

Electronic Supporting Information (ESI)

**A novel COF-based Cu heterogeneous catalyst for green Suzuki cross-coupling
reaction under mild conditions**

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1. Materials and methods

All starting chemicals and reagents were purchased from commercial suppliers and used as received, unless otherwise mentioned. Spectroscopic measurements were conducted under ambient conditions using dry solvents. The FT-IR spectra were recorded using KBr pellets in the range of 4000–400 cm^{-1} on a Varian 660-IR spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker Avance III HD (600 MHz) spectrometer. The chemical shifts are expressed in parts per million (ppm) with TMS as internal standard. Thermogravimetric analysis (TGA) measurements were carried out on a NETZSCH DSC 200F3 instrument equipped with an automatically programmed temperature controller. The TGA curves were measured in an air atmosphere by heating the samples from 25 °C to 800 °C at a rate of 10 °C min^{-1} . Powder X-ray diffraction (PXRD) measurements were carried out in reflection mode on a Rigaku Ultima IV–185 diffractometer with Cu-filtered $K\alpha$ radiation ($\lambda = 1.5404 \text{ \AA}$) and a position-sensitive detector (LynxEye, step size: 0.02°, step time: 10s). The PXRD measurements of COF materials were performed by depositing the powder on a silicon wafer and applying a low scan speed and small angle increments (from $2\theta = 1.5^\circ$ up to 30° with 0.02° increment). Scanning electron microscopy (SEM) images were recorded using a JEOL JSM-7500F instrument under an accelerating voltage of 20–30 kV. X-ray photoelectron spectroscopy (XPS) data were obtained using a Thermo K-Alpha⁺ scientific electron spectrometer using Al $K\alpha$ radiation. The N_2 isotherm measurements were carried out at 77 K in a liquid nitrogen bath. The samples were heated to 120 °C and kept at this temperature for at least 12 hours under vacuum for activation. The dry samples were thereafter loaded into sample tubes and activated under high vacuum (less than 10^{-5} Torr) at 200 °C. The apparent surface areas were calculated from nitrogen adsorption data by multipoint BET analysis. The apparent micropore distributions were calculated from nitrogen adsorption data by the NLDFT method.

Synthesis of Cu-TAPB-BTDA

Firstly, a mixture of tris(4-aminophenyl)benzene (TAPB) (0.2 mmol, 71 mg) and 4,4'-(benzothiadiazole-4,7-diyl)dibenzaldehyde (BTDA) (0.3 mmol, 103 mg) using t-BuOH/mesitylene (3.0/3.0 mL, v/v 1:1) as the solvent with 6 M AcOH (0.5 mL) was stirred at 120 °C for 72 h to generate TAPB-BTDA as bright yellow crystalline solids. The obtained crystalline solids were completely washed with water and MeOH and dried in air (Yield, 85%). Then, TAPB-BTDA (500 mg) was added to an acetonitrile solution (15 mL) containing $\text{Cu}(\text{OAc})_2$ (45 mg 0.25 mmol) and stirred under reflux at 80 °C for 12 h. After that, the resultant residue was recovered by suction filtration and then eluted with the above solvent (acetonitrile). At last, the target heterogeneous

catalyst sample of Cu-TAPB-BTDA was acquired by the vacuum drying of the solid residue with a yield of at 80 °C for 12 h. Yield: 420 mg.

Synthesis of Cu- TAPP-BTDA

Firstly, a mixture of 5,10,15,20-tetra(4-aminophenyl) porphyrin (H₂TAPP) (0.2 mmol, 132 mg) and 4,4'-(benzothiadiazole-4,7-diyl)dibenzaldehyde (BTDA) (0.3 mmol, 103 mg) using t-BuOH/mesitylene (3.0/3.0 mL, v/v 1:1) as the solvent with 6 M AcOH (0.5 mL) was stirred at 120 °C for 72 h to generate TAPP-BTDA as bright yellow crystalline solids. The obtained crystalline solids were completely washed with water and MeOH and dried in air (Yield, 86%). Then, TAPP -BTDA (500 mg) was added to an acetonitrile solution (15 mL) containing Cu(OAc)₂ (45 mg 0.25 mmol) and stirred under reflux at 80 °C for 12 h. After that, the resultant residue was recovered by suction filtration and then eluted with the above solvent (acetonitrile). At last, the target heterogeneous catalyst sample of Cu-TAPP-BTDA was acquired by the vacuum drying of the solid residue with a yield of at 80 °C for 12 h. Yield: 430 mg.

General procedure for the Suzuki-Miyaura coupling reaction

In a typical activity test for the heterogeneous catalyst Cu-TAPB-BTDA, aryl halide (0.30 mmol), phenylboronic acid (0.45 mmol), a base (2.00 mmol), Pd@COFs (0.50 mol%), and 3.0 mL of solvent were added to 10 mL round bottom flask, and the reaction mixture was stirred at ambient temperature and atmosphere for 2.5 h. After the reaction was completed (monitored by TLC), the mixture was centrifuged and the solid was washed with water (3×5 mL) and acetonitrile (3×5 mL). The combined organic phase was washed with water (3×5 mL) to remove the base residue. Then, the organic phase was evaporated under vacuum leaving the crude product, which was purified by column chromatography over silica gel to obtain the final product.

Recycle test

After the completion of coupling reaction between phenylboronic acid and aryl halide, the heterogeneous COF-based Cu catalysts were easily separated by centrifugation. After centrifugation, the solid catalysts were washed with water and acetonitrile and the combined organic solution was concentrated under reduced pressure followed by flash chromatography to give the desired product. The recovered catalyst was then washed with water and EtOH and dried at 80 °C under vacuum for 6h before using for the next catalytic cycle.

2. FT-IR spectrum analysis

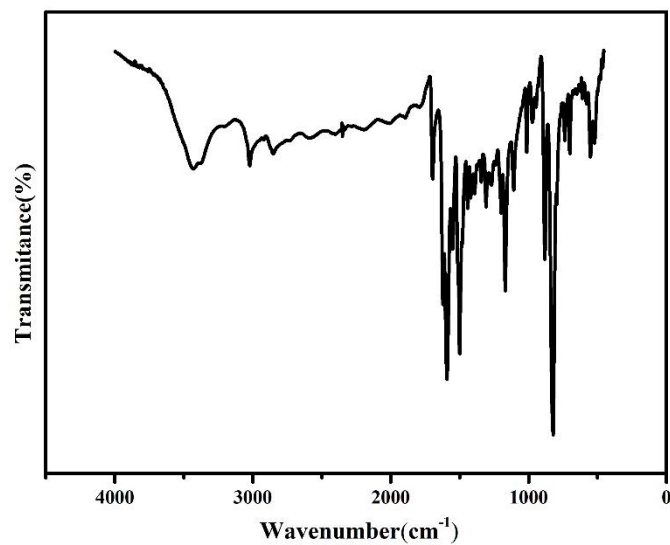


Fig. S1 FT-IR spectra of Cu-TAPB-BTDA.

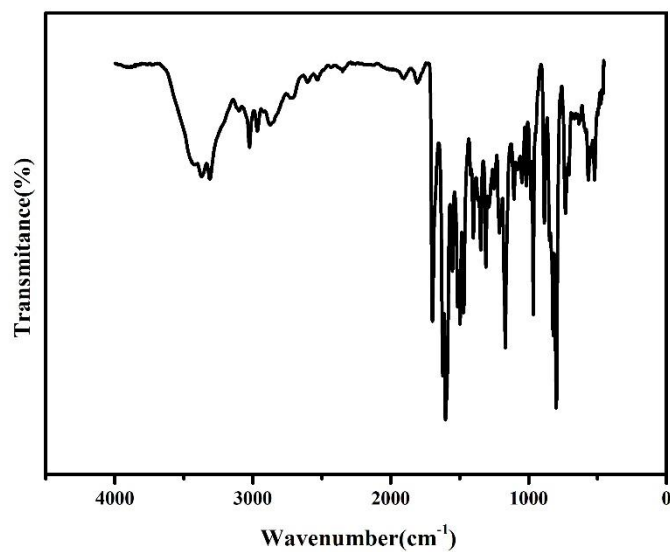


Fig. S2 FT-IR spectra of Cu-TAPP-BTDA.

3. Powder X-ray diffraction analysis

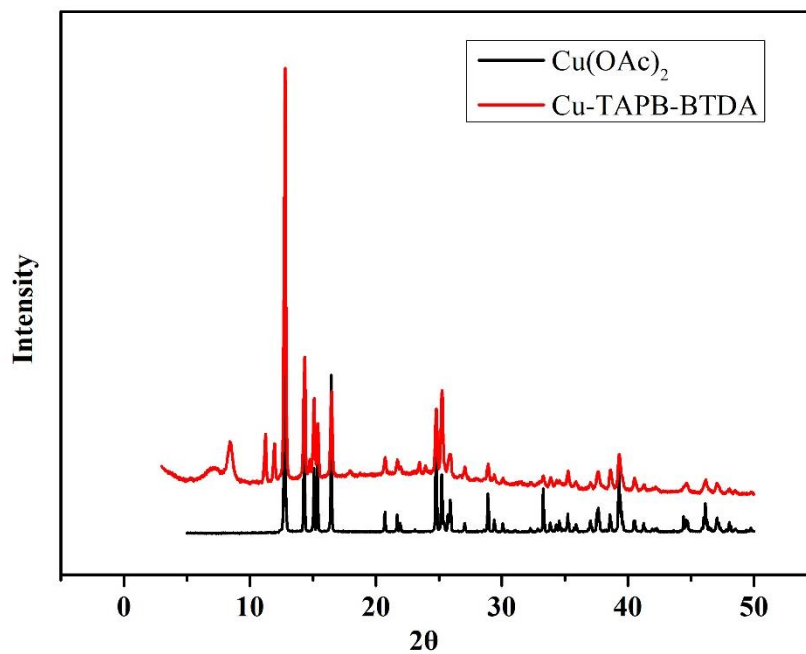


Fig. S3 Powder X-ray diffraction of Cu-TAPB-BTDA and Cu(OAc)₂.

