Supporting information

Polydentate hydrazones as multitasking catalysts in visible-light-induced coupling reactions of amines

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1. General Information

Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The 1H(400MHz) and 13C NMR (100MHz) data were recorded on Bruker AVANCE Ⅱ 400MHz spectrometer using $CDCl_3$ as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. ^1H NMR spectra was recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference.

2. General procedure for synthesis of L_1-L_3

Preparation of L_1：To a 100ml oven-dried flask was added hydrazine hydrate (6.53mL) and 2-fluoropyridine (0.99mL), and heated to 120℃ to reflux. When the reaction was completed, it was diluted with water and extracted with anhydrous ether 3 times. The organic phase was concentrated using the rotary evaporator. Then the flask was added absolute ethanol (20mL) and picolinaldehyde (1.13mL). The reaction mixture was stirred at 90℃ to reflux. When the reaction was completed, removal of solvent followed by column chromatography afforded yellow solid 1.72g, yield 78%.

Preparation of L_2：To a 100 ml ventilated flask was added dodecanohydrazide (2.14 g), absolute ethanol (20 mL) and indoline-2,3-dione (1.32 g). The reaction mixture was stirred to reflux at 90° C. When the reaction was completed, suction filtration to obtain 2.74 g of orange solid with a yield of 80%.

Preparation of L_3: To a 100 mL oven dry flask was added ethanol (20 mL), hydrazine hydrate (6.53 mL) and 2-pyridinecarbaldehyde (1.13 mL). The reaction mixture was stirred at 90°C to reflux. When the reaction was completed, the solvent was removed using a rotary evaporator, deionized water was added and extracted three times with anhydrous ether to remove excess hydrazine hydrate in the system, and the organic phases were combined and the solvent was concentrated. Then add ethanol (20mL) and isatin (1.32g) to the flask again, wait for the reaction to end, and filter the obtained orange-red solid 2.20g with suction.

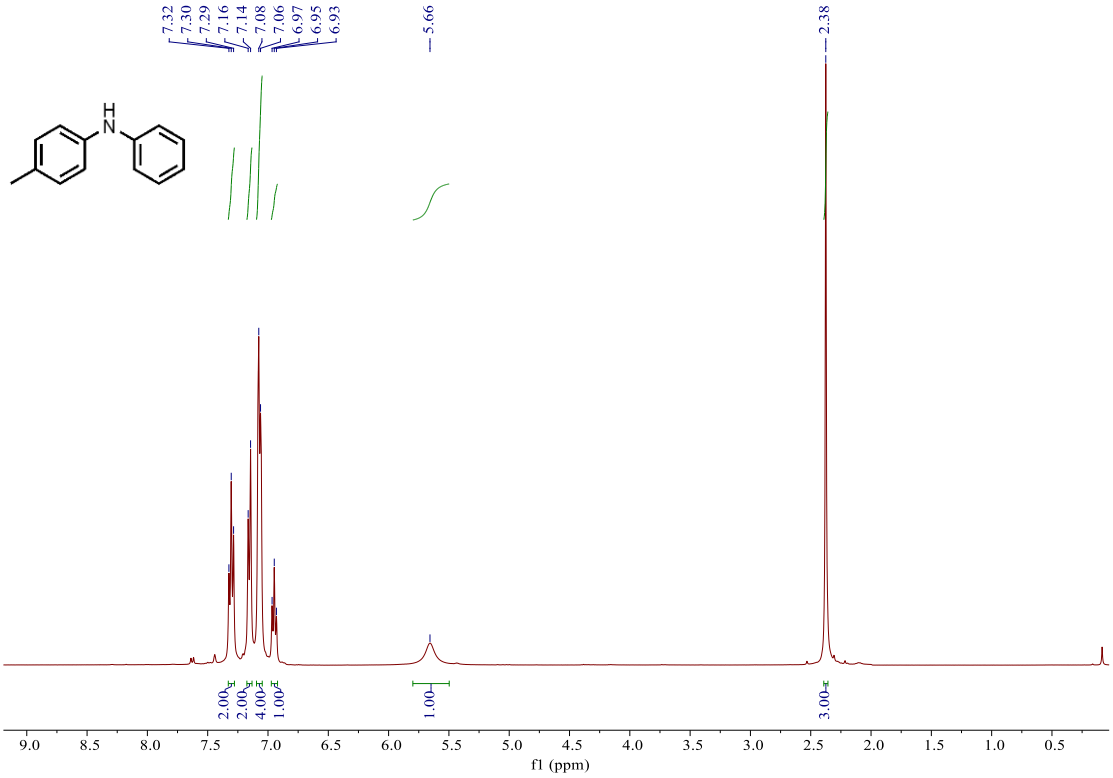
3. General procedure for synthesis of 3aa-3aj and 3ba-3ka,4a-4k

A dry 25 mL reaction tube was charged with arylboronic acid (2.5 mmol), arylamine (1.0 mmol), hydrazone ligand L_1 (0.1 mmol), $CuCl_2 \cdot 2H_2O$ (0.05 mmol), DBU (1.2 mmol) and DMF (2 mL). The reaction mixture was stirred at room temperature under blue LED illumination. The reaction was followed by thin layer chromatography (TLC). When the reaction was complete, the whole was transferred to a separatory funnel, deionized water was added, extracted three times with ethyl acetate, and the organic phases were combined and dried over anhydrous sodium sulfate. Concentration using a rotary evaporator to remove the solvent followed by column chromatography gave the desired product for **3aa-3aj and 3ba-ka.**

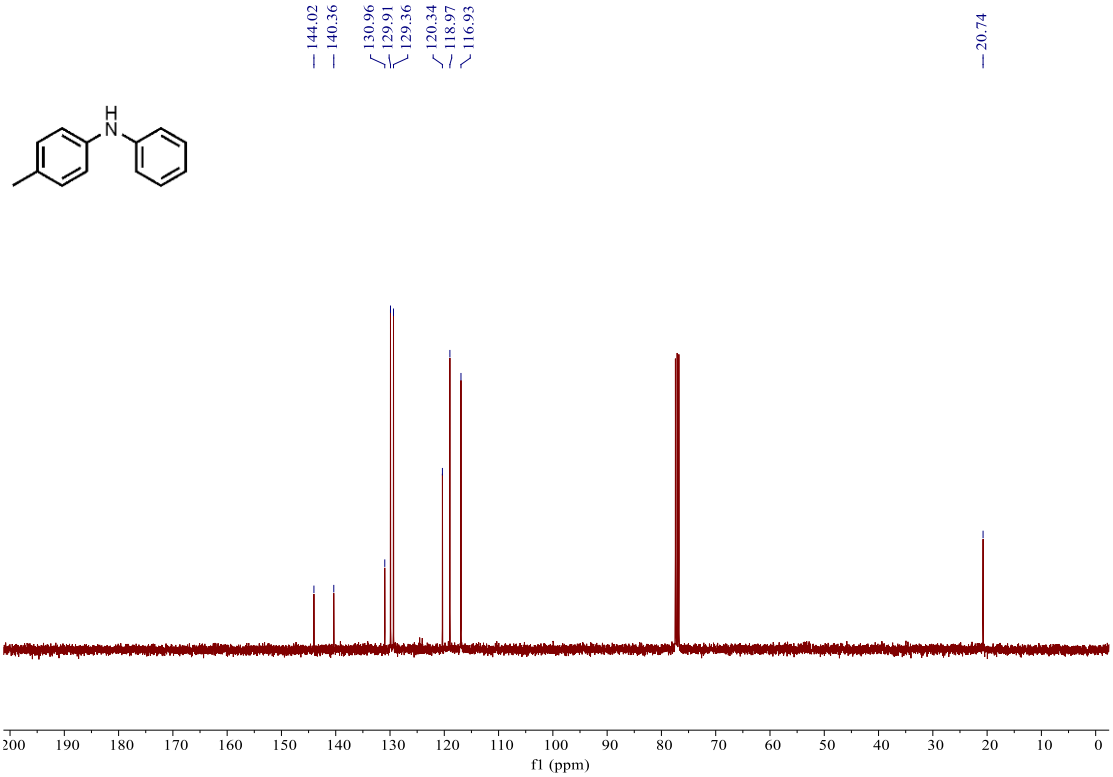
In a dry test tube, add 1.5 mmol of aniline compound, 1.2 mmol of ^{t}BuOK, 0.1 mmol of L_3, 0.05 mmol of copper chloride dihydrate and 2 ml of DMSO. The reaction mixture was stirred at room temperature under the irradiation of blue LED. The reaction was monitored by thin layer chromatography (TLC). When the reaction was completed, the solvent was concentrated using the rotary evaporator. Removal of solvent followed by column chromatography afforded desired products for **4a-4k.**

4. spectroscopic data for products

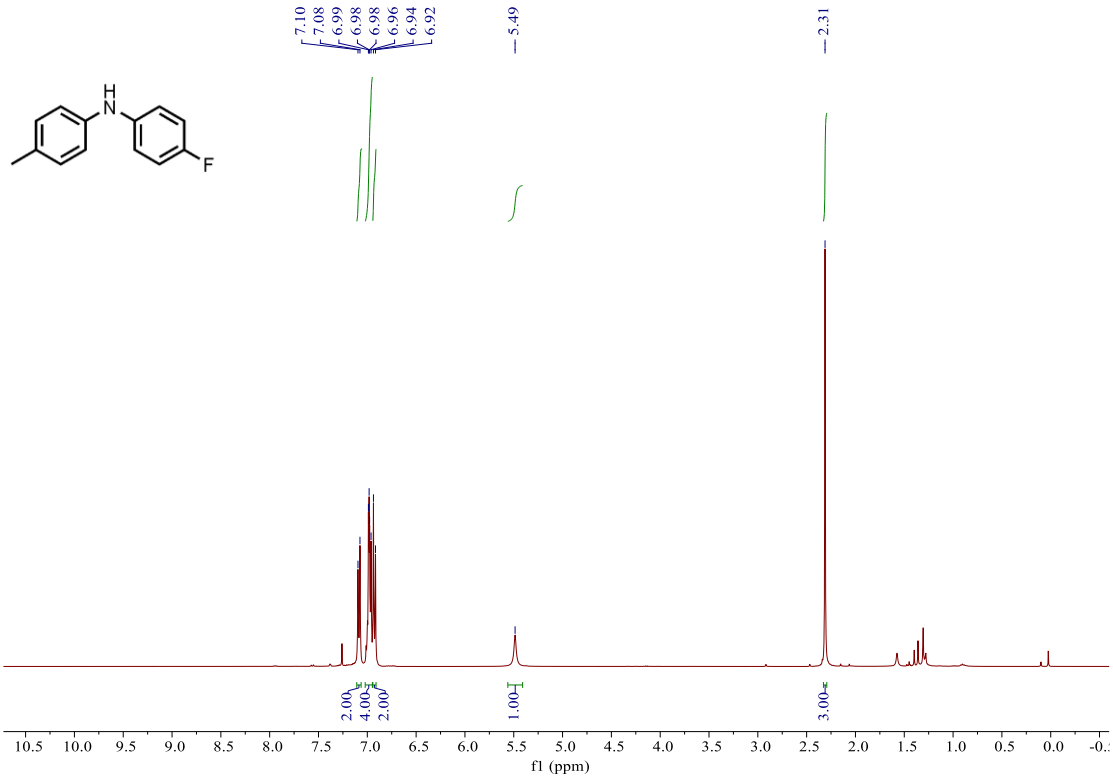
The ^{1}H-NMR spectrum of 3aa



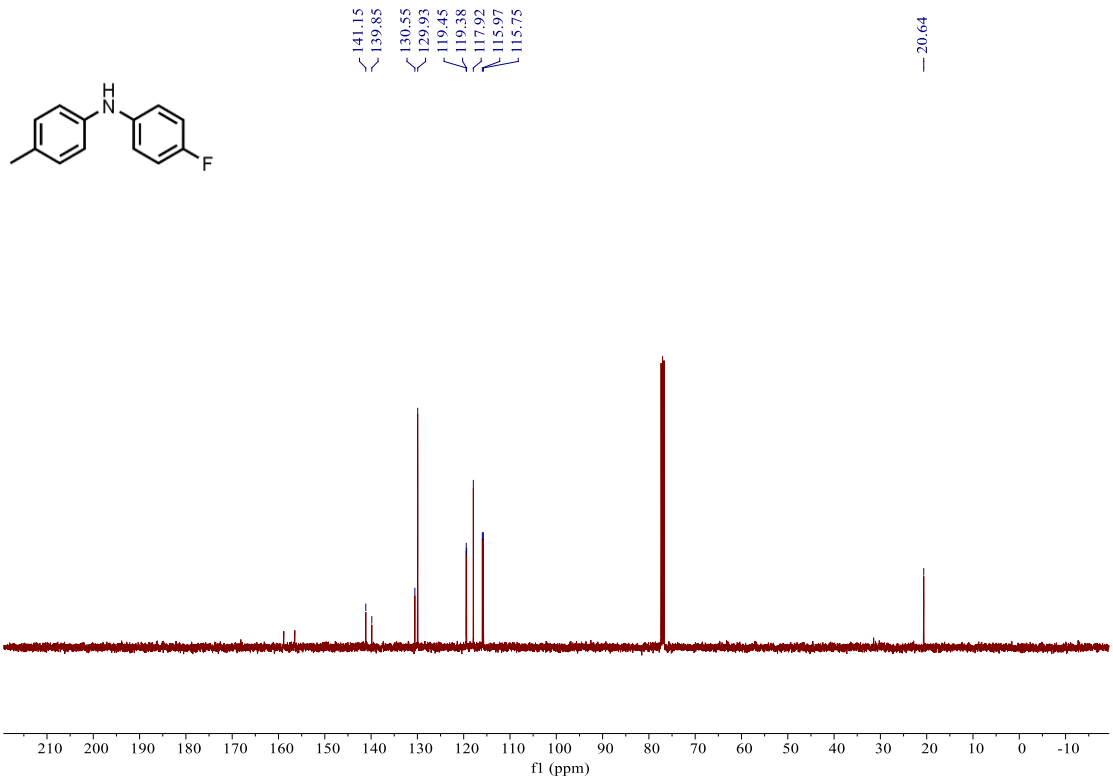
The ^{13}C-NMR spectrum of 3aa



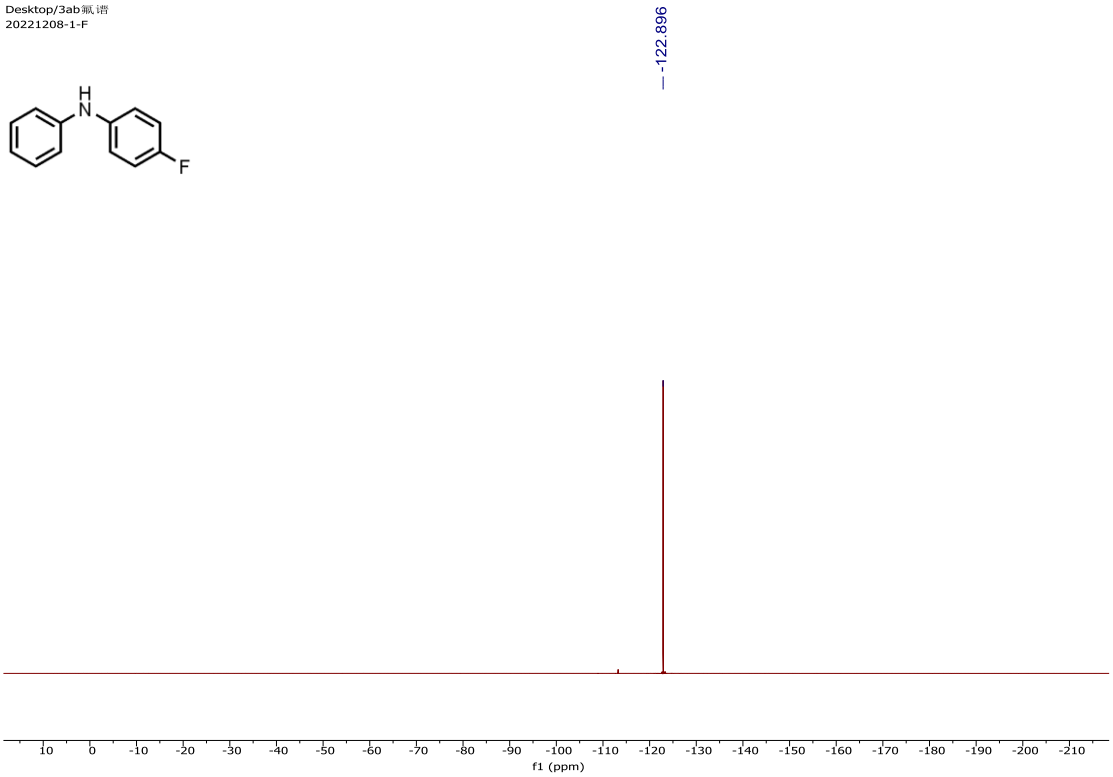
The ^{1}H-NMR spectrum of 3ab



The ^{13}C-NMR spectrum of 3ab



The ^{19}F-NMR spectrum of 3ab



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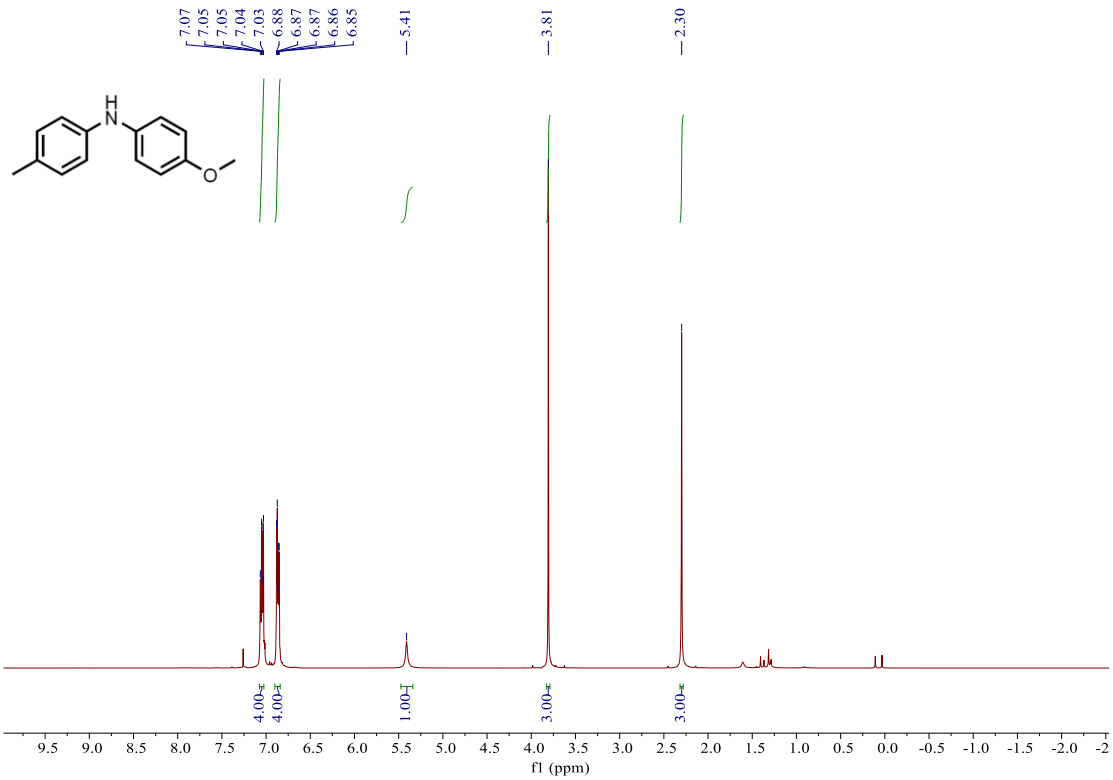

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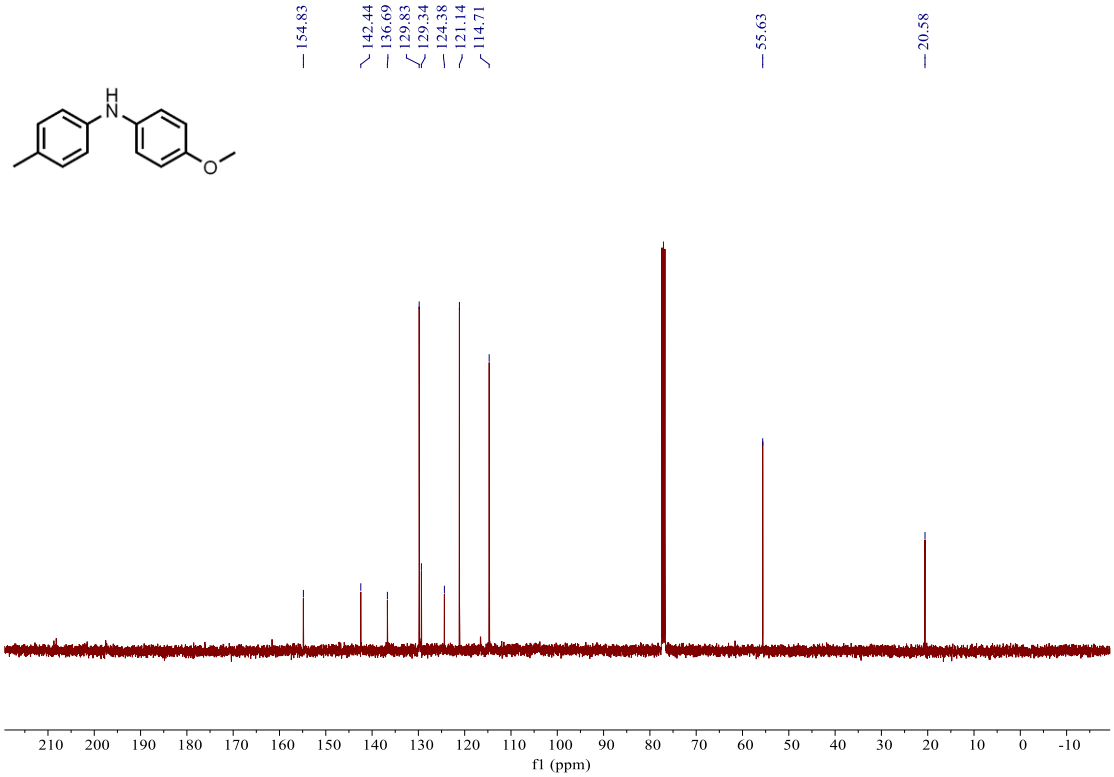

