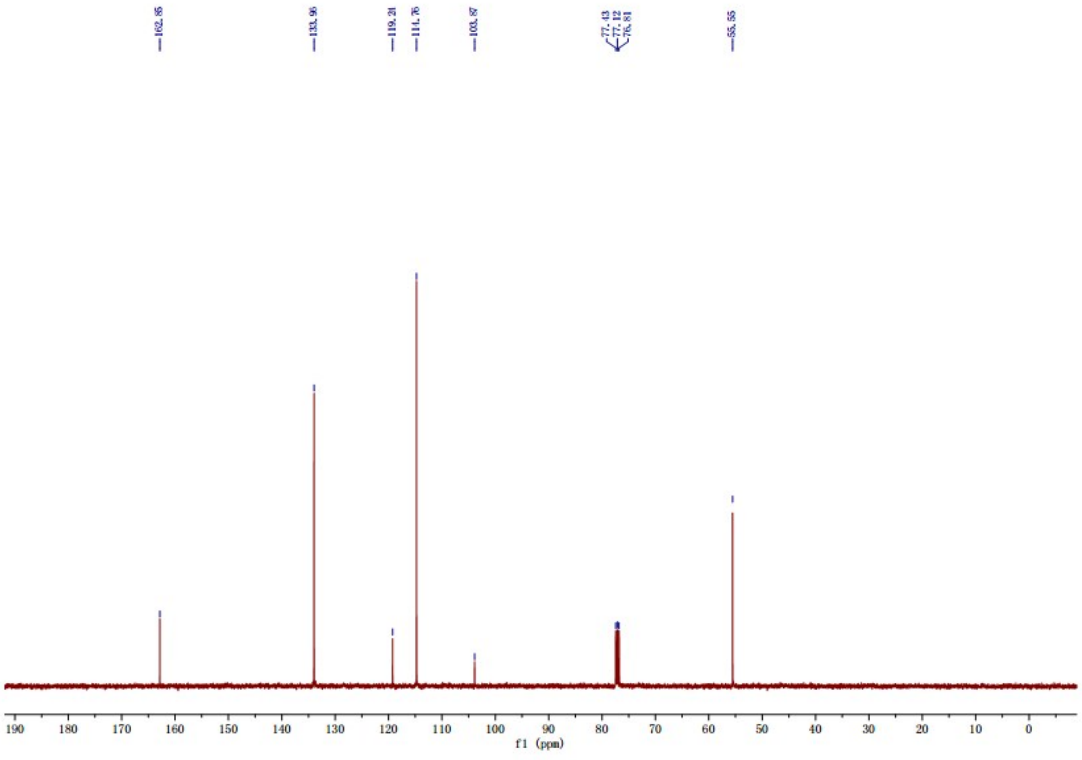
4-methylbenzonitrile:



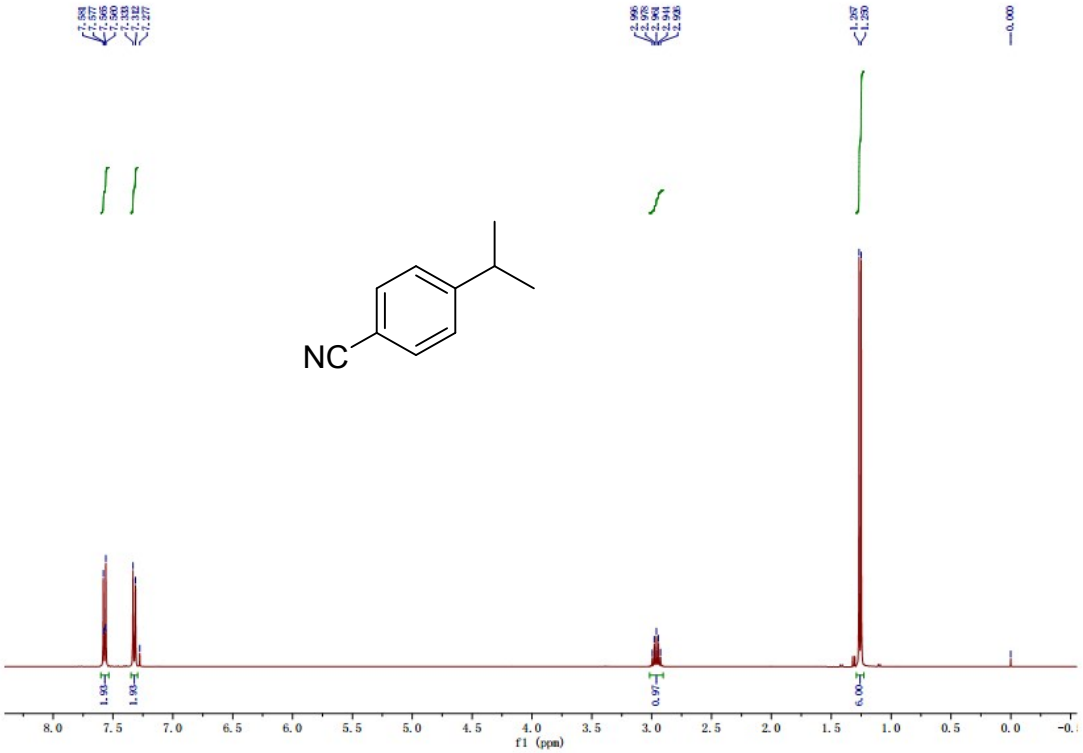


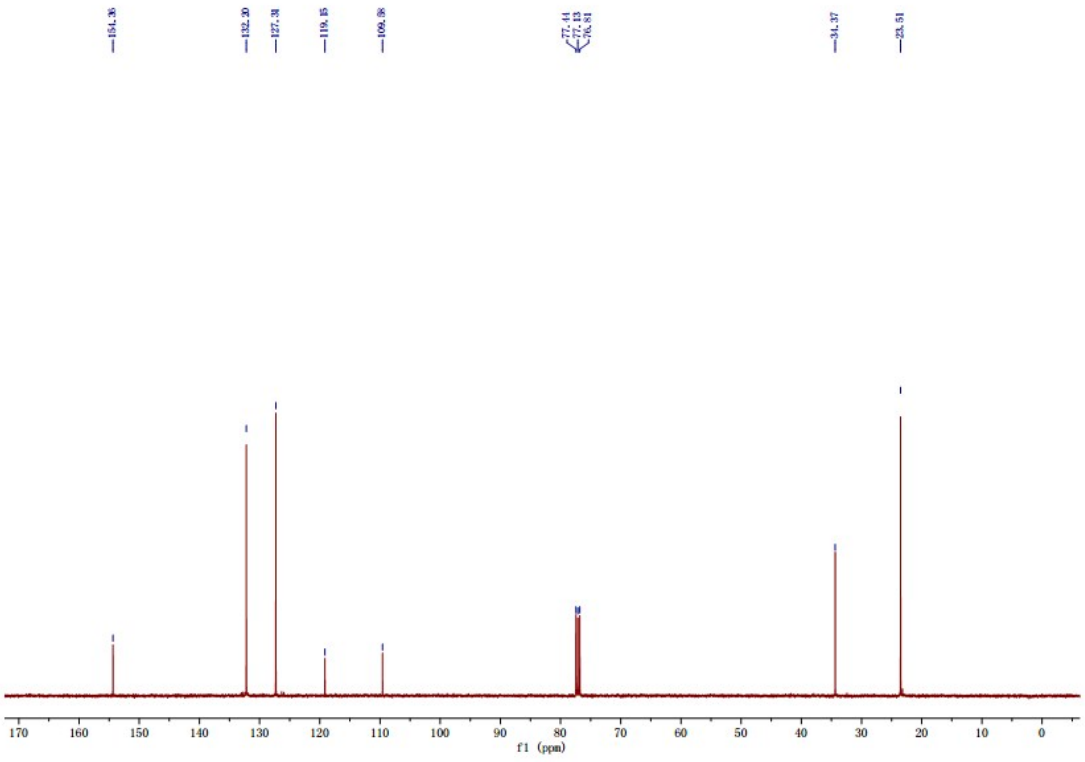
4-methoxybenzonitrile:



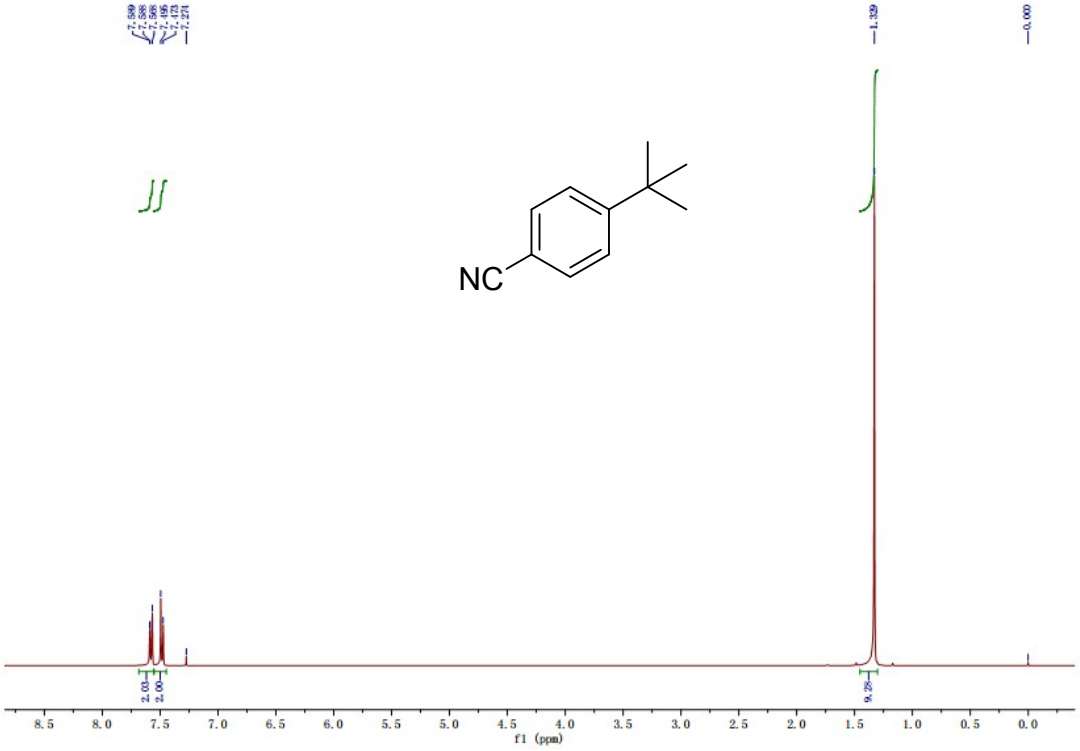


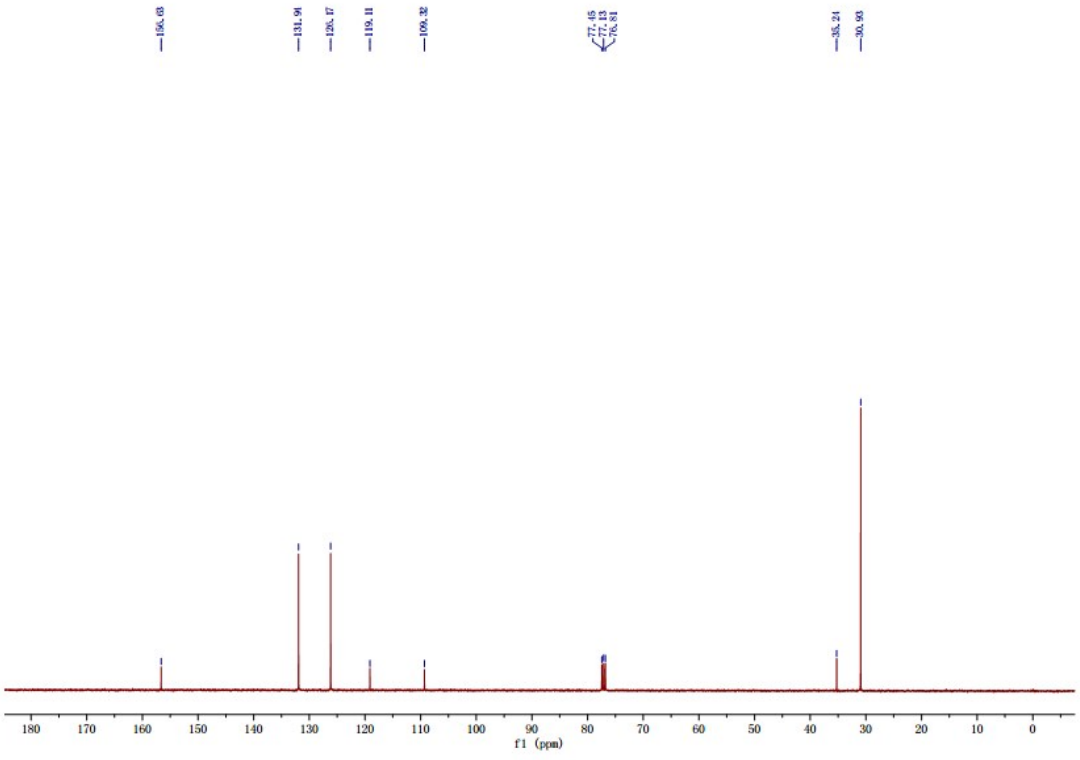
4-isopropylbenzonitrile:





4-(tert-butyl)benzonitrile:





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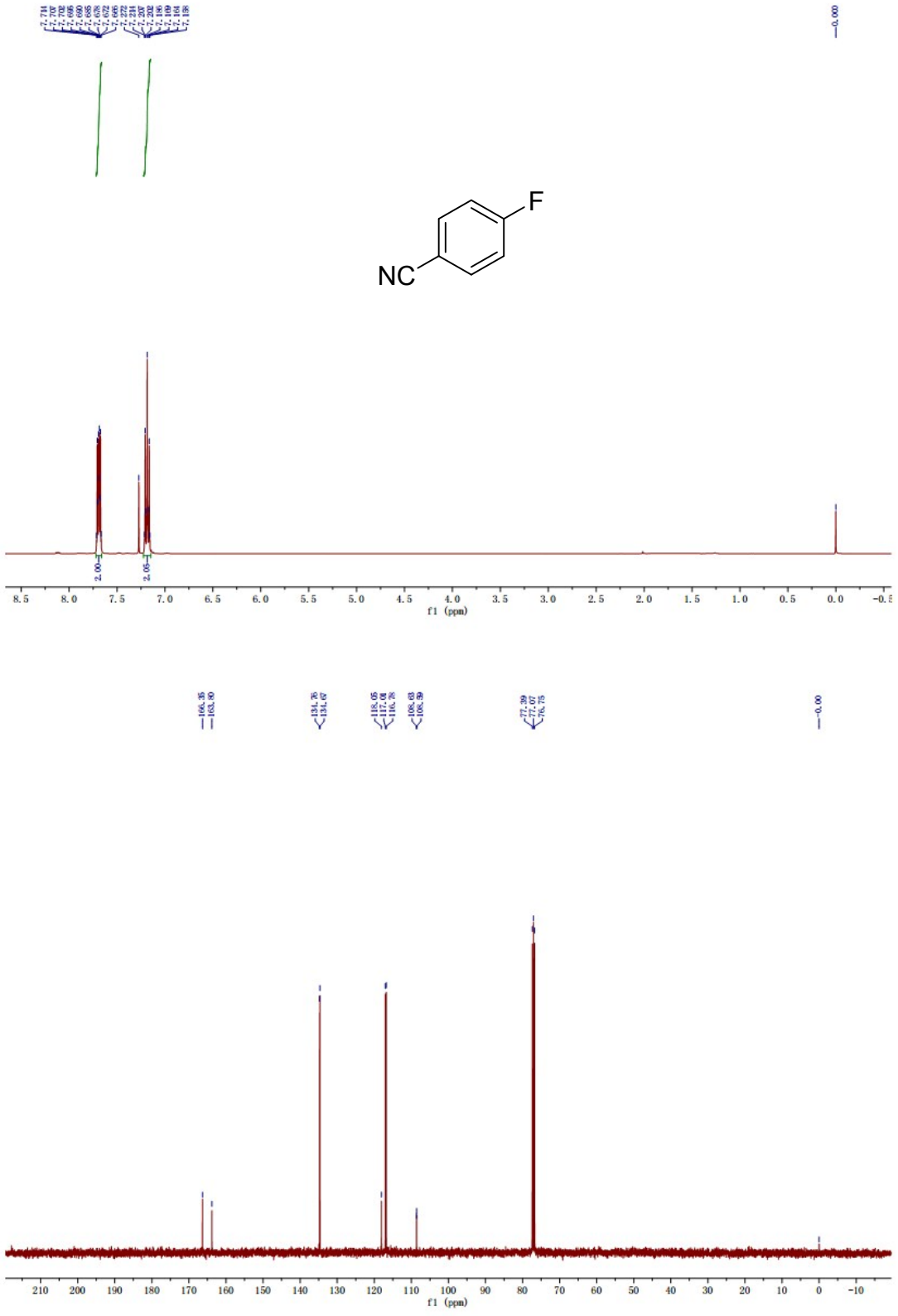