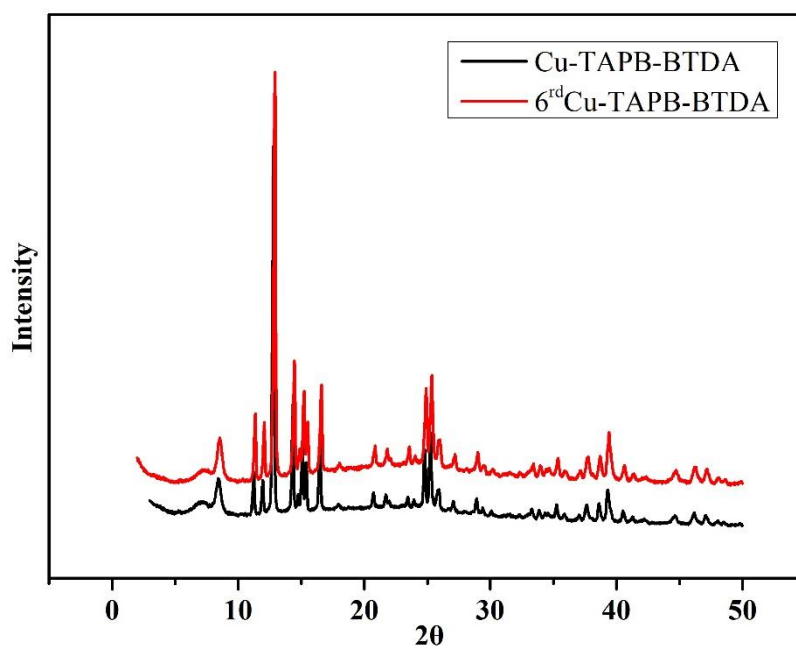


Fig. S4 Powder X-ray diffraction of Cu-TAPB-BTDA and ¹⁰rd Cu-TAPB-BTDA.

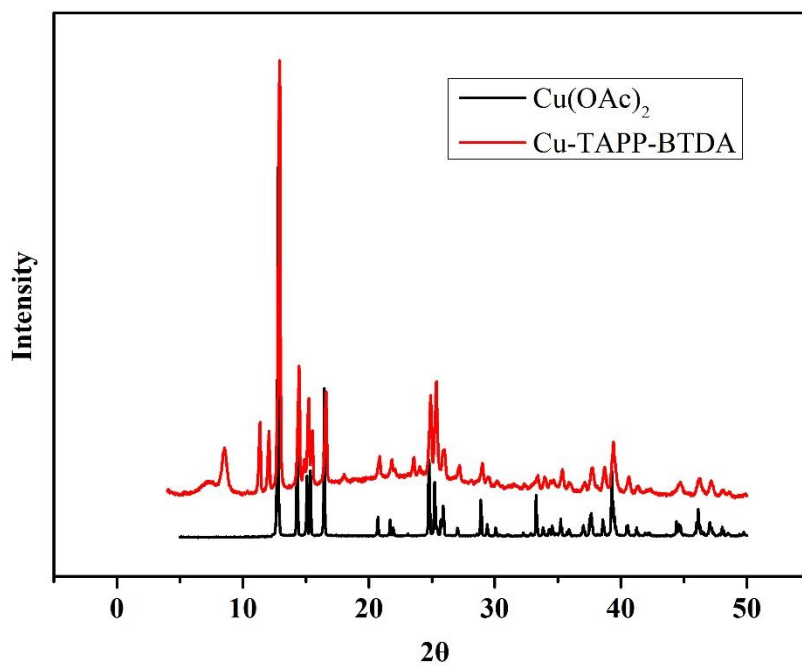


Fig. S5 Powder X-ray diffraction of Cu-TAPP-BTDA and Cu(OAc)₂.

4. Morphology and composition

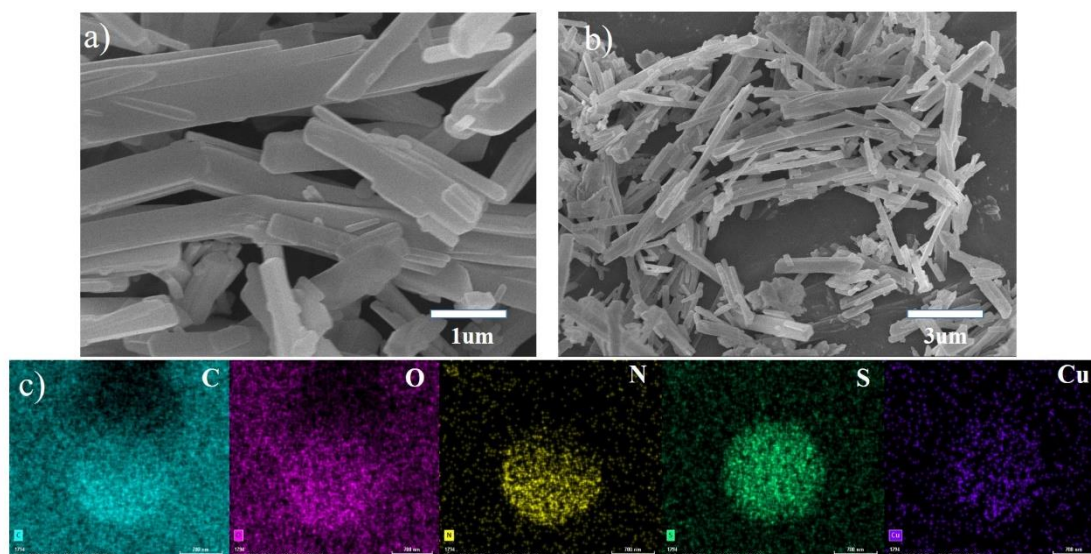


Fig. S6 SEM images of (a) TAPP-BTDA and (b) Cu-TAPP-BTDA. (c) EDS mapping of composition elements C, O, N, S and Cu.

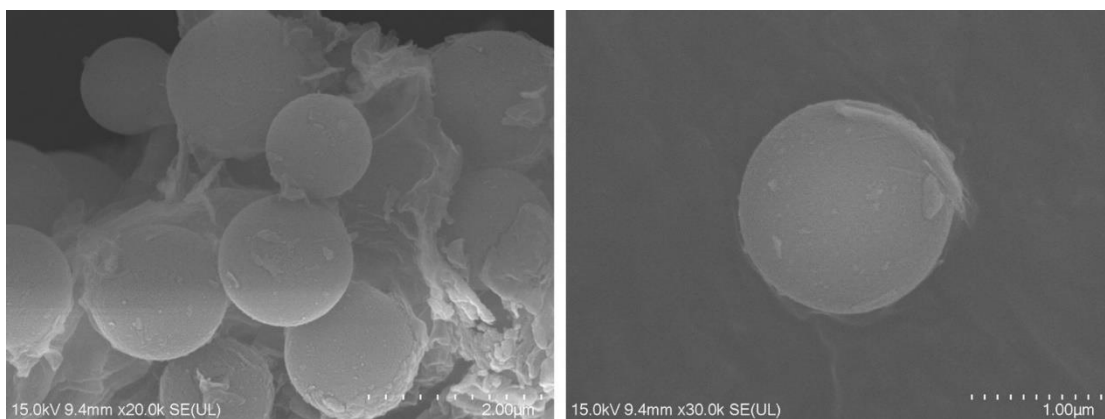


Fig. S7 SEM images of 10rd Cu-TAPB-BTDA.

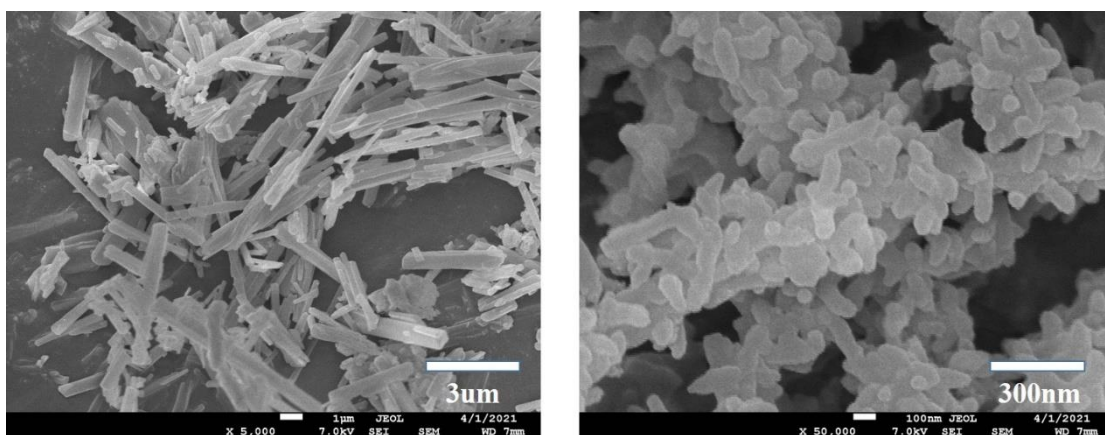


Fig. S8 SEM images of 10rd Cu-TAPP-BTDA.

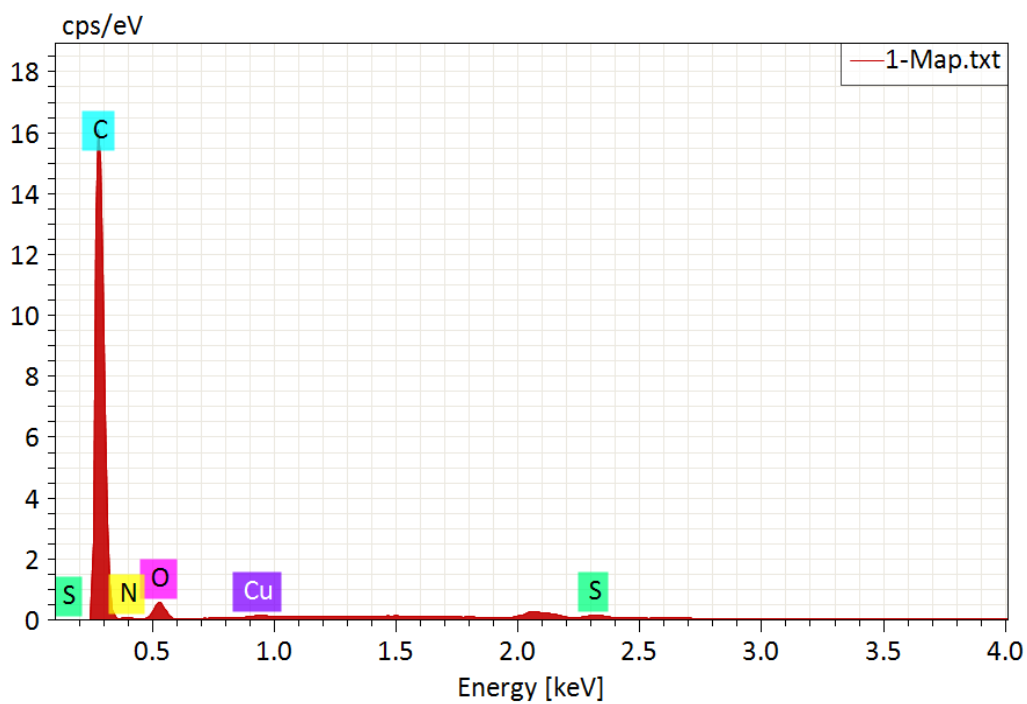


Fig. S9 Energy dispersive spectrum of Cu-TAPB-BTDA.