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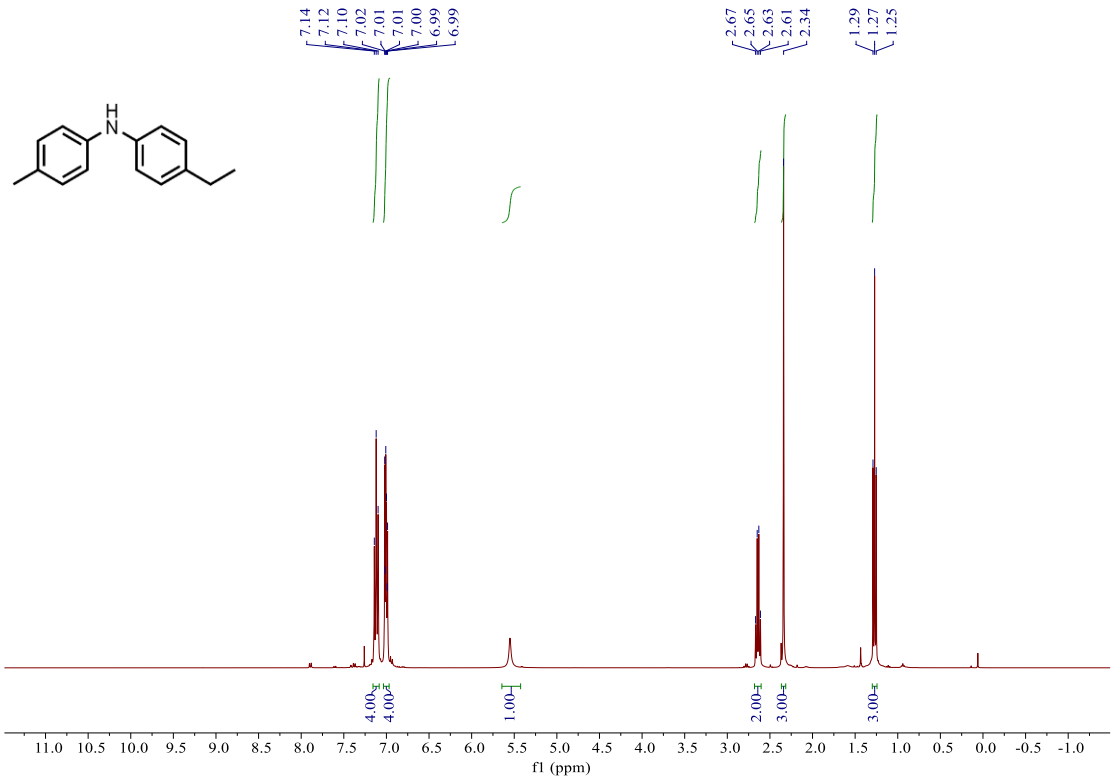

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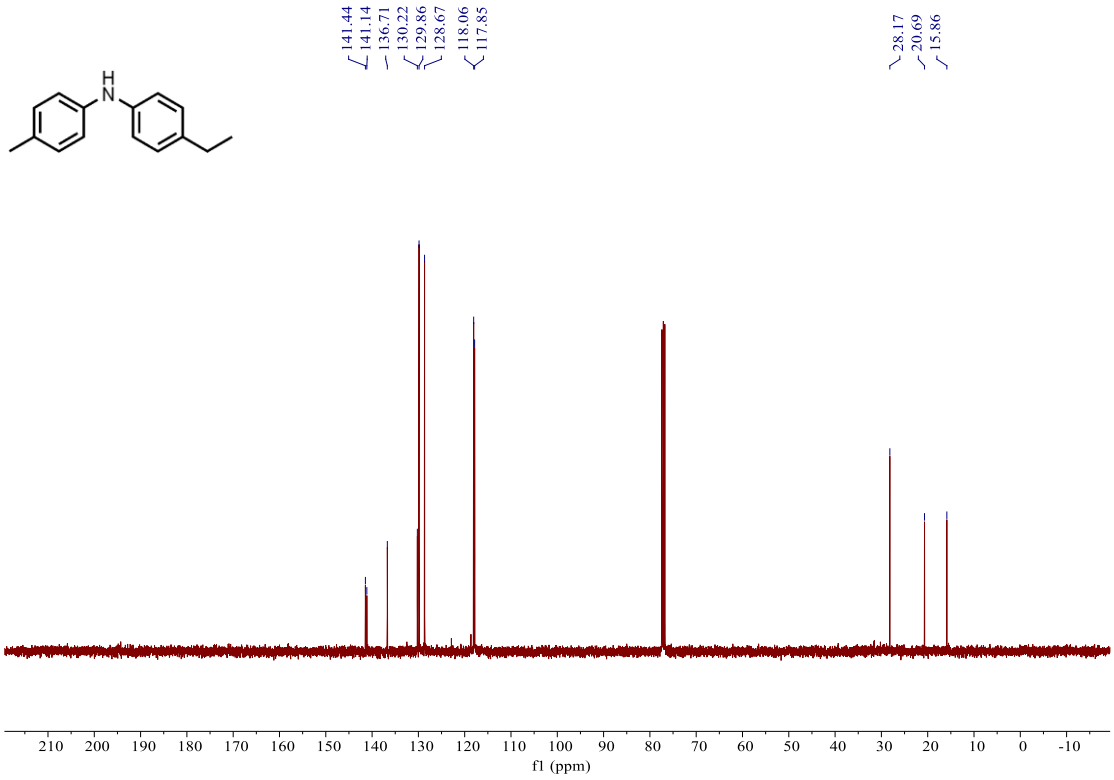
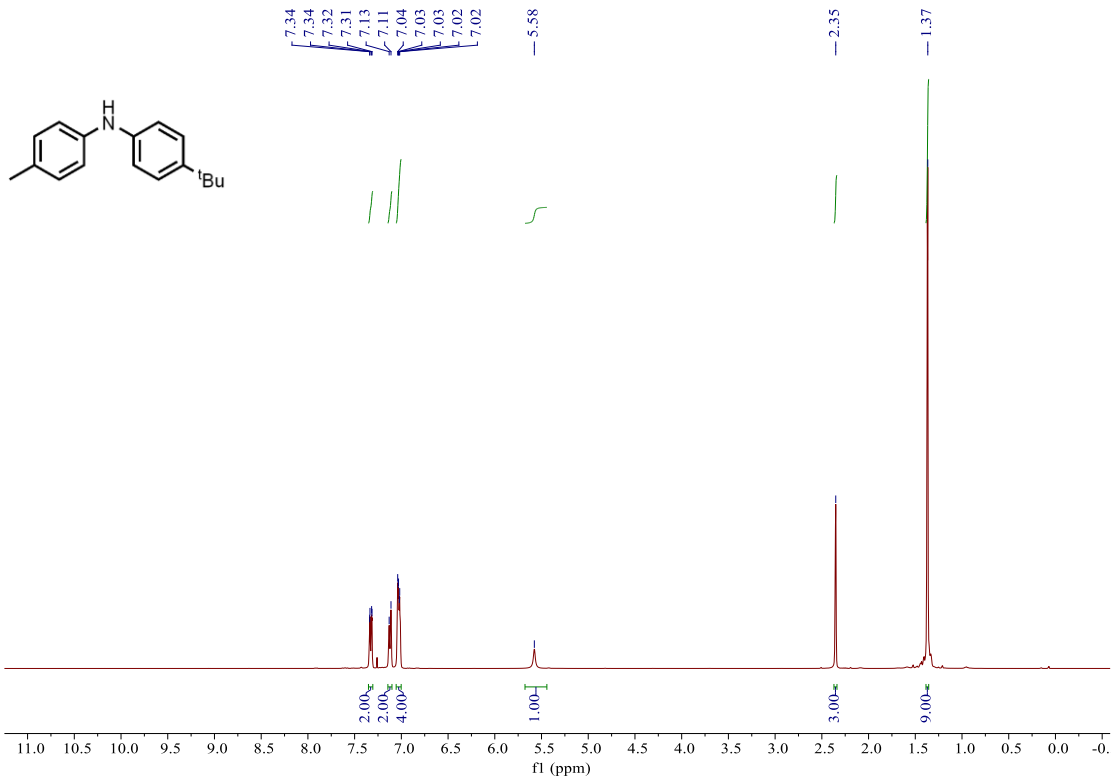
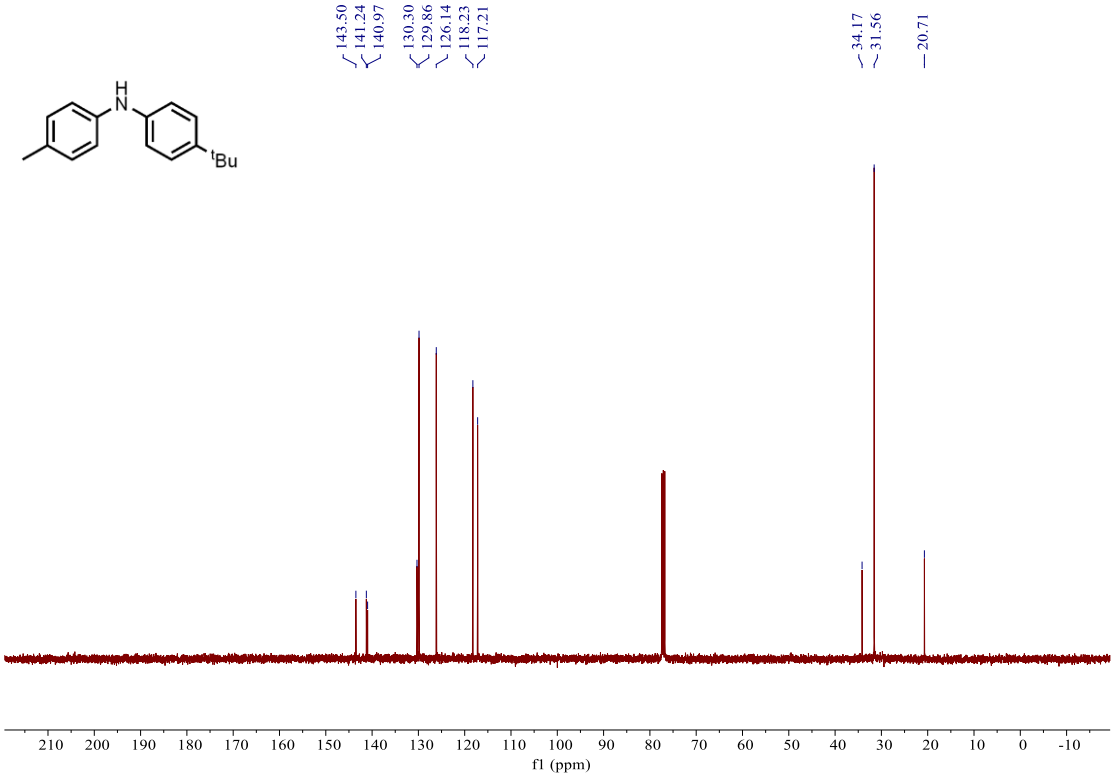


The ^{1}H-NMR spectrum of 3ae



The ^{13}C-NMR spectrum of 3ae



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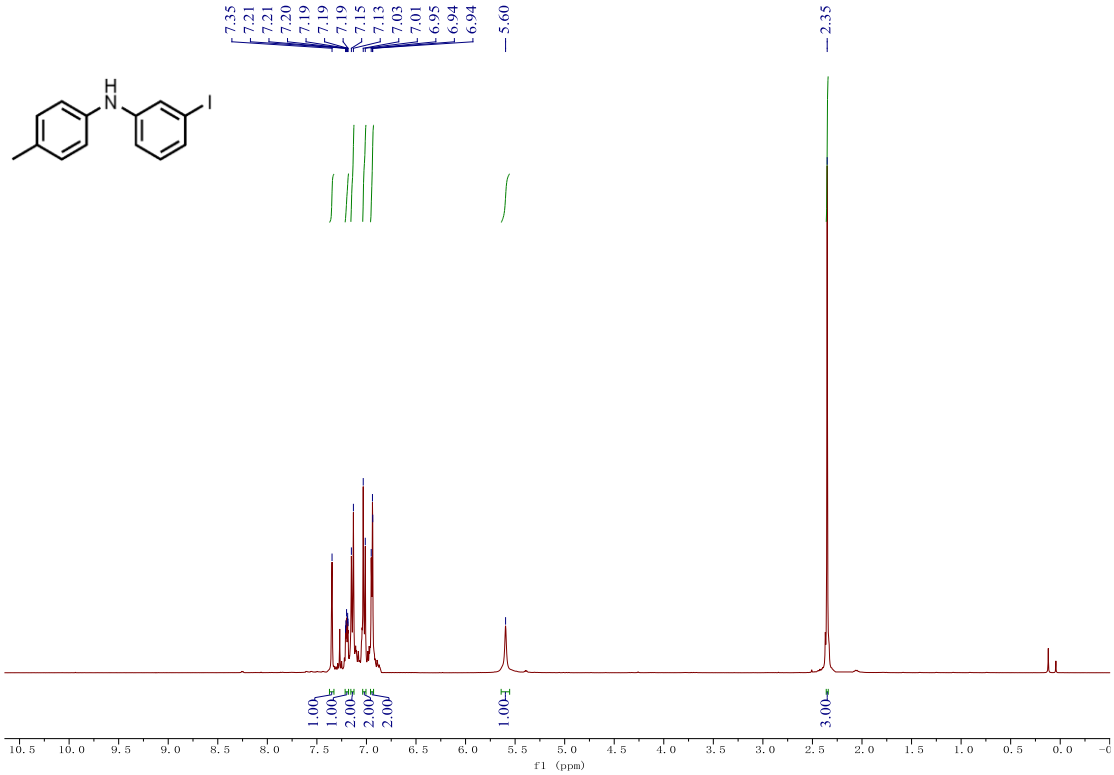

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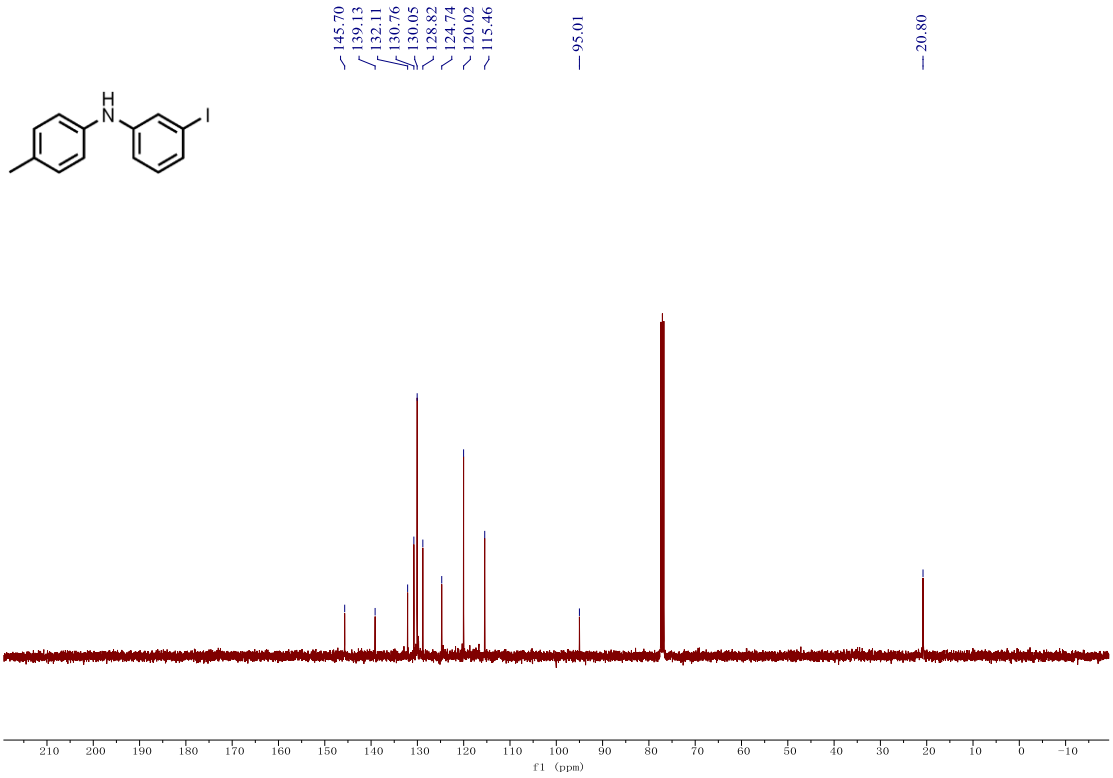

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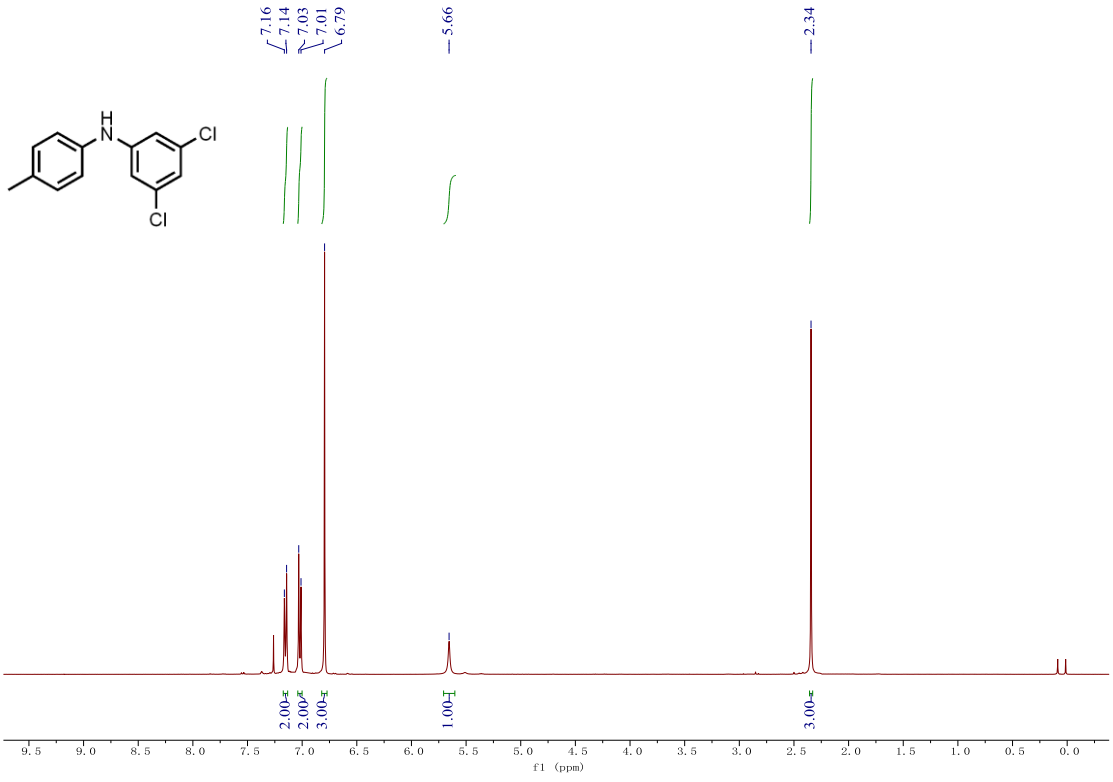

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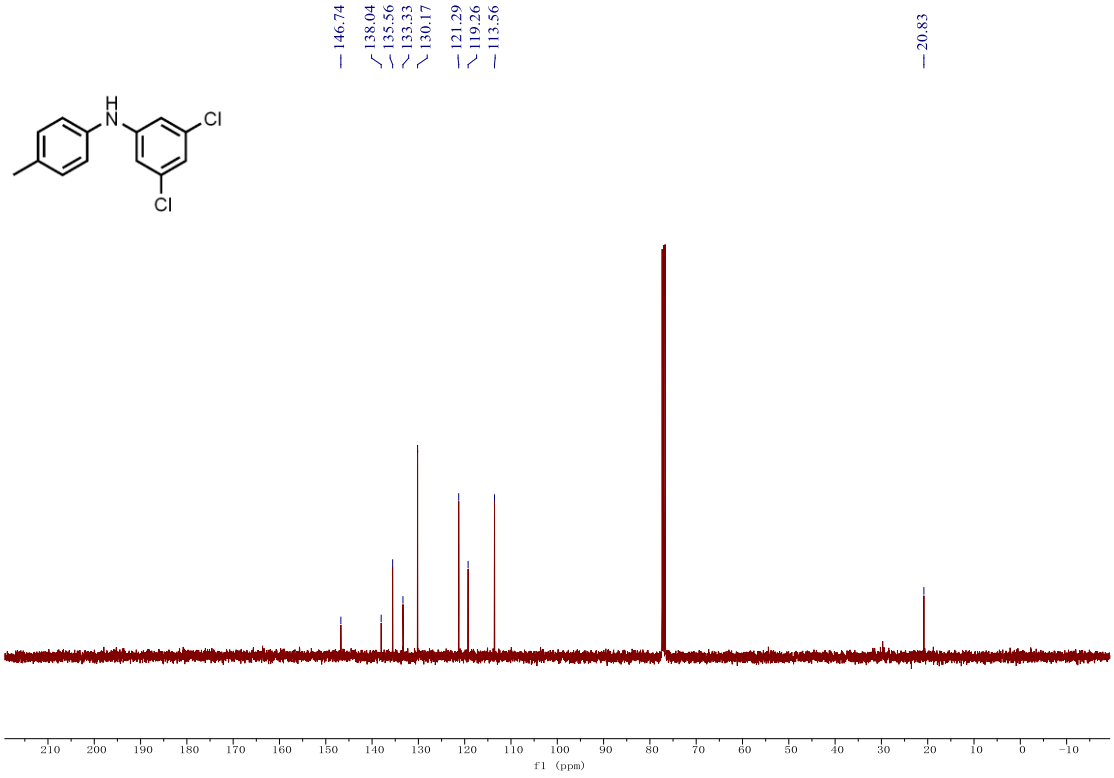