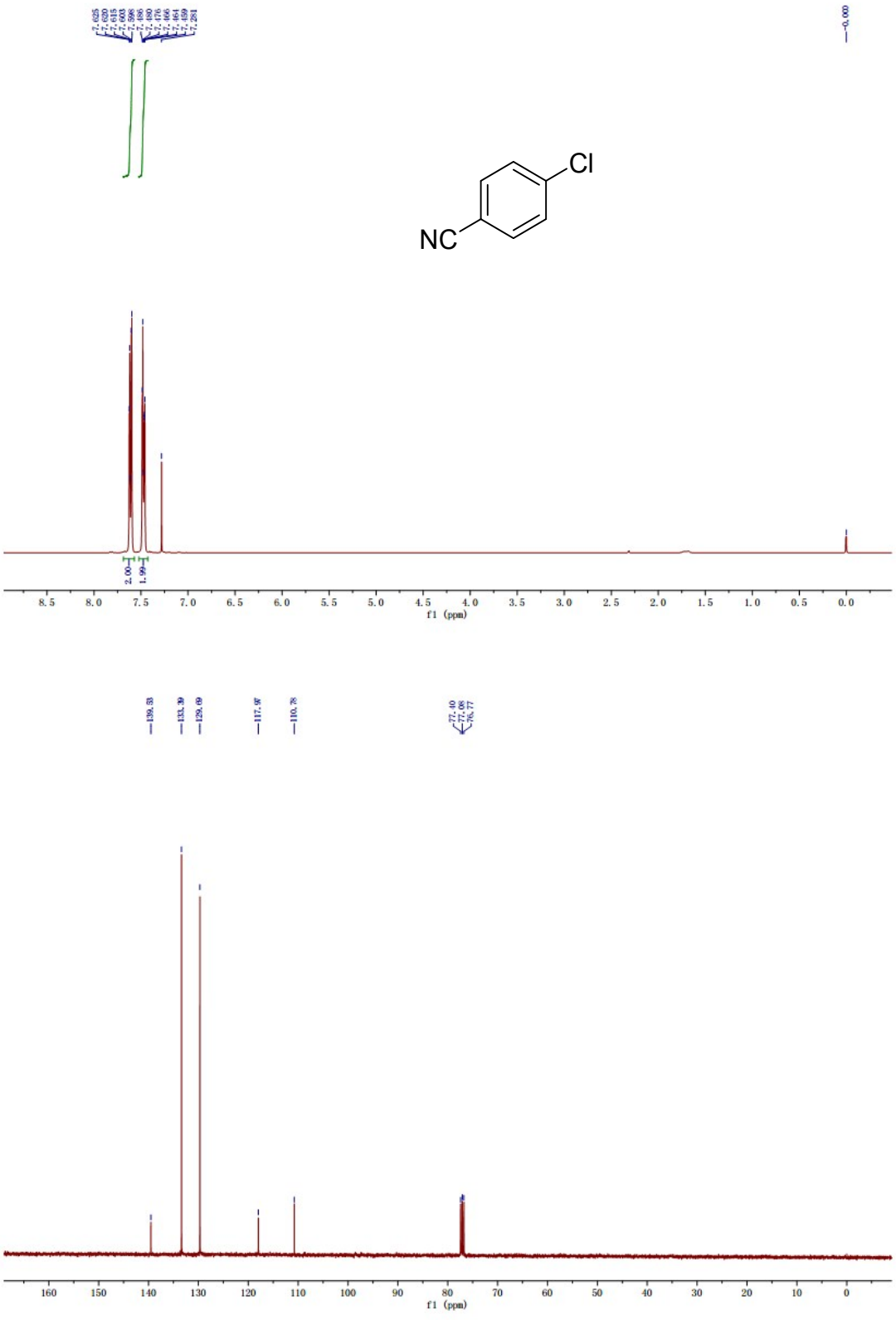
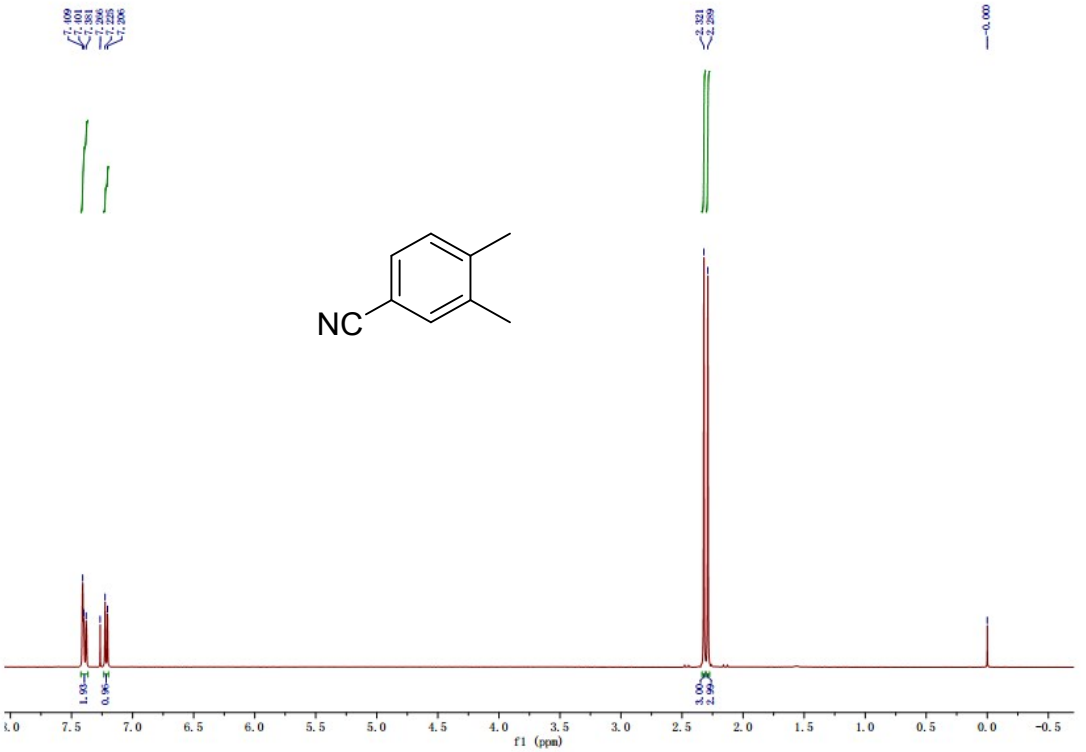
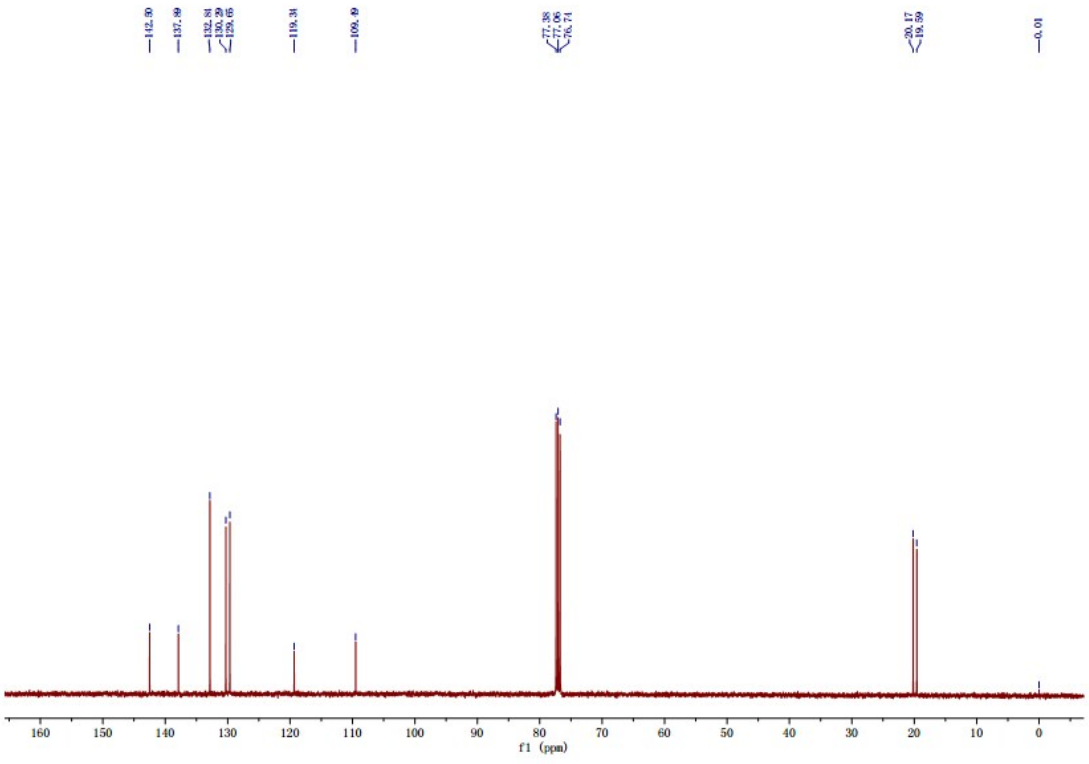