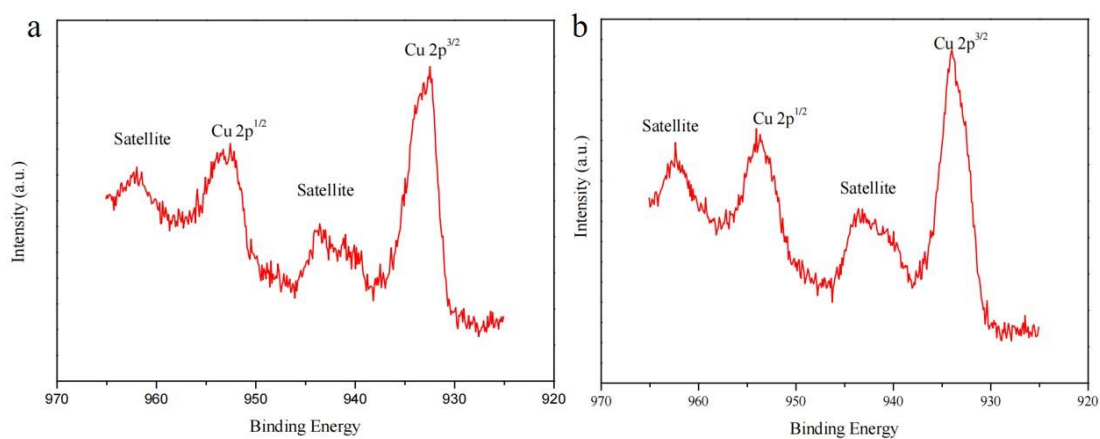


Fig. S10 Cu 2p XPS spectra of (a) 6rd Cu-TAPB-BTDA and (b) 6rd Cu-TAPP-BTDA.

5. Thermal gravimetric analysis

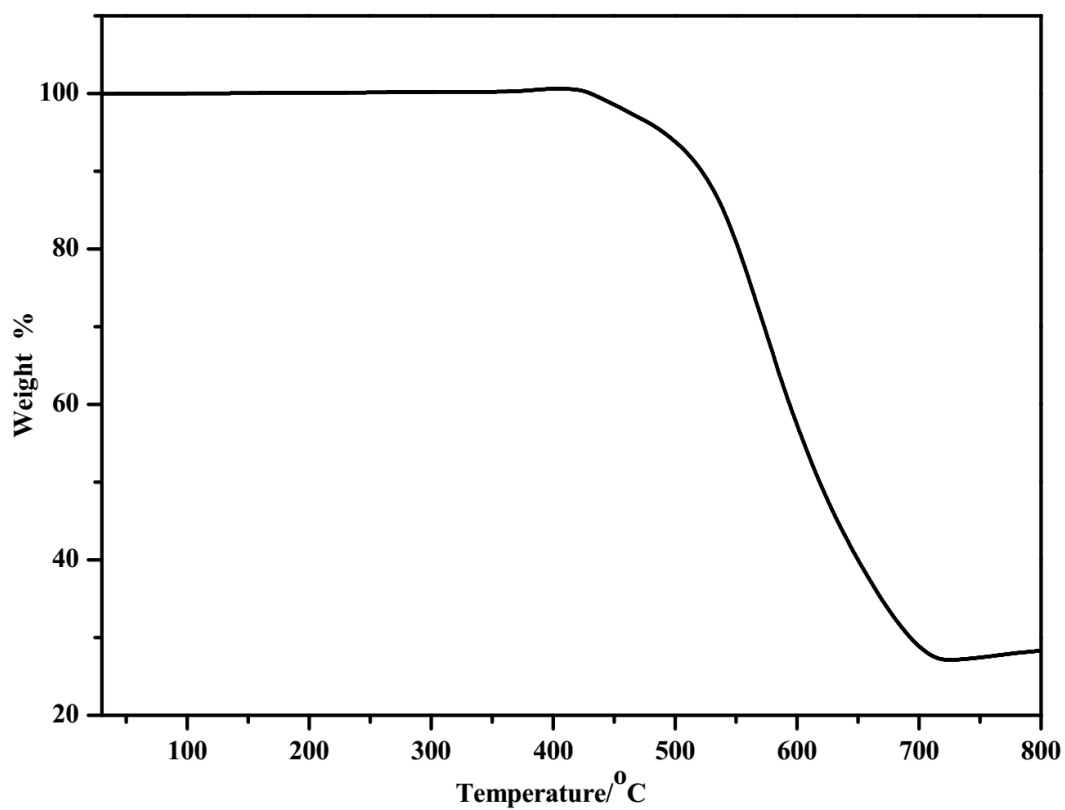


Fig. S11 TGA curve of Cu-TAPB-BTDA. The compound starts to decompose at 425 °C.

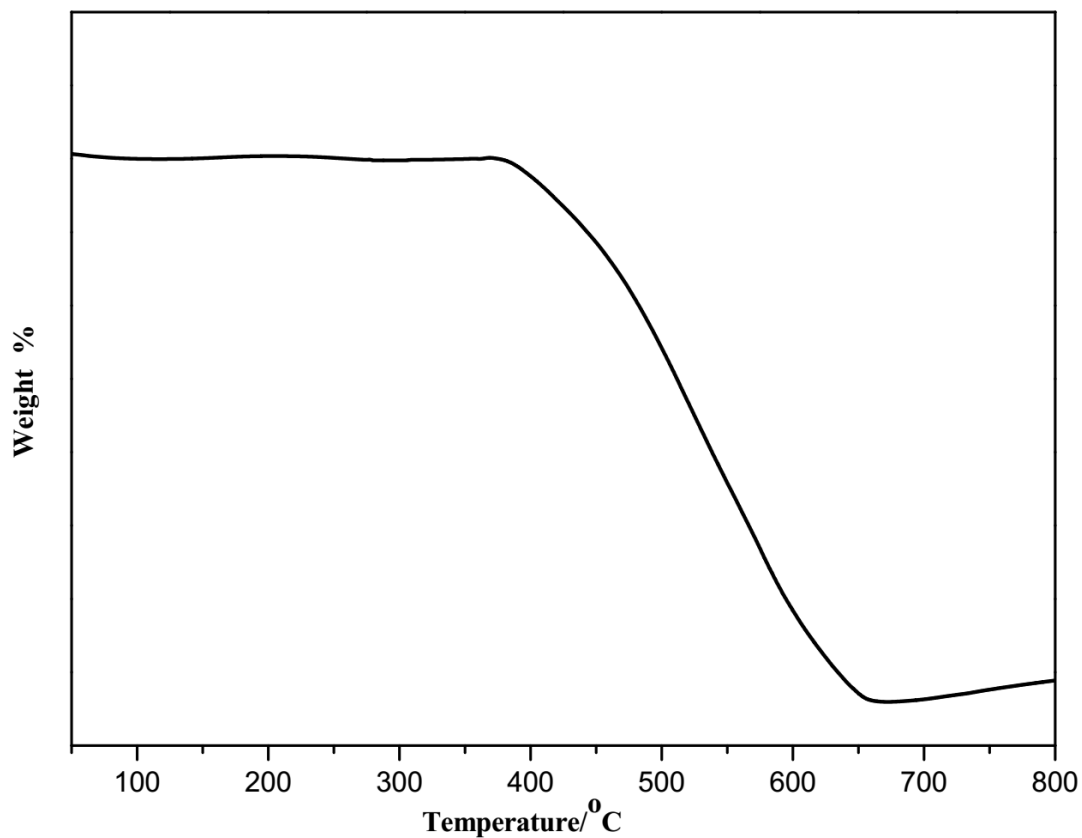


Fig. S12 TGA curve of Cu-TAPP-BTDA. The compound starts to decompose at 378 °C.

6. Nitrogen adsorption–desorption isotherm profiles

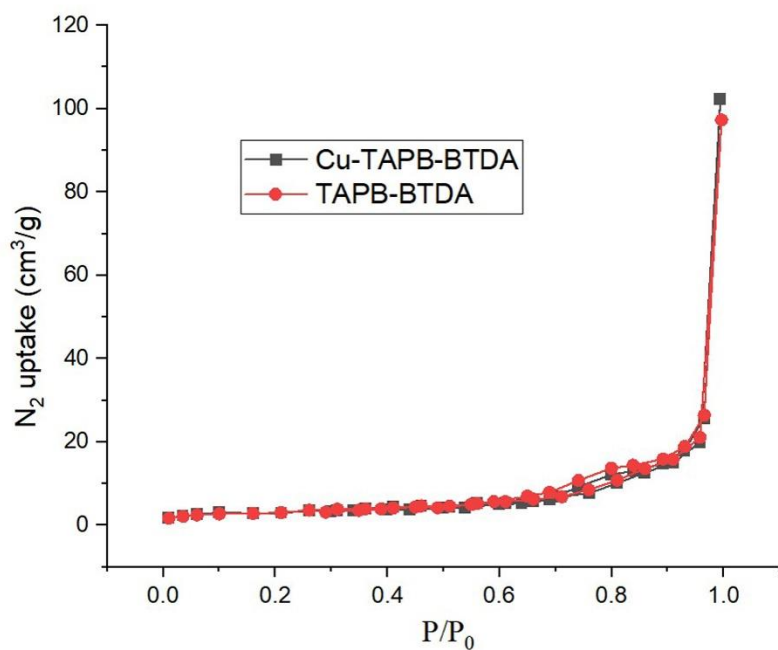


Fig. S13 N₂ adsorption (filled) and desorption (open) isotherm profiles of TAPB-BTDA and Cu-TAPB-BTDA.

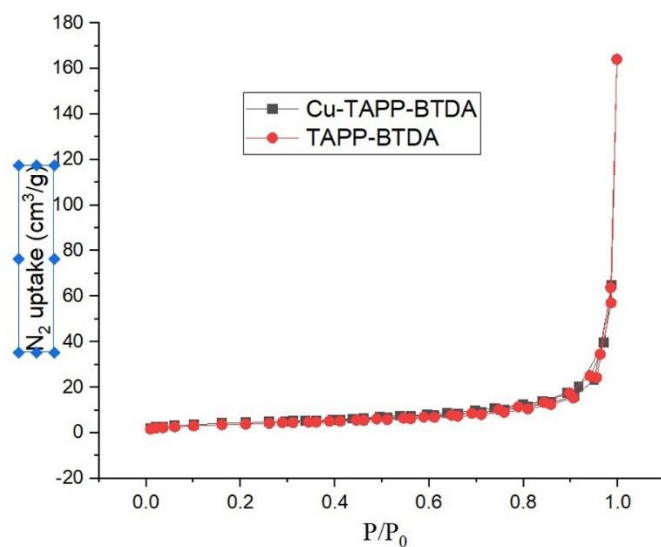


Fig. S14 N₂ adsorption (filled) and desorption (open) isotherm profiles of TAPP-BTDA and Cu-TAPP-BTDA.

7. XPS spectra

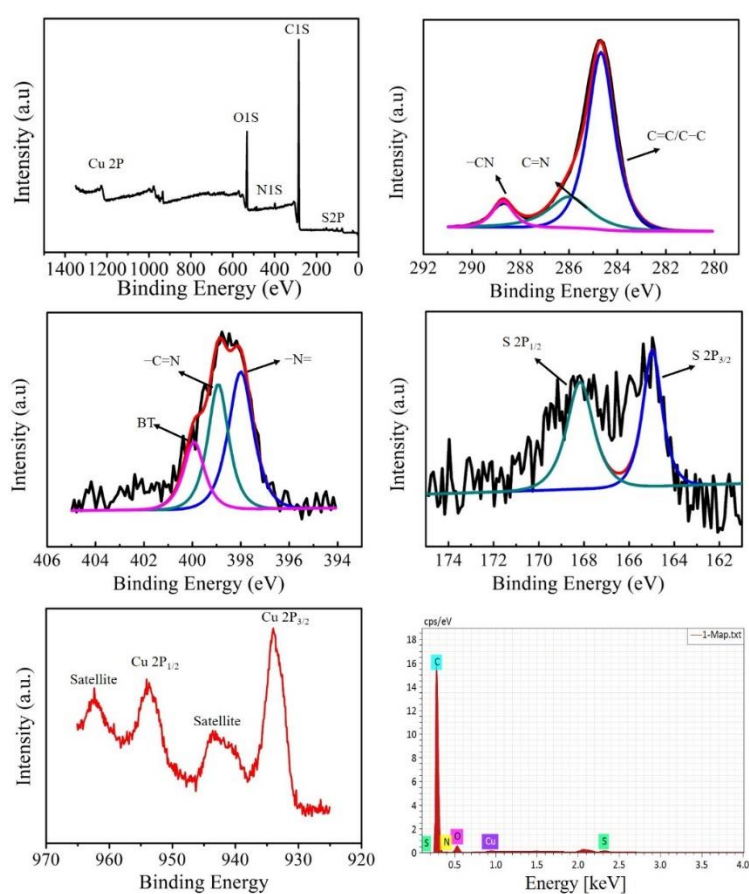
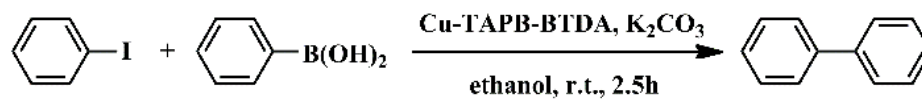


Fig. S15 (a) The survey XPS spectra, (b) C 1s, (c) N 1s, (d) S 2p, (e) Cu 2p high resolution XPS spectra for Cu-TAPP-BTDA and (f) energy dispersive spectrum of Cu-TAPP-BTDA.

8. Catalyst activity results of Cu-TAPB-BTDA

8.1 Stability and reusability of Cu-TAPB-BTDA

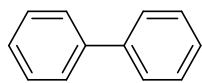
Table S1 Recycle test of Cu-TAPB-BTDA in the Suzuki-Miyaura cross coupling reaction of phenylboronic acid and iodobenzene ^a



Entry	Yield (%) ^b
fresh	99
cycle 1	99
cycle 2	99
cycle 3	99
cycle 4	98
cycle 5	98
cycle 6	99
cycle 7	98
cycle 8	98
cycle 9	97
cycle 10	96

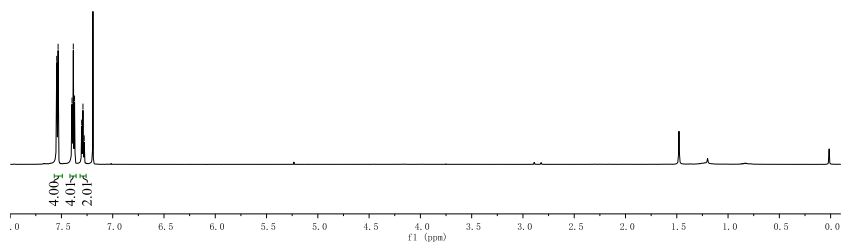
a Reaction condition: iodobenzene (0.30 mmol), phenylboronic acid (0.45 mmol), K₂CO₃ (2.0 mmol), Cu-TAPB-BTDA (0.5 mol%), solution (2.0 mL, ethanol), room temperature for 2.0 h; b Isolated yields.

8.2 NMR spectra of compounds

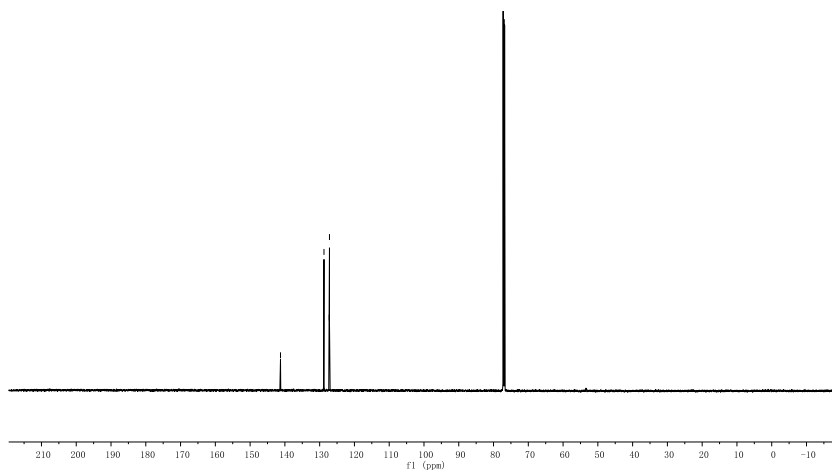


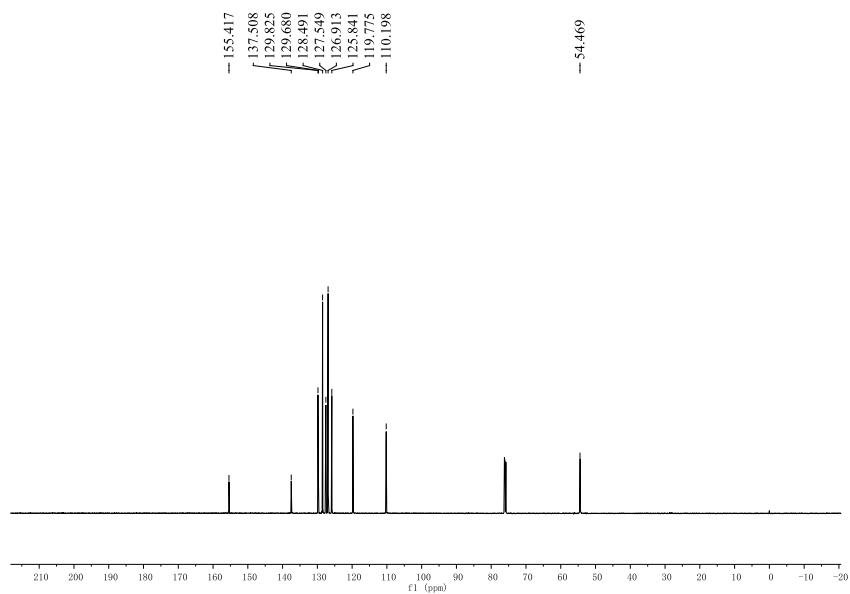
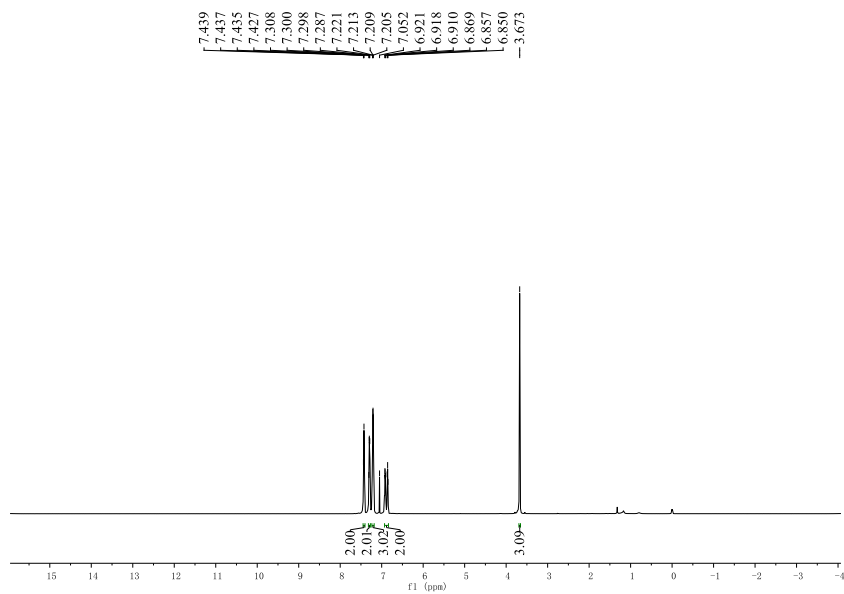
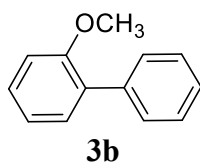
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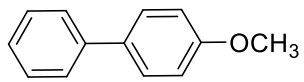
7.546
7.532
7.397
7.384
7.372
7.303
7.290
7.278



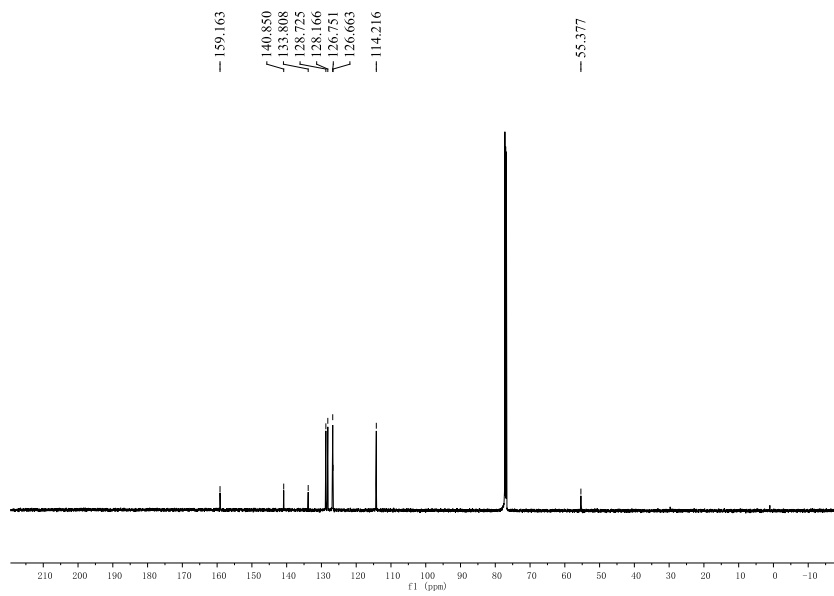
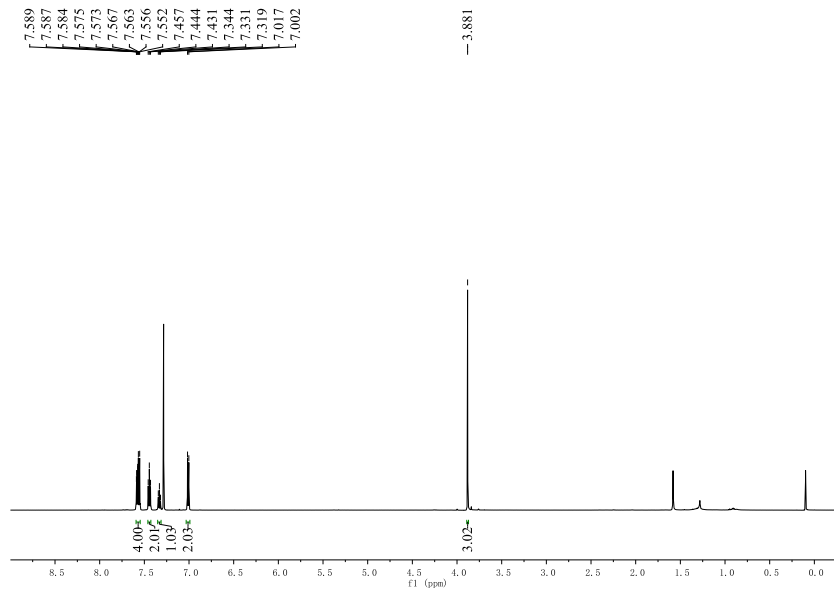
141.261
128.758
127.256
127.178

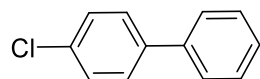




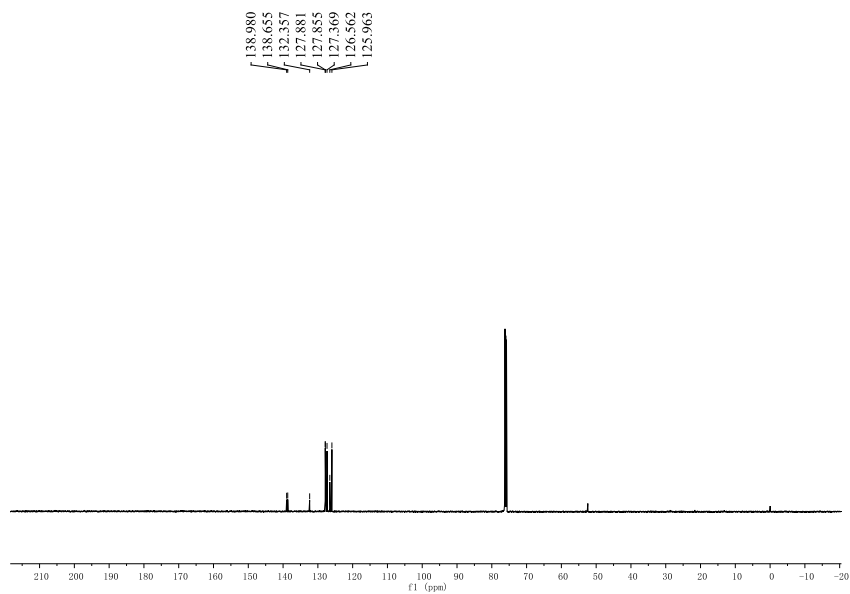
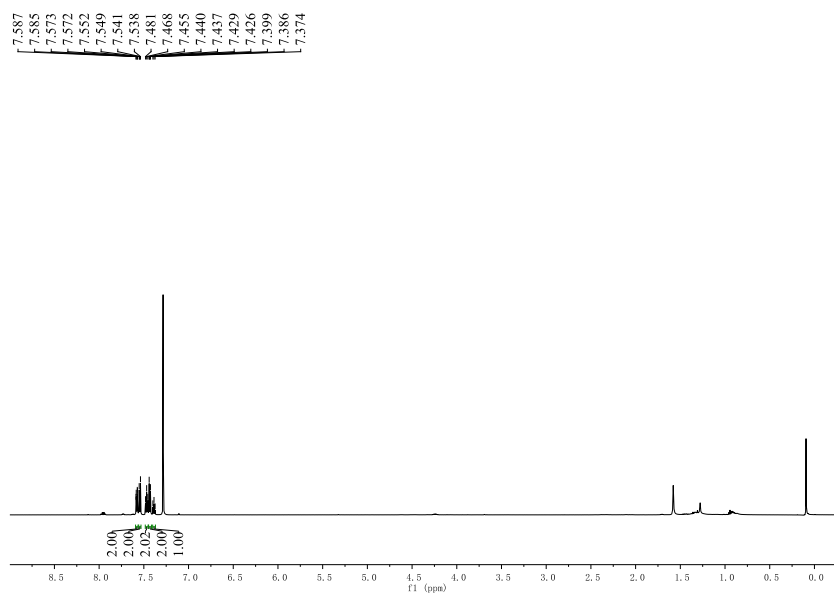


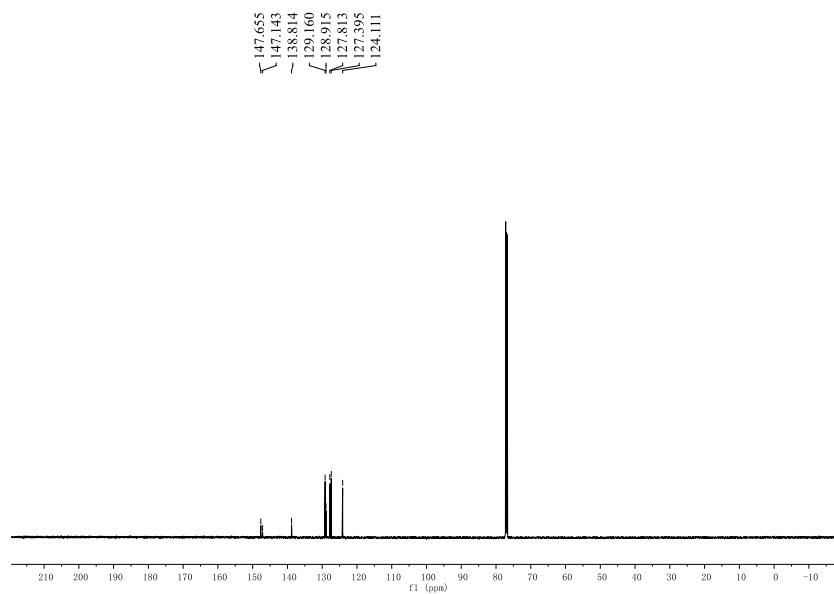
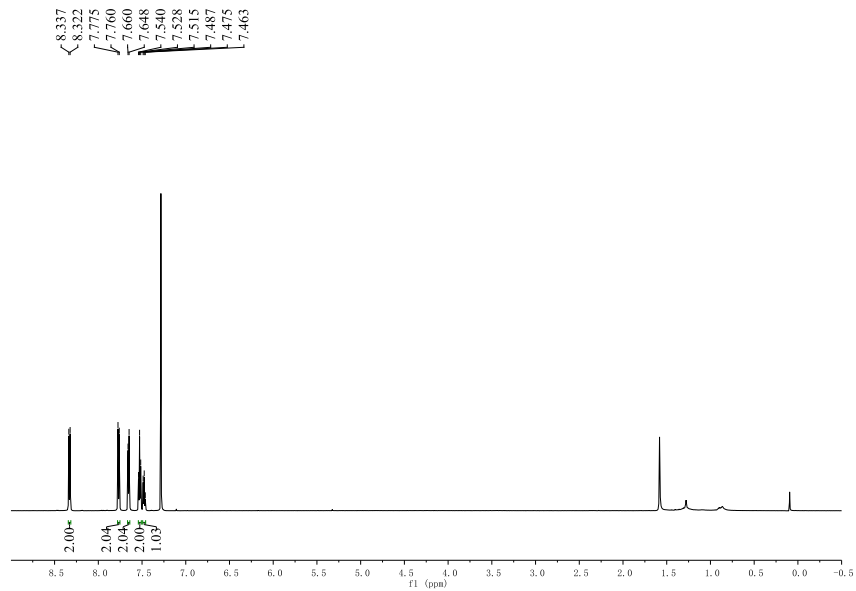
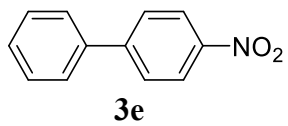
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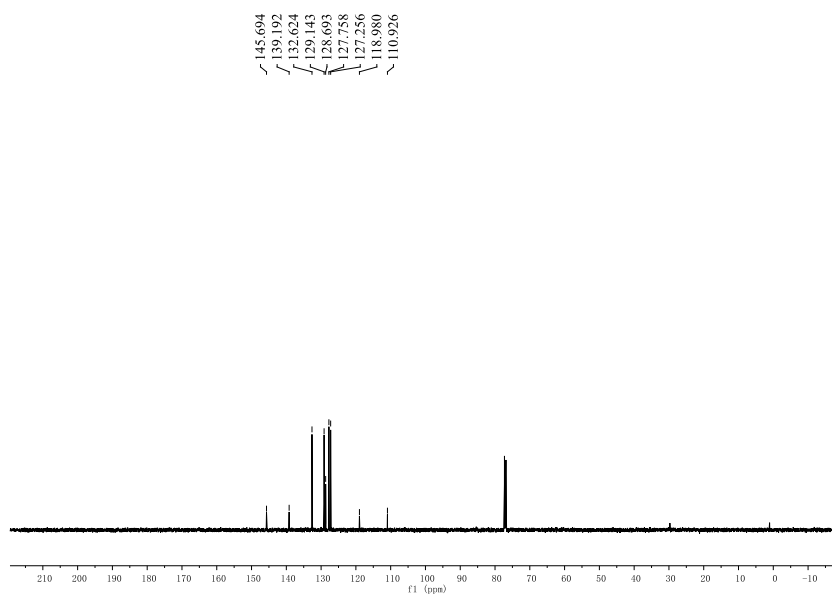
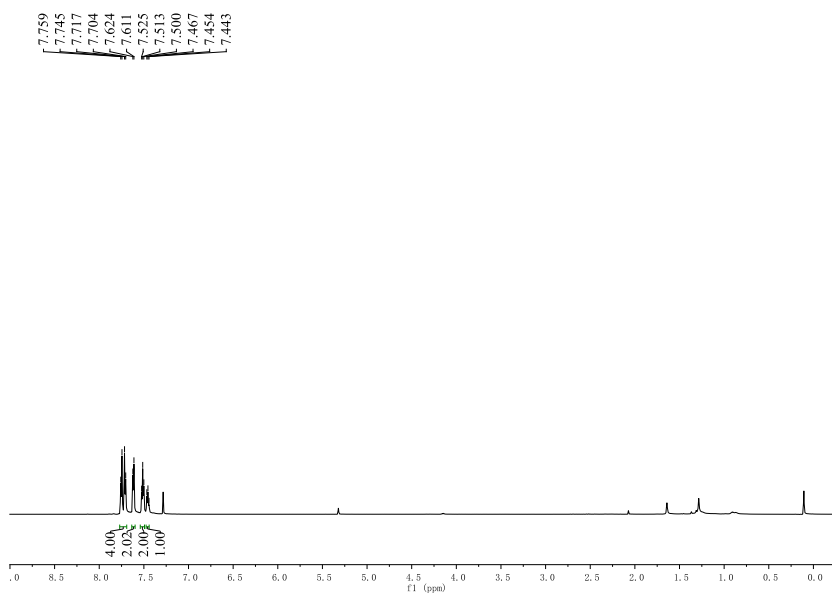
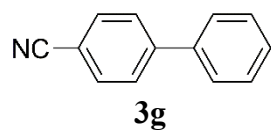


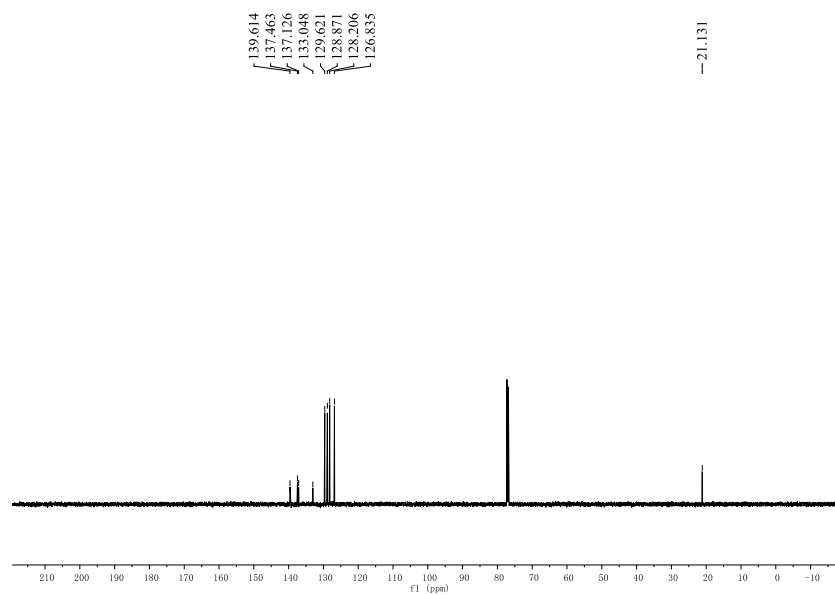
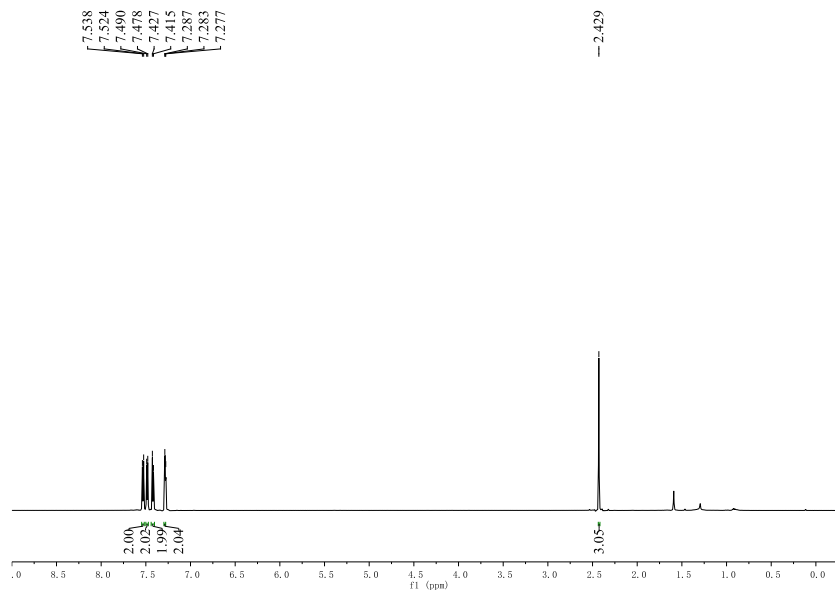
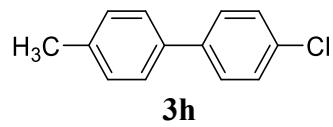


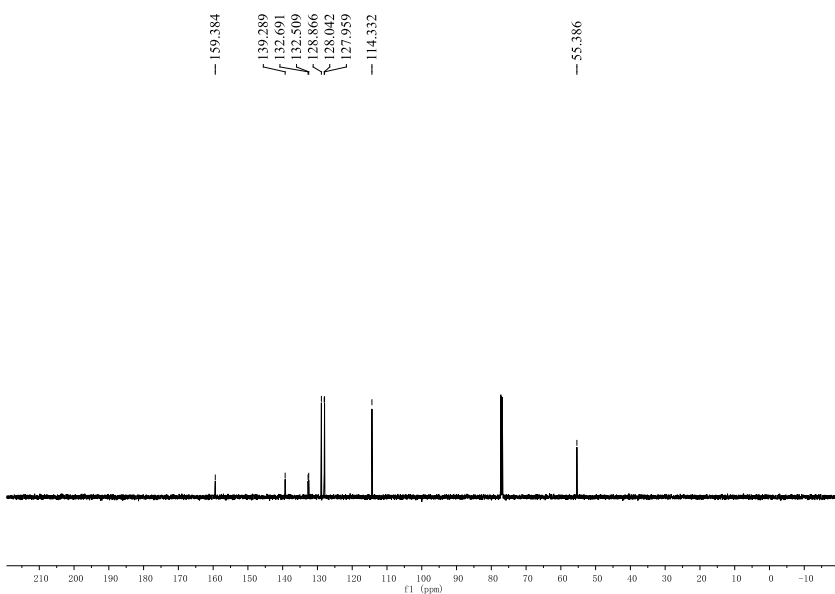
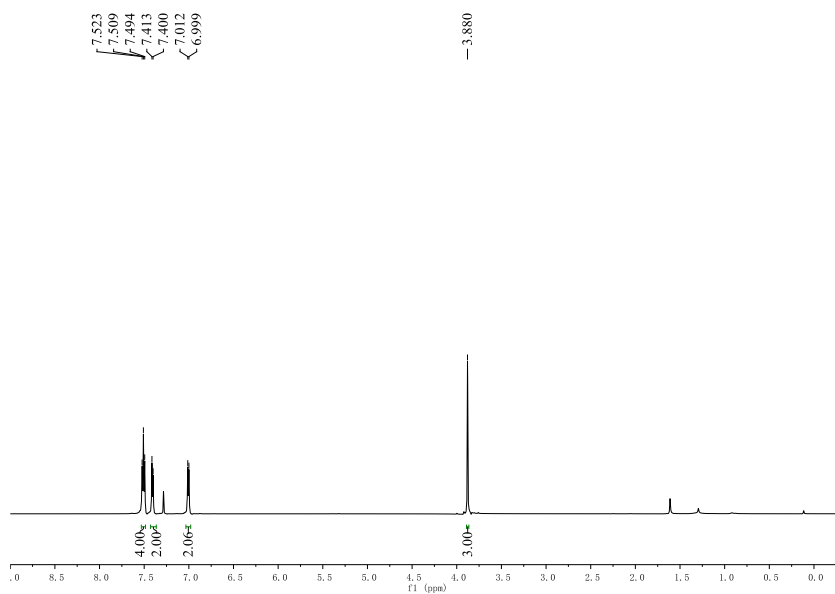
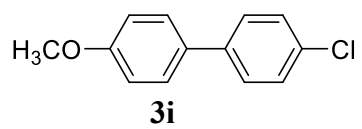
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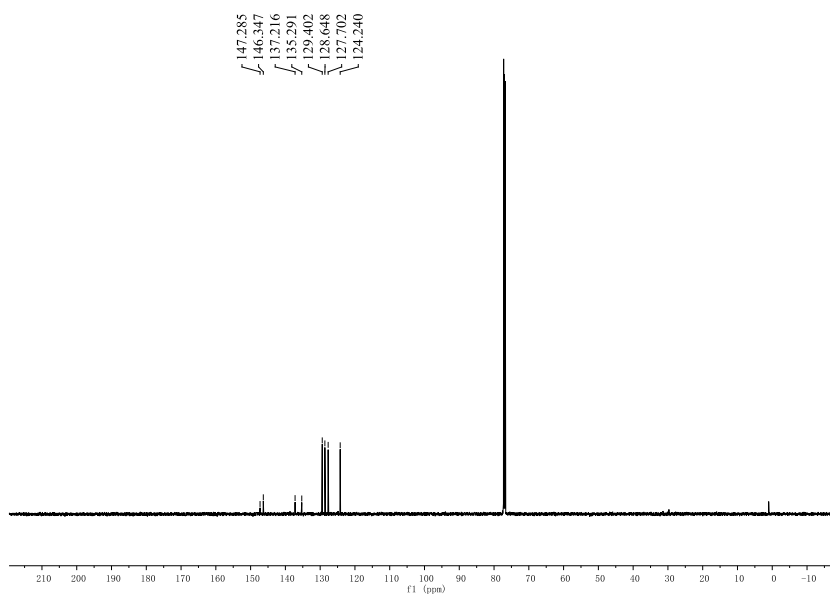
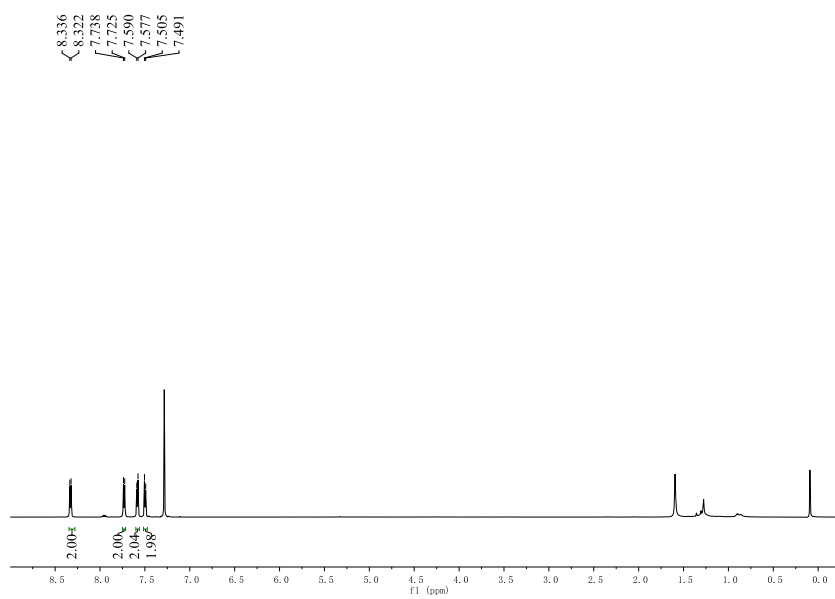
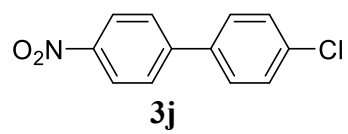


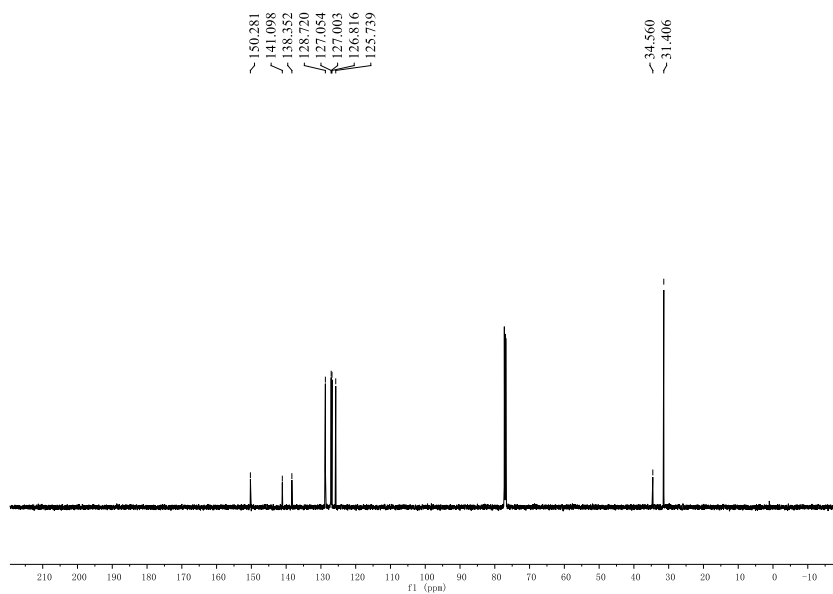
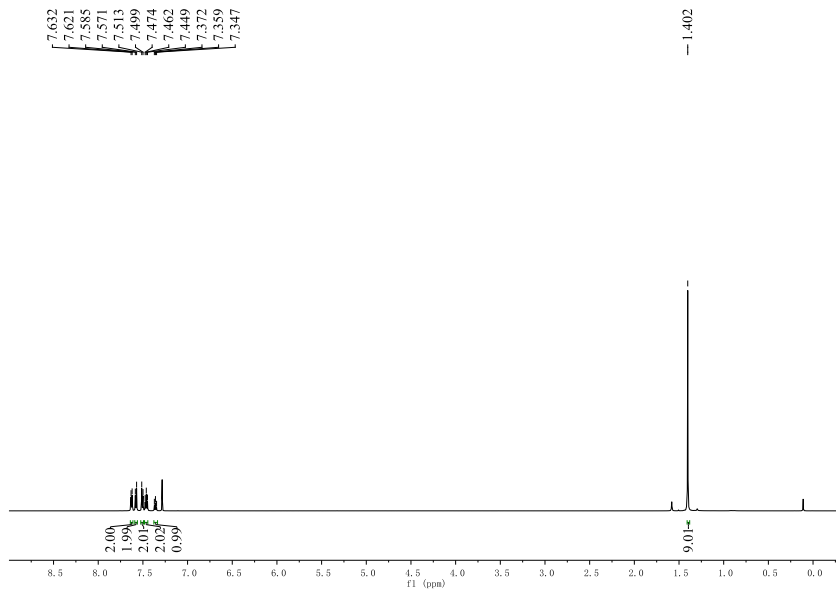
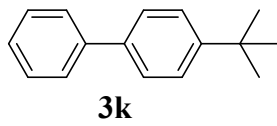


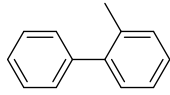




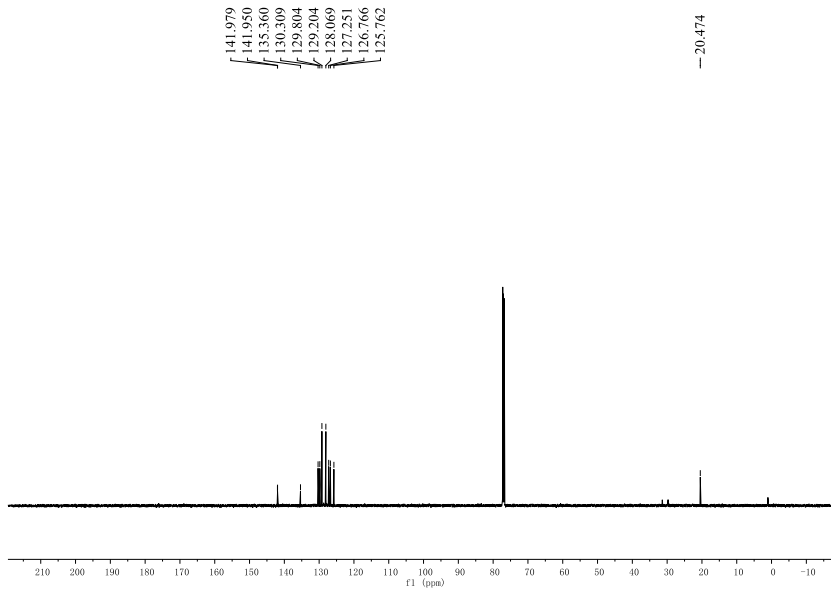
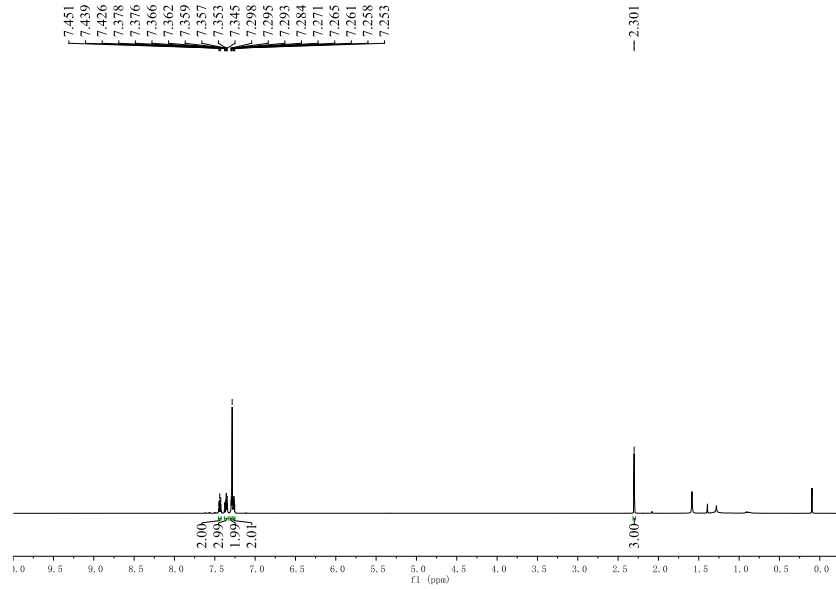


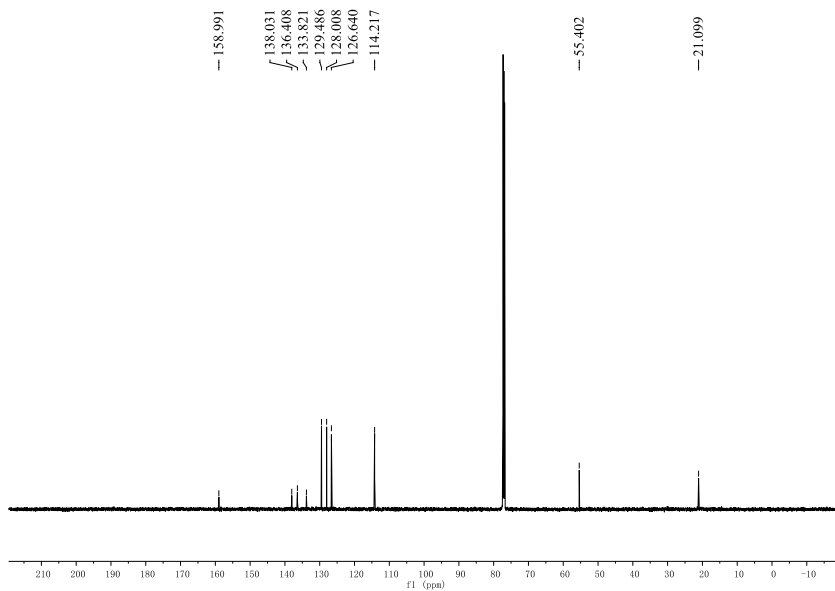
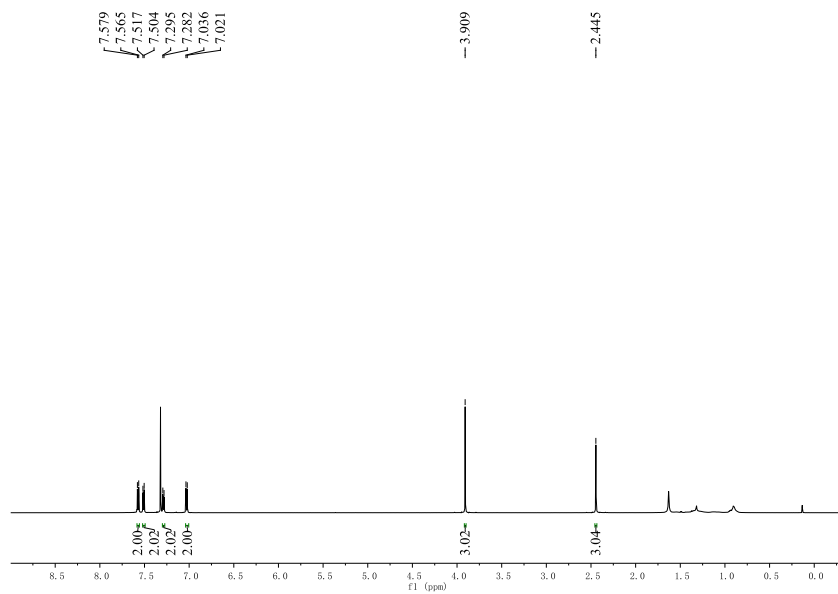
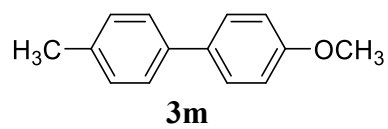


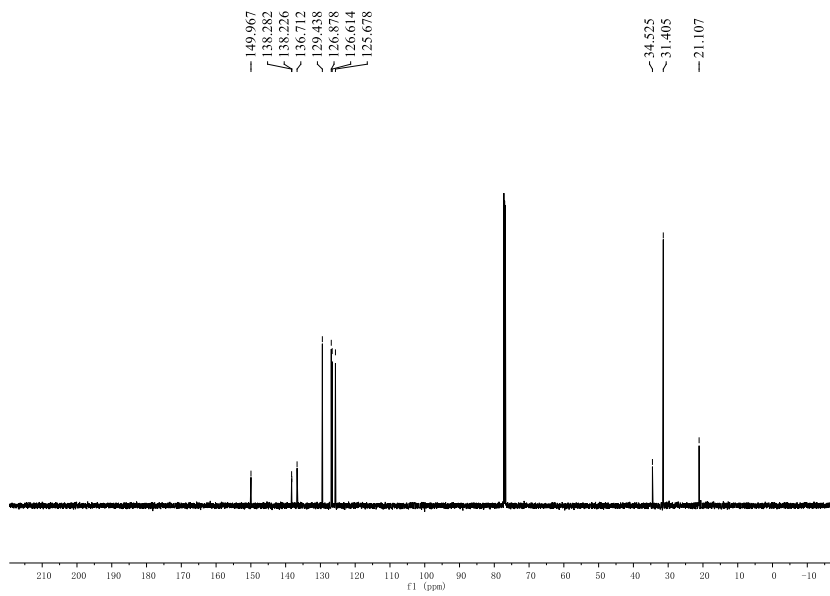
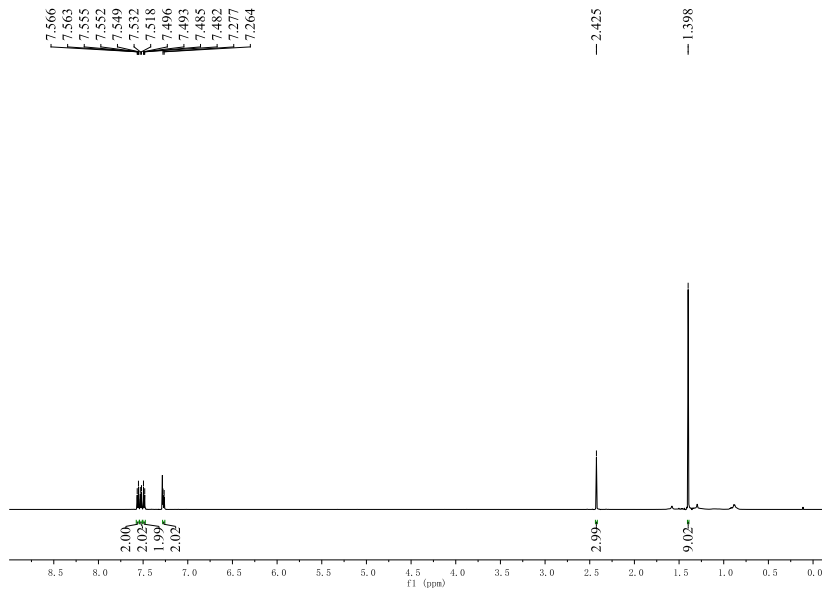
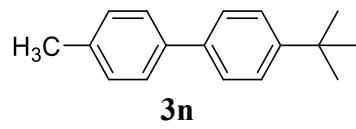


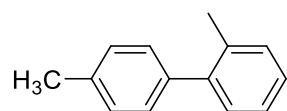


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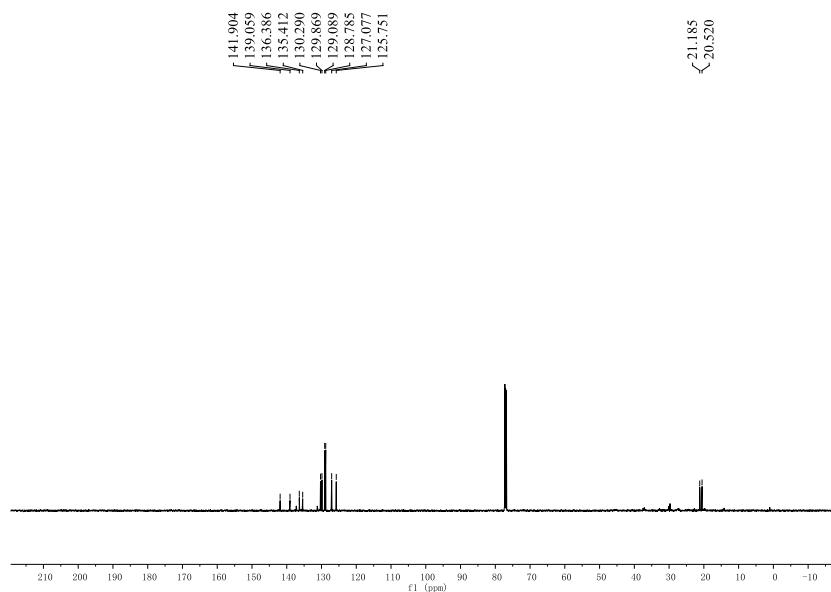
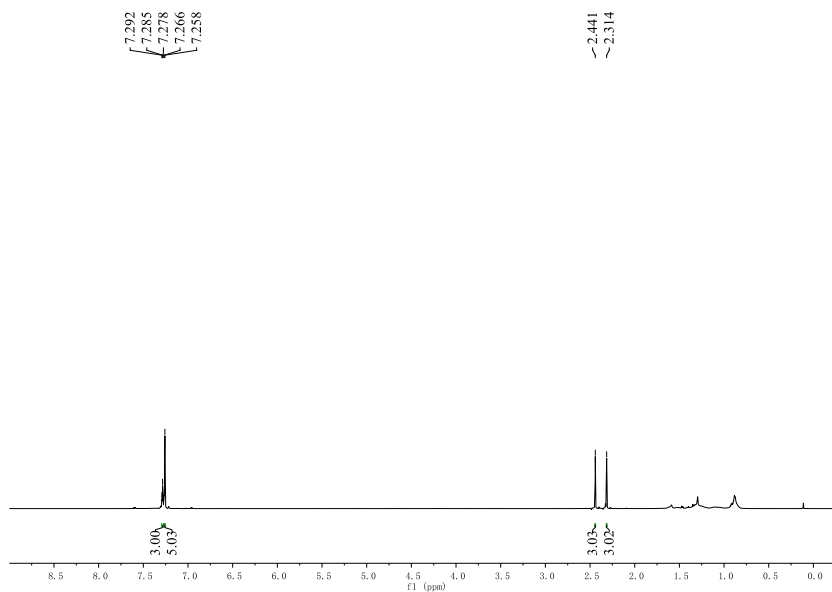


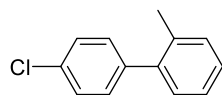






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3p