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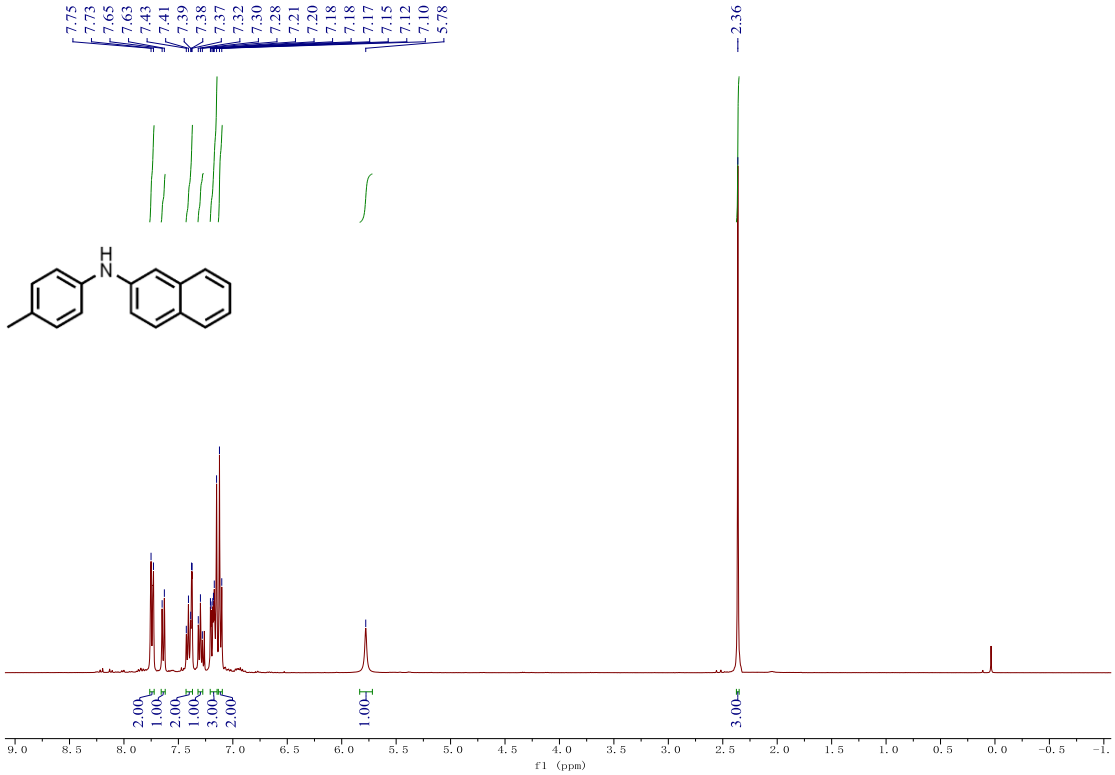
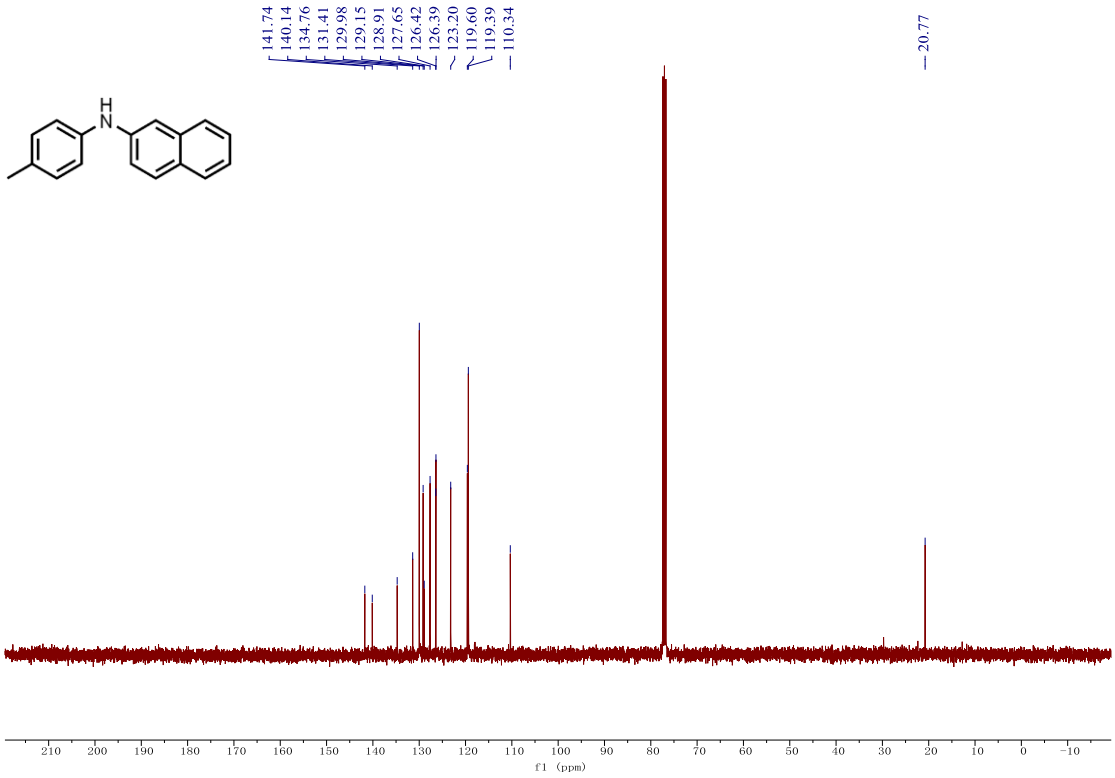


The ^{13}C-NMR spectrum of 3ah



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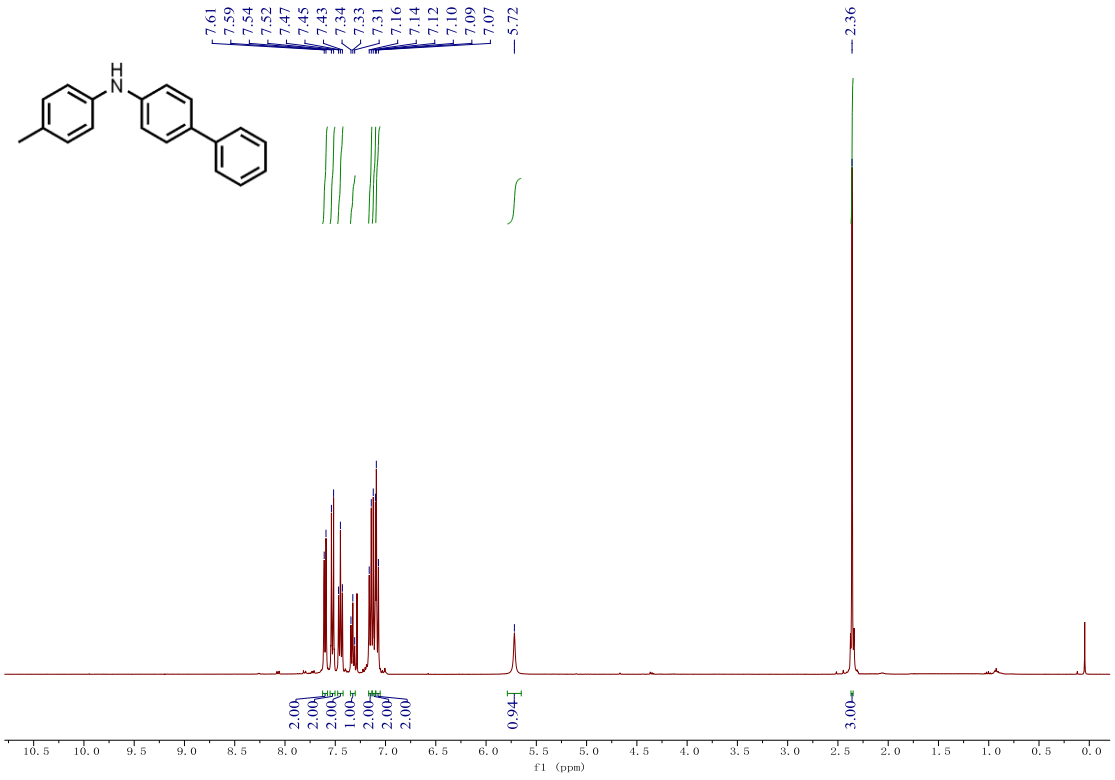

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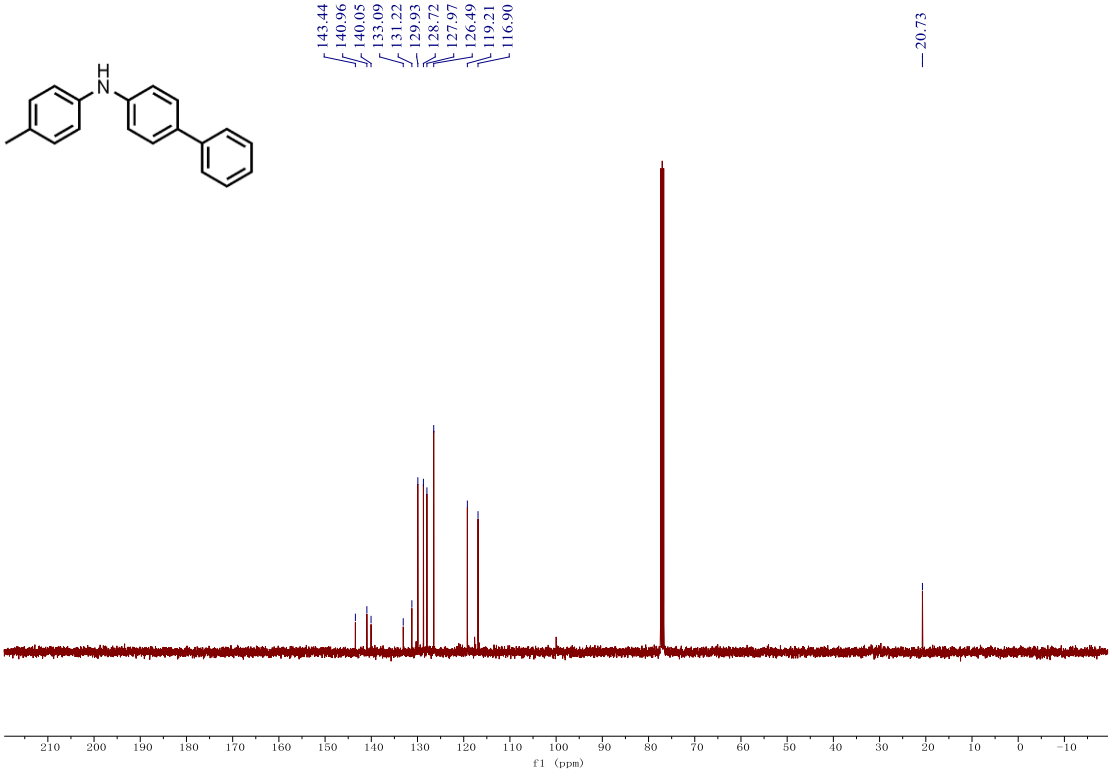

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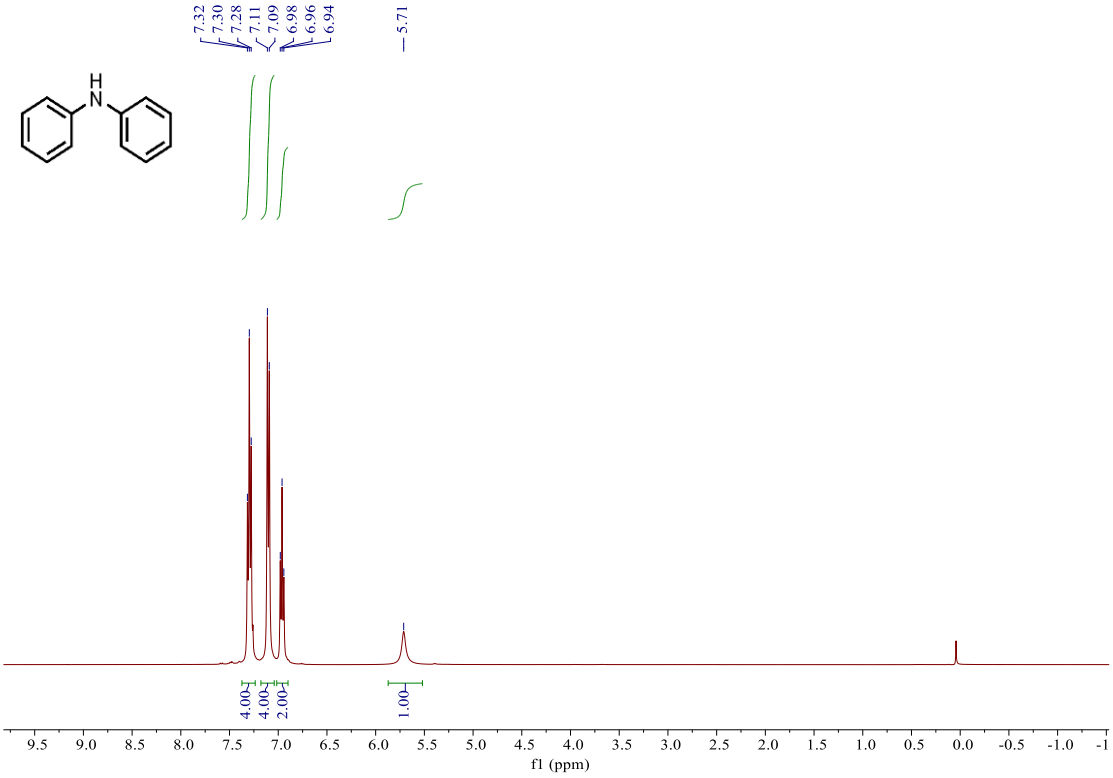

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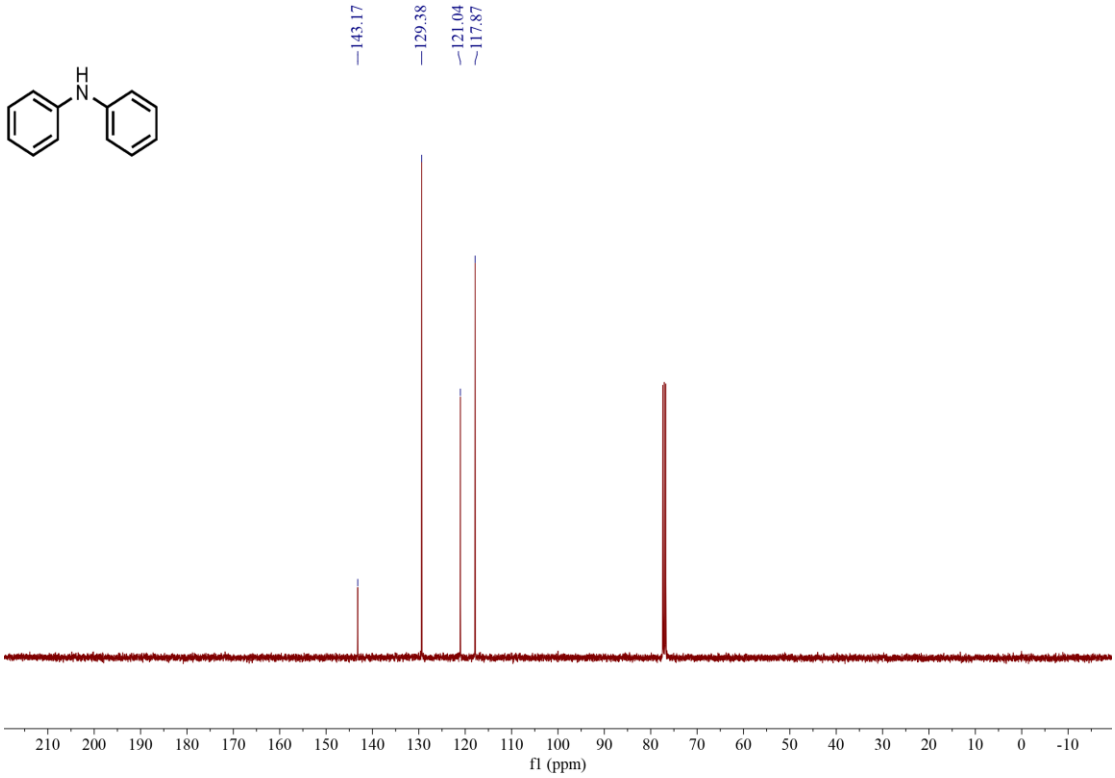

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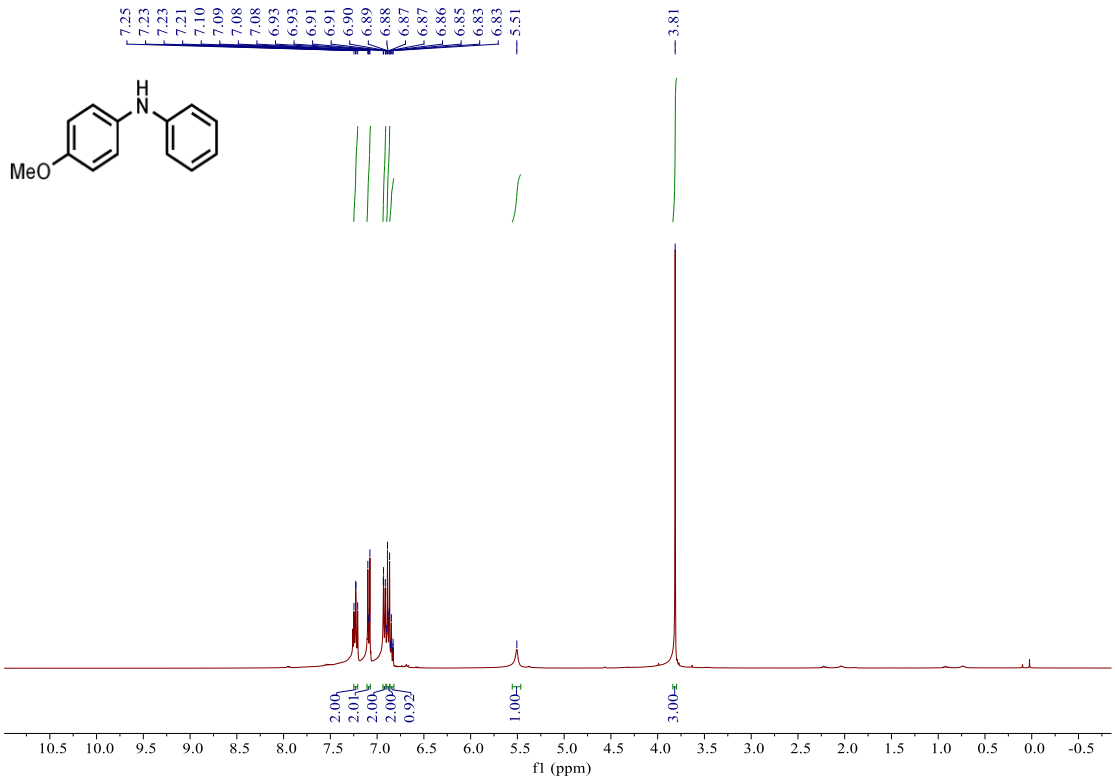
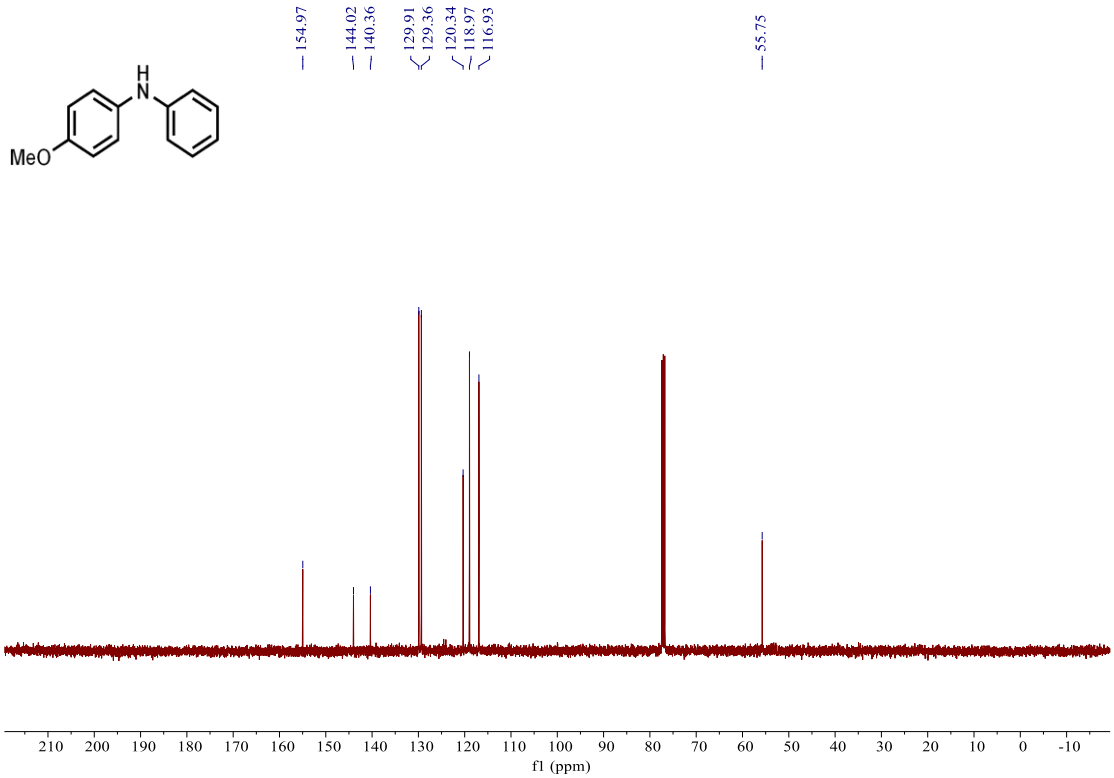


The ^{13}C-NMR spectrum of 3ca



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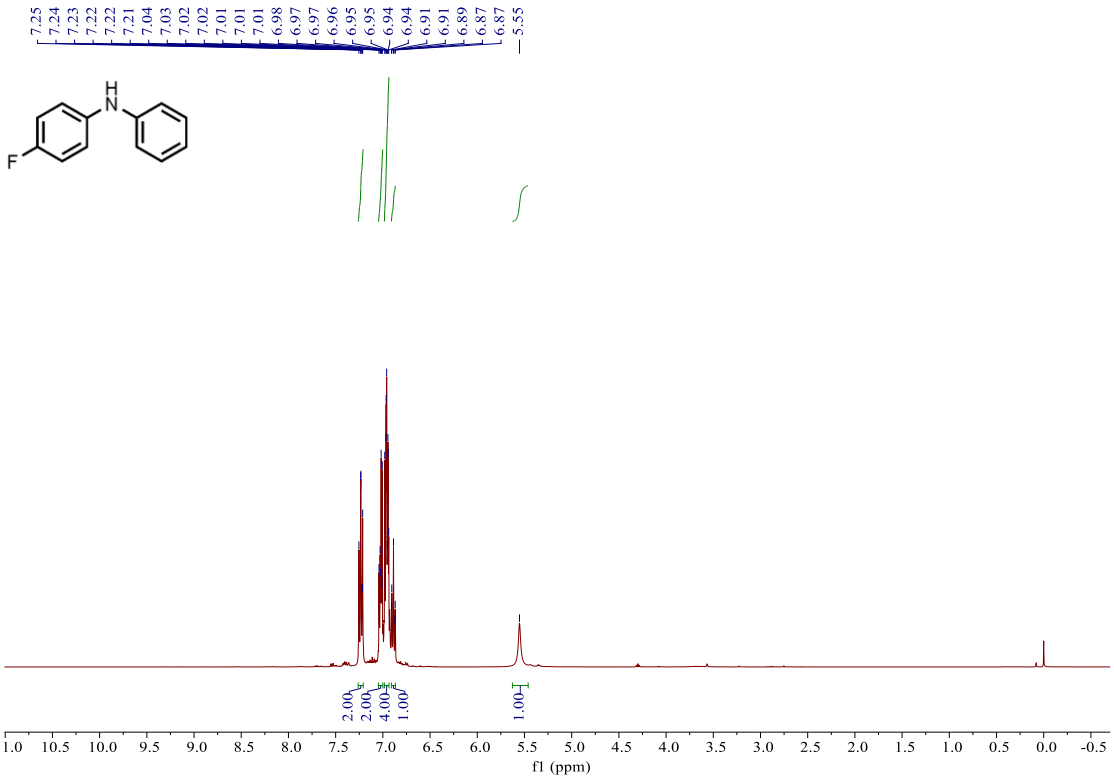
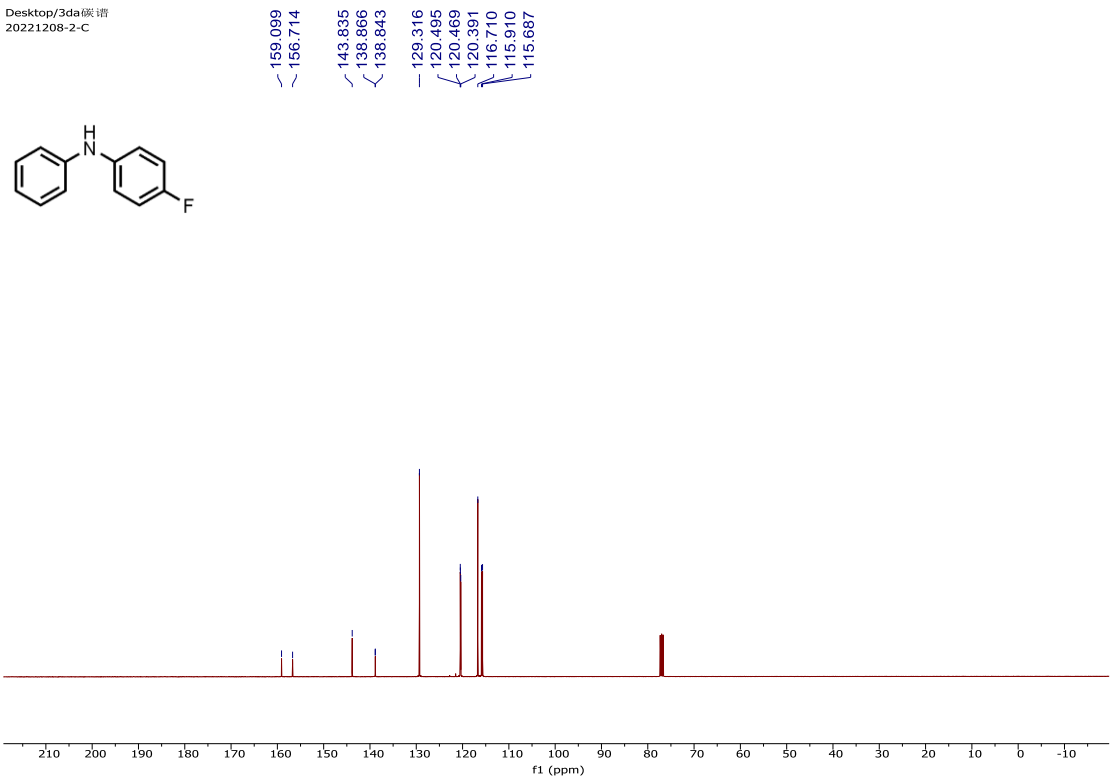
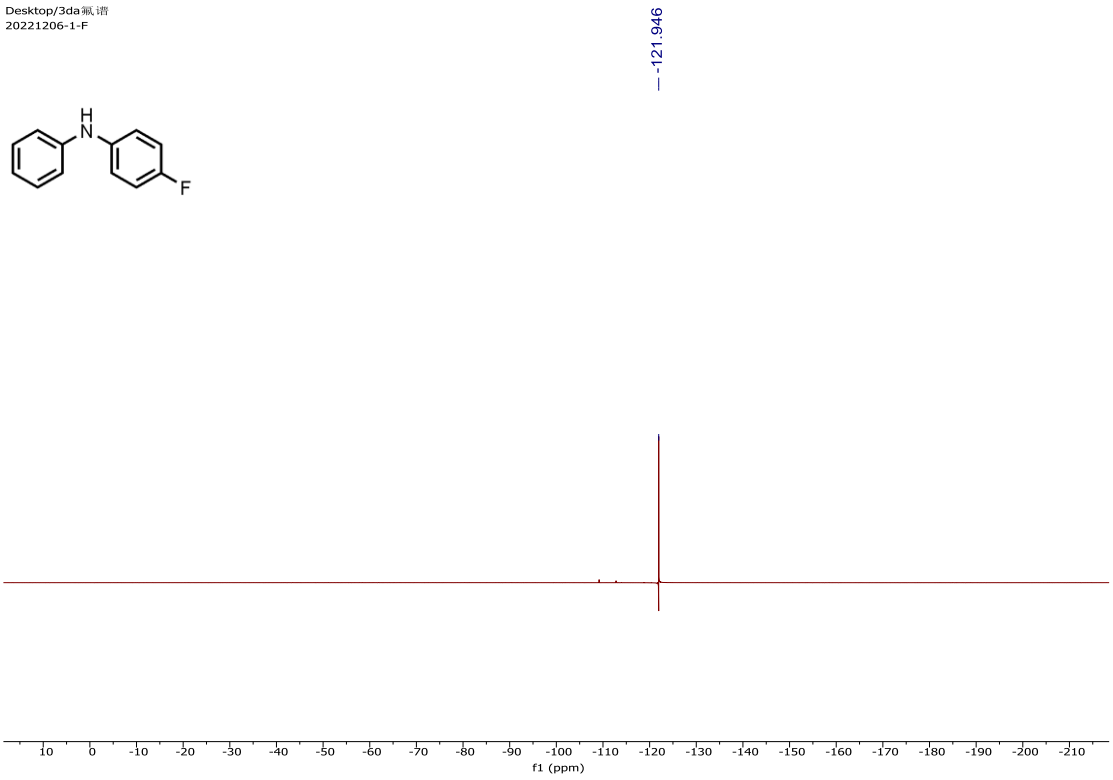


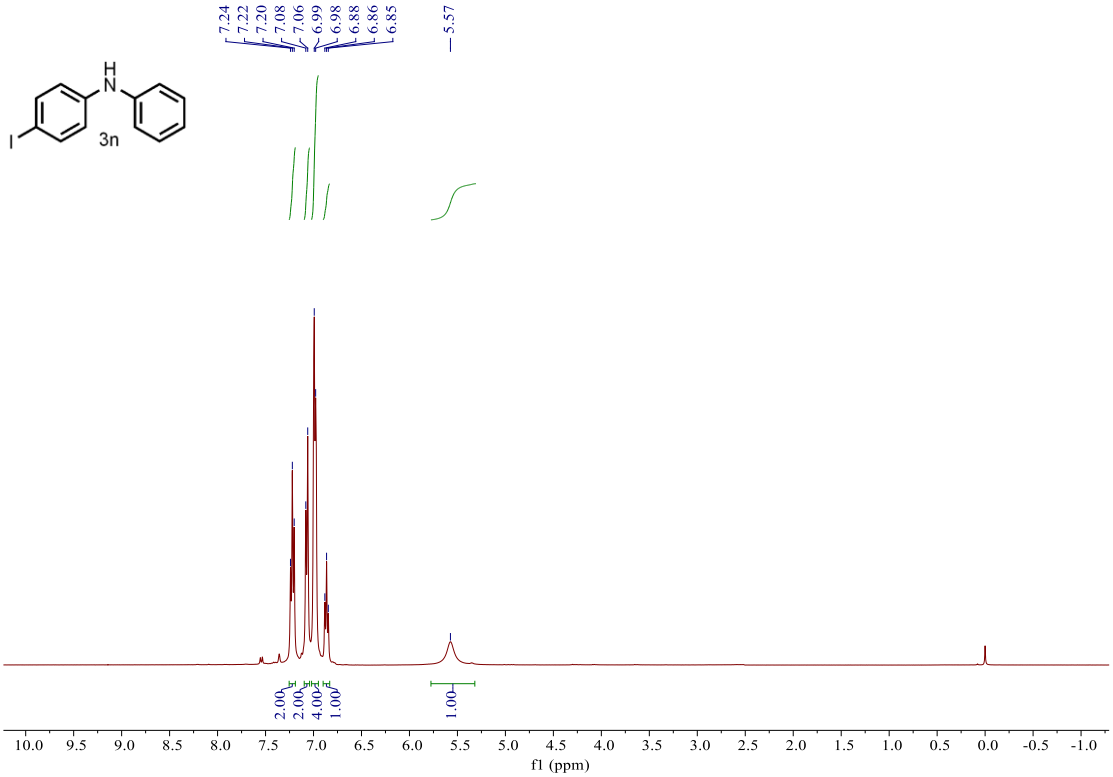
The ^{13}C-NMR spectrum of 3da



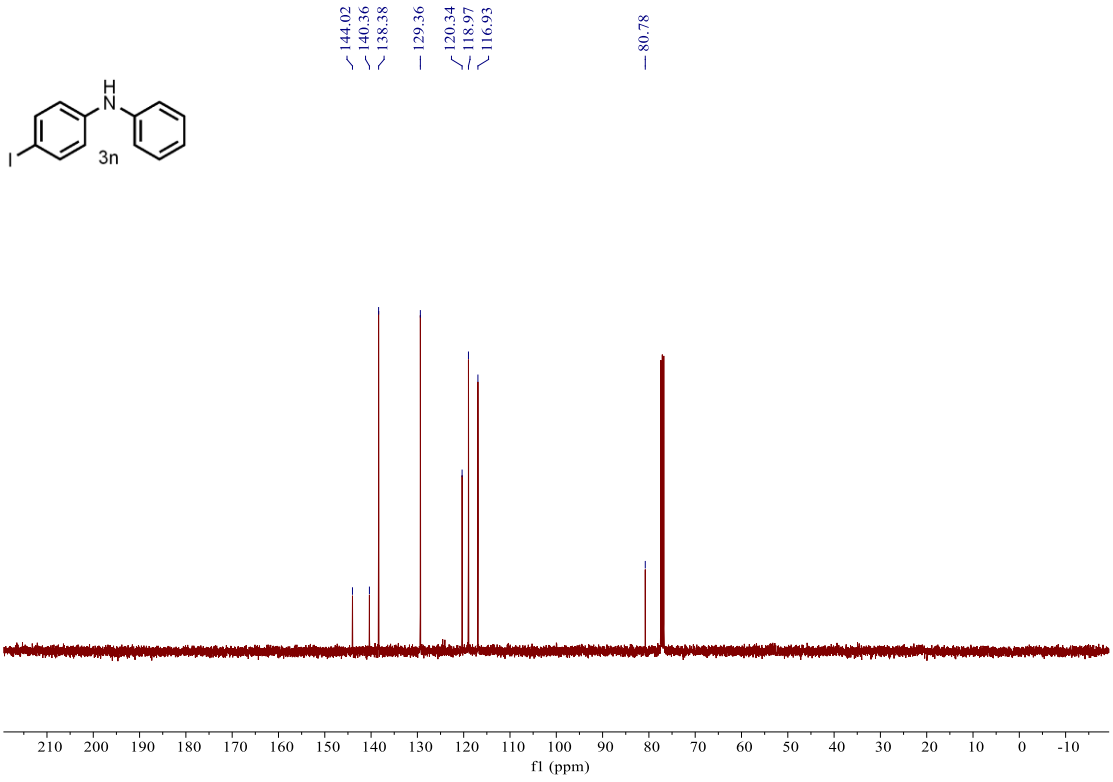
The ^{19}F-NMR spectrum of 3da



The ^{1}H-NMR spectrum of 3ea



The ^{13}C-NMR spectrum of 3ea



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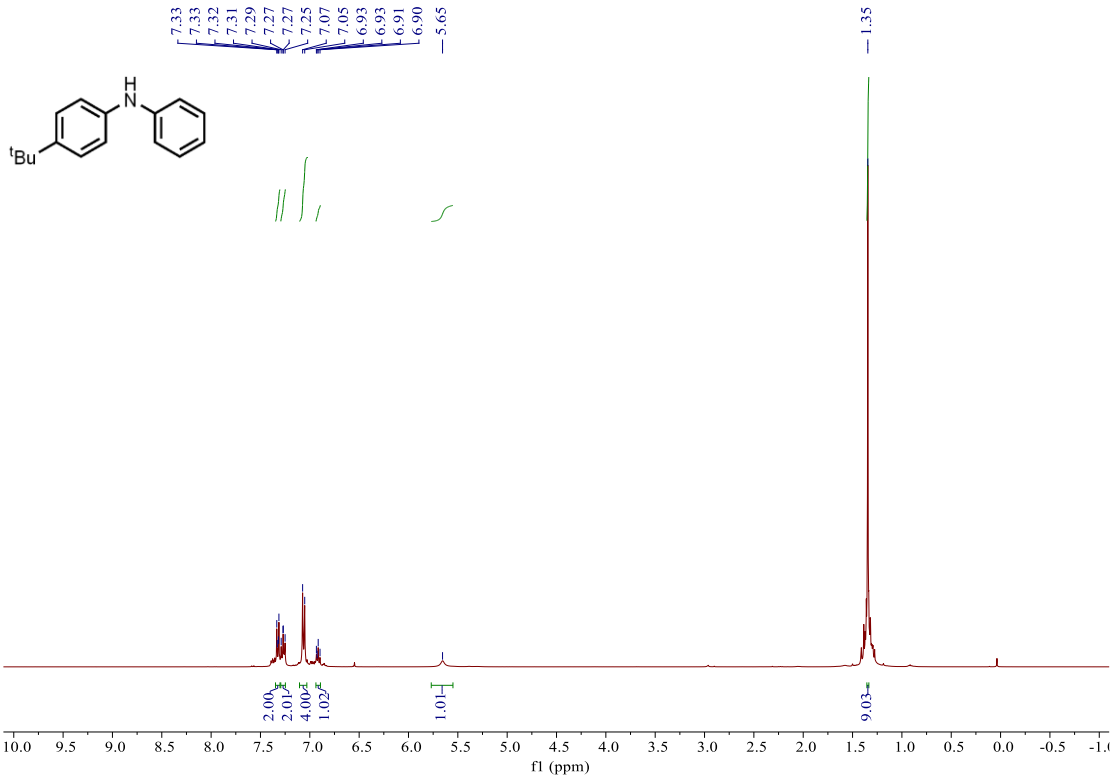

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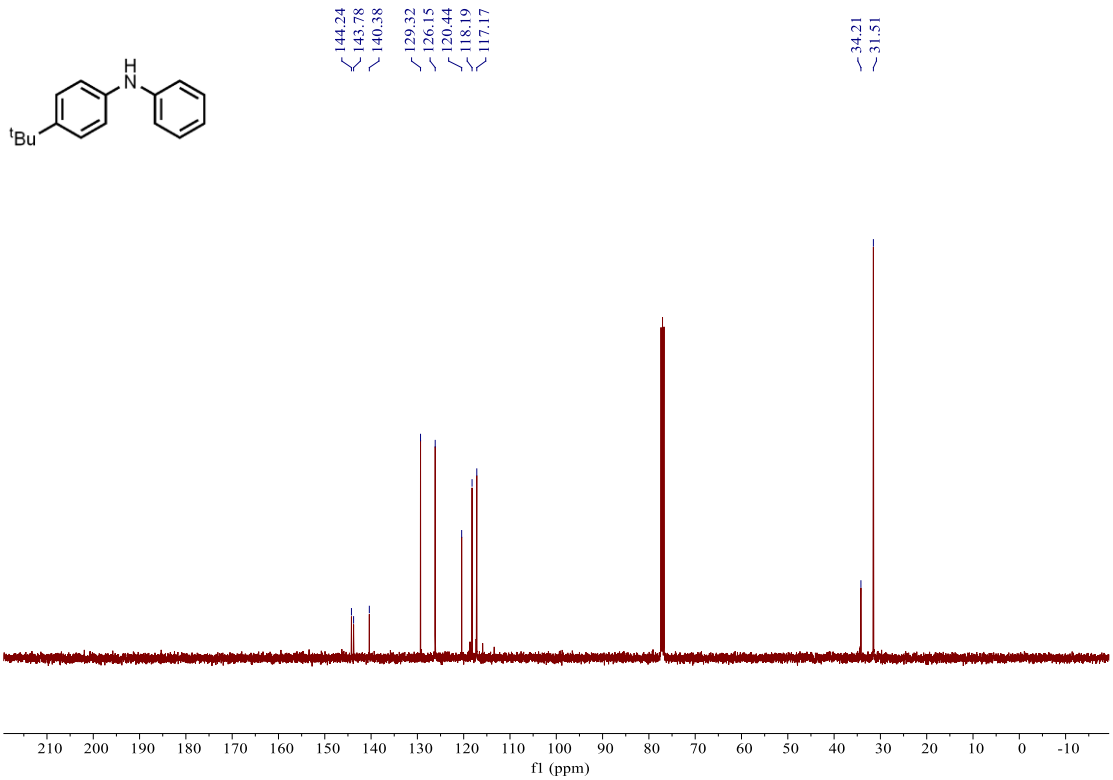

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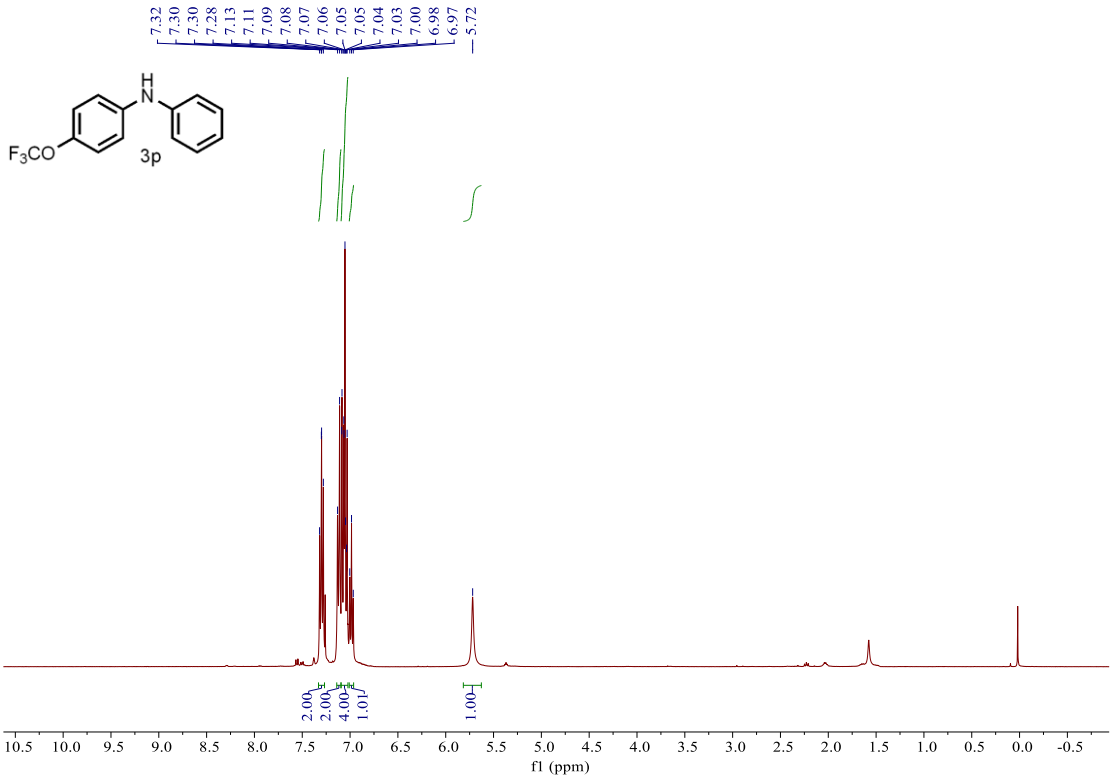

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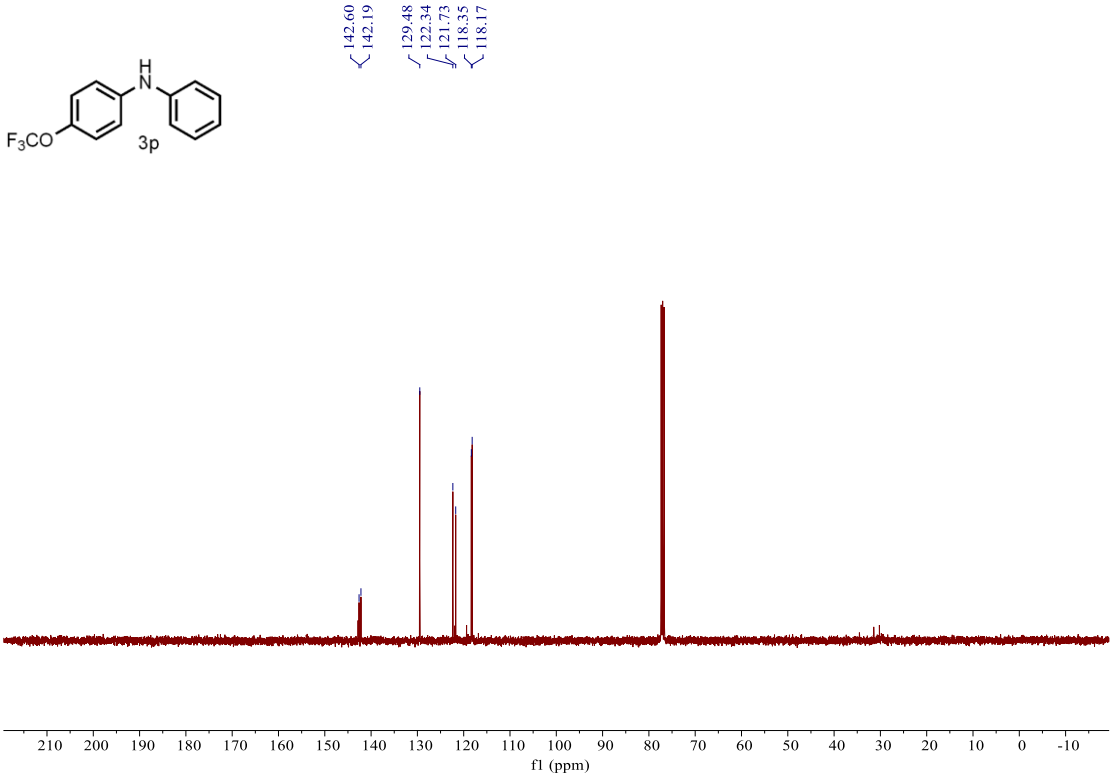
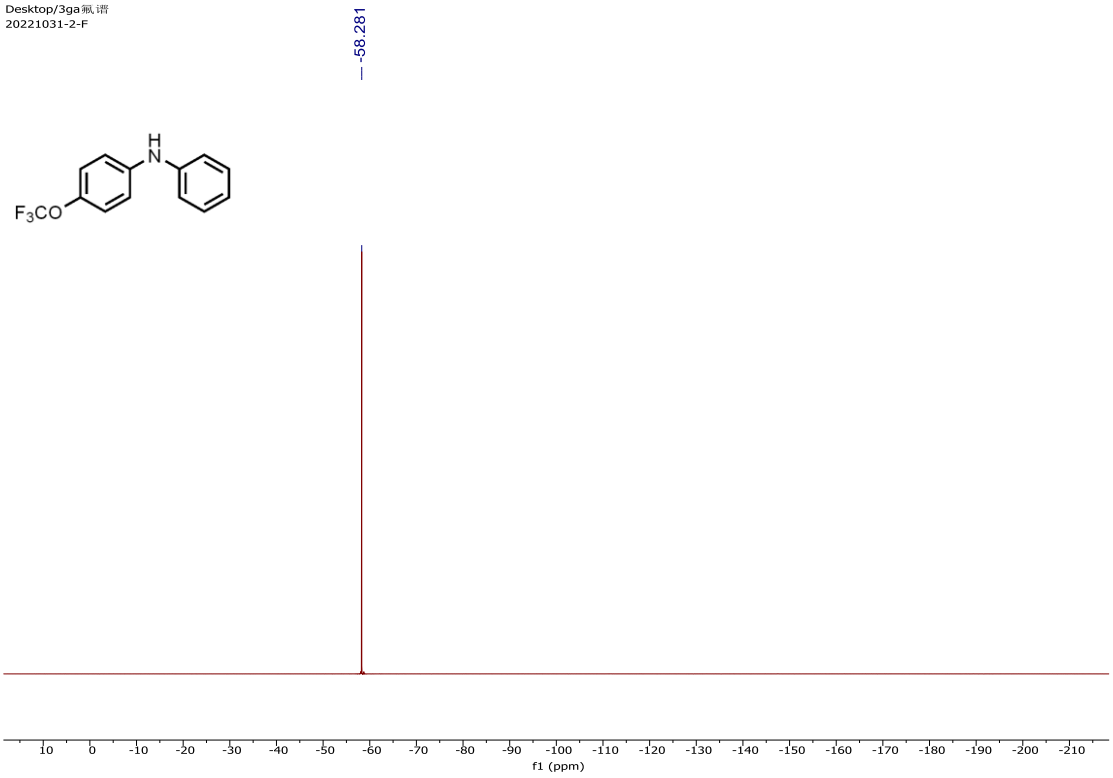


The ^{19}F-NMR spectrum of 3ga



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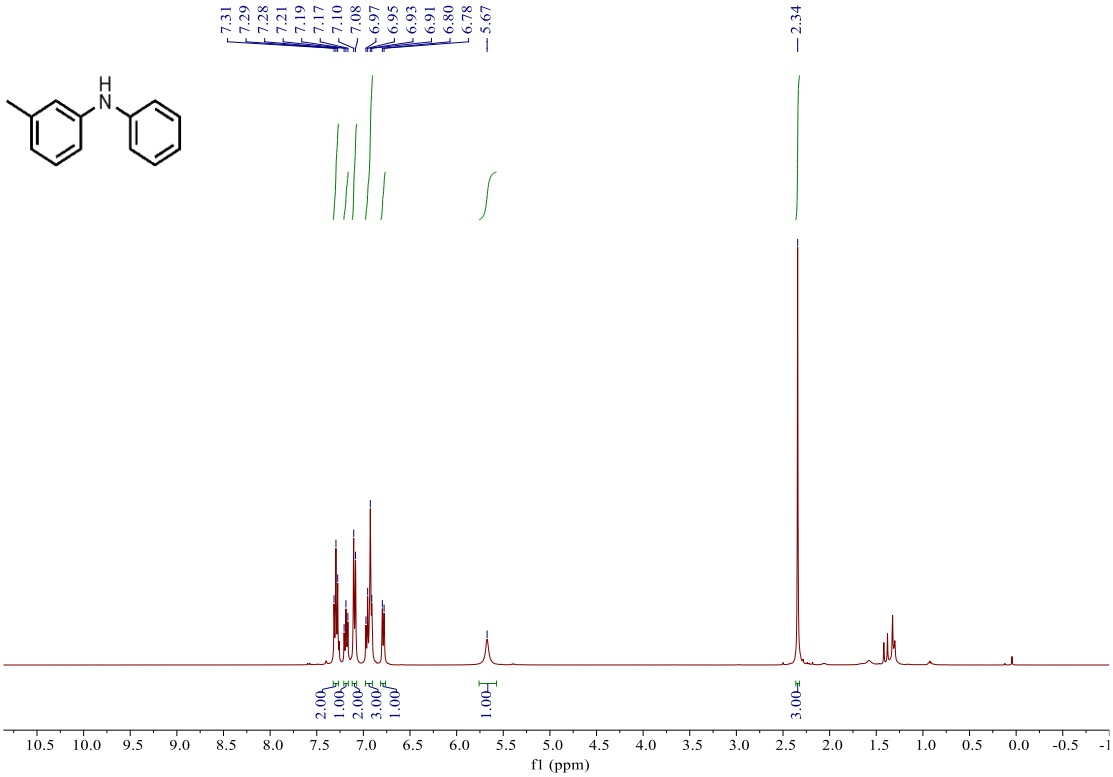
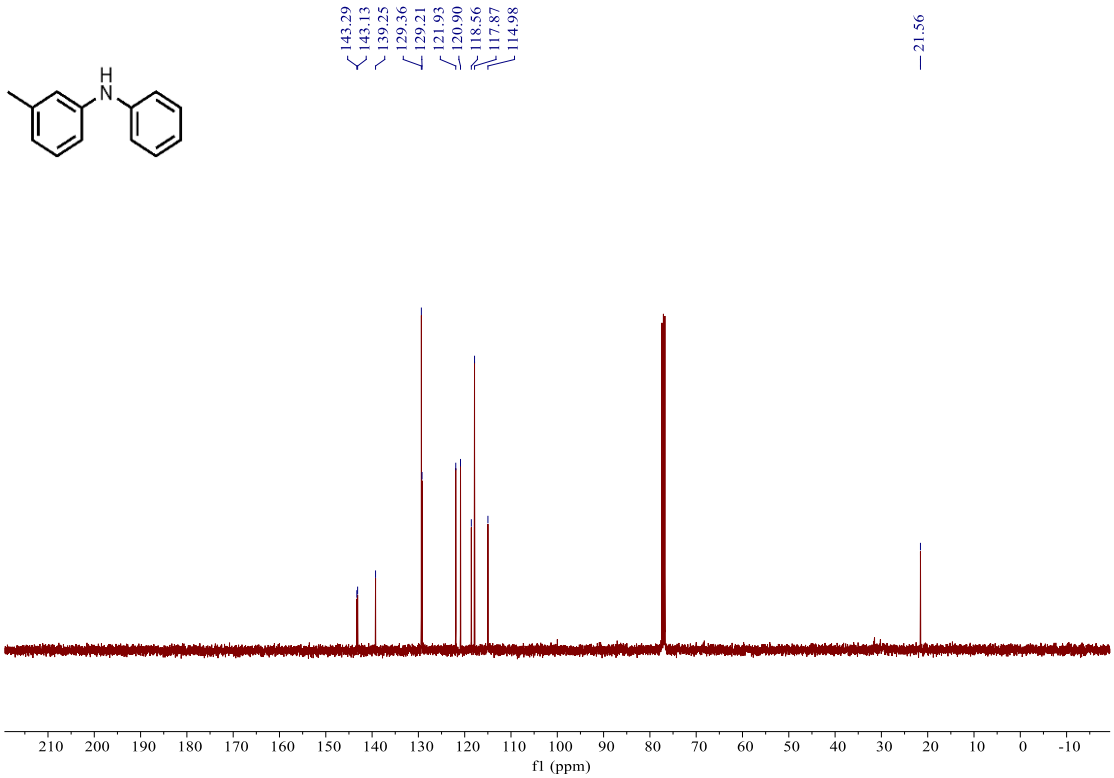


The ^{13}C-NMR spectrum of 3ha



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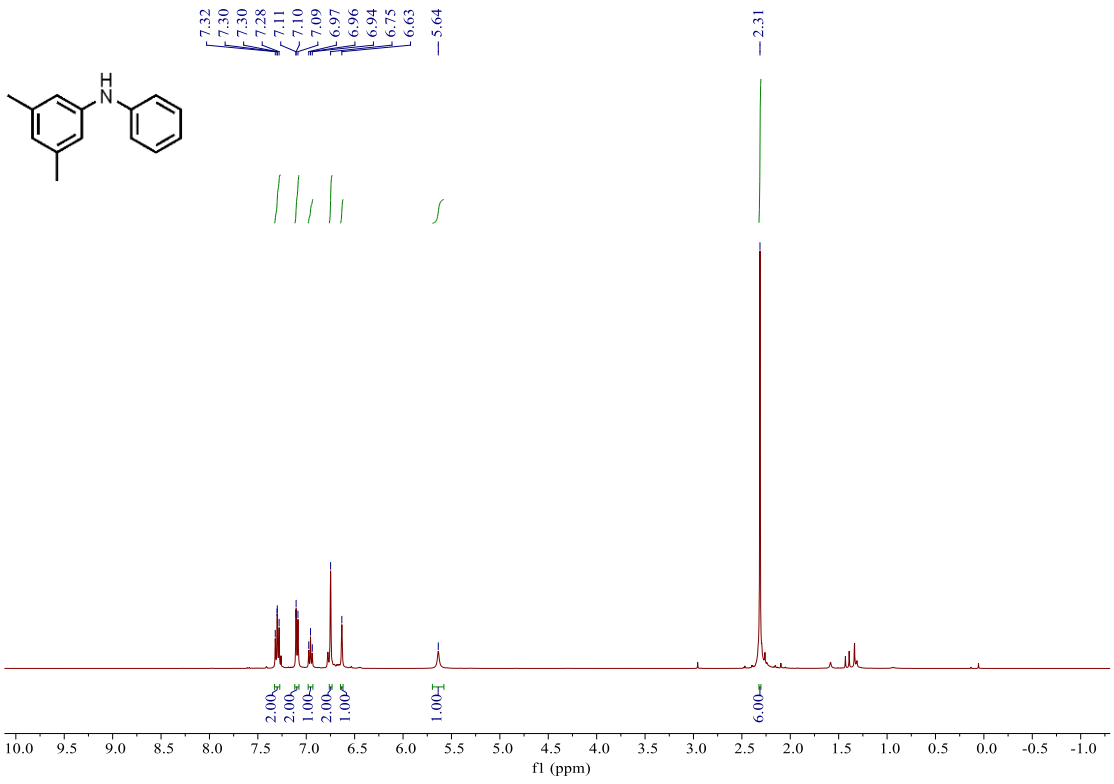

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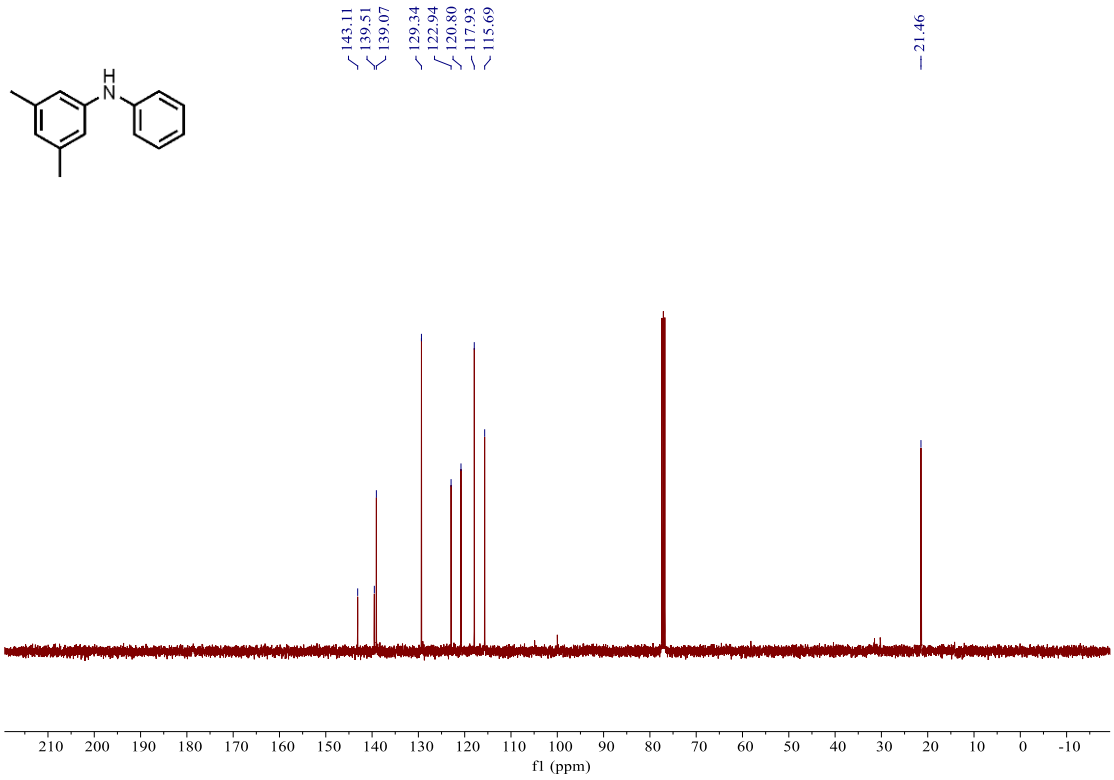

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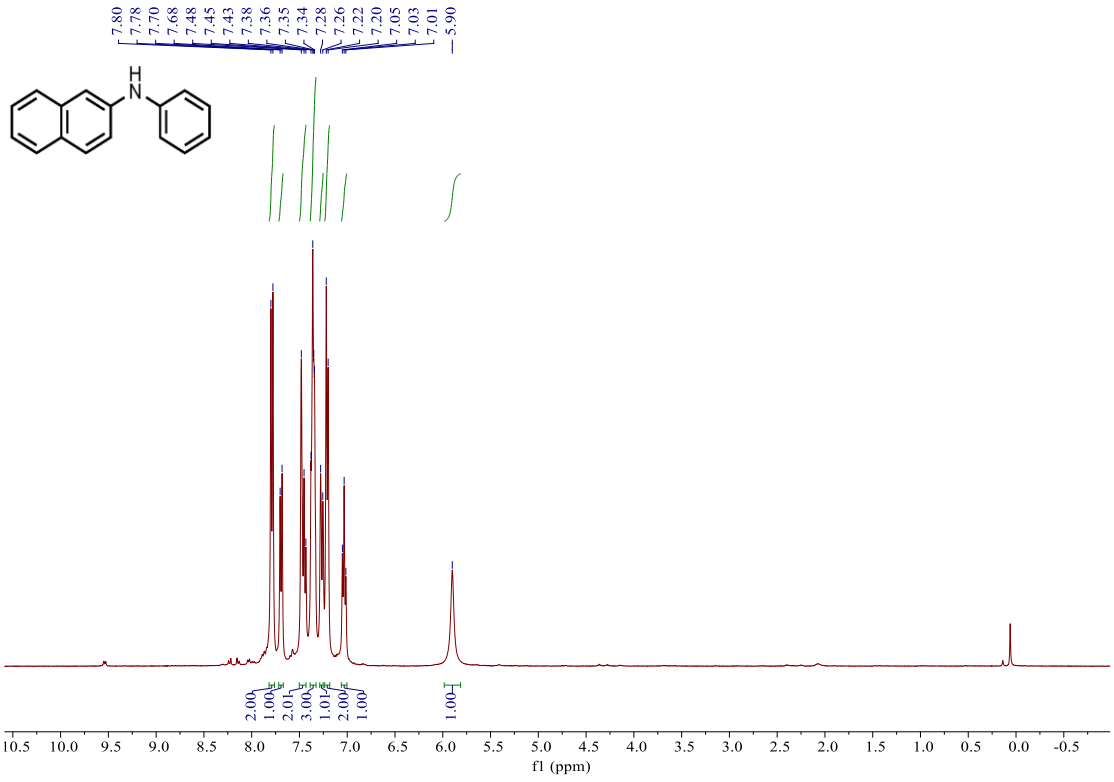
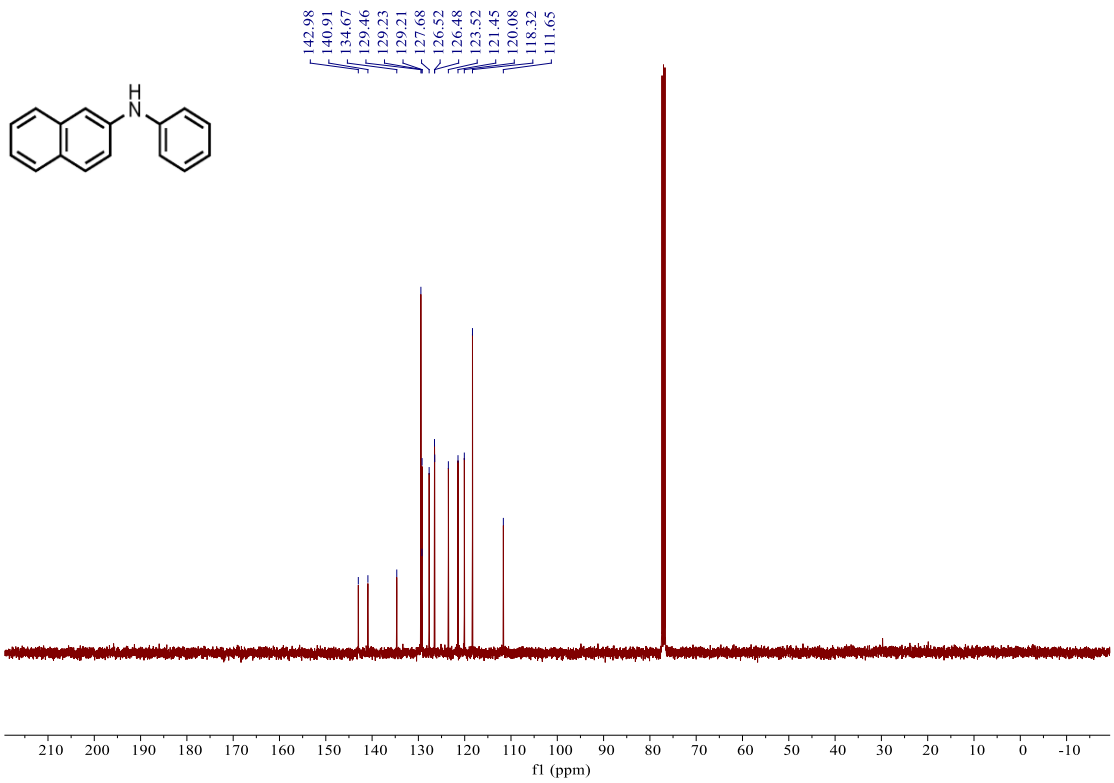
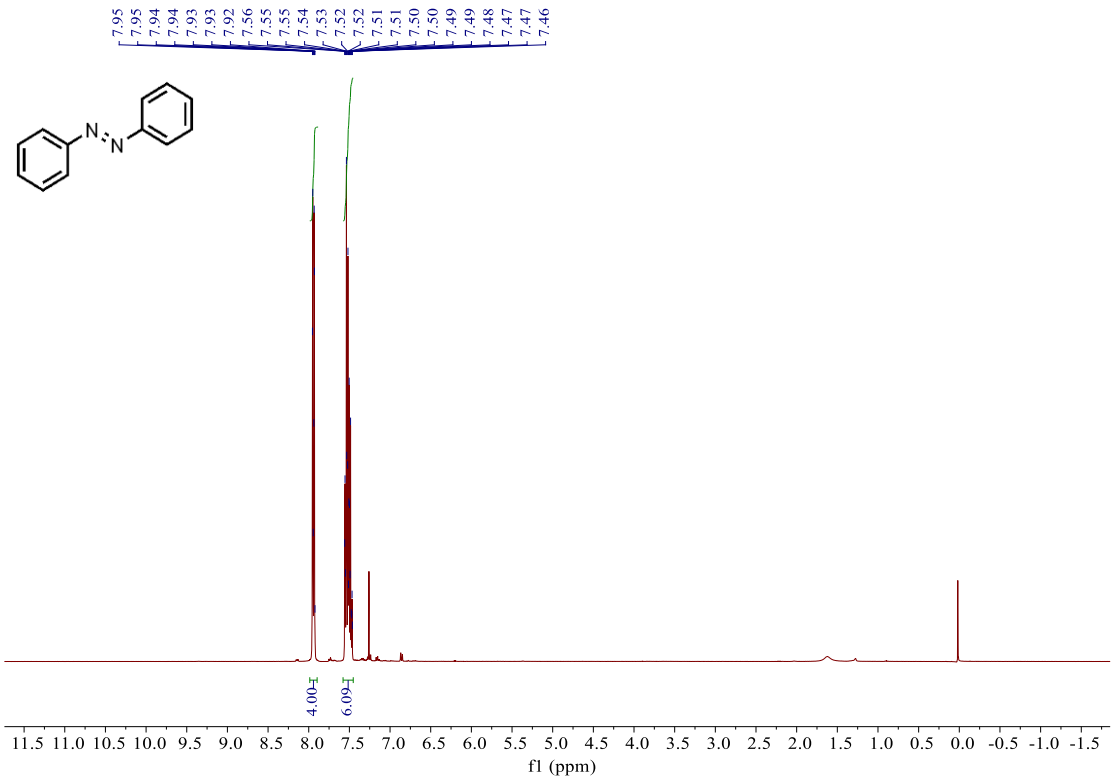


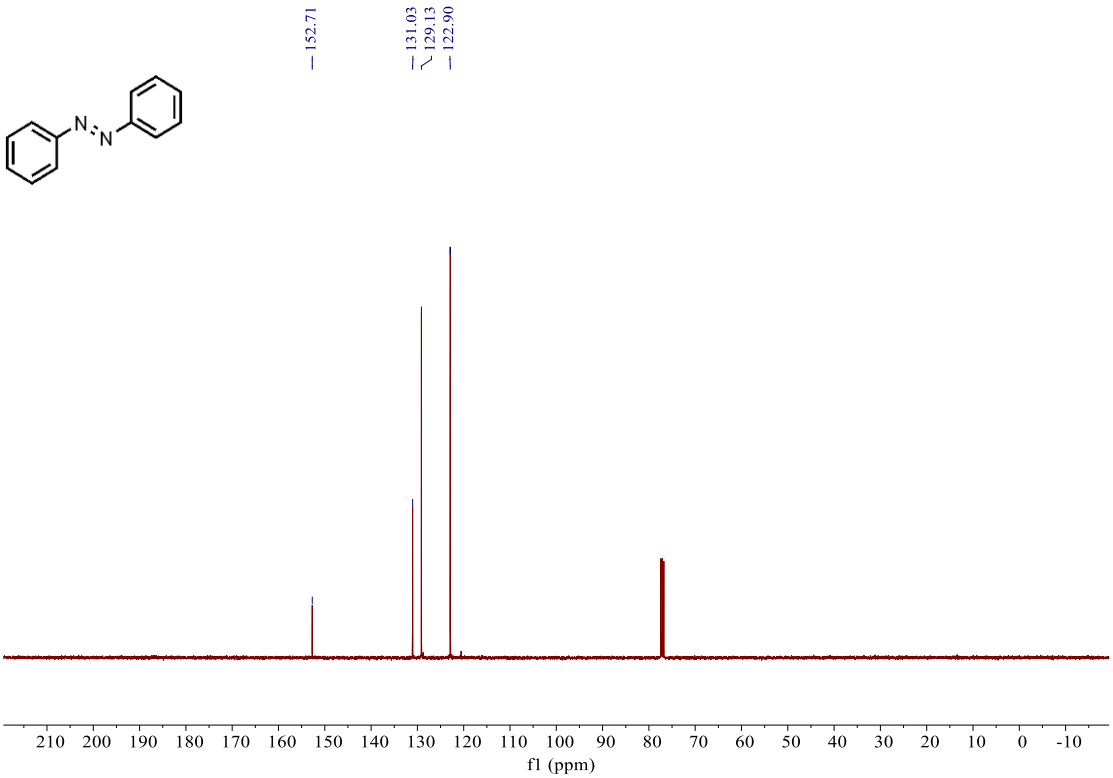
The ^{13}C-NMR spectrum of 3ka



The ^{1}H-NMR spectrum of 4a



The ^{13}C-NMR spectrum of 4a



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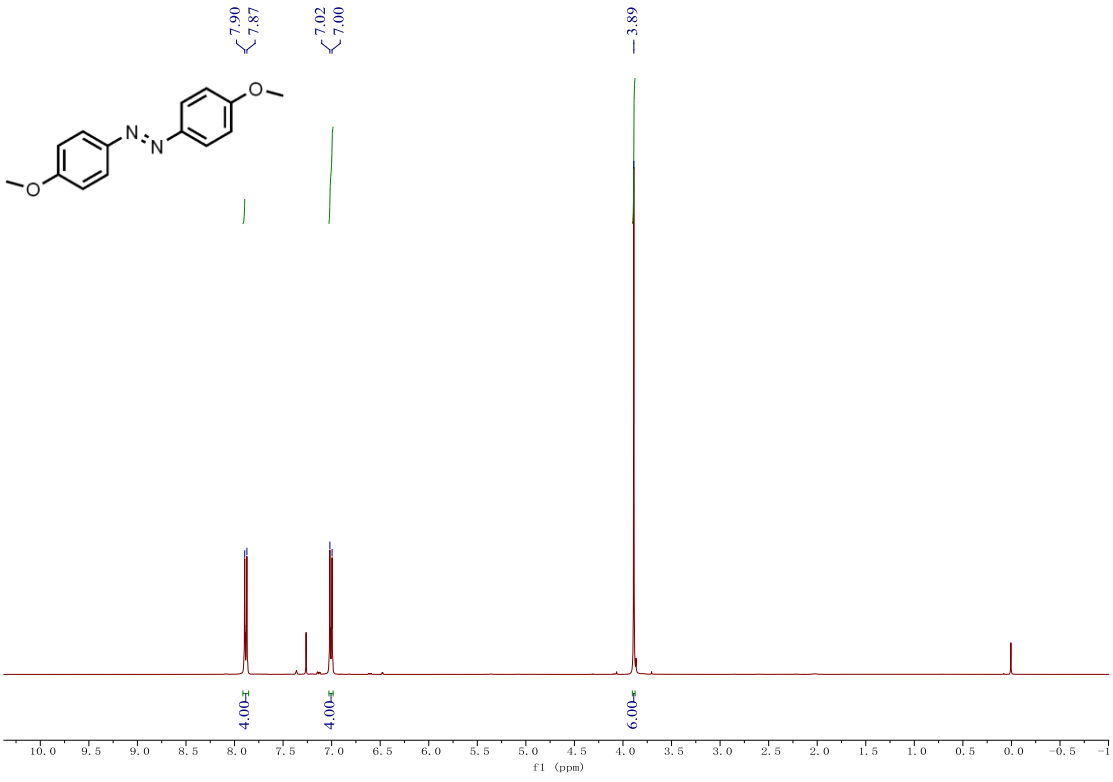

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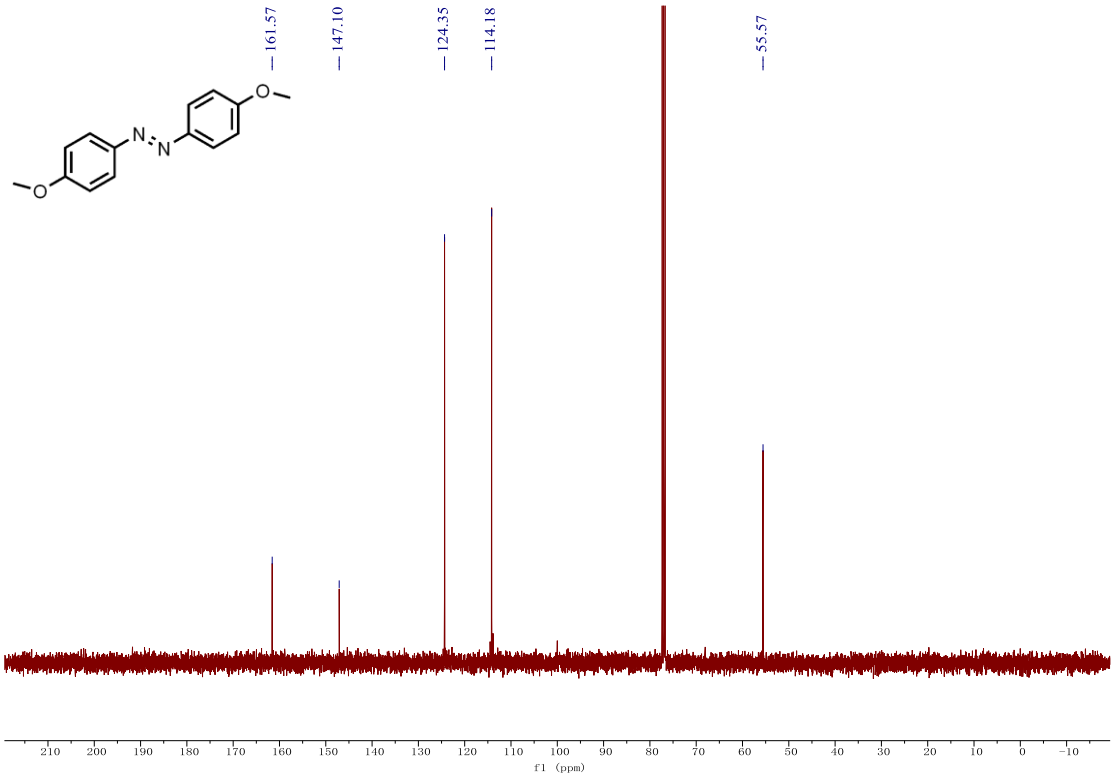

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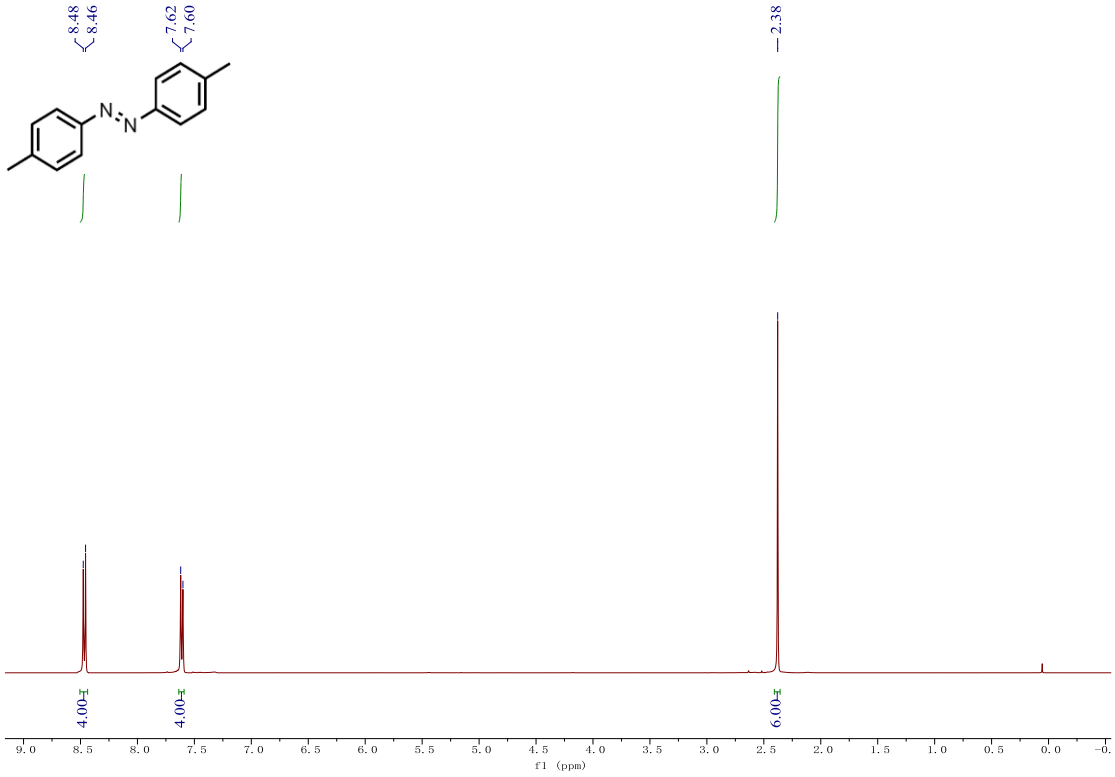

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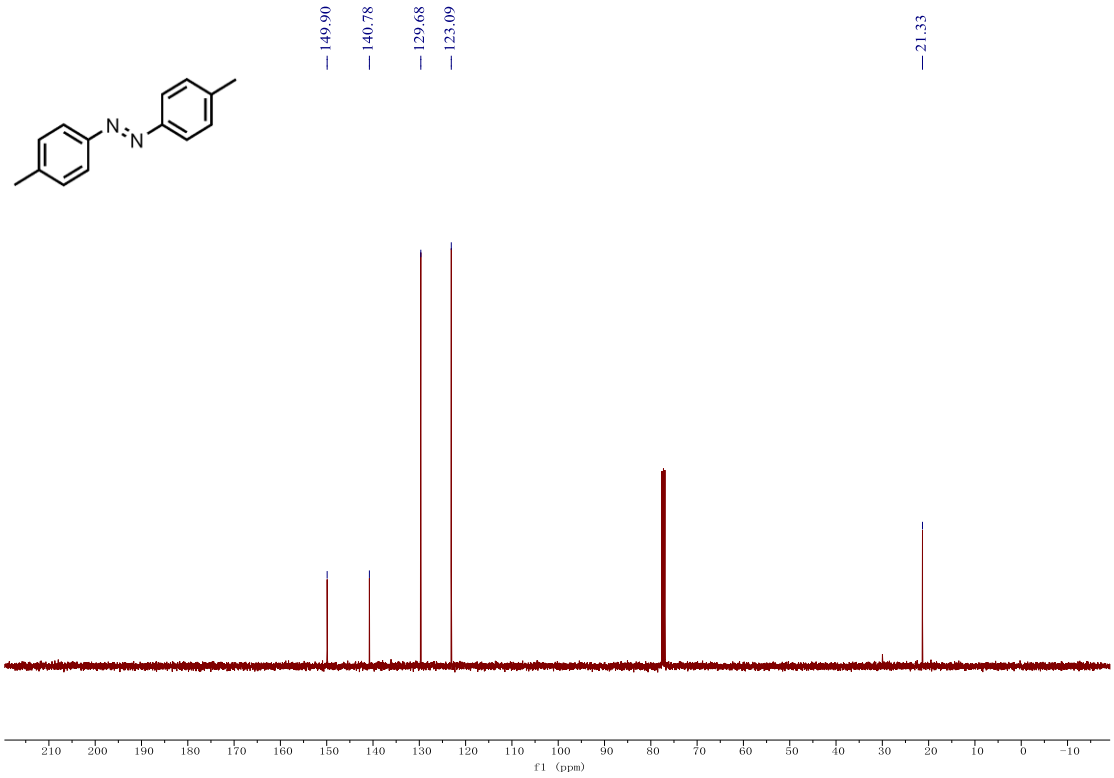

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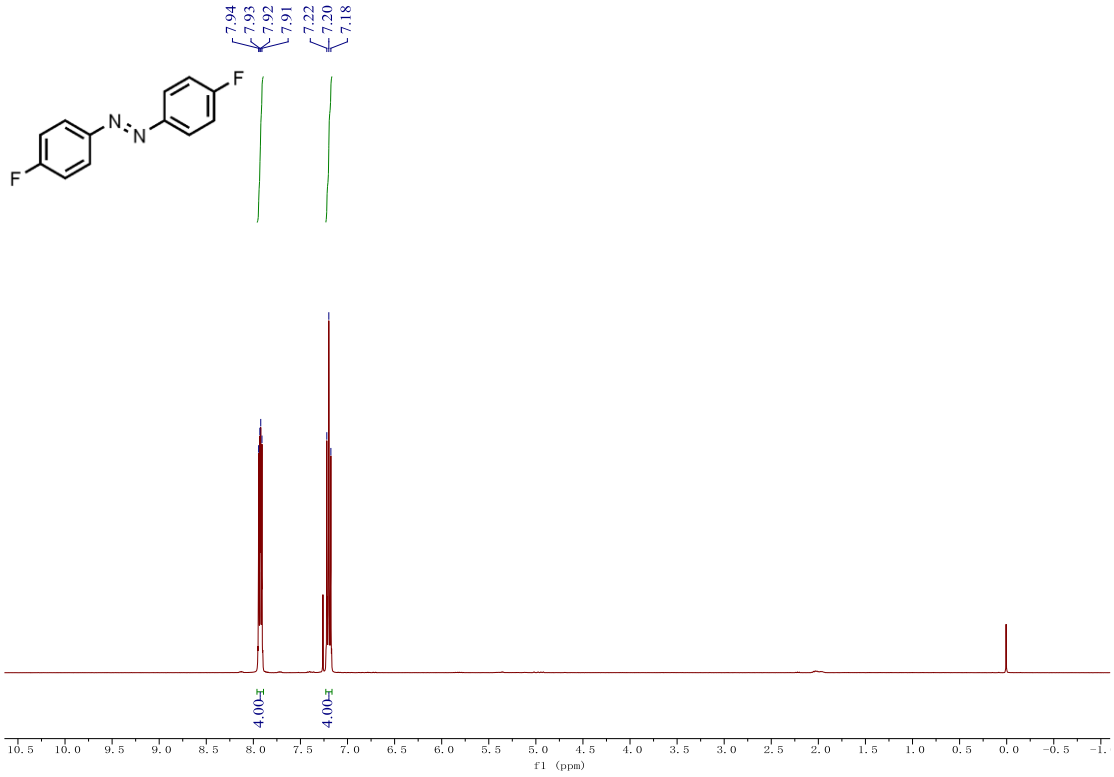
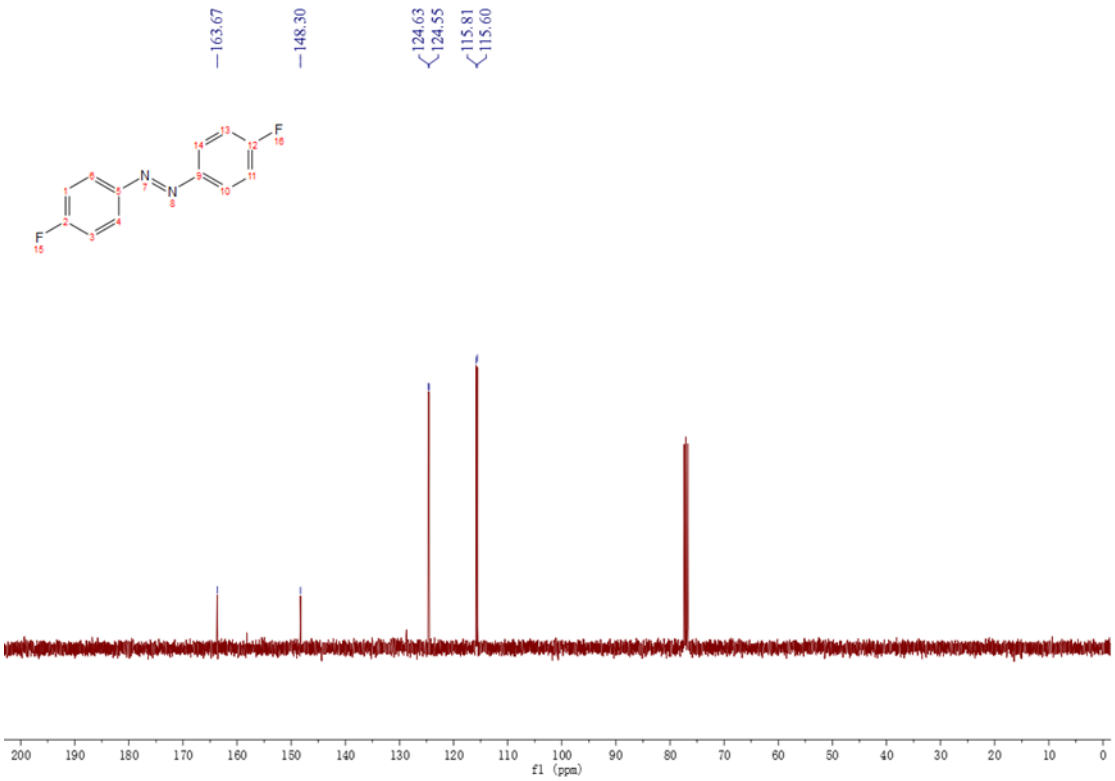
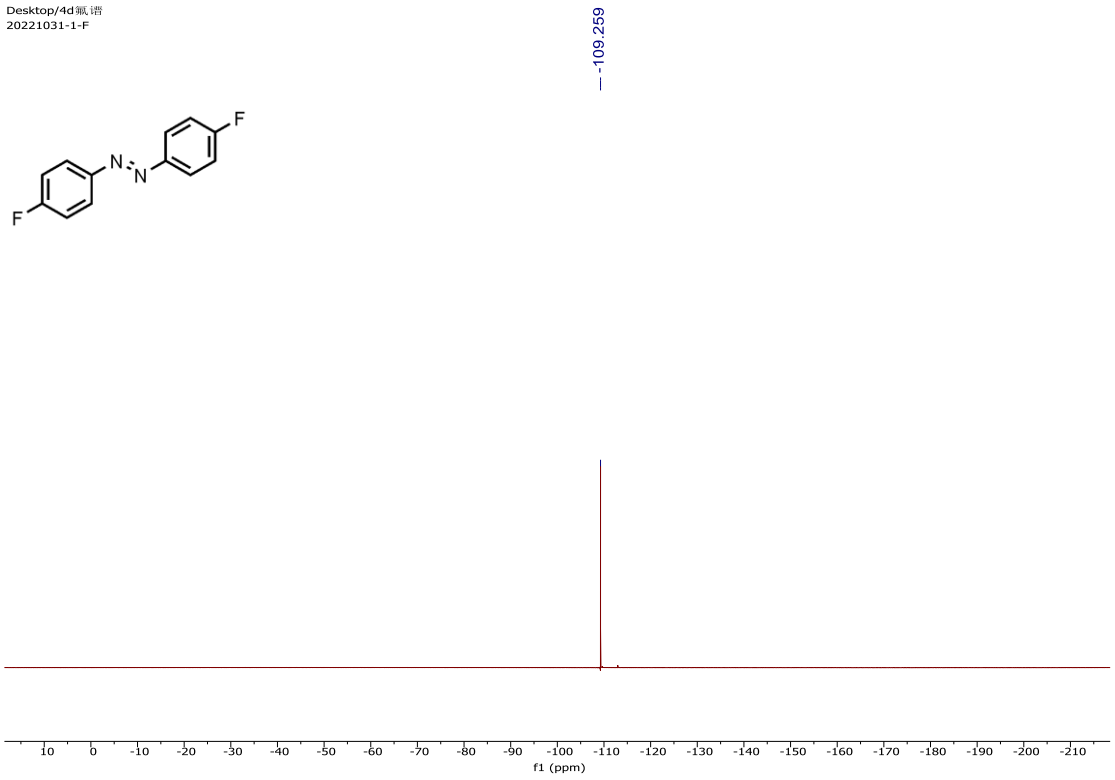


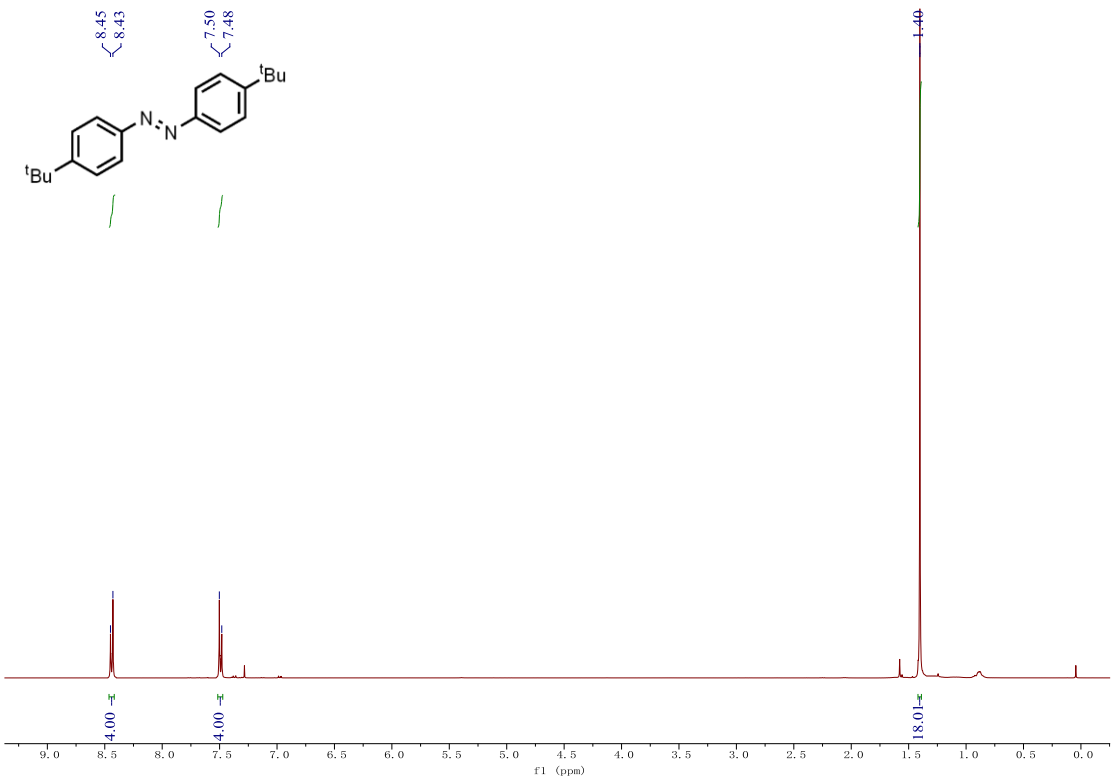
The ^{13}C-NMR spectrum of 4d



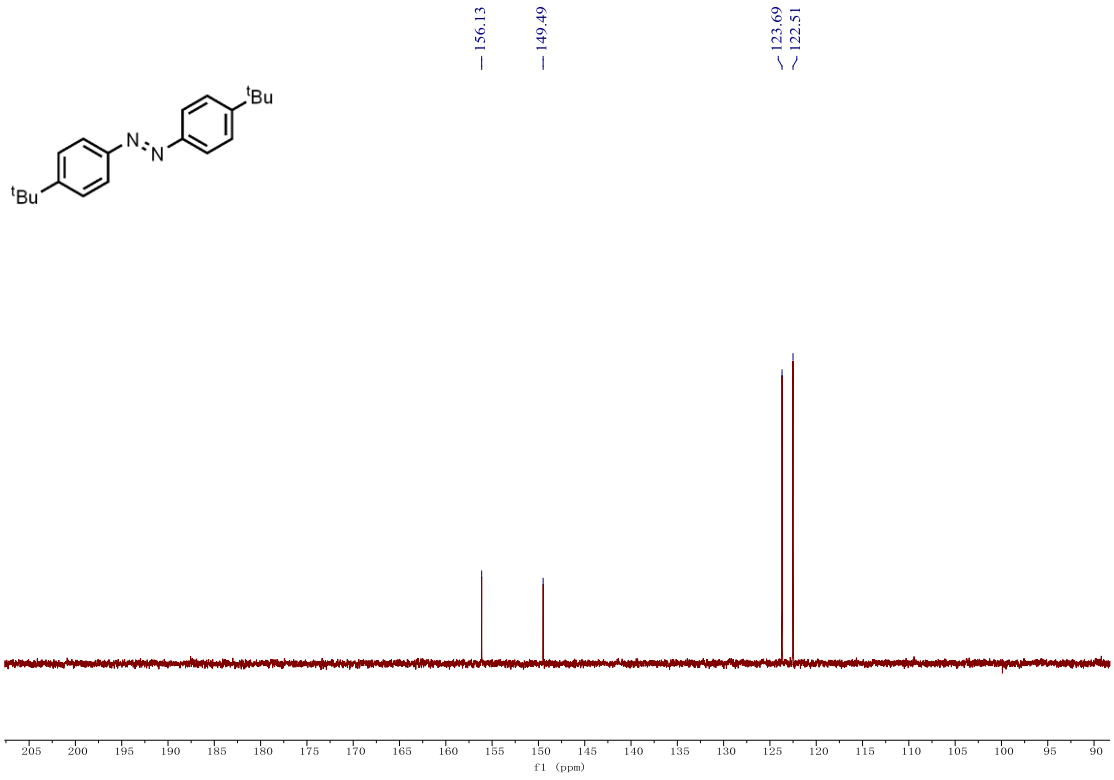
The ^{19}F-NMR spectrum of 4e



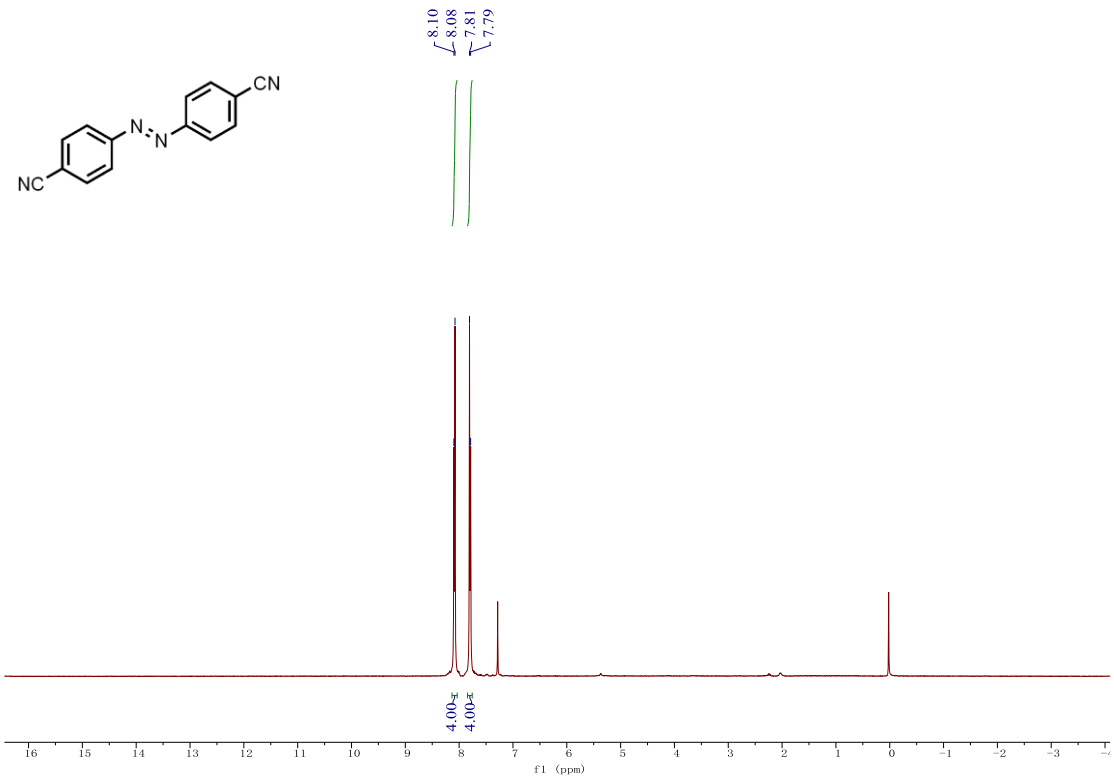
The ^{1}H-NMR spectrum of 4e



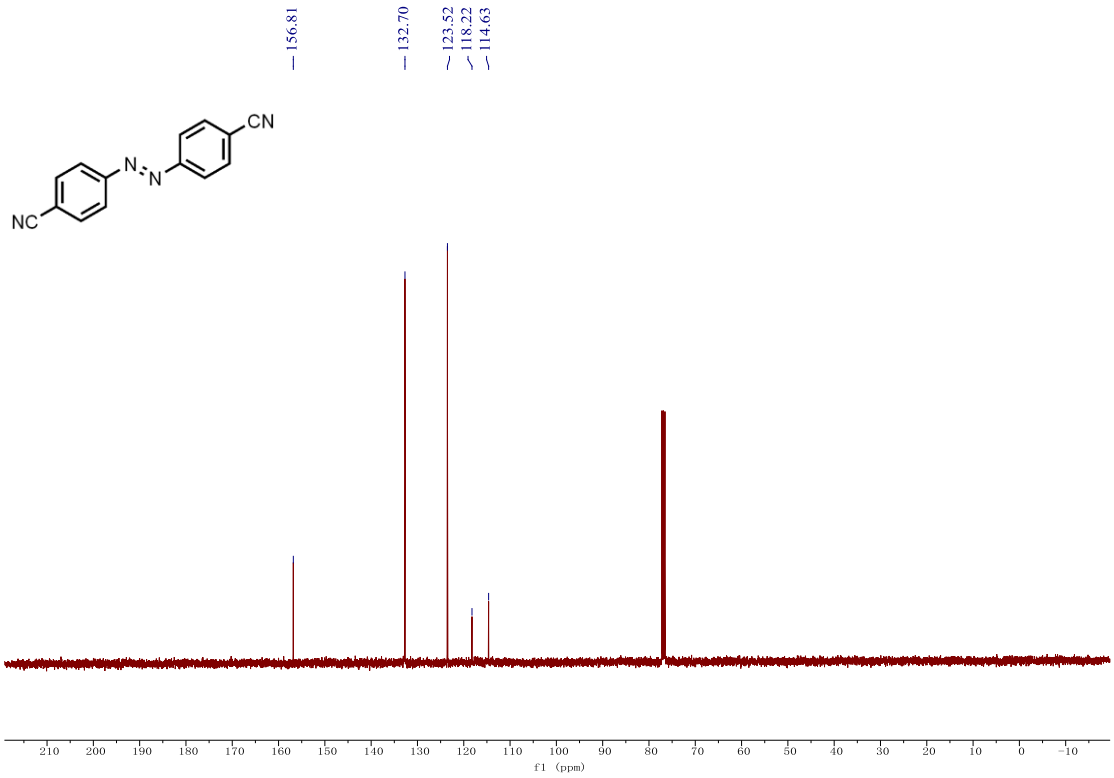
The ^{13}C-NMR spectrum of 4e



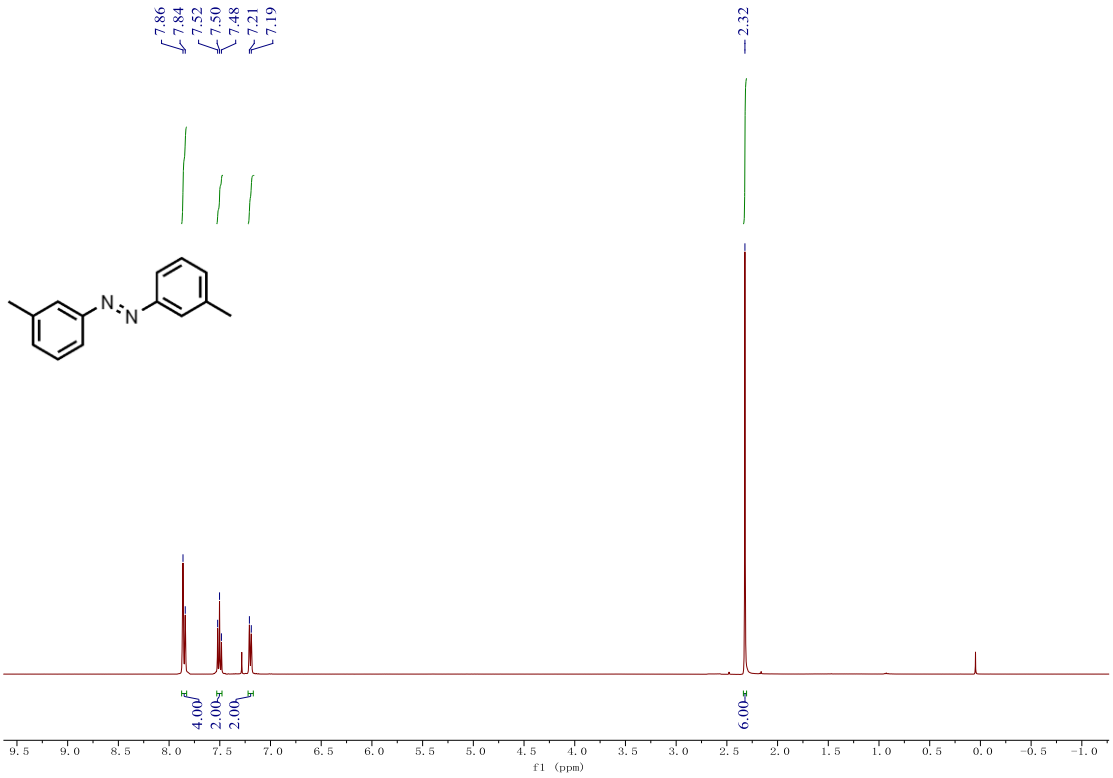
The ^{1}H-NMR spectrum of 4f



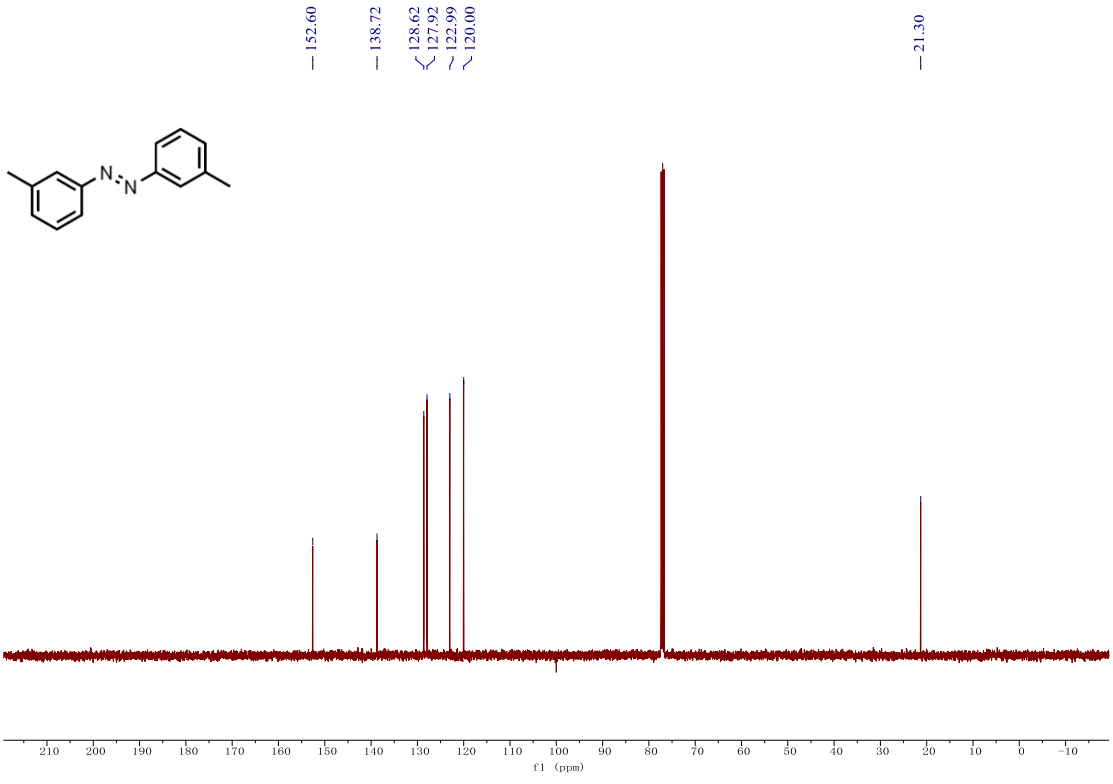
The ^{13}C-NMR spectrum of 4f



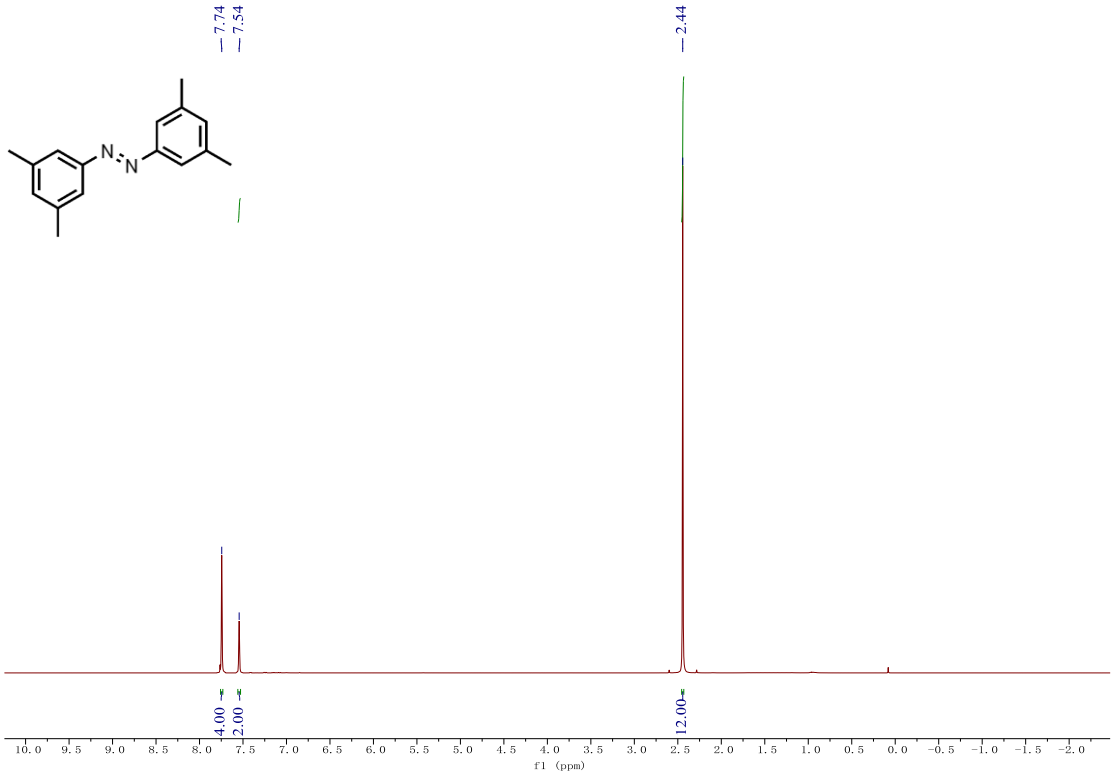
The ^{1}H-NMR spectrum of 4g



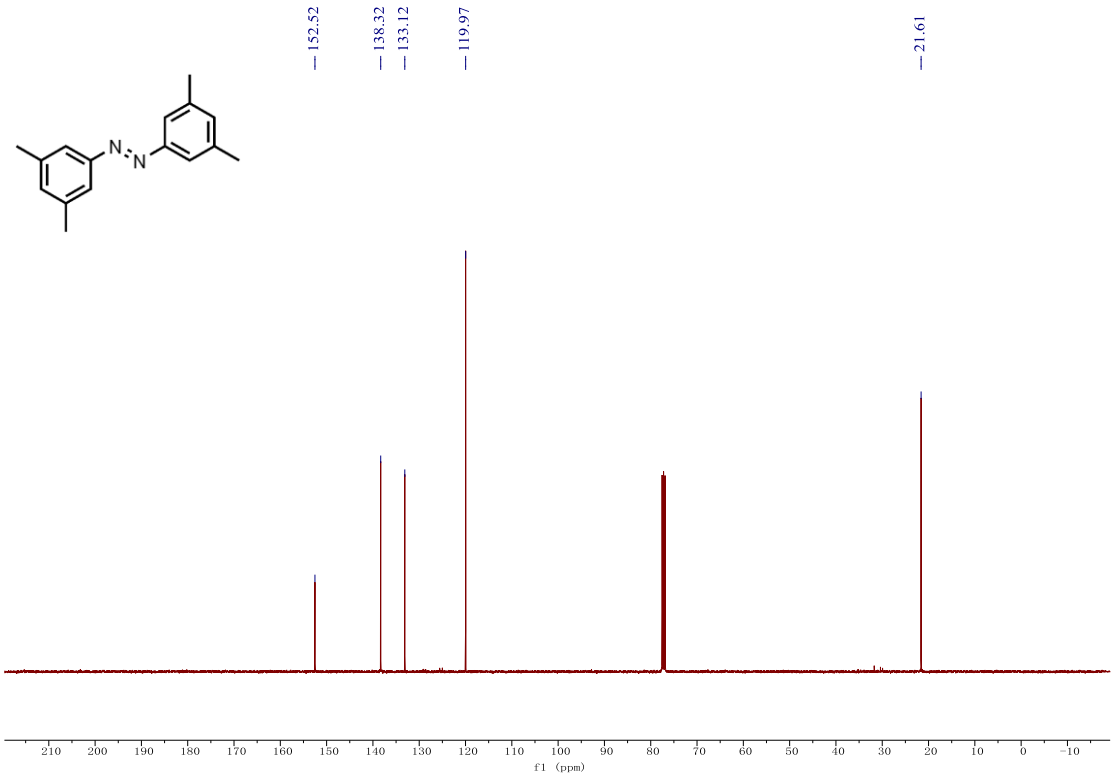
The ^{13}C-NMR spectrum of 4g



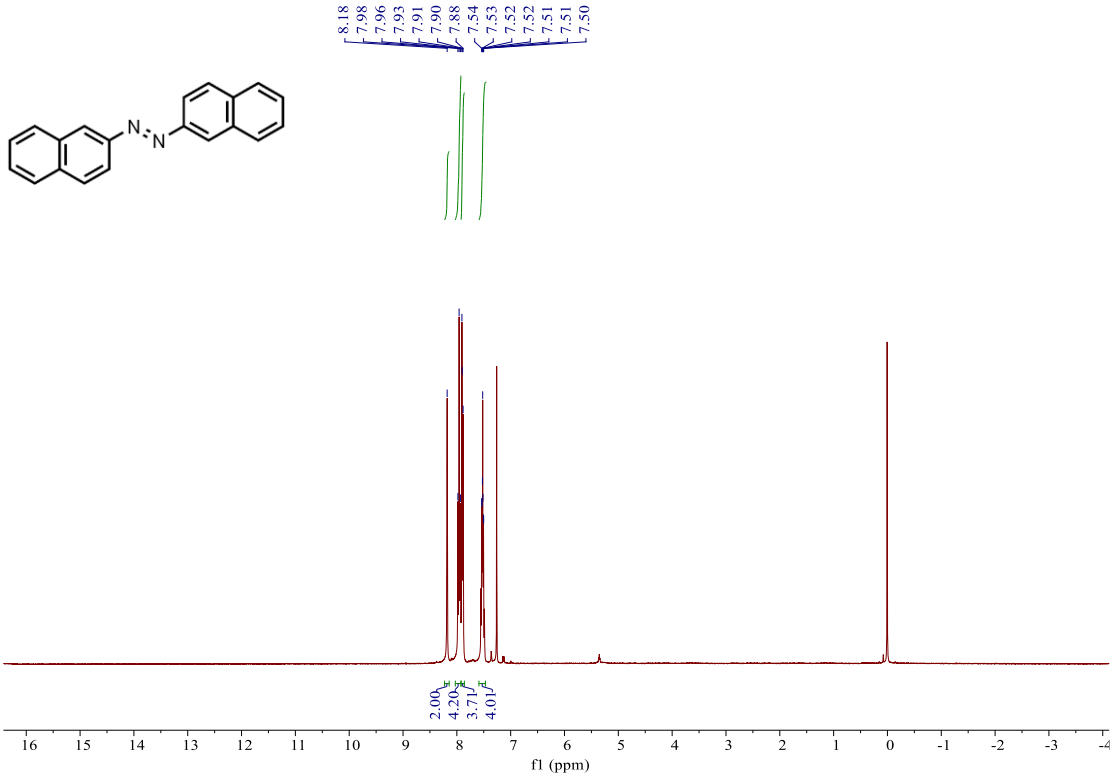
The ^{1}H-NMR spectrum of 4h



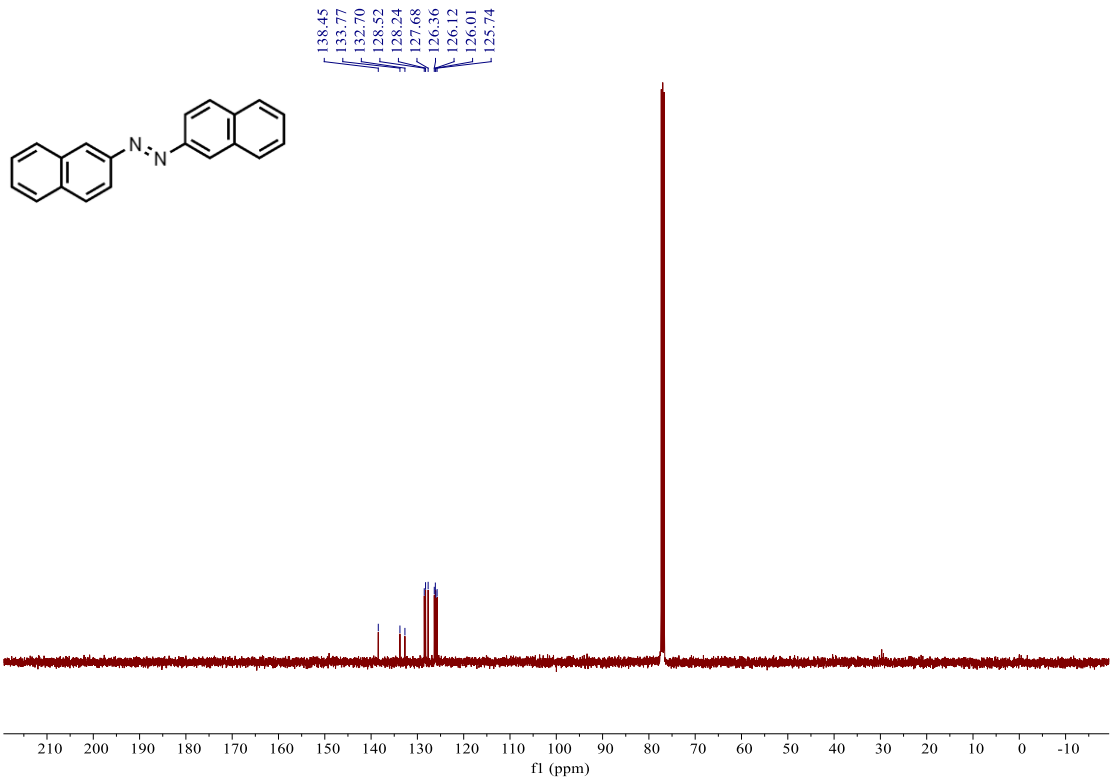
The ^{13}C-NMR spectrum of 4g



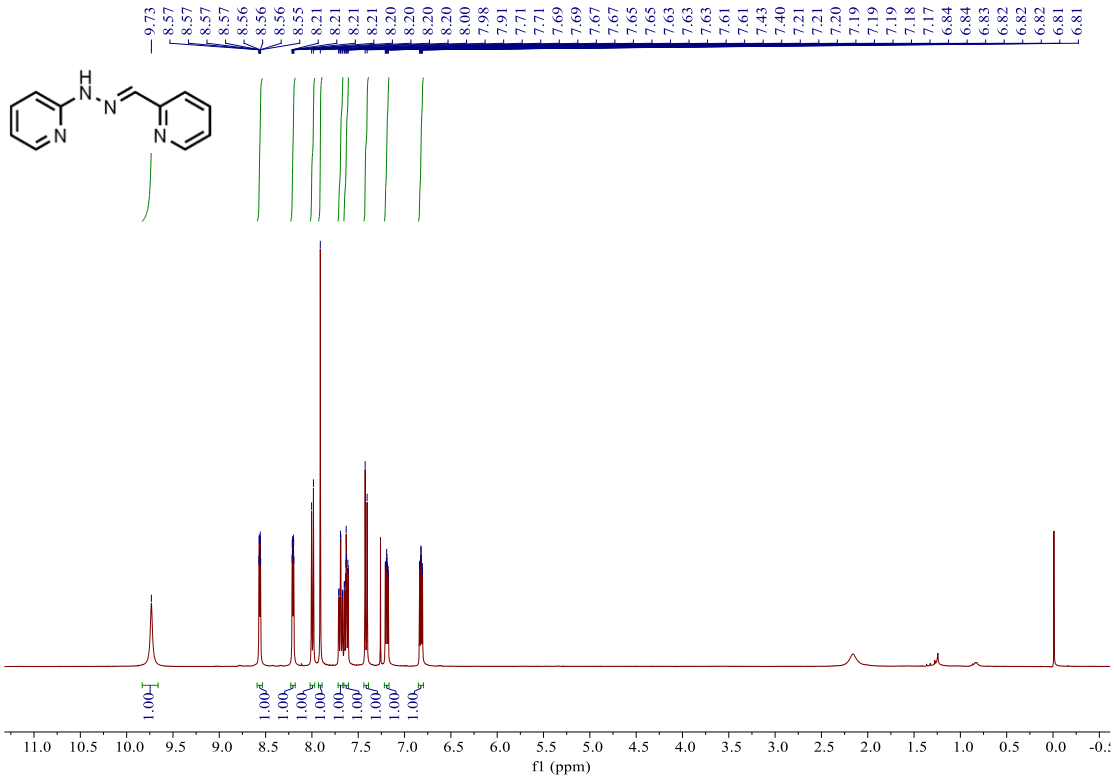
The ^{1}H-NMR spectrum of 4j



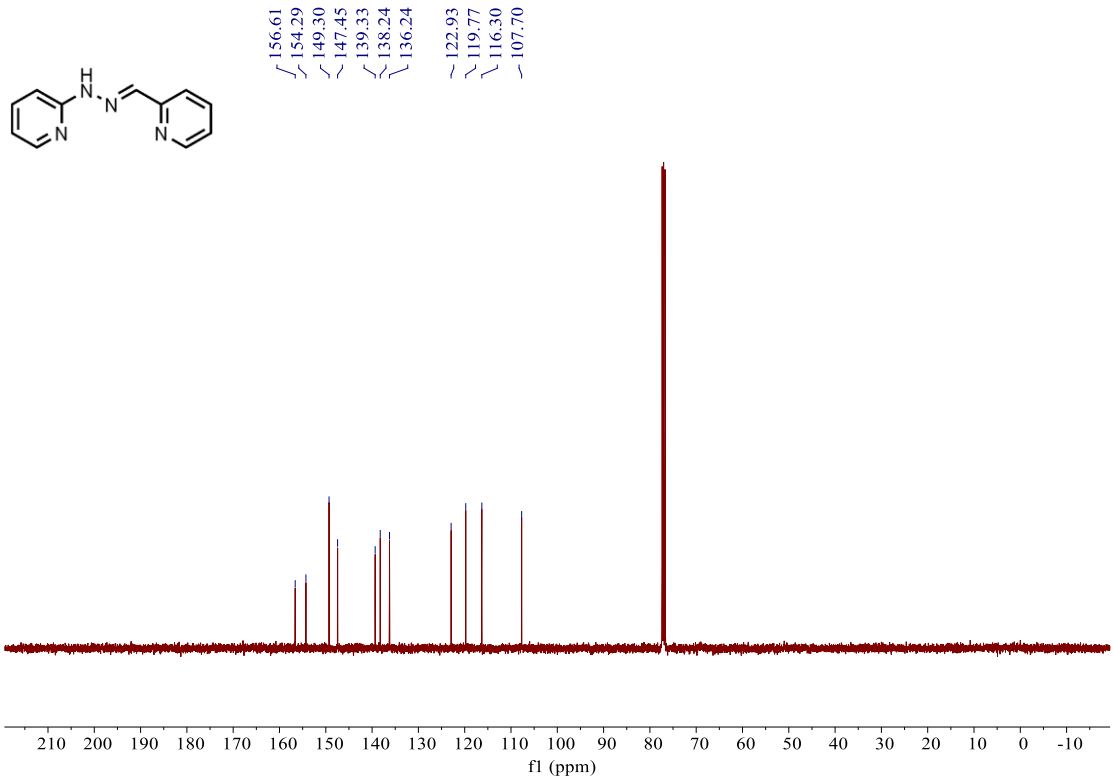
The ^{13}C-NMR spectrum of 4j



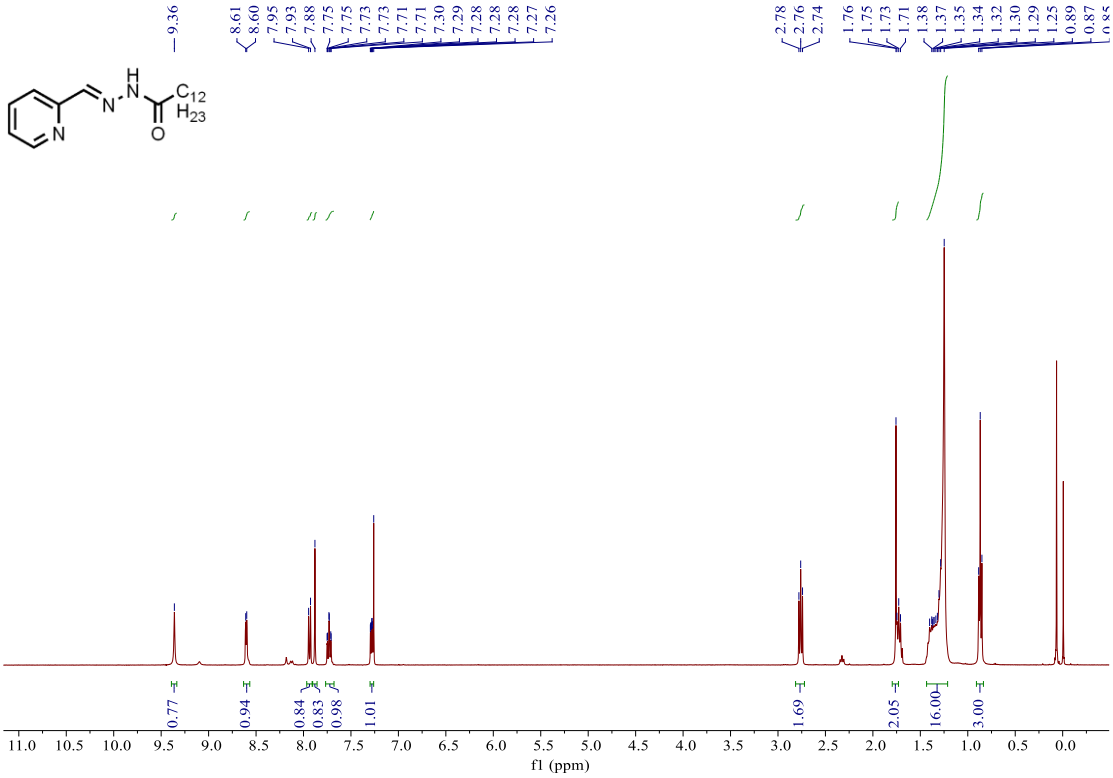
The ^{1}H-NMR spectrum of L_1



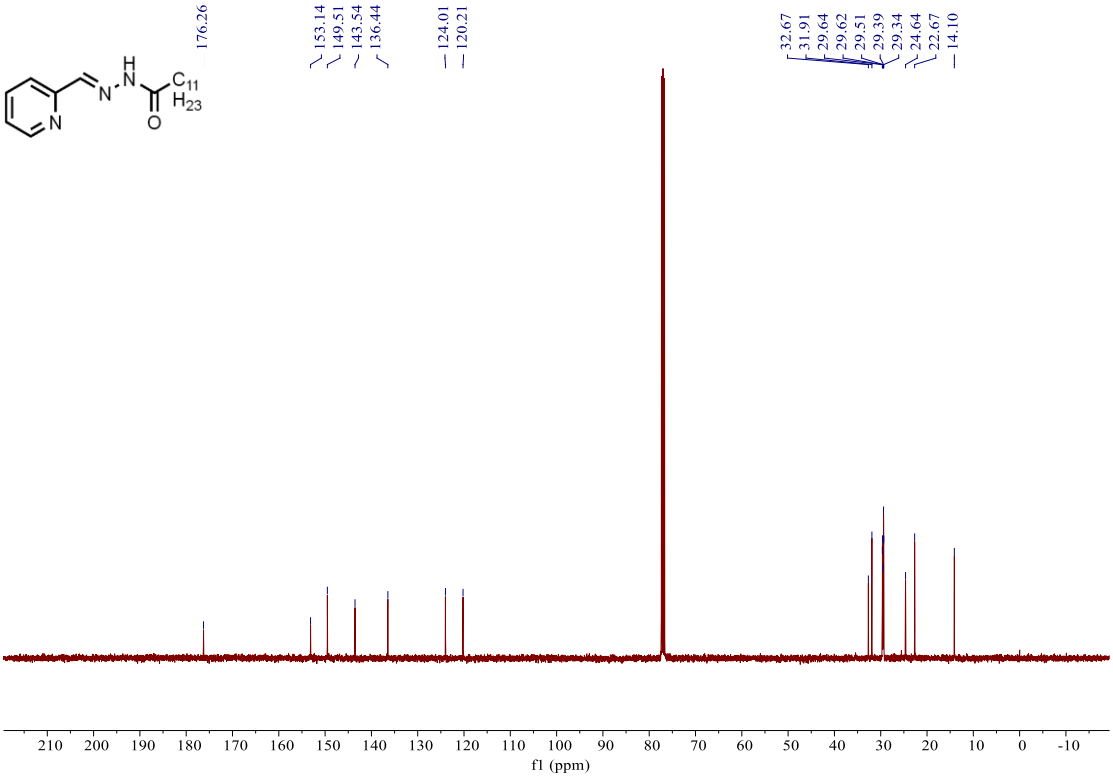
The ^{13}C-NMR spectrum of L_1



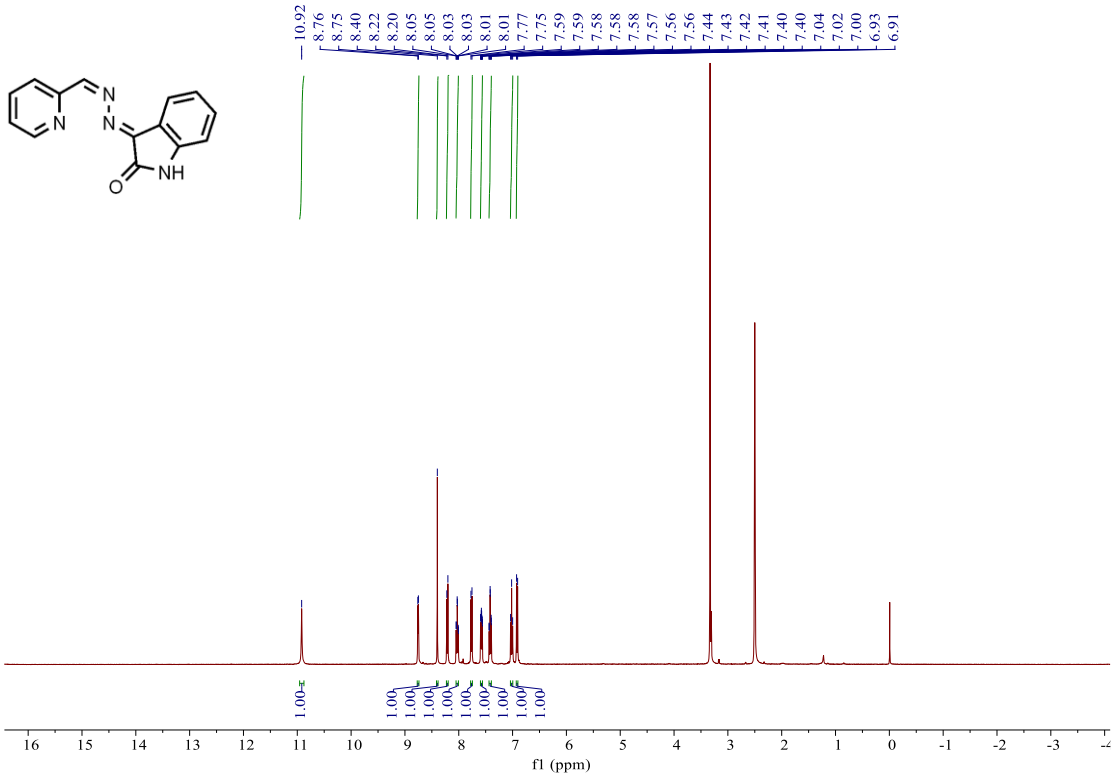
The ^{1}H-NMR spectrum of L_2



The ^{13}C-NMR spectrum of L_2



The ^{1}H-NMR spectrum of L_3



The ^{13}C-NMR spectrum of L_3