4-chlorobenzonitrile:

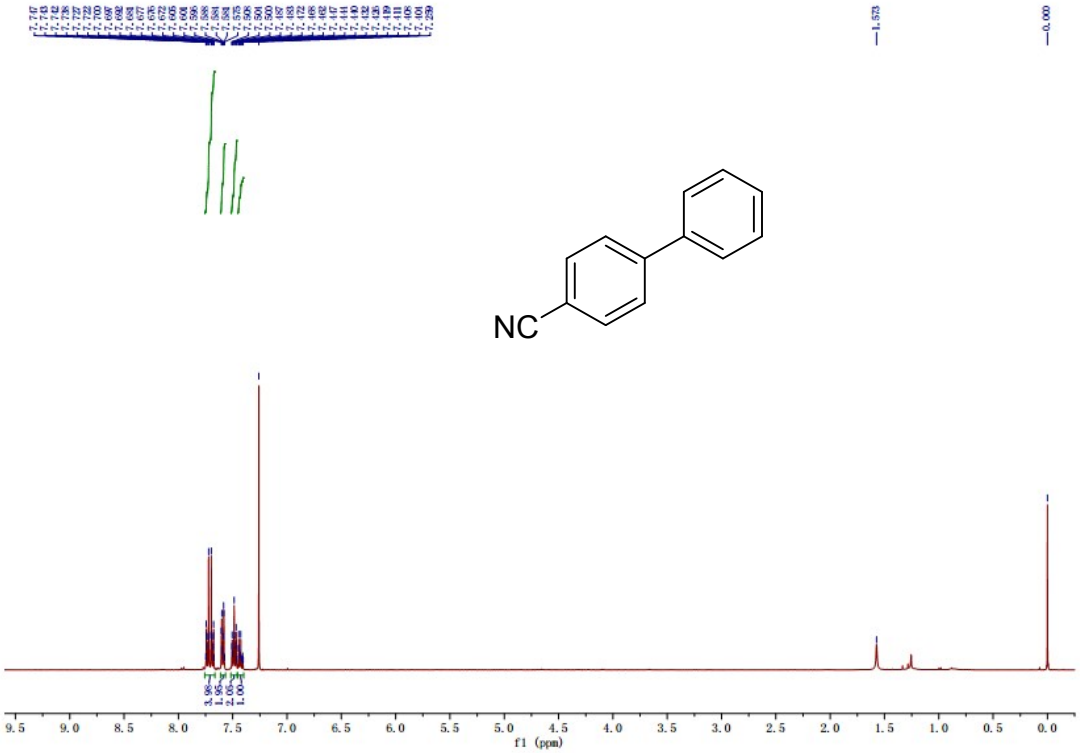


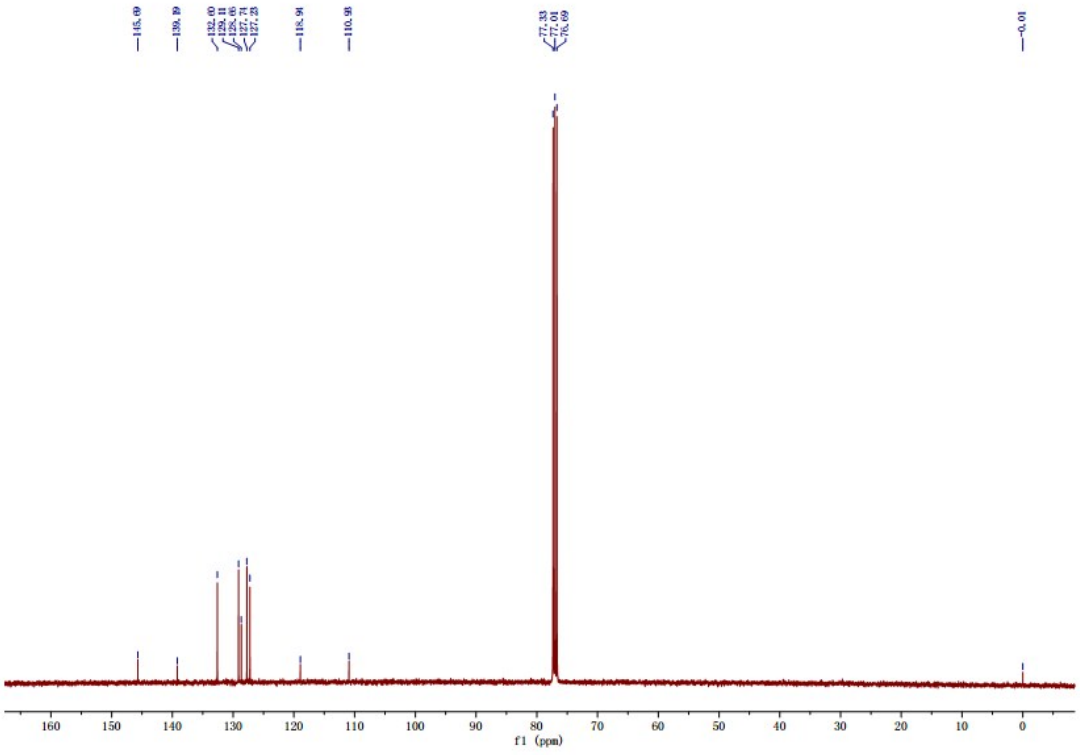
3,4-dimethylbenzonitrile:



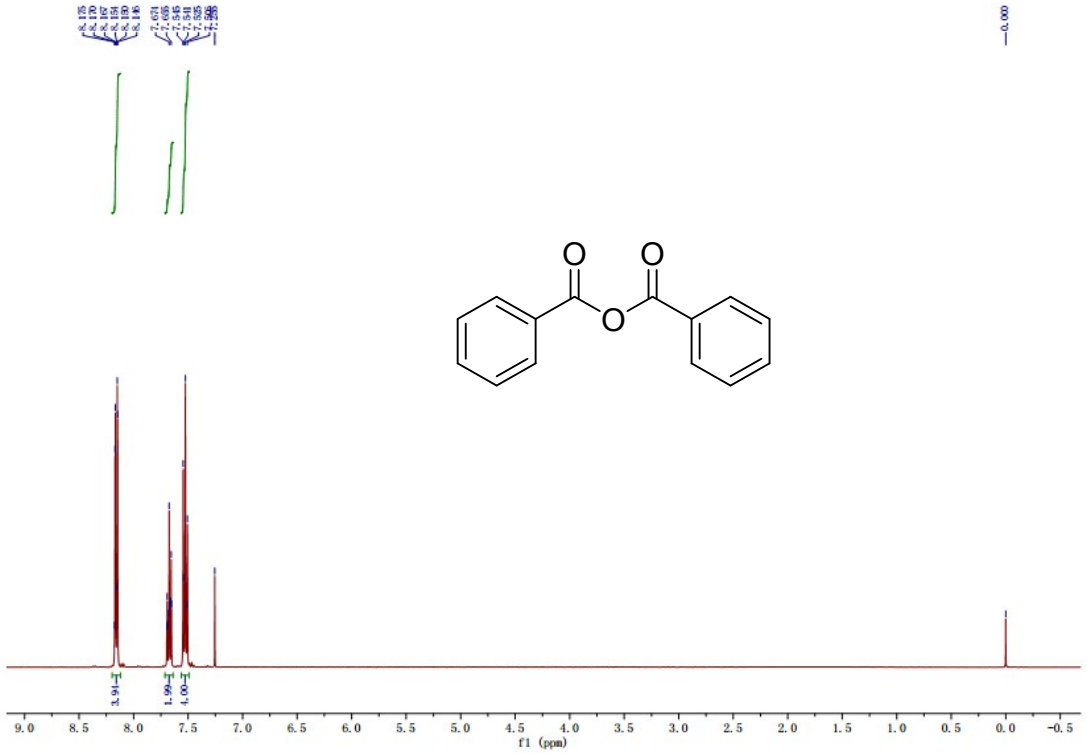


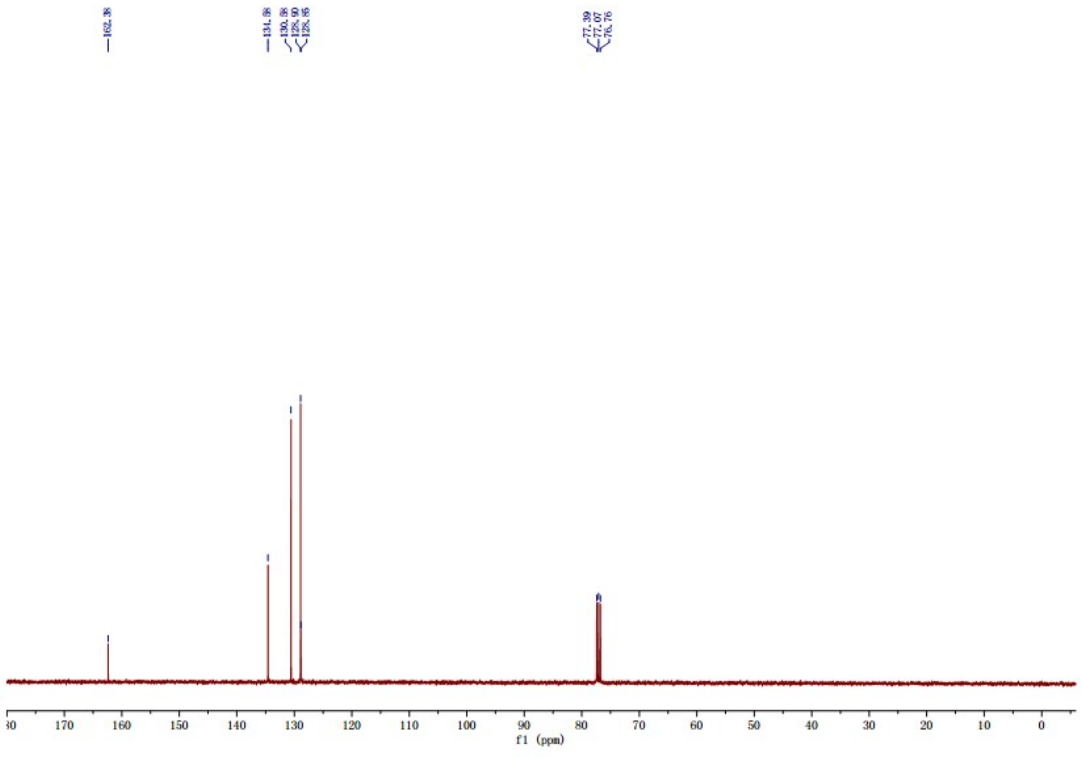
[1,1'-biphenyl]-4-carbonitrile:





benzoic anhydride:





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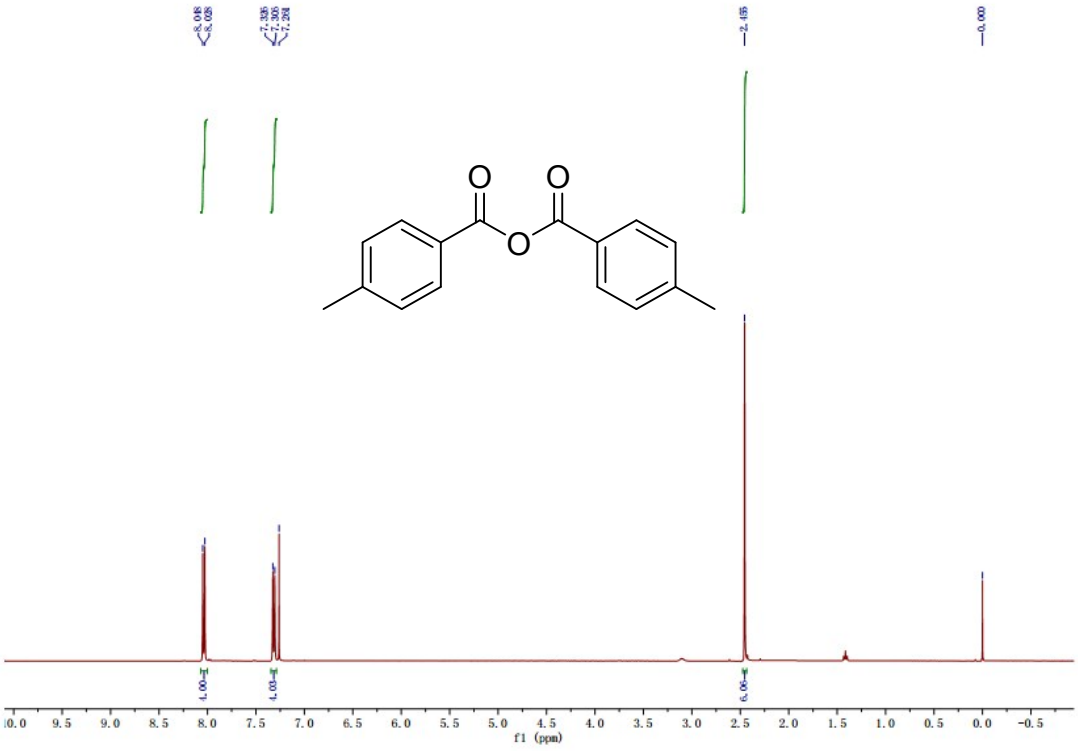
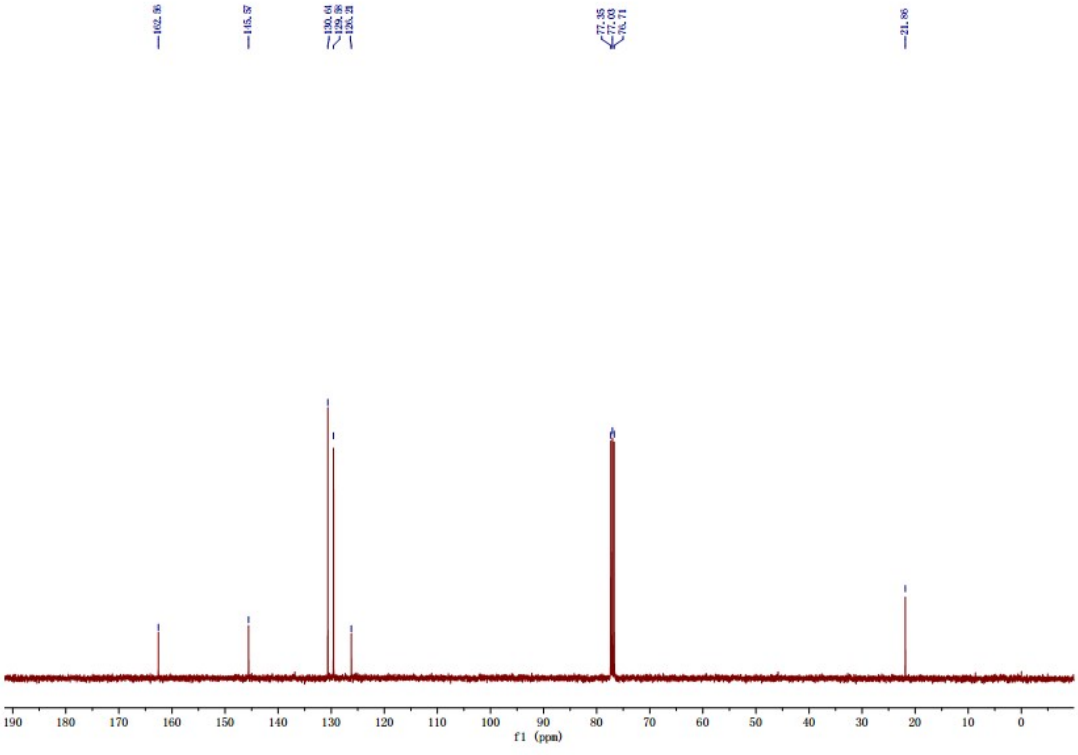
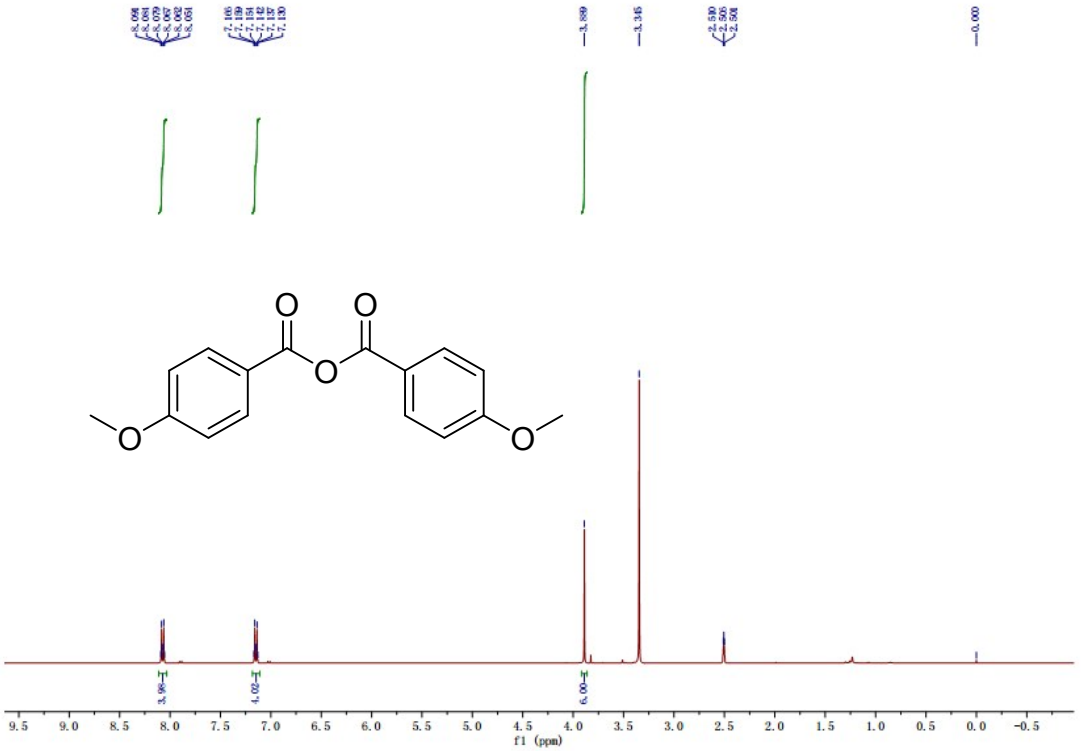
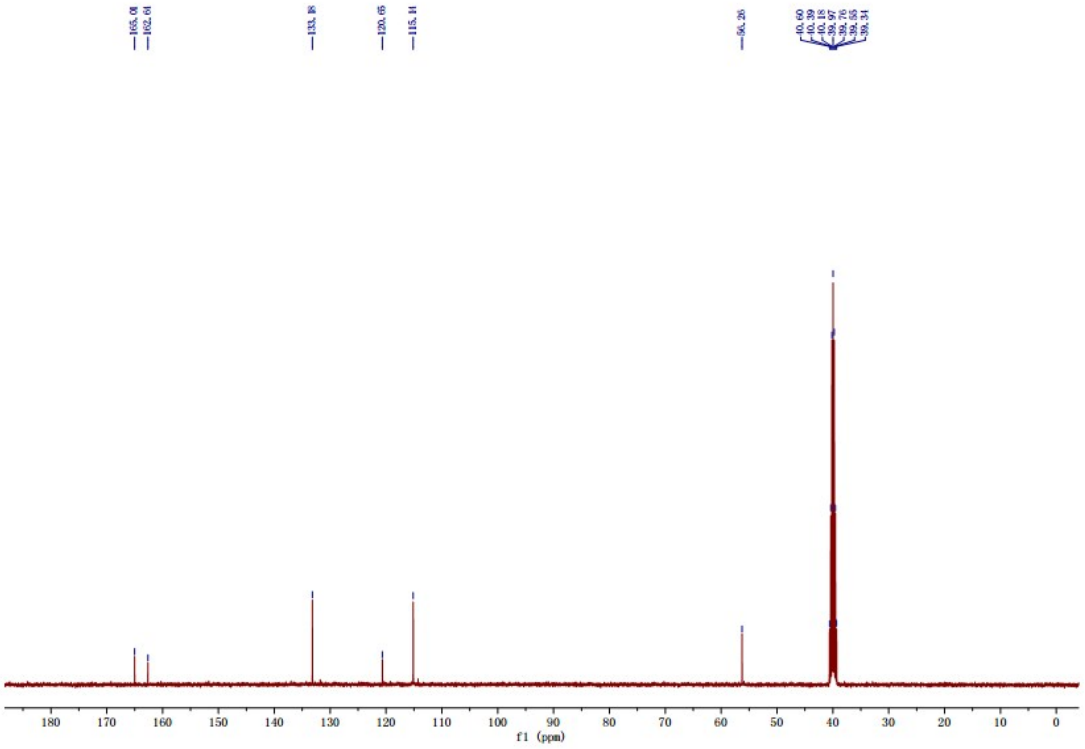


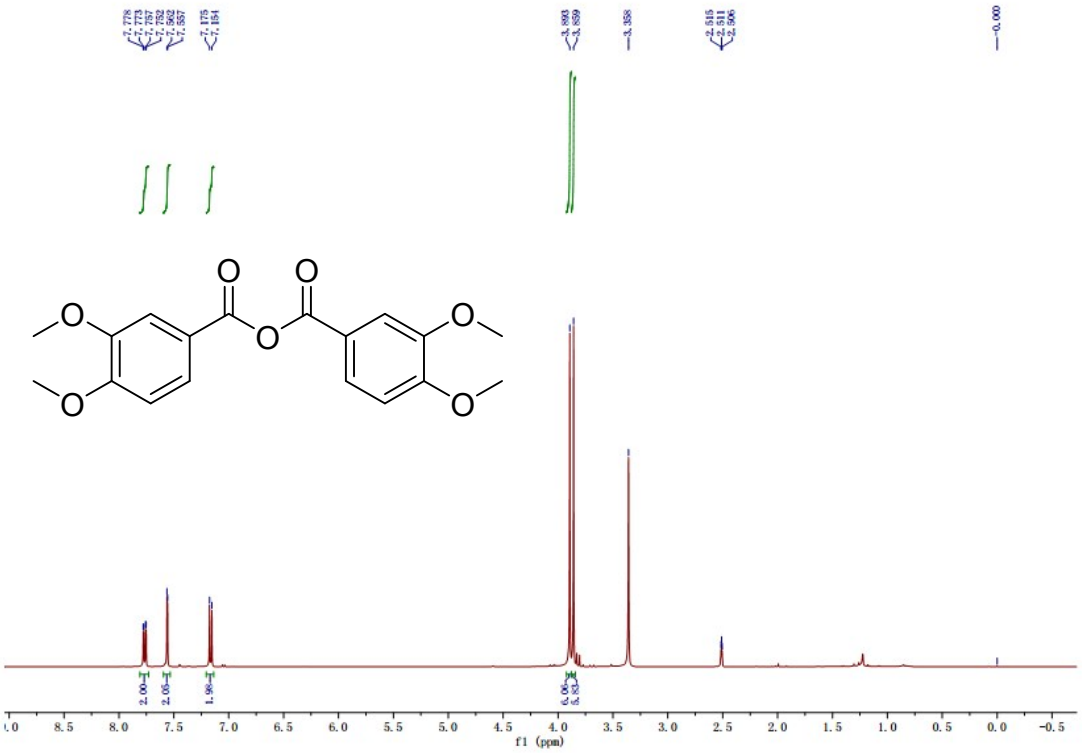


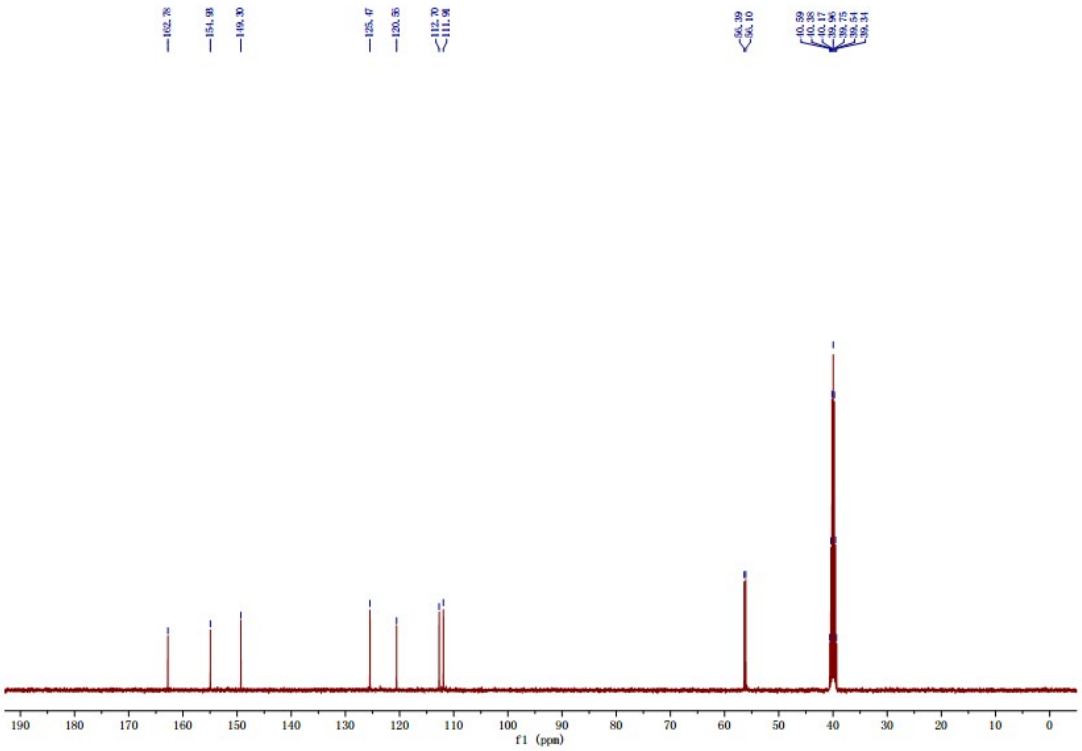
4-methoxybenzoic anhydride:





3,4-dimethoxybenzoic anhydride:





4-chlorobenzoic anhydride: