Electronic Supporting Information (ESI) for New Journal Chemistry

A Recyclable Ciprofloxacin Polymer Ligand for Copper-Catalyzed Coupling of (Hetero)aryl halides Aminations

Dake Song,[a] Yi Qin,[a] Ying Liu,[a] Jifan Wang,[a] Haijie Yang,[a] Zhonghui Zheng,[b] Feng Xu,[a] Xuefei Bao*[a] and Guoliang Chen*[a]

a. Key Laboratory of Structure-Based Drug Design & Discovery of Ministry of Education, Shenyang Pharmaceutical University, Shenyang 110016, Liaoning, P. R. of China.

b. Shandong Xinhua Pharmaceutical Co, Ltd, Zibo 255086, Shandong, P. R. of China

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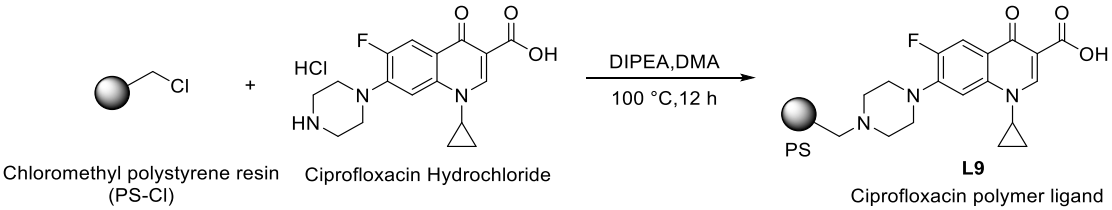
1. General information

Unless otherwise noted, all chemical reagents and solvents were obtained from commercial sources and were used without further purification. Chloromethyl Polystyrene Resin cross-linked with 1 % DVB (100-200 mesh, 1-1.24 mmol/g). TLC was performed on silicagel 60 GF254 and monitored under UV light. Melting points (m.p) were measured with Hanon MP420 melting point apparatus and was uncorrected. Column chromatography was performed on 200-400 mesh silica gel under pressure. NMR spectra were obtained on a Bruker AVIII-HD-400 and 600 spectrometer (^{1}H and ^{13}C), TMS as internal standard and chemical shifts (δ) were given ppm. The following abbreviations were applied in reporting NMR data: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublets of triplet), td (triplets of doublet) and m (multiplet). The mass spectral date were obtained on Waters ACQUITY QDa Mass Detector. HPLC analyses was performed on Shimadzu LC-2010AHT HPLC. The infrared spectral data were measured on FTIR-650 Fourier transform infrared spectrometer.

2. Synthesis of ciprofloxacin polymer ligand L9

2.1 General procedure for the preparation ciprofloxacin polymer ligand L9



Chloromethyl polystyrene resin (PS-Cl) | Ciprofloxacin Hydrochloride | Ciprofloxacin polymer ligand

Figure S1. Synthesis of L9

Chloromethyl polystyrene resin 5.000 g (5-6.20 mmol -Cl) swelled in 120 mL DMA for 12 h. Then ciprofloxacin hydrochloride (11.402 g, 9.30 mmol), DIPEA (8.013 g, 4.65 mmol) were added to the mixture. The mixture was stirred at 100 ℃ in an oil bath for 12 h. After cooling to room temperature, the mixture was filtered, and the filter cake was washed with deionized water, acetonitrile and ethanol, and then dried under vacuum to give ligand **L9 (**6.350 g) as a yellow solid. The filtrate was added 100 mL water and filtered to recover the excess ciprofloxacin.

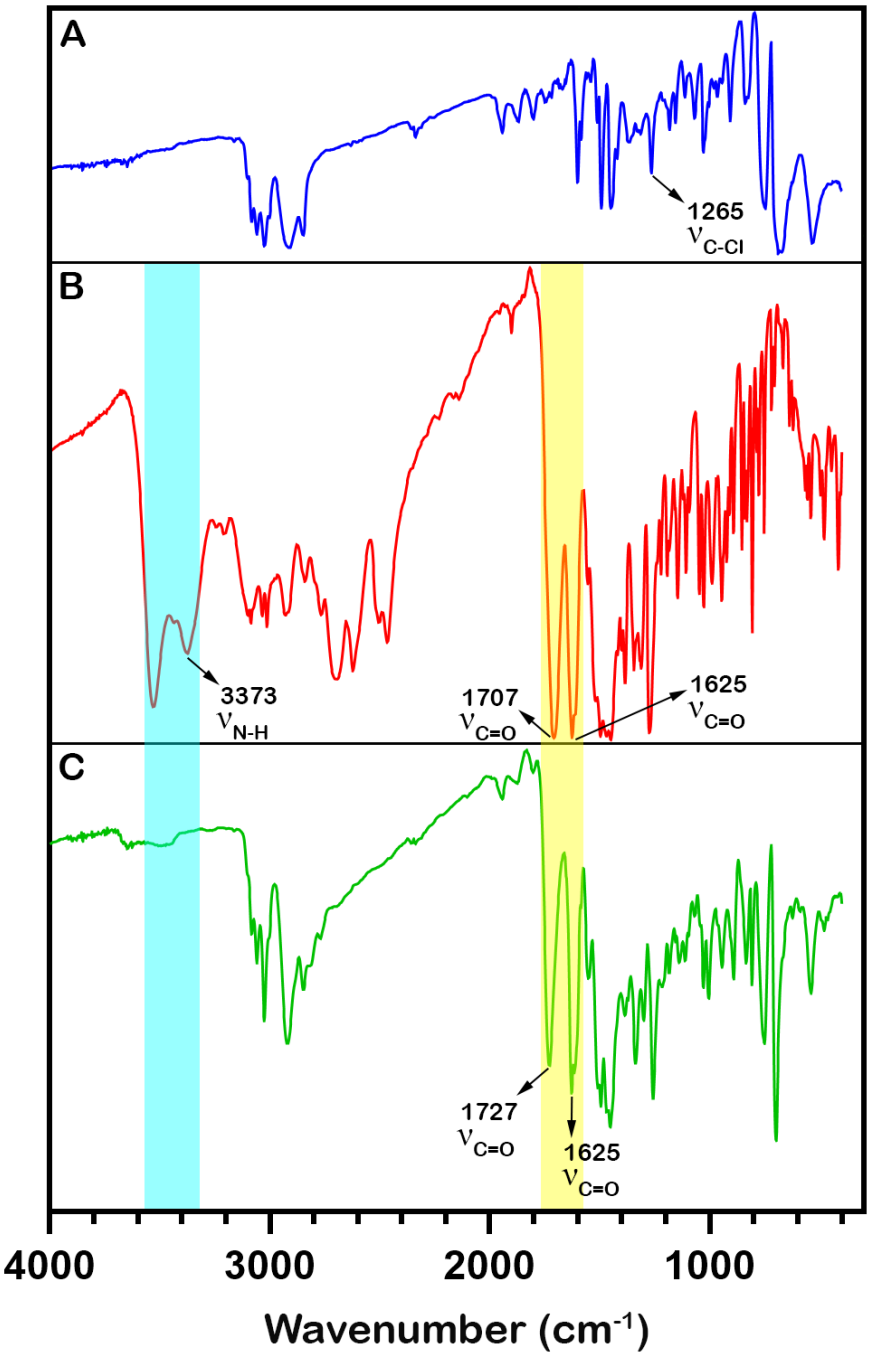


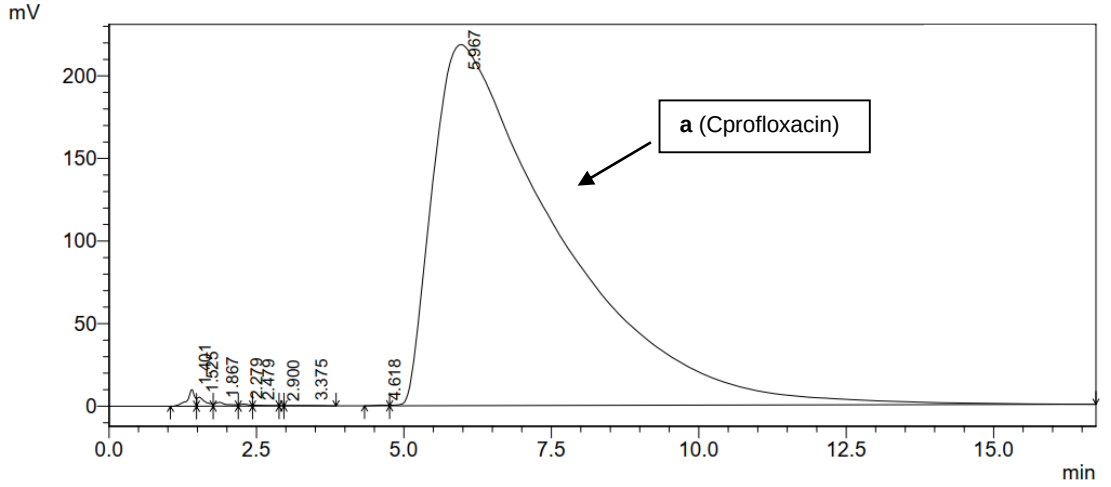
Figure S2. FTIR spectra of A (Chloromethyl polystyrene resin), B (Ciprofloxacin hydrochloride) and C (Ligand L9)

2.2 Fourier transform infrared (FTIR) spectra of ligand L9

Compared with the FTIR spectrum of ciprofloxacin hydrochloride, the most significant change in the infrared spectrum of **L9** was the disappearance of the N-H stretching vibration peak at 3373 cm^{-1} of ciprofloxacin hydrochloride, indicating that hydrogen on piperazine was replaced. The strong absorption peaks at 1727 cm^{-1} and 1625 cm^{-1} in the FTIR spectrum of **L9** correspond to the stretching vibration peaks of the carbonyl in the carboxyl group and ketone carbonyl group, respectively. (**Figure S2**)

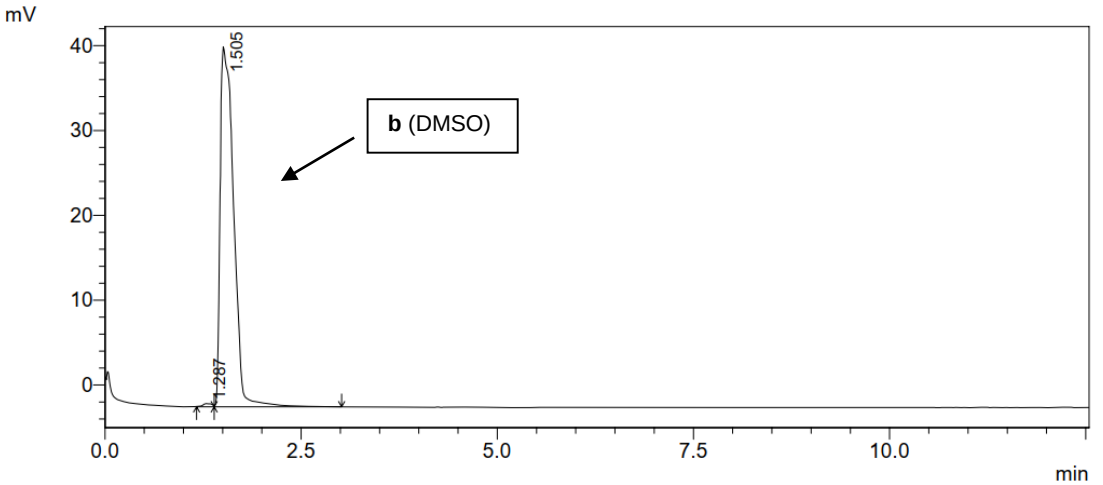
2.3 Determination of ciprofloxacin in reaction wastewater by high performance liquid chromatography (HPLC)

A: HPLC conditions: Agilent ZORBAX Extend-C18, 4.6×150 mm, 5 um, 10 % acetonitrile/90 % H_2O eluent, 0.5 mL/min, 254 nm.



Peak#	Ret.Time	Height	Area %
1	1.401	10017	0.264
2	1.525	5390	0.161
3	1.867	2311	0.101
4	2.279	1237	0.040
5	2.479	549	0.031
6	2.900	235	0.003
7	3.375	301	0.032
8	4.618	420	0.019
9	5.967	218623	99.349

B: HPLC conditions: Agilent ZORBAX Extend-C18, 4.6×150 mm, 5 um, 10 % acetonitrile/90 % H_2O eluent, 0.5 mL/min, 254 nm.

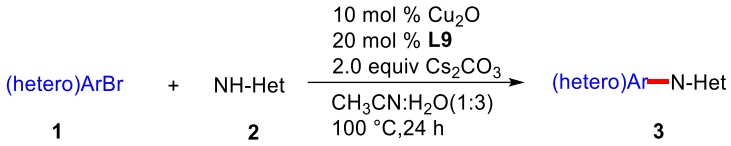


Peak#	Ret.Time	Height	Area %
1	1.287	378	0.614
2	1.505	42449	99.386

Figure S3 HPLC of reaction wastewater. Reaction conditions: (**A**) 4-Bromotoluene (3 mmol), pyrazole (3.75 mmol), Cu_2O (0.3 mmol), **L4** (0.47 g, 0.3 mmol), Cs_2CO_3 (6 mmol) and 6 mL 50 % DMSO aqueous; (**B**) 4-Bromotoluene (3 mmol), pyrazole (3.75 mmol), Cu_2O (0.3 mmol), **L9** (0.47 g, 0.3 mmol), Cs_2CO_3 (6 mmol) and 6 mL 50 % DMSO aqueous,

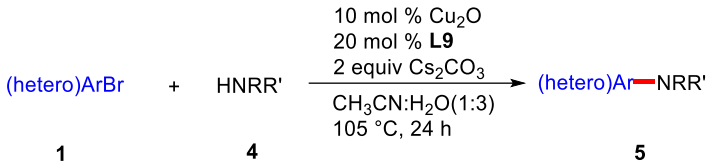
3. General procedure for amination

3.1 General procedure for the Cu_2O-catalyzed coupling of (hetero)aryl bromides with nitrogen aromatic heterocycles



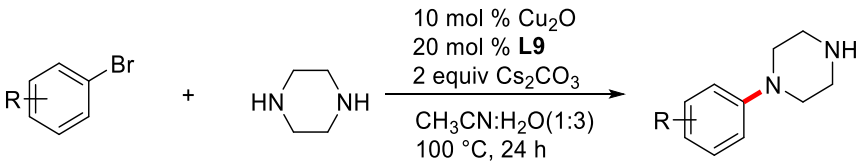
A 10 mL of seal tube with a magnetic stirring bar was charged with aryl bromides (3 mmol), amines (3.75 mmol), Cu_2O (0.04 g, 0.3 mmol), ligand **L9** (0.47 g, 0.3 mmol), Cs_2CO_3 (1.95 g, 6 mmol), 1 mL CH_3CN and 3 mL H_2O. The mixture was stirred at 100 ℃ in an oil bath for 24 h. The reaction mixture was cooled to ambient temperature, suction filtration to recover the ligand **L9**. The filtrate was diluted by 20 mL water and extracted with ethyl acetate (3×30 mL). The combined extracts was wash with brine and dried with $MgSO_4$. Filtered and evaporated under vacuum to give the crude product, which was purified with column chromatography on silica gel and eluting with petroleum ether /ethyl acetate or dichloromethane/methanol to give pure desired products.

3.2 General procedure for the Cu_2O-catalyzed coupling of (hetero)aryl bromides with cyclic secondary amines



To a 50 mL seal tube with a magnetic stirring bar was charged with aryl bromides (3 mmol), amines (3.75 mmol), Cu_2O (0.04 g, 0.3 mmol), ligand **L9** (0.47 g, 0.3 mmol), Cs_2CO_3 (1.95 g, 6 mmol), 1 mL CH_3CN and 3 mL H_2O. The mixture was stirred at 105 ℃ in an oil bath for 24 h. After cooling to room temperature, the mixture was filtered to recover the ligand **L9**. The filtrate was diluted by 20 mL water and extracted with ethyl acetate (3×30 mL). The combined extracts was wash with brine and dried with $MgSO_4$. Filtered and evaporated under vacuum to give the crude product, which was purified with column chromatography on silica gel and eluting with petroleum ether /ethyl acetate or dichloromethane/methanol to give pure desired products.

3.3 General procedure for scaled-up coupling reactions of aryl bromides with piperazine



5r, **5s**, **5u** and **5v**

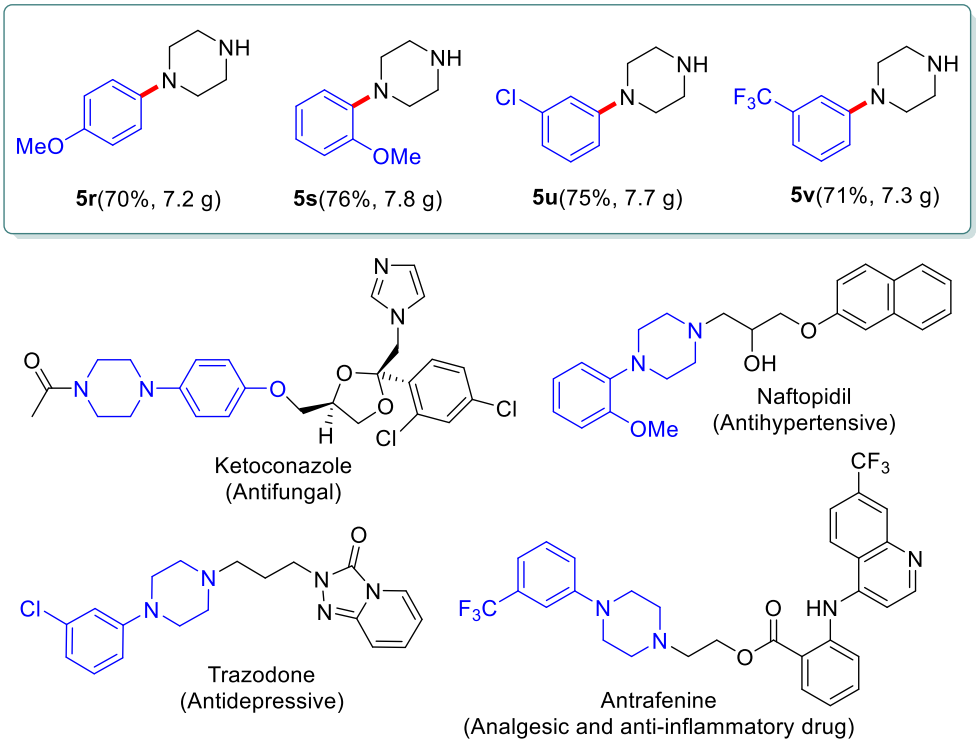
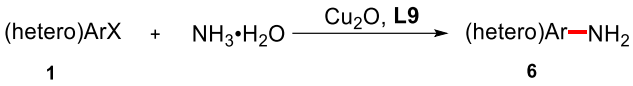


Figure S4 Scaled-up coupling reactions of aryl bromides with piperazine

To a 100 mL flask with a magnetic stirring bar was charged with aryl bromides (10 g, 1 eq), piperazine (4 eq), Cu_2O (0.1 eq), ligand **L9** (0.2 eq), Cs_2CO_3 (2 eq), 10 mL CH_3CN and 30 mL H_2O. The mixture was stirred at 100 ℃ in an oil bath for 24 h under argon. After cooling to room temperature, the mixture was filtered to recover the ligand **L9**. Recovery of acetonitrile from filtrate under reduced pressure and the residue was extracted with ethyl acetate (3×30 mL). The combined extracts was wash with brine and dried with $MgSO_4$. Filtered and evaporated under vacuum to give the crude product, which was purified with column chromatography on silica gel and eluting with petroleum ether /ethyl acetate or dichloromethane/methanol to give pure desired products (**5r**, **5s**, **5u** and **5v**).

3.4 General procedure for the Cu_2O-catalyzed coupling of (hetero)aryl bromides and chlorides with ammonia solution



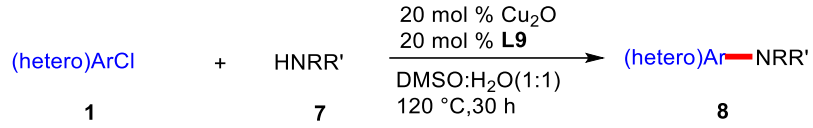
X = Br:10 mol % Cu_2O,10 mol % **L9**,100 °C,24 h

X = Cl: 20 mol % Cu_2O,20 mol % **L9**,DMSO,120 °C,24 h

For aryl bromides: A 30 mL of seal tube with a magnetic stirring bar was charged with aryl bromides (3 mmol), 25 % ammonia aqueous solution (3 mL), Cu_2O (0.04 g, 0.3 mmol) and ligand **L9** (0.47 g, 0.3 mmol). The resulting solution was stirred at 100 ℃ in an oil bath for 24 h. The reaction mixture was cooled to ambient temperature, suction filtration to recover the ligand **L9**. The filtrate was diluted by 20 mL water and extracted with ethyl acetate (3×30 mL). The combined extracts was dried over $MgSO_4$, filtered and evaporated under vacuum to give the crude product, which was purified with petroleum ether /ethyl acetate or dichloromethane/methanol to give pure desired products.

For aryl chlorides: A 30 mL of seal tube with a magnetic stirring bar was charged with aryl bromides (3 mmol), 25 % ammonia aqueous solution (3 mL), Cu_2O (0.08 g, 0.6 mmol), ligand **L9** (0.94 g, 0.6 mmol) and 3 mL DMSO. The resulting solution was stirred at 120 ℃ in an oil bath for 24 h. The reaction mixture was cooled to ambient temperature, suction filtration to recover the ligand **L9**. The filtrate was diluted by 20 mL water and extracted with ethyl acetate (3×30 mL).The combined extracts was dried over $MgSO_4$, filtered and evaporated under vacuum to give the crude product, which was purified with petroleum ether /ethyl acetate or dichloromethane/methanol to give pure desired products.

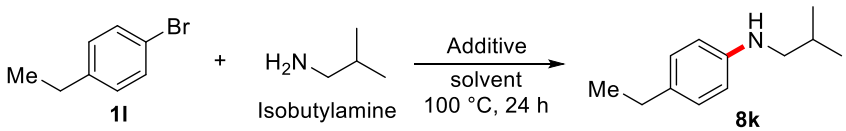
3.5 General procedure for the Cu_2O-catalyzed coupling of (hetero)aryl chlorides with primary and secondary alkylamines



A 30 mL of seal tube with a magnetic stirring bar was charged with aryl chlorides (3 mmol), amines (24 mmol), Cu_2O (0.08 g, 0.6 mmol), ligand **L9** (0.94 g, 0.6 mmol), 1 mL DMSO and 3 mL H_2O. The resulting solution was stirred at 120 ℃ in an oil bath for 30 h. The reaction mixture was cooled to ambient temperature, suction filtration to recover the ligand **L9**. The filtrate was diluted by 0 mL water and extracted with ethyl acetate (3×30 mL). The combined extracts was dried over $MgSO_4$, filtered and evaporated under vacuum to give the crude product, which was purified with column chromatography on silica gel and eluting with petroleum ether /ethyl acetate or dichloromethane/methanol to give pure desired products.

3.6 Preparation of 4-ethyl-N-isobutylaniline (8k)

3.6.1 Optimization of additive and solvent



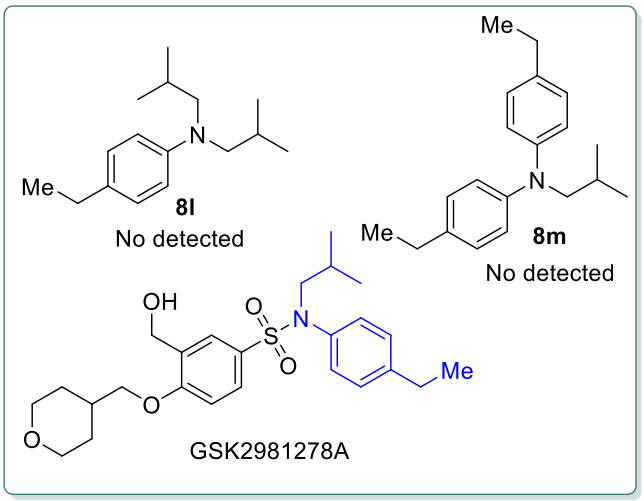


Table S1. Optimization of additive and solvent

Entry	Additive	Solvent	Yield (%)[a, b]
1	10 mol % Cu_2O	CH_3CN/H_2O (*v*/*v* = 1:3)	36
2	10 mol % Cu_2O + 20 mol % **PS-Cl**	CH_3CN/H_2O (*v*/*v* = 1:3)	32
3	10 mol % Cu_2O + 20 mol % **L9**	CH_3CN/H_2O (*v*/*v* = 1:3)	94
4	10 mol % Cu_2O + 10 mol % **L9**	CH_3CN/H_2O (*v*/*v* = 1:3)	93
5	10 mol % Cu_2O + 10 mol % **L9**	H_2O	85

[a] General conditions:**1l** (3 mmol), *iso*butylamine (18 mmol), additive, solvent (6 mL), 100 ℃, 24 h.

[b] Yields of isolated products are given.

In the coupling reaction of 4-bromoethylbenzene and *iso*butylamine, the compound **8k** was obtained with only 36 % yield in the absence of ligand **L9** (**Table S1**, entry **1**). A lower yield of 32 % could be obtained when using 10 mol % Cu_2O and 20 mol % PS-Cl as the catalyst, indicating that PS-Cl did not promote the coupling reaction (entry **2**). Additionally, reduce the loading of ligand **L9** to 10

mol % did not affect the conversion (entry **3** *vs* entry **4**). On this basis, the yield of compound **8k** was reduced when changing the solvent to H_2O (entry **5**). Therefore, we used 10 mol % Cu_2O and 10 mol % **L9** as the catalyst system in the subsequent investigations.

3.6.2 Procedure for 4-ethyl-N-isobutylaniline (8k)

A 100 mL of flask with a magnetic stirring bar was charged with 4-Bromoethylbenzene (10 g, 54.04 mmol), *Iso*butylamine (32 mL, 324.42 mmol), Cu_2O (0.77 g, 5.40 mmol), ligand **L9** (1.79 g, 5.40 mmol), 10 mL CH_3CN and 30 mL H_2O. The resulting solution was stirred at 100 ℃ in an oil bath for 24 h. The reaction mixture was cooled to ambient temperature, suction filtration to recover the ligand **L9**. Recovery of acetonitrile from filtrate under reduced pressure and the residue was extracted with ethyl acetate (3×30 mL). The combined extracts was dried over $MgSO_4$, filtered and evaporated under vacuum to give the crude product, which was purified with petroleum ether /ethyl acetate to give compound **8k** as a colorless oil (8.91 g; yield: 93 %). The ligand **L9** was washed with water and acetone, and reusing under as is condition for the next catalytic cycle.

4. A possible reaction mechanism

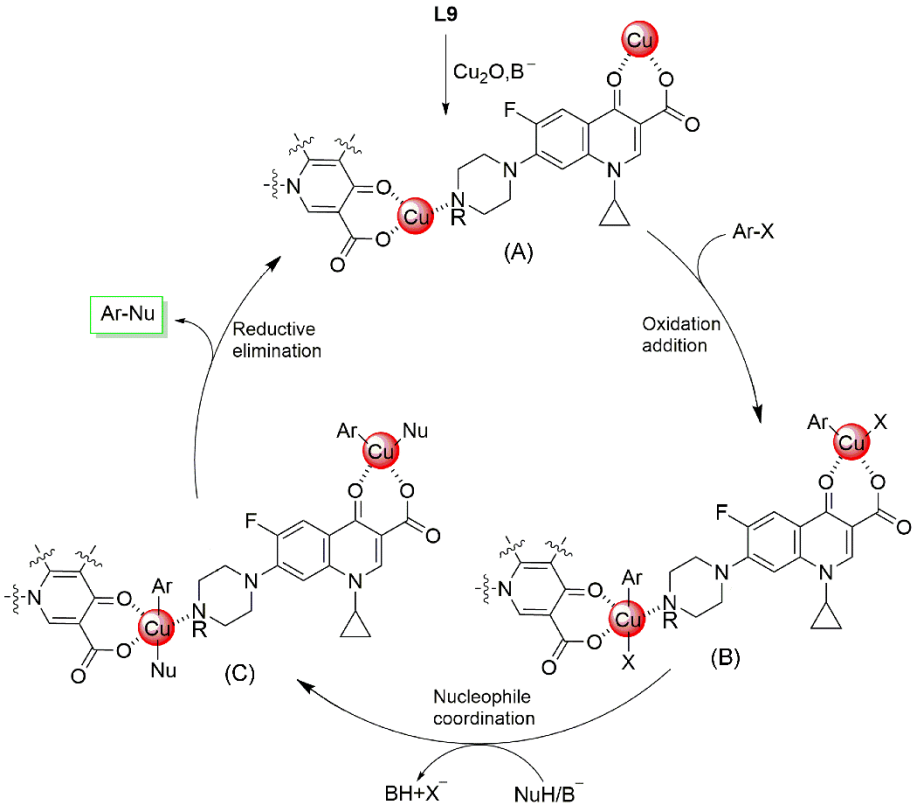
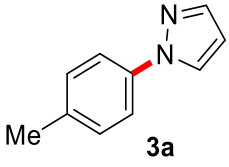


Figure S5. Possible Cu(I)/Cu(III) catalytic cycle mechanism for the Ullmann coupling reaction

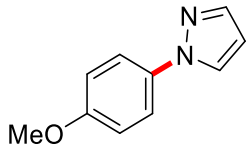
Furthermore, we proposed a possible reaction mechanism to explain the copper-catalyzed coupling reaction. As described in **Figure S5**, the cross-coupling reaction might go through a prototypical Cu(I)/Cu(III) catalytic cycle via an oxidative addition and reductive elimination pathway. First, the coordination of the quinolones C3, C4, C7 substituents carboxyl, ketone carbonyl and a nitrogen atom in piperazine to the Cu(I) center formed the reactive species A, and then the chelating aryl halides to afford complexes B via oxidative addition process. Secondly, the complexes B react with amine to afford intermediate C under the action of base. Finally, the desired product was obtained by reductive elimination process and release the reactive species A ready to re-enter the next catalytic cycle.

5. Characterization



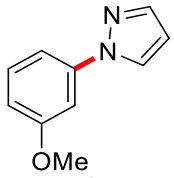
3a

1-p-Tolyl-1H-pyrazole **(3a):** Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.4 Hz, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.59-7.54 (m, 2H), 7.24 (s, 2H), 6.45 (t, *J* = 2.1 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.74, 136.27, 129.93, 126.70, 119.22, 107.31, 20.93. [1]



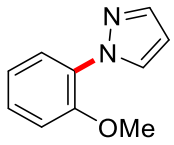
3b

1-(4-Methoxyphenyl)-1H-pyrazole **(3b):** Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.69 (s, 1H), 7.61-7.56 (m, 2H), 6.99-6.94 (m, 2H), 6.43 (q, *J* = 4.1, 2.0 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.25, 140.56, 133.99, 126.84, 120.90, 114.51, 107.17, 55.56.[2]



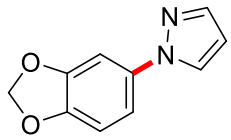
3c

1-(3-Methoxyphenyl)-1H-pyrazole **(3c):** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 2.5, 0.6 Hz, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.33 (t, *J* = 8.1 Hz, 1H), 7.32-7.29 (m, 1H), 7.23 (ddd, *J* = 7.9, 2.1, 1.0 Hz, 1H), 6.83 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 6.46 (dd, *J* = 2.5, 1.8 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.55, 141.32, 140.99, 130.16, 126.92, 112.43, 111.17, 107.60, 105.09, 55.52. [2]



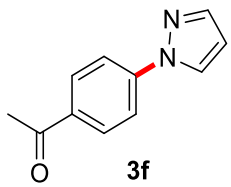
3d

1-(2-Methoxyphenyl)-1H-pyrazole **(3d):** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.4 Hz, 1H), 7.73 (s, 1H), 7.73-7.70 (dd, *J* = 7.9, 4.2 Hz, 1H), 7.34-7.29 (m, 1H), 7.10-7.04 (m, 2H), 6.45 (t, *J* = 2.1 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.35, 140.03, 131.58, 128.05, 125.34, 121.18, 112.29, 106.16, 77.21, 55.99, 29.71. [2]



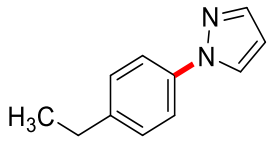
3e

1-(Benzo[d][1,3]dioxol-5-yl)-1H-pyrazole **(3e):** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 2.4, 0.6 Hz, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.22 (d, *J* = 2.2 Hz, 1H), 7.10 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.43 (dd, *J* = 2.4, 1.8 Hz, 1H), 6.02 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.39,146.26, 140.68, 135.21, 127.00, 112.63, 108.29, 107.29, 101.96, 101.70.



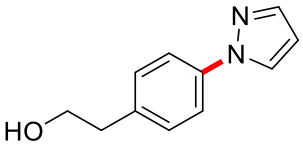
3f

1-p-Tolyl-1H-pyrazole **(3f):** White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 6.8, 1.9 Hz, 2H), 8.02 (d, *J* = 2.5 Hz, 1H), 7.81(dd, *J* = 6.7, 1.8 Hz, 2H), 7.77 (d, *J* = 1.7 Hz, 1H), 6.52 (t, *J* = 2.2, 1.9 Hz, 1H), 2.63 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.71, 143.19, 141.92, 134.73, 129.91, 126.79, 118.32, 108.48, 26.50.



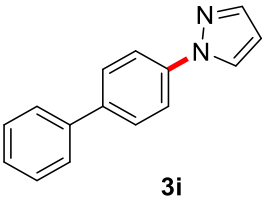
3g

***1-(4-Ethylphenyl)-1H-pyrazole* (3g):** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.5 Hz, 1H), 7.71 (d, *J* = 1.7 Hz, 1H), 7.62-7.57 (m, 2H), 7.30-7.26 (m, 2H), 6.45 (t, *J* = 2.1 Hz, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.69, 140.74, 138.12, 128.76, 126.73, 119.33, 107.31, 28.34, 15.58. [3]



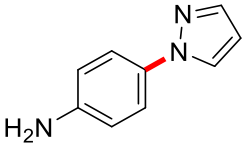
3h

***2-(4-(1H-pyrazol-1-yl)phenyl)ethanol* (3h):** Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.5 Hz, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.63 (dt, *J* = 6.2, 4.4 Hz, 2H), 7.31 (dt, *J* = 6.3, 4.4 Hz, 2H), 6.46 (t, *J* = 2.2 Hz, 1H), 3.89 (t, *J* = 6.5 Hz, 2H), 2.90 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.95, 138.79, 136.99, 130.00, 126.79, 119.49, 107.53, 76.77, 63.54, 38.59.



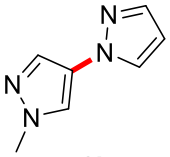
3i

***1-[1,1'-Biphenyl]-4-yl-1*H*-pyrazole* (3i):** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.4 Hz, 1H), 7.81-7.74 (m, 3H), 7.72-7.66 (m, 2H), 7.65-7.58 (m, 2H), 7.48-7.44 (m, 2H), 7.40-7.34 (m, 1H), 6.50 (t, *J* = 2.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.15, 140.11, 139.38, 139.35, 128.88, 128.07, 127.50, 126.97, 126.74, 119.47, 107.72. [2]



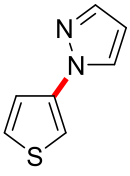
3j

***4-(1H-Pyrazol-1-yl)aniline* (3j)**: White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.4 Hz, 1H), 7.66 (d, *J* = 1.8 Hz, 1H), 7.42 (dt, *J* = 9.7, 3.2 Hz, 2H), 6.72 (dt, *J* = 9.7, 3.2 Hz, 2H), 6.40 (t, *J* = 2.1 Hz, 1H), 3.73 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.26, 140.24, 132.45, 126.70, 121.10, 115.46, 106.81. [4]



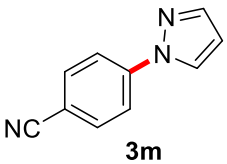
3k

***1-Methyl-4-(1H-pyrazol-1-yl)-1H-pyrazole* (3k):** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.69 (s, 1H), 7.66-7.63 (m, 2H), 6.40 (t, *J* = 2.2 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.31, 130.53, 128.01 , 121.95, 106.72, 39.56. [4]



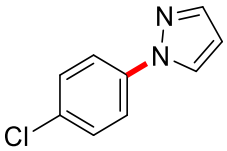
3l

***1-(3-Thienyl)-1H-pyrazole* (3l):** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.4 Hz, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 7.40-7.32 (m, 3H), 6.41 (t, *J* = 2.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.60, 139.83, 127.46, 126.48, 120.32, 110.62, 107.05. [4]



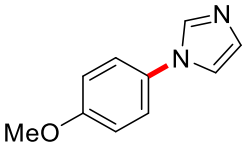
3m

***1-(4-Cyanophenyl)-1H-pyrazole* (3m):** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.5 Hz, 1H), 7.73 (d, *J* = 1.7 Hz, 1H), 7.63 (dt, *J* = 9.7, 3.0 Hz, 2H), 7.41 (dt, *J* = 9.8, 3.1 Hz, 2H), 6.48 (dd, *J* = 2.5, 1.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.35 , 138.74 , 131.91 , 129.52 , 126.69 , 120.32 , 107.98. [1]



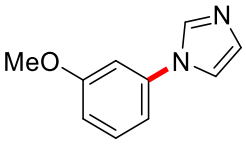
3n

1-(4-Bromophenyl)-1H-pyrazole **(3n):** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.5 Hz, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.64 (dt, *J* = 6.7, 3 Hz, 2H), 7.41 (dt, *J* = 9.7, 3.1 Hz, 2H), 6.48 (t, *J* = 2.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ141.36 , 138.75 , 131.91 , 129.52 , 126.69 , 120.32 , 107.98. [3]



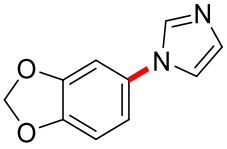
3o

1-(4-Methoxyphenyl)-1H-imidazole **(3o):** Light brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.30 (dt, *J* = 10.2, 3.4 Hz, 2H), 7.22 (s, 1H), 7.20 (s, 1H), 6.99 (dt, *J* = 10.2, 3.5 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.95, 130.77, 130.11, 123.25, 114.91, 55.62.[5]



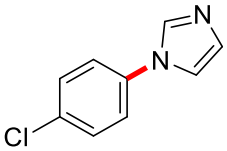
3p

1-(3-Methoxyphenyl)-1H-imidazole **(3p)**: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (t, *J* = 1.1 Hz, 1H), 7.38 (td, *J* = 8.0, 0.7 Hz, 1H), 7.28 (t, *J* = 1.4 Hz, 1H), 7.20 (t, *J* = 1.2 Hz, 1H), 6.98 (ddd, *J* = 7.9, 2.0, 0.9 Hz, 1H), 6.95-6.86 (m, 2H), 3.86 (s, 3H), 1.27 (d, *J* = 11.1 Hz, 0H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.69, 138.46, 135.62, 130.72, 130.33, 118.28, 113.67, 112.66, 107.75, 55.55. [5]



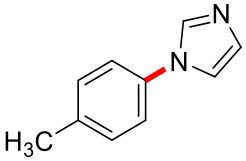
3q

1-(Benzo[d][1,3]dioxol-5-yl)-1H-imidazole **(3q):** Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.18 (s, 2H), 6.89-6.82 (m, 3H), 6.05 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.63, 147.12, 135.95, 131.81, 130.07, 118.91, 115.30, 108.68, 103.76, 101.97. [6]



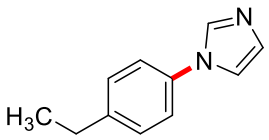
3r

1-(4-Chlorophenyl)-1H-imidazole **(3r):** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (t, *J* = 1.2 Hz, 1H), 7.46 (dt, *J* = 9.5, 2.9 Hz, 2H), 7.33 (dt, *J* = 9.6, 3.0 Hz, 2H), 7.26 (t, *J* = 1.4 Hz, 1H), 7.23 (t, *J* = 1.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.87, 135.52, 133.29, 130.62, 130.07, 122.75, 118.23. [2]



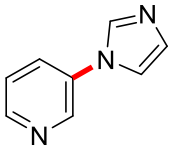
3s

1-p-Tolyl-1H-imidazole **(3s):** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.28 (s, 4H), 7.25 (t, *J* = 1.4 Hz, 1H), 7.21 (d, *J* = 1.2 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.55, 135.60, 134.97, 130.38, 130.05, 121.49, 118.43, 20.98. [5]



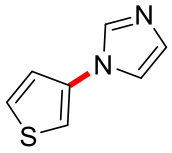
3t

***1-(4-Ethylphenyl)-1H-imidazole* (3t):** Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (t, *J* = 1.1 Hz, 1H), 7.30 (s, 4H), 7.26 (d, *J* = 1.3 Hz, 1H), 7.20 (d, *J* = 1.2 Hz, 1H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.86, 135.64, 135.16, 130.14, 129.21, 121.59, 118.42, 28.38, 15.55. [7]



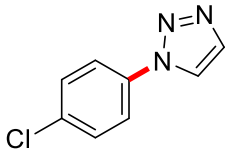
3u

***3-(1H-Imidazol-1-yl)pyridine* (3u):** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 2.6 Hz, 1H), 8.65 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.91 (s, 1H), 7.74 (dq, *J* = 8.2, 2.7, 1.5 Hz, 1H), 7.46 (dd, *J* = 8.2, 4.7 Hz, 1H), 7.32 (s, 1H), 7.28 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.88, 142.98, 133.91, 131.14, 128.85, 124.29, 118.13. [5]



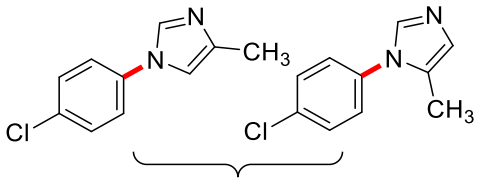
3v

***1-(3-Thienyl)-1H-imidazole* (3v):** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.43 (dd, *J* = 5.2, 3.2 Hz, 1H), 7.27-7.11 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.19, 129.85, 127.22, 121.45, 118.70, 113.35. [5]



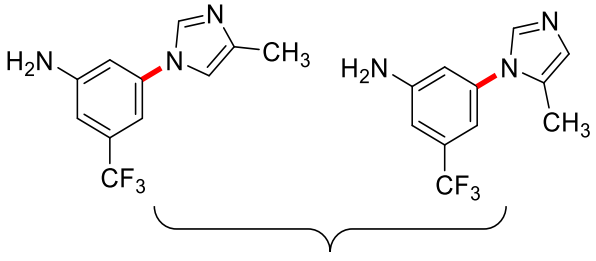
3w

***1-(4-Chlorophenyl)-1H-1, 2, 3-triazole* (3w):** White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.11 (s, 1H), 7.64 (dt, *J* = 9.8, 3.1 Hz, 2H), 7.49 (dt, *J* = 9.8, 3.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.75, 140.84, 135.52, 133.96, 129.97, 121.24.[8]



3x(10:1)

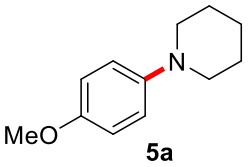
***4-Methyl-1-(4-chlorophenyl)-1H-imidazole* and *2-Methyl-1-(4-chlorophenyl)-1H-imidazole* (3x):** White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.4 Hz, 1H), 7.43 (dt, *J* = 9.7, 3.1 Hz, 2H), 7.30 (dt, *J* = 9.8, 3.2 Hz, 2H), 6.98 (s, 1H), 2.30 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.52, 135.88, 134.44, 132.94, 130.01, 129.84, 126.88, 122.33, 114.64, 29.70, 13.50.



3y(2:1)

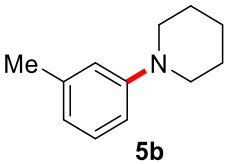
***3-(4-Methyl-1H-imidazol-1-yl)-5-(trifluoromethyl)aniline* and *3-(2-Methyl-1H-imidazol-1-yl)-5-(trifluoromethyl)aniline* (3y):** White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.56 (s, 0H), 6.99 (s, 1H), 6.94 (s, 2H), 6.90 (s, 1H), 6.87 (s, 1H), 6.84 (s, 1H), 6.78

(s, 1H), 6.70 (s, 0H), 4.12 (s, 3H), 2.29 (s, 3H), 2.19 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.25, 148.05, 139.67, 138.80, 137.92, 134.38, 133.27, 127.51, 124.28, 114.36, 114.23, 111.63, 111.61, 110.92, 109.77, 109.75, 109.53, 107.20, 13.55, 9.78.[9]



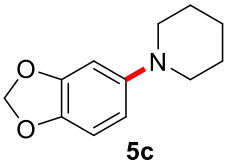
5a

***1-(4-Methoxyphenyl)piperidine* (5a):** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 8.8 Hz, 2H), 6.82 (dt, *J* = 10.3, 3.6 Hz, 2H), 3.76 (s, 3H), 3.02 (t, *J* = 5.4 Hz, 4H), 1.75-1.70 (m, 4H), 1.57-1.51 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 118.75, 114.25, 55.48, 52.29, 25.97, 24.03.[18]



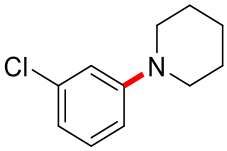
5b

***1-(3-Methylphenyl)piperidine* (5b):** Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.7 Hz, 1H), 6.77 (s, 2H), 6.65 (d, *J* = 7.4 Hz, 1H), 3.14 (t, *J* = 5.5 Hz, 4H), 2.31 (s, 3H), 1.74-1.68 (m, 4H), 1.60-1.54 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.64, 128.85, 120.15, 117.48, 113.71, 50.84, 25.88, 24.32, 21.78.[11]



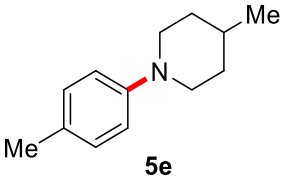
5c

***1-(Benzo[d][1,3]dioxol-5-yl)piperidine* (5c):** Yellowish solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.71 (d, *J* = 8.4 Hz, 1H), 6.58 (s, 1H), 6.38 (s, 1H), 5.88 (s, 2H), 3.01 (t, *J* = 5.5 Hz, 4H), 1.71 (s, 4H), 1.56-1.52 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.04, 108.05, 100.82, 100.57, 52.85, 25.71, 23.86.[12]



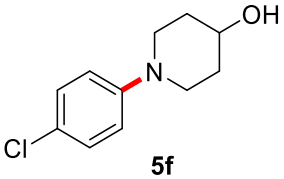
5d

***1-(3-Chlorophenyl)piperidine* (5d):** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (t, *J* = 8.1 Hz, 1H), 6.83-6.78 (m, 1H), 6.75-6.65 (m, 2H), 3.11-3.06 (m, 4H), 1.64-1.59 (m, 4H), 1.53-1.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.04, 133.81, 128.87, 117.56, 114.98, 113.24, 49.10, 24.57, 23.19.



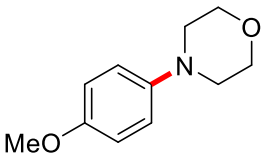
5e

***4-Methyl-1-(p-tolyl)piperidine* (5e):** Yellowish solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 3.57 (dt, *J* = 11.7, 2.5 Hz, 2H), 2.64 (td, *J* = 12.0, 2.5 Hz, 2H), 2.26 (s, 3H), 1.77-1.68 (m, 2H), 1.50-1.44 (m, 1H), 1.43-1.30 (m, 2H), 0.97 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.55, 116.95, 50.71, 34.21, 30.70, 21.91, 20.44.



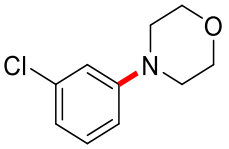
5f

***1-(4-Chlorophenyl)piperidin-4-ol* (5f):** Yellowish solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 1H), 3.51 (d, *J* = 13.4 Hz, 2H), 2.91 (t, *J* = 11.2 Hz, 2H), 1.99 (s, 2H), 1.70-1.67 (m, 2H), 1.46 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.97, 117.72, 109.31, 67.65, 47.28, 34.00.



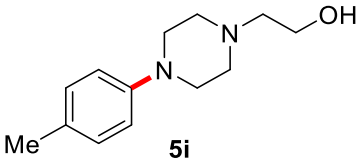
5g

***4-(4-Methoxyphenyl)morpholine* (5g):** White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 3.86 (t, *J* = 4.5 Hz, 4H), 3.77 (s, 3H), 3.06 (t, *J* = 4.6 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 117.75, 114.44, 66.94, 55.49, 50.77.[13]



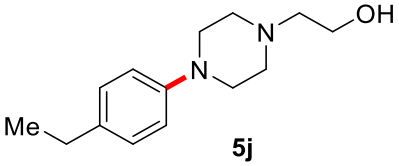
5h

***4-(3-Chlorophenyl)morpholine* (5h):** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 8.1 Hz, 1H), 6.87 (t, *J* = 2.2 Hz, 1H), 6.84 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.88-3.82 (m, 4H), 3.17-3.13 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.26, 135.06, 130.11, 119.80, 115.58, 113.66, 66.72, 48.96.[13]



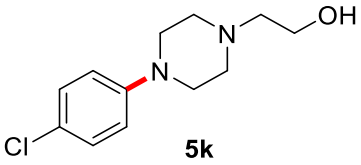
5i

***2-(4-(p-Tolyl)piperazin-1-yl)ethan-1-ol* (5i):** Yellowish solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.3 Hz, 2H), 6.84 (dt, *J* = 9.4, 3.1 Hz, 2H), 3.67 (t, *J* = 5.4 Hz, 2H), 3.17 (m, 4H), 2.79 (s, 1H), 2.72-2.67 (m, 4H), 2.62 (t, *J* = 5.4 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.10, 129.66, 129.41, 116.48, 59.33, 57.73, 52.95, 49.77, 20.43; ESI-MS (*m/z*):221.11 [M+H$^+$].



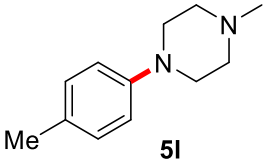
5j

***2-(4-(4-Ethylphenyl)piperazin-1-yl)ethan-1-ol* (5j):** Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 3.92 (t, *J* = 5.0 Hz, 2H), 3.39 (t, *J* = 5.1 Hz, 4H), 3.16 (s, 4H), 3.01 (t, *J* = 5.3 Hz, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.60, 128.66, 117.26, 59.97, 56.33, 53.10, 47.65, 27.87, 15.59.



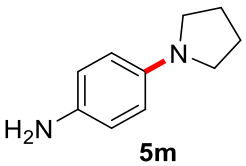
5k

***2-(4-(4-Chlorophenyl)piperazin-1-yl)ethan-1-ol* (5k)**: White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (dt, *J* = 12.0, 2.2 Hz, 2H), 6.77 (dt, *J* = 12.0, 2.1 Hz, 2H), 3.69 (t, *J* = 5.2 Hz, 2H), 3.20 (t, *J* = 5.0 Hz, 4H), 2.77 (t, *J* = 5.0 Hz, 4H), 2.68 (t, *J* = 5.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.33, 128.97, 125.09, 117.48, 59.57, 57.31, 52.76, 48.65.[18]



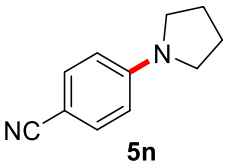
5l

***1-(p-Tolyl)-4-methylpiperazine* (5l):** Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 3.19 (t, *J* = 5.0 Hz, 4H), 2.62 (s, 4H), 2.38 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.91, 129.68, 116.60, 54.97, 49.35, 45.79, 29.71, 20.43. [10]



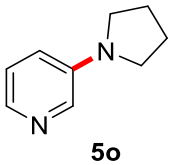
5m

***4-(Pyrrolidin-1-yl)aniline* (5m):** Brown oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.67 (d, *J* = 8.2 Hz, 2H), 6.48 (d, *J* = 8.2 Hz, 2H), 3.42 (s, 2H), 3.21 (s, 4H), 2.00-1.94 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.28, 135.99, 117.02, 112.95, 48.26, 25.19.[14]



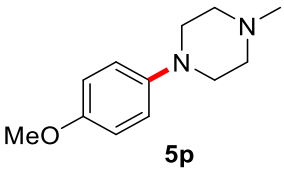
5n

***4-(Pyrrolidin-1-yl)benzonitrile* (5n):** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dt, *J* = 9.7, 2.8 Hz, 2H), 6.51 (dt, *J* = 9.6, 2.8 Hz, 2H), 3.36-3.31 (m, 4H), 2.07-2.02 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.01, 133.47, 121.01, 111.46, 96.62, 47.50, 25.43.[10]



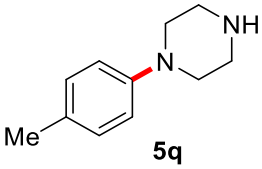
5o

***3-(Pyrrolidin-1-yl)pyridine* (5o):** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.98 (s, 1H), 7.12 (t, *J* = 6.3 Hz, 1H), 6.82 (ddd, *J* = 8.4, 3.0, 1.2 Hz, 1H), 3.34-3.27 (m, 4H), 2.06-2.00 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.62, 134.08, 117.86, 47.30, 29.71, 25.39.[15]



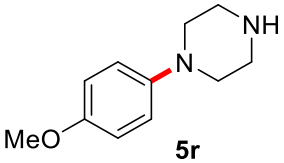
5p

***1-(4-Methoxyphenyl)-4-methylpiperazine* (5p):** White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90 (dt, *J* = 10.6, 3.7 Hz, 2H), 6.84 (dt, *J* = 10.6, 3.9 Hz, 2H), 3.77 (s, 3H), 3.12 (t, *J* = 4.9 Hz, 4H), 2.61 (t, *J* = 4.9 Hz, 4H), 2.37 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.74, 145.54, 118.13, 114.35, 55.49, 55.15, 50.42, 45.97.[16]



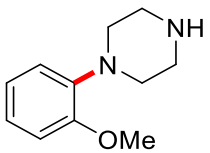
5q

***1-(1-(p-Tolyl)piperazine* (5q):** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 8.4, 2.2 Hz, 2H), 6.84 (dt, *J* = 8.5, 2.1 Hz, 2H), 3.12-3.10 (m, 4H), 3.09-2.99 (m, 4H), 2.43 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.67, 129.64, 129.41, 116.56, 50.83, 46.05, 20.43. ESI-MS (*m/z*):177.37 [M+H$^+$]. [17]



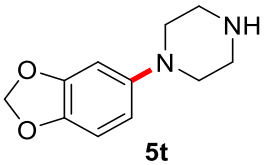
5r

***1-(4-Methoxyphenyl)piperazine* (5r):** Yellowish solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90 (dt, *J* = 10.4, 4.0 Hz, 2H), 6.84 (dt, *J* = 10.3, 3.6 Hz, 2H), 3.77 (s, 3H), 3.10 (s, 8H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.54, 145.20, 119.05, 114.53, 55.56, 50.16, 44.94; ESI-MS (*m/z*): 193.24 [M+H$^+$]. [18]



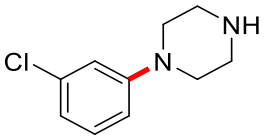
5s

***1-(2-Methoxyphenyl)piperazine* (5s):** Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ6.95-6.91 (m, 1H), 6.89-6.83 (m, 2H), 6.79 (dd, *J* = 8.0, 1.3 Hz, 1H), 3.79 (s, 3H), 3.02-3.00 (m, 4H), 3.00-2.95 (m, 4H), 2.40 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.20, 141.59, 122.89, 120.90, 118.18, 111.13, 55.27, 51.79, 46.13; ESI-MS (*m/z*): 193.21 [M+H$^+$]. [18]



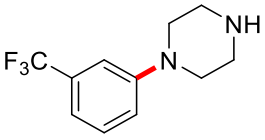
5t

***1-(Benzo[d][1,3]dioxol-5-yl)piperazine* (5t):** White solid; m.p. 67-68 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.72 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.37 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.90 (s, 2H), 3.03 (s, 8H), 2.11 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.23, 147.66, 141.79, 109.32, 108.18, 100.91, 100.19, 51.64, 45.86; ESI-MS (*m/z*): 207.11 [M+H$^+$]. [18]



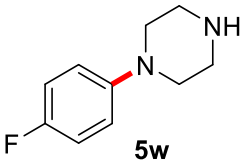
5u

***1-(3-Chlorophenyl)piperazine* (5u):** Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 8.1 Hz, 1H), 6.87 (t, *J* = 2.2 Hz, 1H), 6.83-6.76 (m, 2H), 3.18-3.11 (m, 4H), 3.04-3.01 (m, 4H), 1.89 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.81, 134.95, 130.00, 119.32, 115.81, 113.95, 49.86, 45.98. ESI-MS (*m/z*): 197.09, 199.10 [M+H$^+$]. [18]



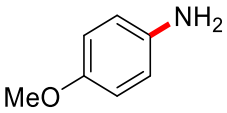
5v

***1-(3-(Trifluoromethyl)phenyl)piperazine* (5v):** Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.06 (s, 1H), 7.01 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.40 (t, *J* = 5.0 Hz, 4H), 3.26 (t, *J* = 5.0 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.45, 129.79, 119.77, 117.59, 113.33, 113.30, 47.23, 43.83; ESI-MS (*m/z*): 231.25 [M+H$^+$]. [18]



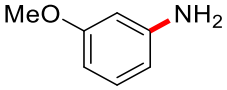
5w

***1-(4-Fluorophenyl)piperazine* (5w):** Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.92-6.87 (m, 2H), 6.83-6.79 (m, 2H), 3.01 (d, *J* = 5.4 Hz, 4H), 2.99 (d, *J* = 5.9 Hz, 4H), 2.41 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.97, 117.95, 117.90, 115.51, 115.36, 51.12, 45.90. ESI-MS (*m/z*): 181.19 [M+H$^+$]. [18]



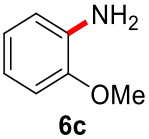
6a

***4-Methoxybenzenamine* (6a):** Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (dt, *J* = 10.8, 3.4 Hz, 2H), 6.65 (dt, *J* = 9.9, 3.5 Hz, 2H), 3.74 (s, 3H), 3.24 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.75, 139.81, 116.35, 114.73, 55.66.[19]



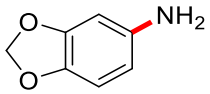
6b

***3-Methoxybenzenamine*(6b):** Brown oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (t, *J* = 7.8 Hz, 1H), 6.32 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.27 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.23 (q, *J* = 2.2 Hz, 1H), 3.74 (s, 3H), 3.64 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.69, 147.73, 130.04, 107.86, 103.88, 101.01, 55.01.[19]



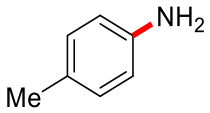
6c

***2-Methoxybenzenamine* (6c):** Brown oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.80-6.76 (m, 2H), 6.75-6.69 (m, 2H), 3.83 (s, 3H), 3.70 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.27, 136.08, 121.02, 118.41, 114.98, 110.39, 55.36.[20]



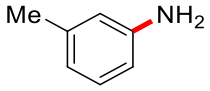
6d

***1,3-Benzodioxol-5-amine* (6d):** Grey solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (d, *J* = 8.1 Hz, 1H), 6.28 (d, *J* = 2.2 Hz, 1H), 6.12 (d, *J* = 8.1 Hz, 1H), 5.86 (s, 2H), 3.34 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.13, 141.24, 140.30, 108.48, 106.80, 100.57, 97.99.[21]



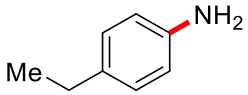
6e

***4-Methylaniline* (6e):** White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 (dd, *J* = 8.2, 2.3 Hz, 2H), 6.59 (dd, *J* = 8.2, 1.7 Hz, 2H), 3.50 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.72, 129.67, 127.71, 115.18, 20.38.[19]



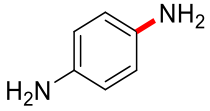
6f

***3-Methylaniline* (6f)**: Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (t, *J* = 7.6 Hz, 1H), 6.58 (m, 1H), 6.59-6.56 (m, 2H), 3.51 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.26, 139.05, 129.10, 119.40, 115.87, 112.20, 21.38.[22]



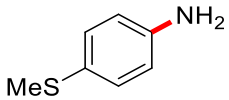
6g

***4-Ethylaniline* (6g):** Brown oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.1 Hz, 2H), 3.52 (s, 2H), 2.53 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.04, 134.51, 128.62, 115.32, 28.02, 15.99.[23]



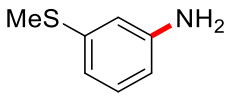
6h

***p-Phenylenediamine* (6h):** Brown white; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.56 (s, 4H), 3.32 (s, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.60, 116.72.[24]



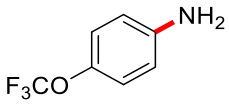
6i

***4-(Methylthio)aniline* (6i):** Brown oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (dt, *J* = 9.6, 3.2 Hz, 2H), 6.61 (dd, *J* = 8.4, 2.1 Hz, 2H), 3.61 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.14, 131.09, 125.79, 115.76, 18.82.[21]



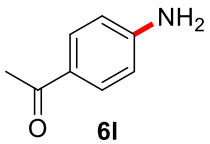
6j

***3-(Methylthio)aniline* (6j):** Brown oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (t, *J* = 7.8 Hz, 1H), 6.65 (ddd, *J* = 7.7, 1.8, 0.9 Hz, 1H), 6.57 (t, *J* = 2.0 Hz, 1H), 6.45 (ddd, *J* = 7.9, 2.2, 1.0 Hz, 1H), 3.65 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.69, 139.28, 129.57, 116.62, 112.85, 112.04, 15.59.[25]



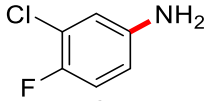
6k

***4-(Trifluoromethoxy)aniline* (6k):** Yellowish oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.4 Hz, 2H), 6.62 (dt, *J* = 10.1, 3.7 Hz, 2H), 3.68 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.23, 141.31, 132.91, 122.40, 115.47.[26]



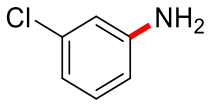
6l

***4-Aminoacetophenone* (6l):** White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 1H), 6.65 (dd, *J* = 8.4, 3.0 Hz, 1H), 4.12 (s, 1H), 2.51 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.33, 150.94, 130.70, 127.87, 113.63, 26.00.[23]



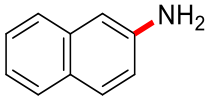
6m

***3-Chloro-4-fluoroaniline* (6m):** White solid; m.p. 43-44 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.91 (t, *J* = 8.8 Hz, 1H), 6.69 (dd, *J* = 6.1, 2.8 Hz, 1H), 6.50-6.48 (m, 1H), 3.58 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.31, 150.73, 143.03, 143.02, 120.94, 120.81, 116.82, 116.68, 116.31, 114.18, 114.13.[27]



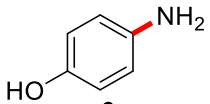
6n

***3-Chloroaniline* (6n):** Brown oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 (t, *J* = 8.0 Hz, 1H), 6.71 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.65 (s, 1H), 6.55-6.50 (m, 1H), 3.67 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.57, 134.76, 130.25, 118.37, 114.85, 113.12.[23]



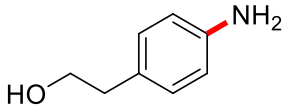
6o

***2-Naphthylamine* (6o):** Brown solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.49 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.26 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.08 (ddd, *J* = 8.0, 6.7, 1.2 Hz, 1H), 6.93 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.81 (d, *J* = 2.2 Hz, 1H), 5.37 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.10, 134.92, 129.22, 127.98, 127.72, 126.35, 125.80, 122.48, 118.23, 108.60.[20]



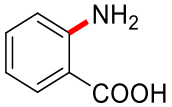
6p

***4-Aminophenol* (6p):** White solid; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.32 (s, 1H), 6.47 (dt, *J* = 8.4, 1.4 Hz, 2H), 6.41 (dt, *J* = 8.4, 1.4 Hz, 2H), 4.36 (s, 2H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 148.57, 141.01, 115.90, 115.59, 40.42.[19]



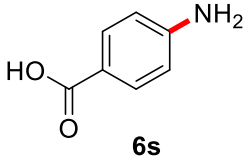
6q

***4-Aminobenzyl alcohol* (6q):** Yellowish solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (dt, *J* = 9.0, 2.8 Hz, 2H), 6.46 (dt, *J* = 9.0, 2.8 Hz, 2H), 4.79 (s, 2H), 4.49 (t, *J* = 5.3 Hz, 1H), 3.48 (td, *J* = 7.4, 5.2 Hz, 2H), 2.53 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.76, 129.78, 128.14, 115.34, 63.82, 38.24.[28]



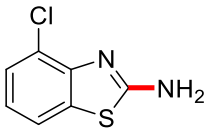
6r

***2-Aminobenzoic acid* (6r):** White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.60 (m 2H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 7.30 (td, *J* = 7.7, 1.8 Hz, 1H), 6.14 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.06, 136.52, 133.49, 131.60, 129.87, 127.52, 119.10, 109.89.[24]



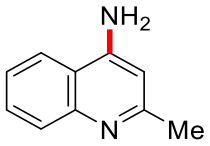
6s

***4-Aminobenzoic acid* (6s):** White solid; ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.94 (s, 1H), 7.61 (d, J = 8.3 Hz, 2H), 6.54 (d, J = 8.3 Hz, 2H), 5.86 (s, 2H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.84, 153.50, 131.57, 117.23, 112.91, 40.44.[22]



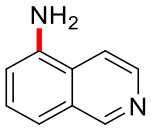
6t

***2-Amino-4-chlorobenzothiazole* (6t):** White solid; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.83 (s, 2H), 7.62 (d, J = 7.7 Hz, 1H), 7.28 (d, J = 7.9 Hz, 1H), 6.99 (td, J = 7.9, 1.3 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.68, 149.82, 132.52, 125.92, 121.83, 121.63, 120.21.[29]



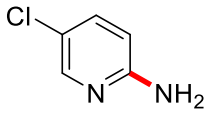
6u

***4-Amino-2-methylquinoline* (6u):** White solid; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.08 (d, J = 8.3 Hz, 1H), 7.66 (d, J = 8.3 Hz, 1H), 7.54 (dd, J = 8.4, 6.8 Hz, 1H), 7.30 (dd, J = 8.3, 6.8 Hz, 1H), 6.63 (s, 2H), 6.43 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 158.57, 151.84, 148.84, 129.12, 128.49, 123.08, 122.43, 117.63, 102.36, 25.23.[30]



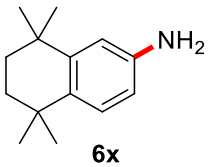
6v

***5-Aminoisoquinoline* (6v):** Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.49 (d, J = 6.0 Hz, 1H), 7.58 (d, J = 6.0 Hz, 1H), 7.41 (d, J = 4.3 Hz, 2H), 6.96 (t, J = 4.3 Hz, 1H), 4.19 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.92, 141.96, 141.30, 129.41, 127.80, 126.01, 118.01, 114.08, 113.11.



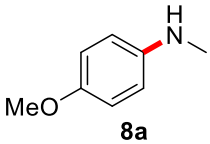
6w

***2-Amino-5-chloropyridine* (6w):** White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 2.5 Hz, 1H), 7.37 (dd, J = 8.7, 2.6 Hz, 1H), 6.45 (d, J = 8.7 Hz, 1H), 4.56 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.71, 146.30, 137.45, 120.84, 109.33.[31]



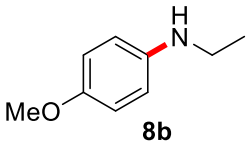
6x

***5,6,7,8-Tetrahydro-5,5,8,8-tetramethyl-2-naphthylamine* (6x):** White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (d, J = 8.3 Hz, 1H), 6.70 (d, J = 2.5 Hz, 1H), 6.58 (dd, J = 8.3, 2.5 Hz, 1H), 4.25 (s, 2H), 1.65 (s, 4H), 1.25 (s, 6H), 1.23 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.84 , 143.67 , 135.37 , 127.40 , 113.65 , 112.89 , 35.30 , 34.24 , 33.58 , 32.06 , 31.86.[32]



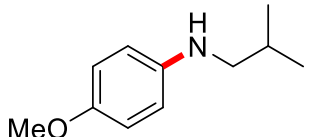
8a

***4-Methoxy-N-methylaniline* (8a)**: White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (dt, J = 10.3, 3.6 Hz, 2H), 6.78 (dt, J = 10.2, 3.7 Hz, 2H), 3.74 (s, 3H), 3.30 (s, 1H), 2.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.16, 143.64, 114.95, 113.72, 55.88, 31.67.[33]



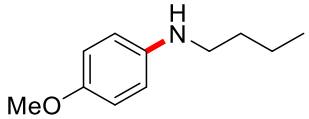
8b

***N-Ethyl-4-methoxyaniline* (8b):** Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ6.78 (dt, *J* = 10.2, 3.6 Hz, 2H), 6.58 (dt, *J* = 10.2, 3.6 Hz, 2H), 3.74 (s, 3H), 3.21 (s, 1H), 3.10 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.17, 142.64, 114.93, 114.24, 55.84, 39.56, 14.97.[34]



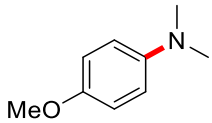
8c

***N-(isobutyl)-4-methoxyaniline* (8c):** Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (dt, *J* = 10.2, 3.6 Hz, 2H), 6.57 (dt, *J* = 10.2, 3.7 Hz, 2H), 3.73 (s, 3H), 3.50 (s, 1H), 2.88 (d, *J* = 6.8 Hz, 2H), 1.91-1.82 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.95, 142.83, 114.95, 114.04, 55.87, 52.96, 28.06, 20.54.[35]



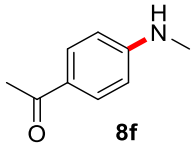
8d

***N-Butyl-4-methoxyaniline* (8d):** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (dt, *J* = 10.2, 3.6 Hz, 2H), 6.58 (dt, *J* = 10.2, 3.7 Hz, 2H), 3.74 (s, 3H), 3.39 (s, 1H), 3.06 (t, *J* = 7.1 Hz, 2H), 1.63-1.55 (m, 2H), 1.46-1.37 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.06, 142.72, 114.92, 114.14, 55.85, 44.82, 31.77, 20.34, 13.95.[36]



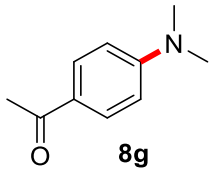
8e

***4-Methoxy-N, N-dimethylaniline* (8e):** Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (dt, *J* = 10.2, 3.5 Hz, 2H), 6.77 (dt, *J* = 10.3, 3.6 Hz, 2H), 3.76 (s, 3H), 2.87 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.66, 115.06, 114.68, 55.78, 41.93.[36]



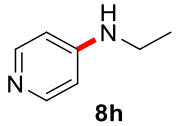
8f

***1-(4-(Methylamino)phenyl)ethanone* (8f):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dt, *J* = 9.5, 2.7 Hz, 2H), 6.58 (dt, *J* = 9.6, 2.8 Hz, 2H), 4.44 (s, 1H), 2.90 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.34, 152.93, 130.75, 126.79, 111.17, 30.19, 25.99.[37]



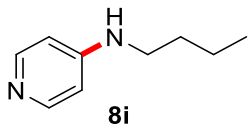
8g

***1-(4-(Dimethylamino)phenyl)ethanone* (8g):** Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (dt, *J* = 9.9, 3.1 Hz, 2H), 6.66 (dt, *J* = 10.1, 3.1 Hz, 2H), 3.06 (s, 6H), 2.51 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.37 , 153.31 , 130.52 , 125.53 , 110.71 , 40.11 , 26.00; ESI-MS (*m/z*):164.11 [M+H^{+}].[38]



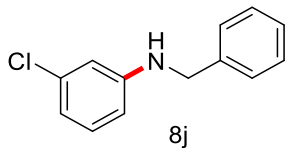
8h

***N-propylpyridin-4-amine* (8h):** Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 5.3 Hz, 2H), 6.44 (d, *J* = 5.5 Hz, 2H), 4.48 (s, 1H), 3.25-3.14 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.61, 149.33, 107.46, 37.27, 14.39.[39]



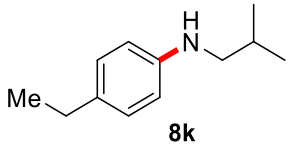
8i

***N-isobutylpyridin-4-amine* (8i):** Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 5.5 Hz, 2H), 6.42 (d, *J* = 5.9 Hz, 2H), 4.33 (s, 1H), 3.14 (q, *J* = 7.0 Hz, 2H), 1.60 (p, *J* = 7.3 Hz, 2H), 1.42 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.51, 149.87, 107.44, 42.34, 31.20, 20.16, 13.80.[39]



8j

(8j): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.4 Hz, 4H), 7.32-7.25 (m, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.67 (ddd, *J* = 7.8, 1.9, 0.9 Hz, 1H), 6.61 (t, *J* = 2.2 Hz, 1H), 6.48 (ddd, *J* = 8.2, 2.4, 0.9 Hz, 1H), 4.30 (s, 2H), 4.10 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.23, 138.75, 135.04, 130.22, 128.75, 127.48, 127.45, 117.43, 112.50, 111.14, 48.12.



8k

4-Ethyl-N-isobutylaniline (**8k**): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (dt, *J* = 9.4, 3.0 Hz, 2H), 6.56 (dt, *J* = 9.2, 3.0 Hz, 2H), 3.96 (s, 1H), 2.91 (d, *J* = 6.8 Hz, 2H), 2.53 (q, *J* = 7.6 Hz, 2H), 1.91-1.83 (m, 1H), 1.18 (t, *J* = 7.6 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.21, 133.18, 128.54, 113.08, 52.42, 27.98, 27.93, 20.52, 15.98.[40]

6. References

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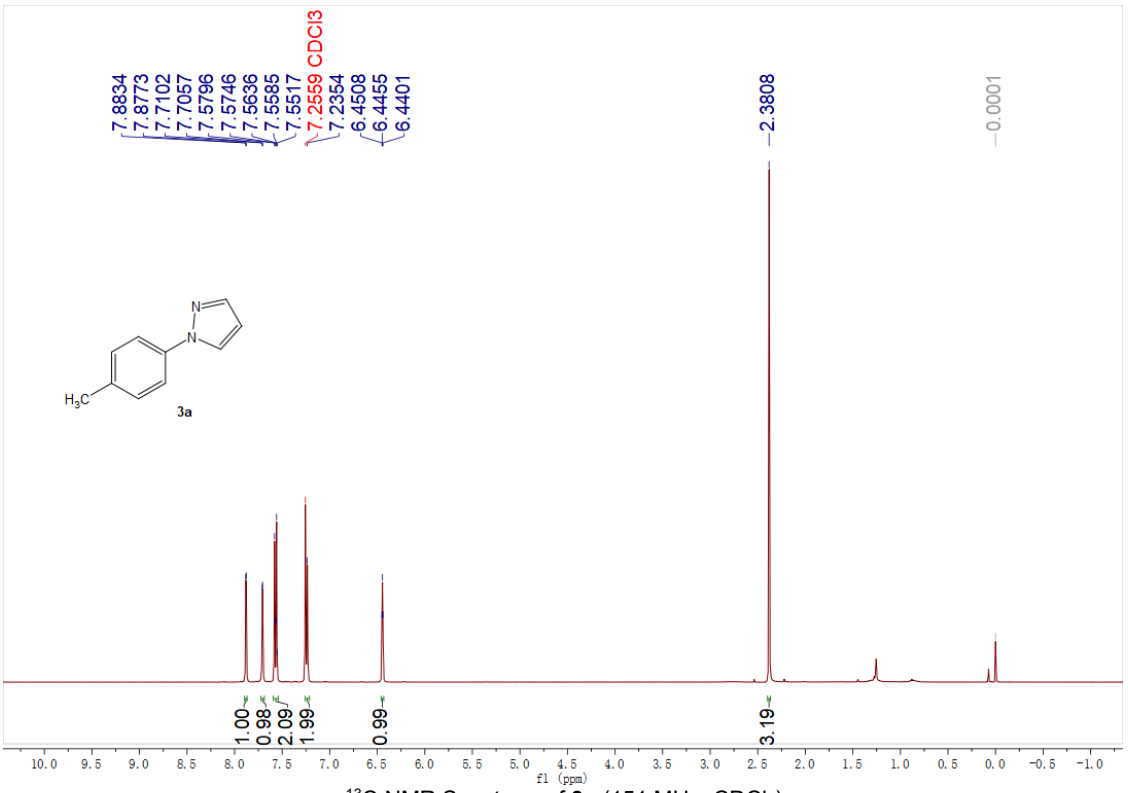
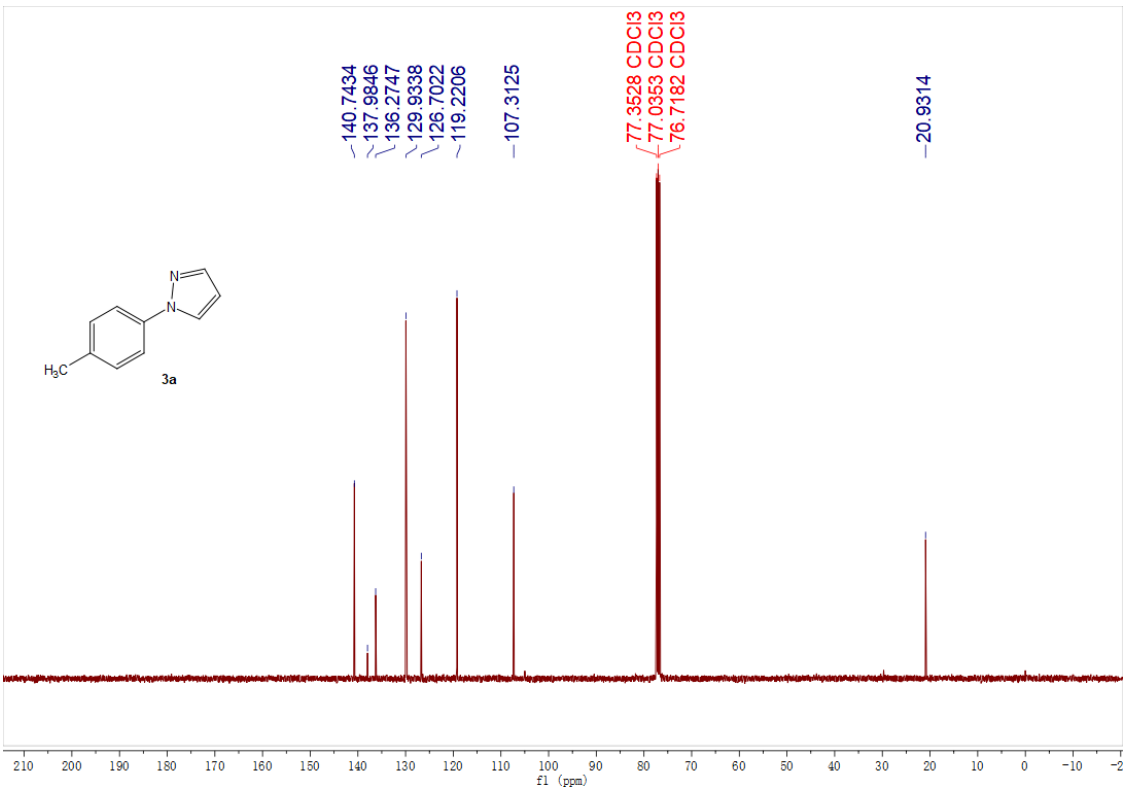
7. *Copies of ^{1}H and ^{13}C NMR spectrum of products*

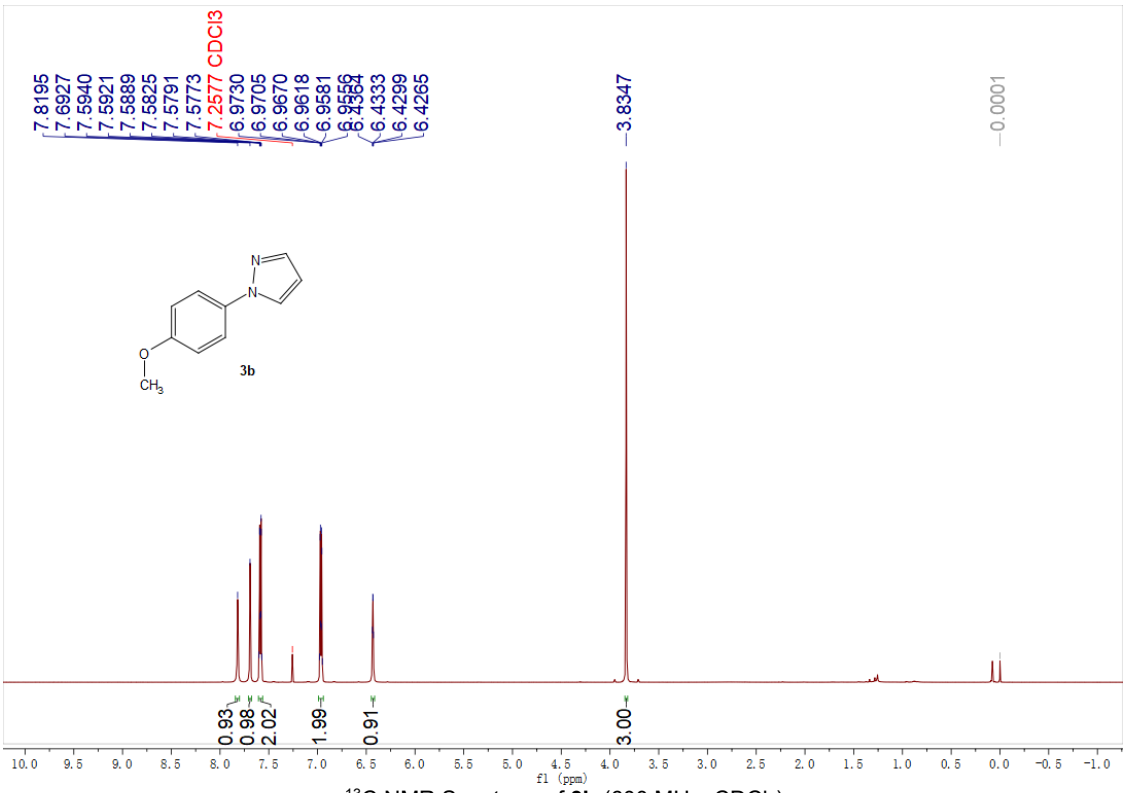
^{1}H NMR Spectrum of **3a** (600 MHz, $CDCl_3$)



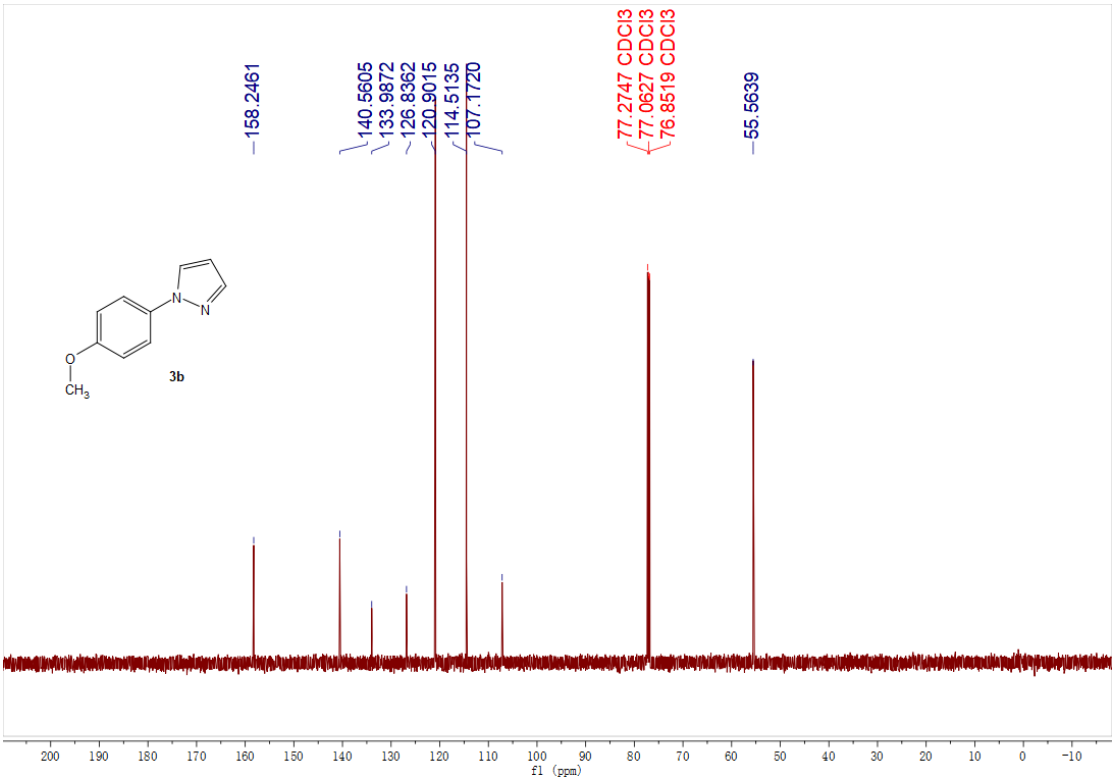
^{13}C NMR Spectrum of **3a** (151 MHz, $CDCl_3$)



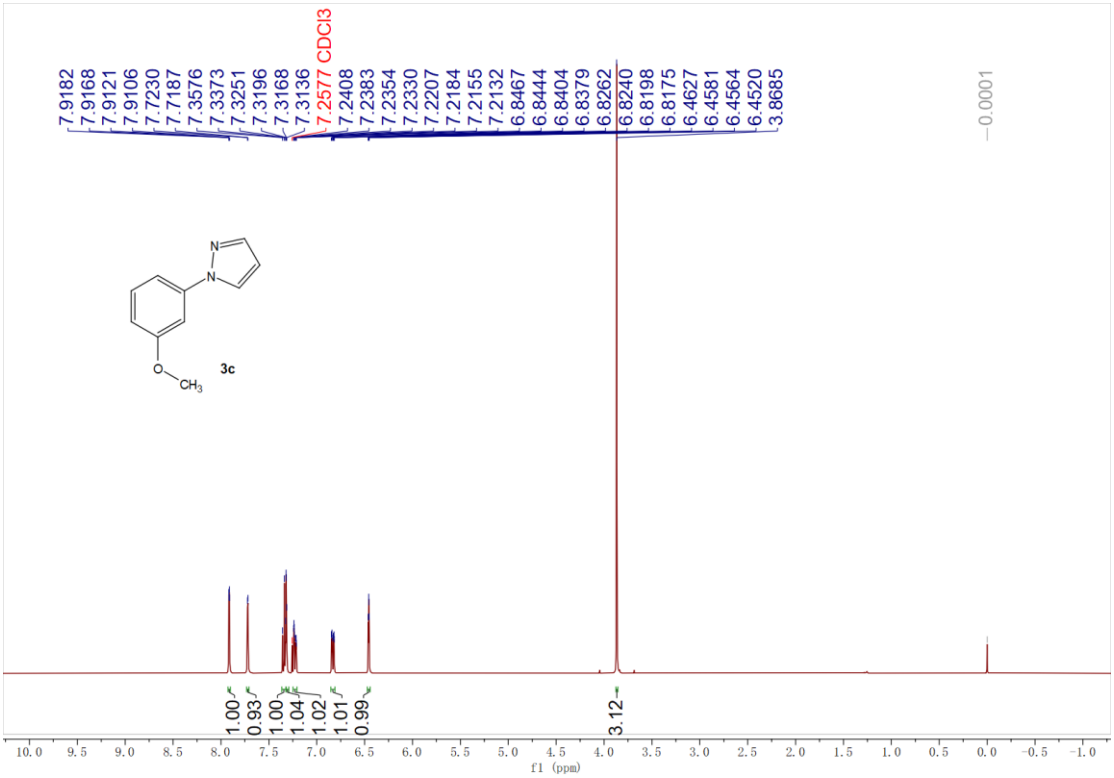
^{1}H NMR Spectrum of **3b** (600 MHz, $CDCl_3$)



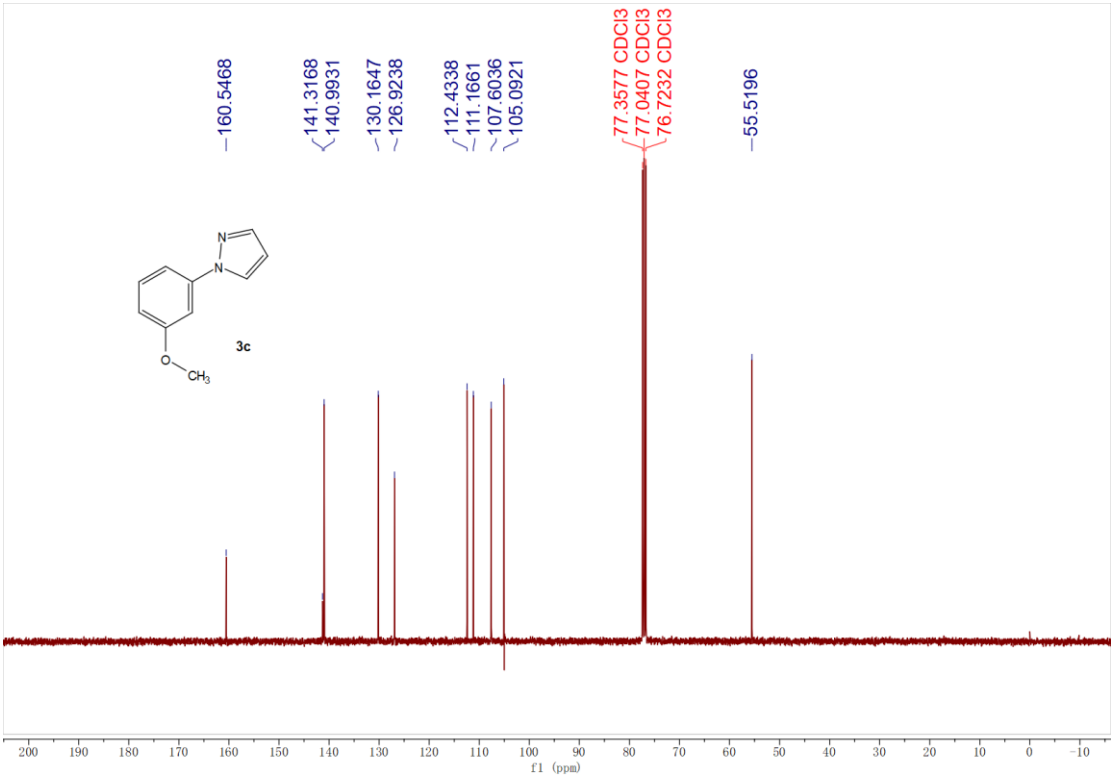
^{13}C NMR Spectrum of **3b** (600 MHz, $CDCl_3$)



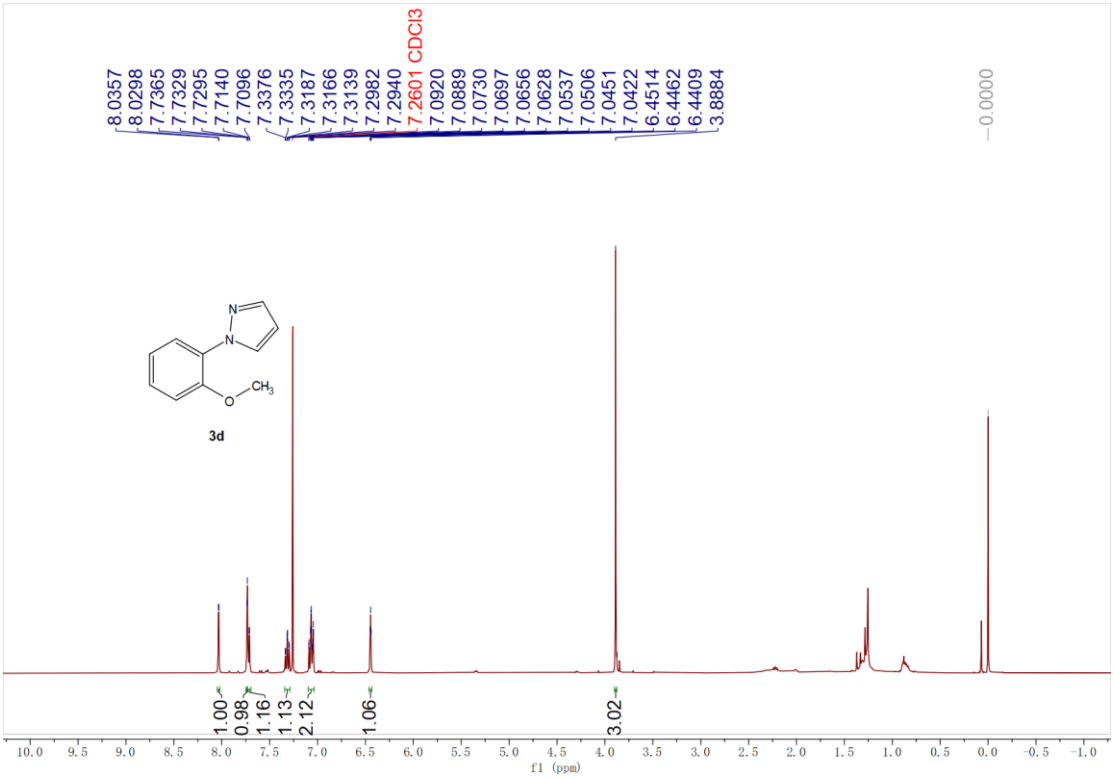
^{1}H NMR Spectrum of **3c** (400 MHz, $CDCl_3$)



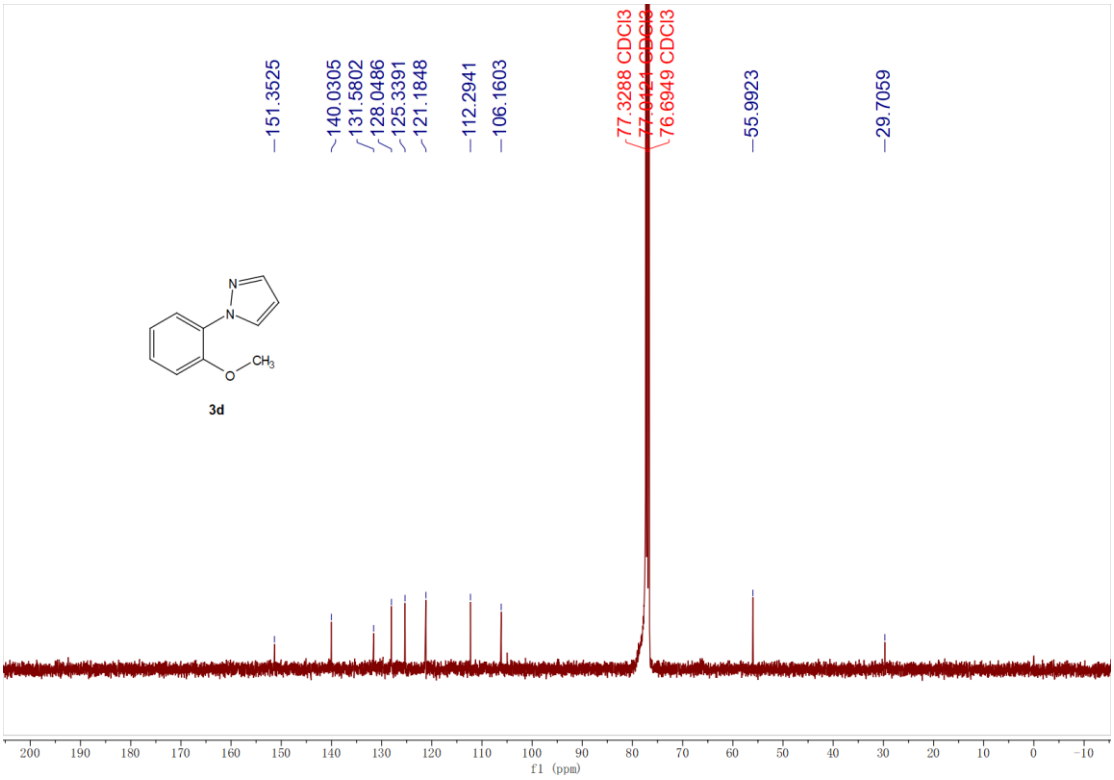
^{13}C NMR Spectrum of **3c** (101 MHz, $CDCl_3$)



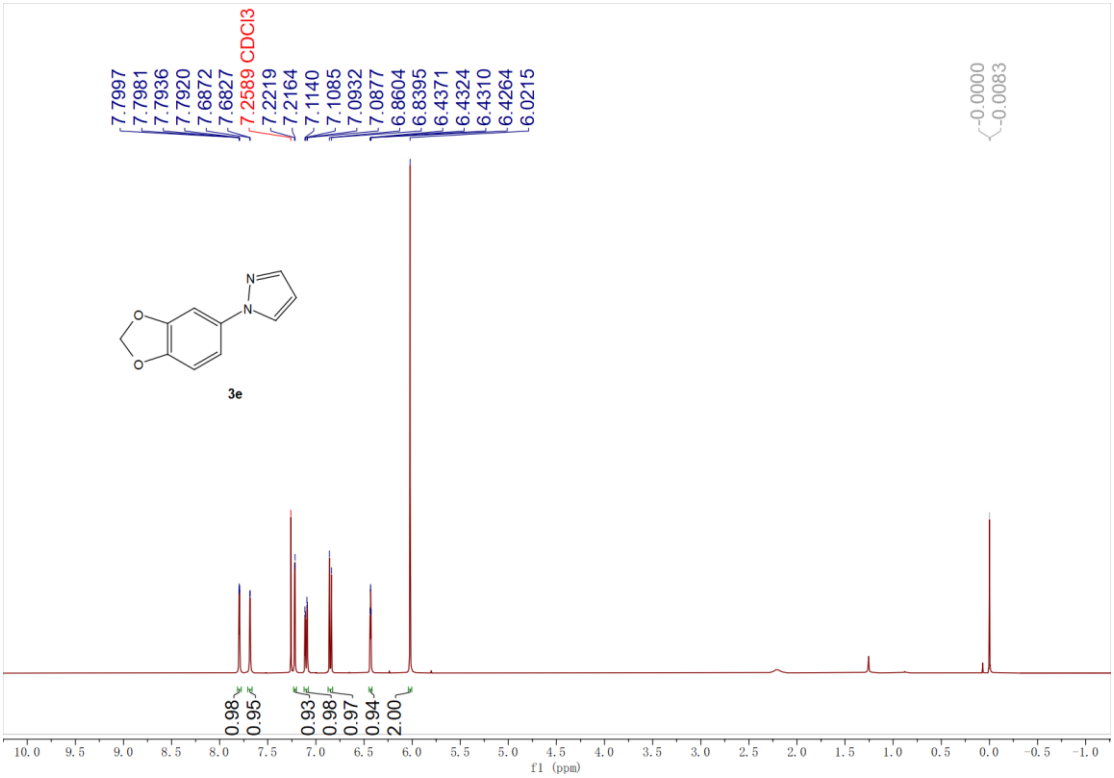
^{1}H NMR Spectrum of **3d** (400 MHz, $CDCl_3$)



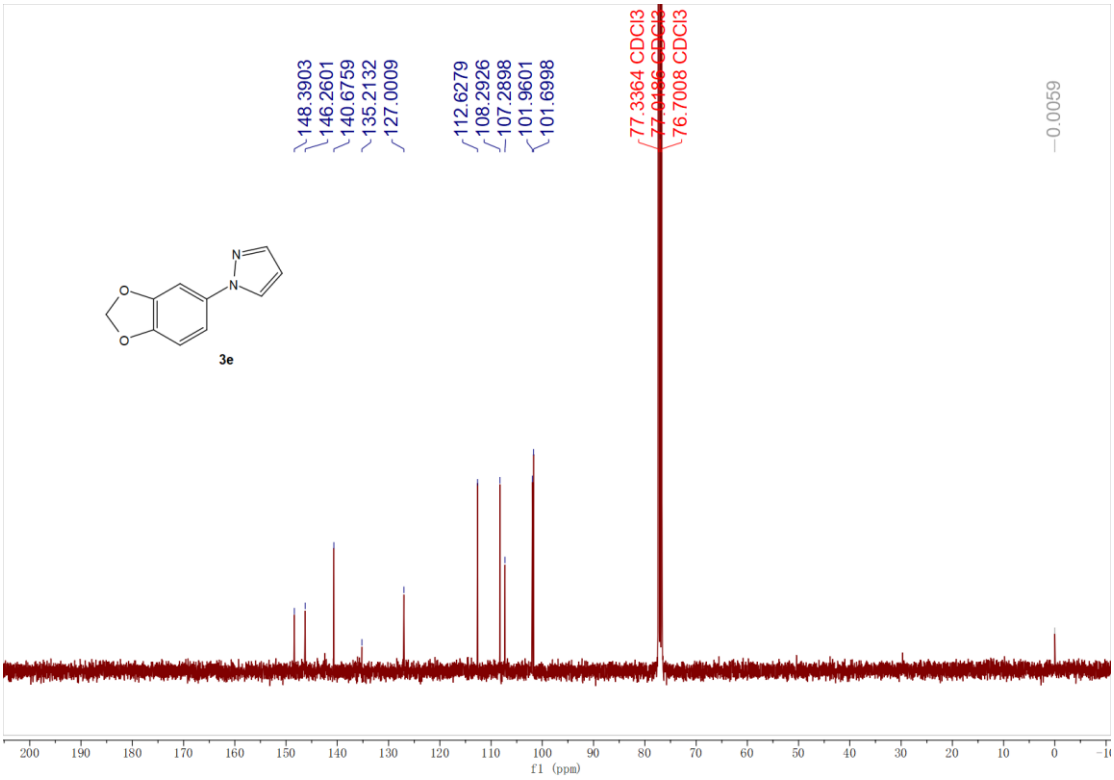
^{13}C NMR Spectrum of **3d** (101 MHz, $CDCl_3$)



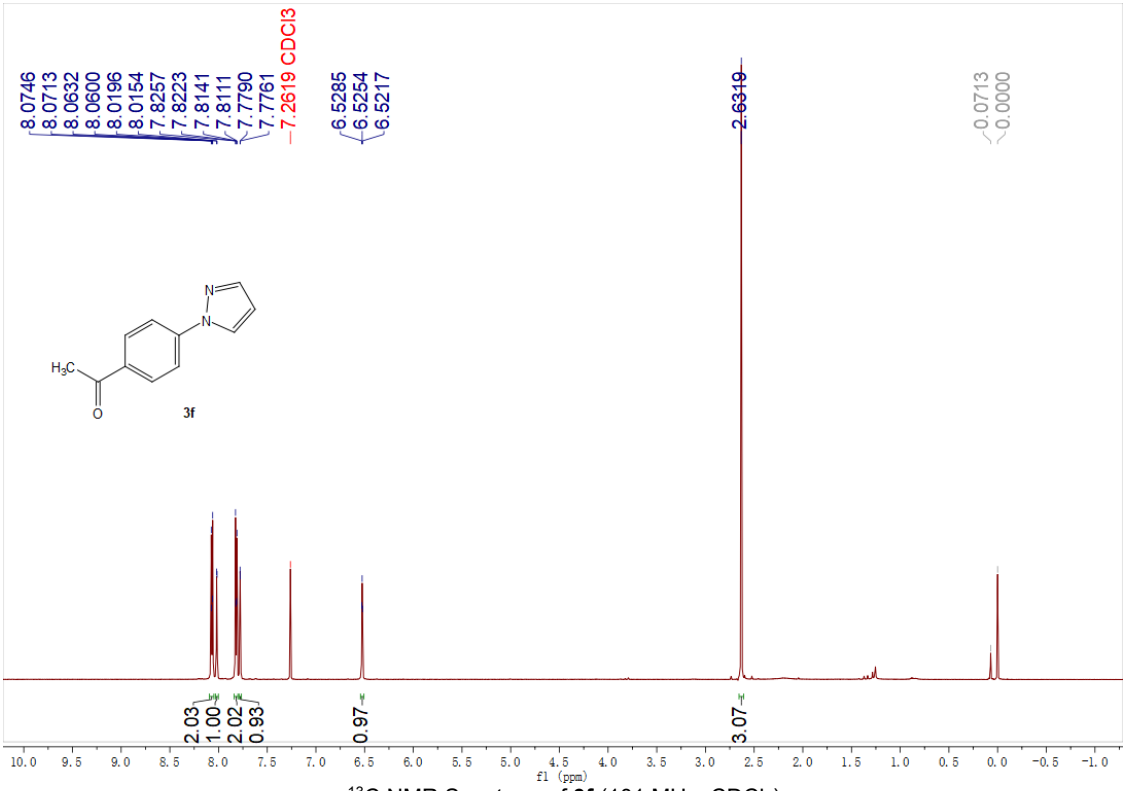
^{1}H NMR Spectrum of **3e** (400 MHz, $CDCl_3$)



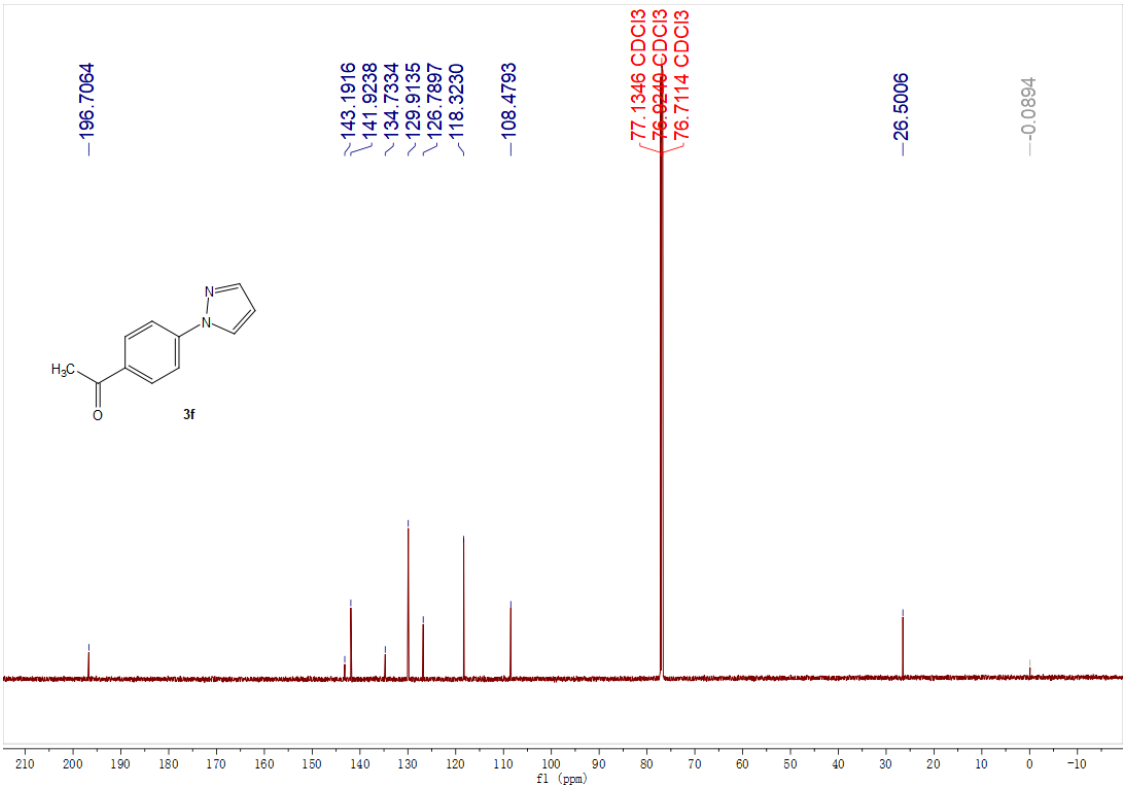
^{13}C NMR Spectrum of **3e** (101 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **3f** (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **3f** (101 MHz, $CDCl_3$)



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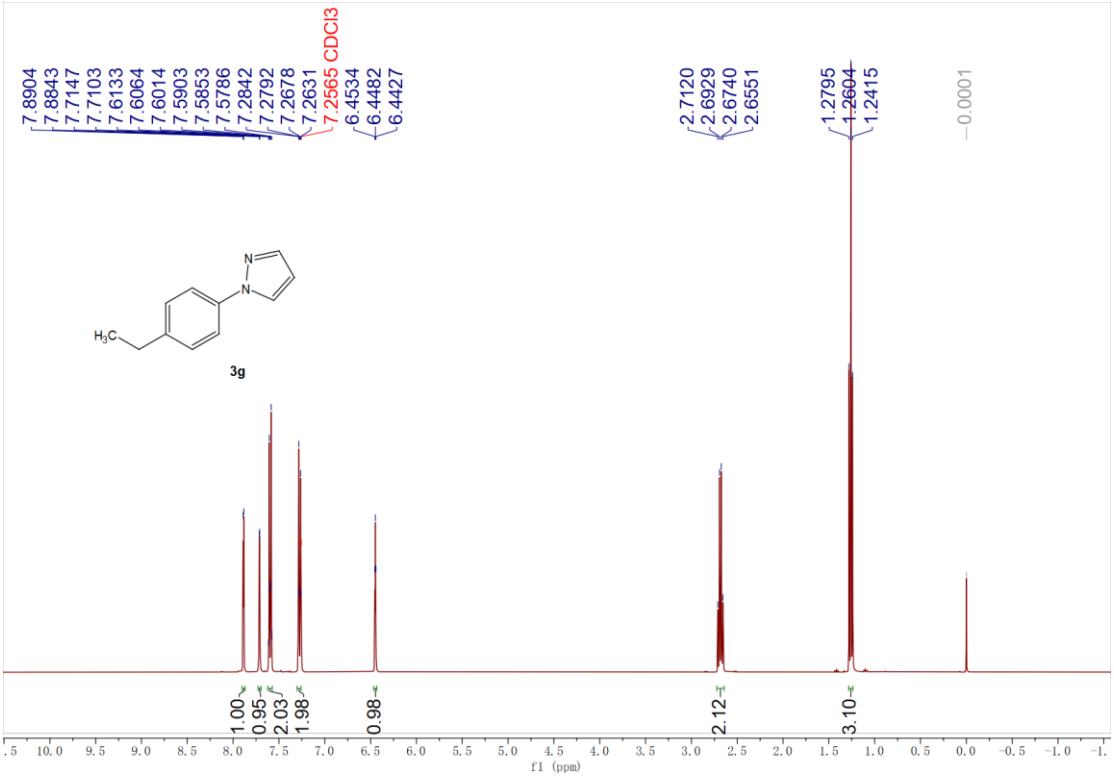
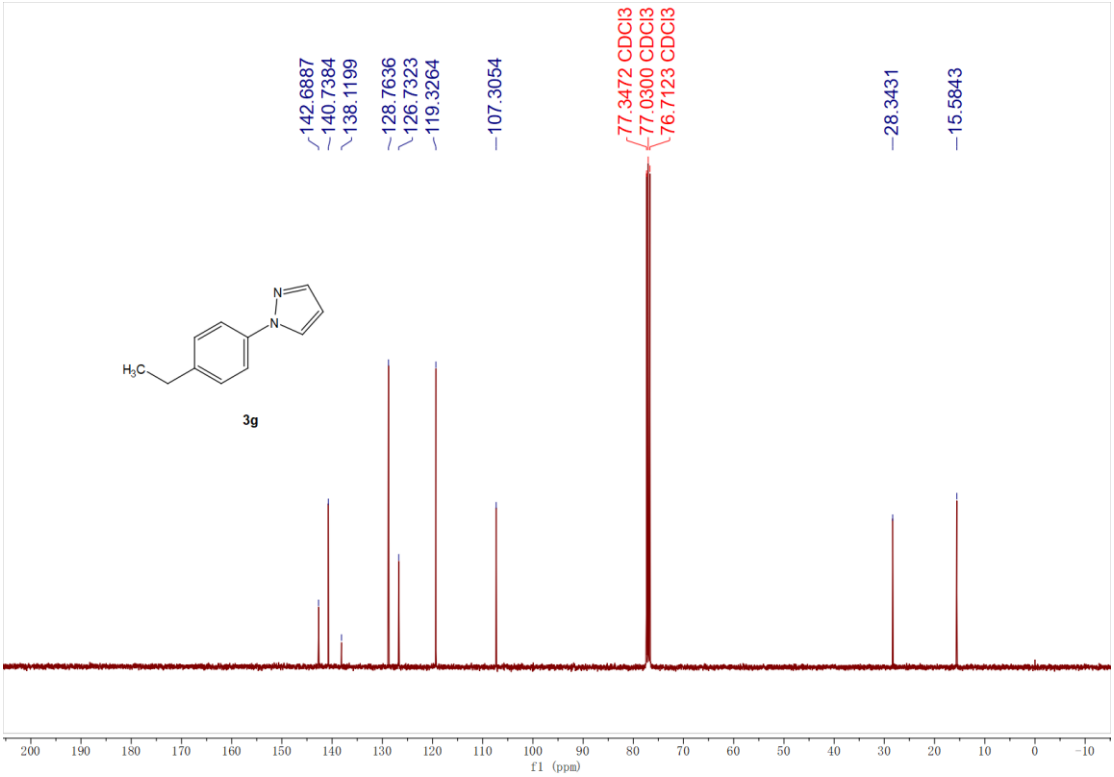


^{13}C NMR Spectrum of **3g** (101 MHz, $CDCl_3$)



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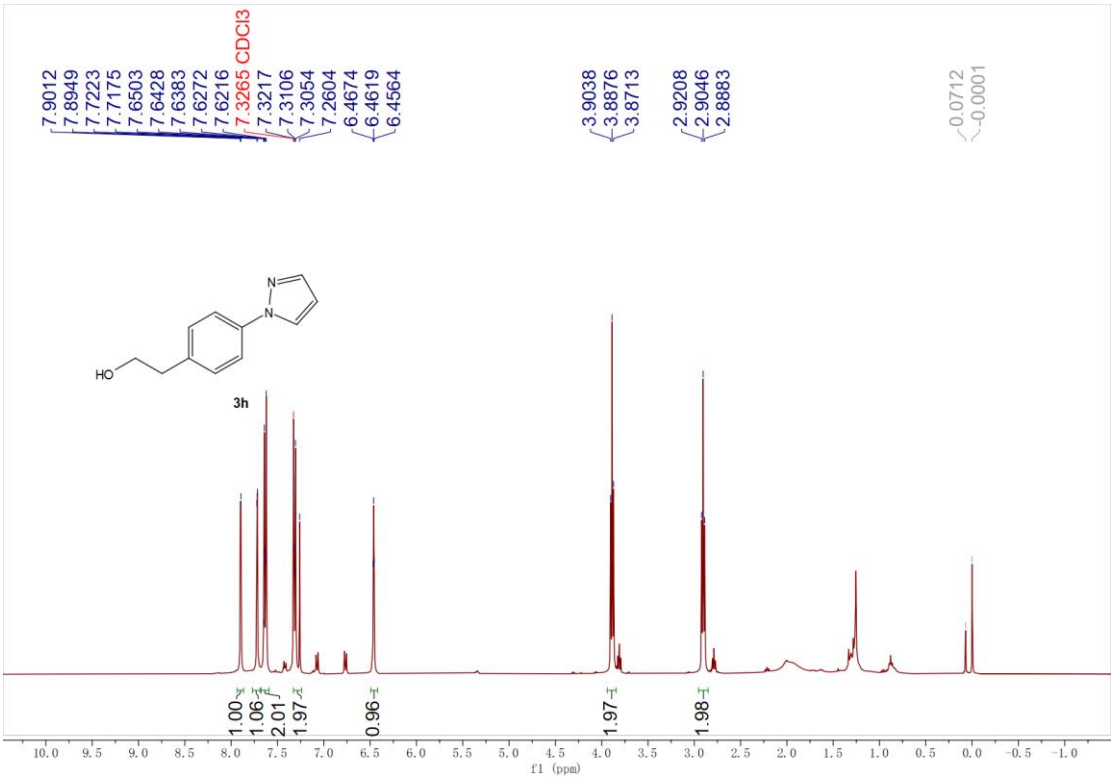
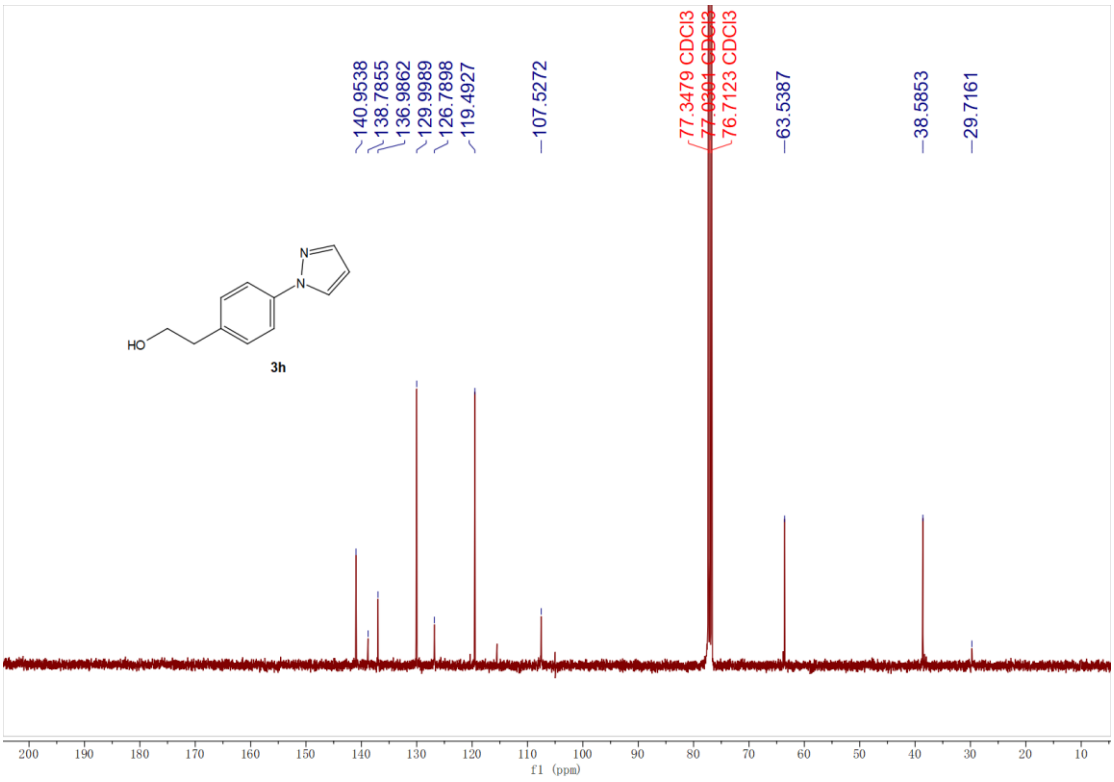
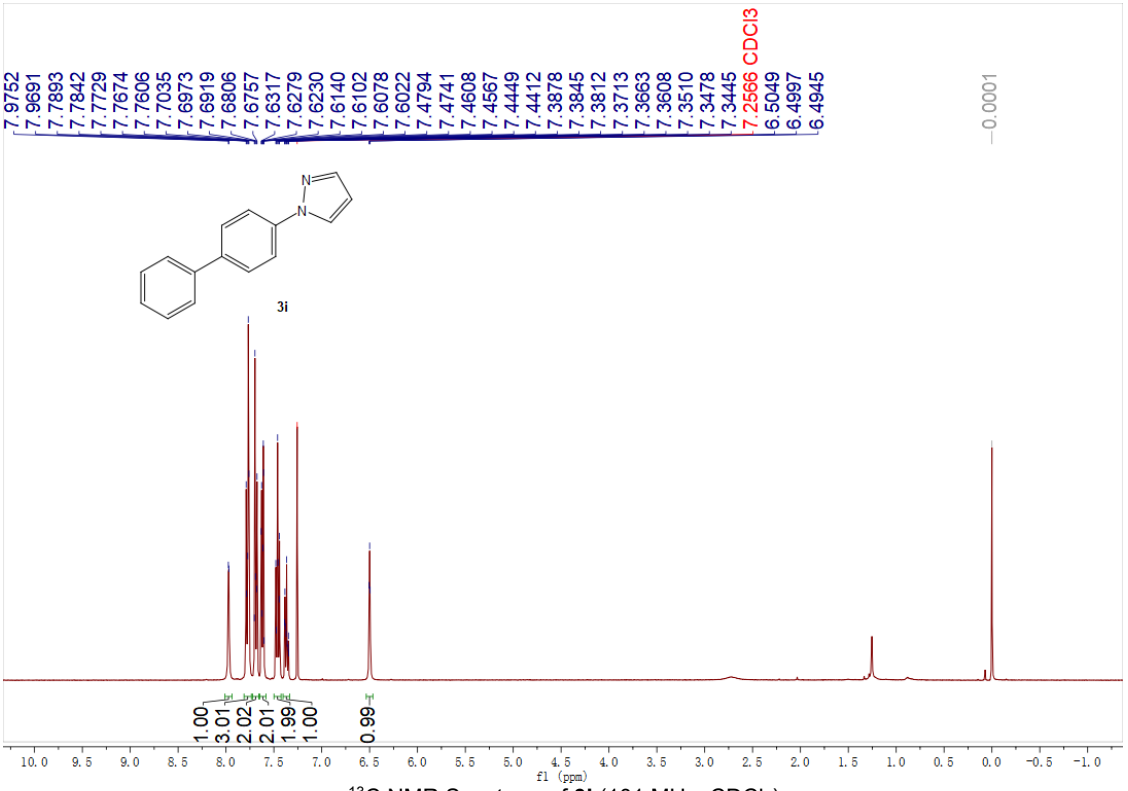


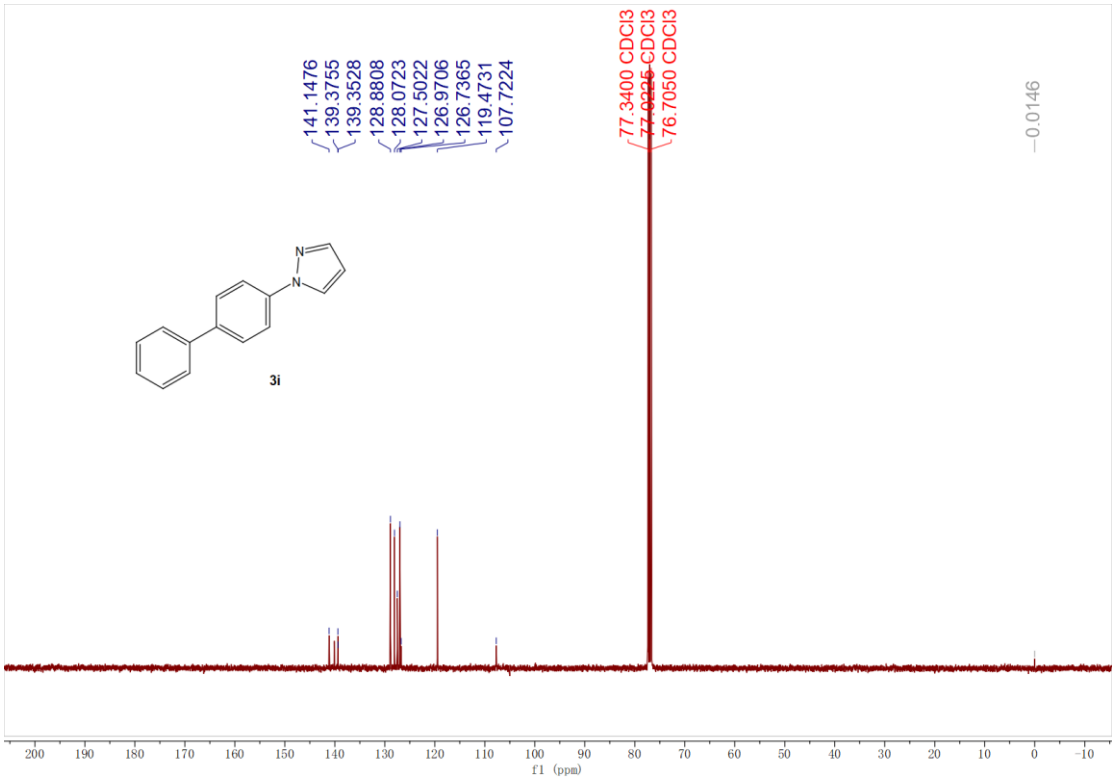
^{13}C NMR Spectrum of **3h** (101 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **3i** (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **3i** (101 MHz, $CDCl_3$)



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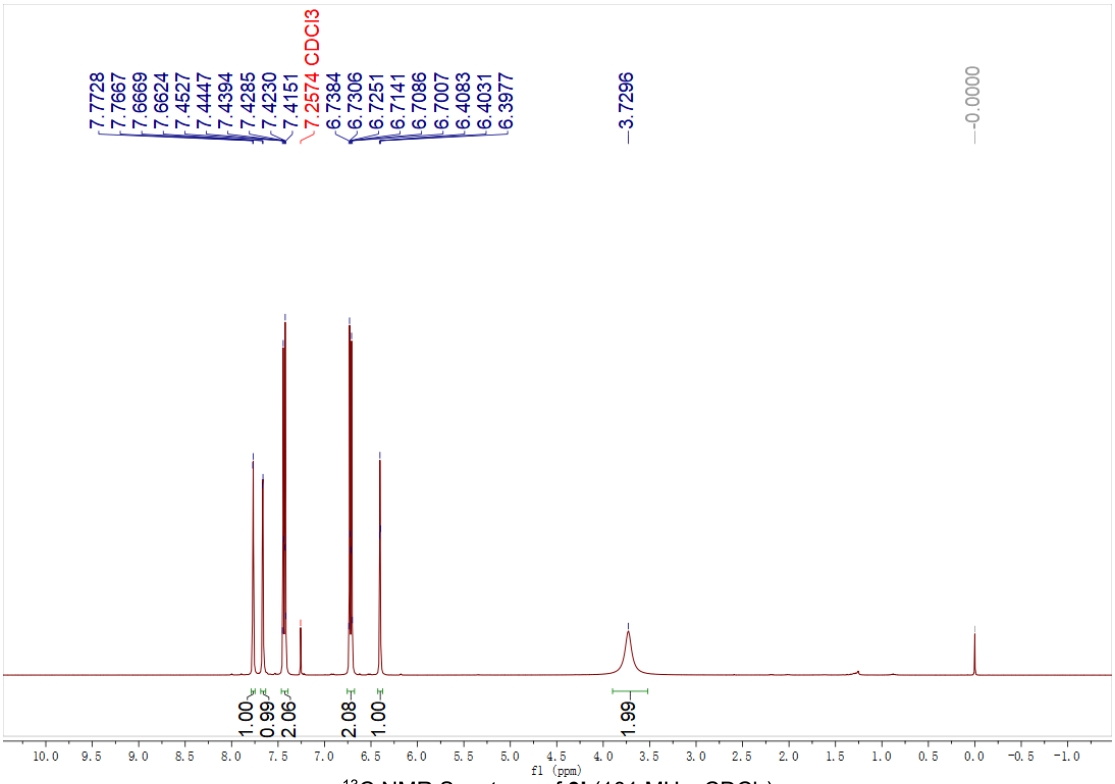

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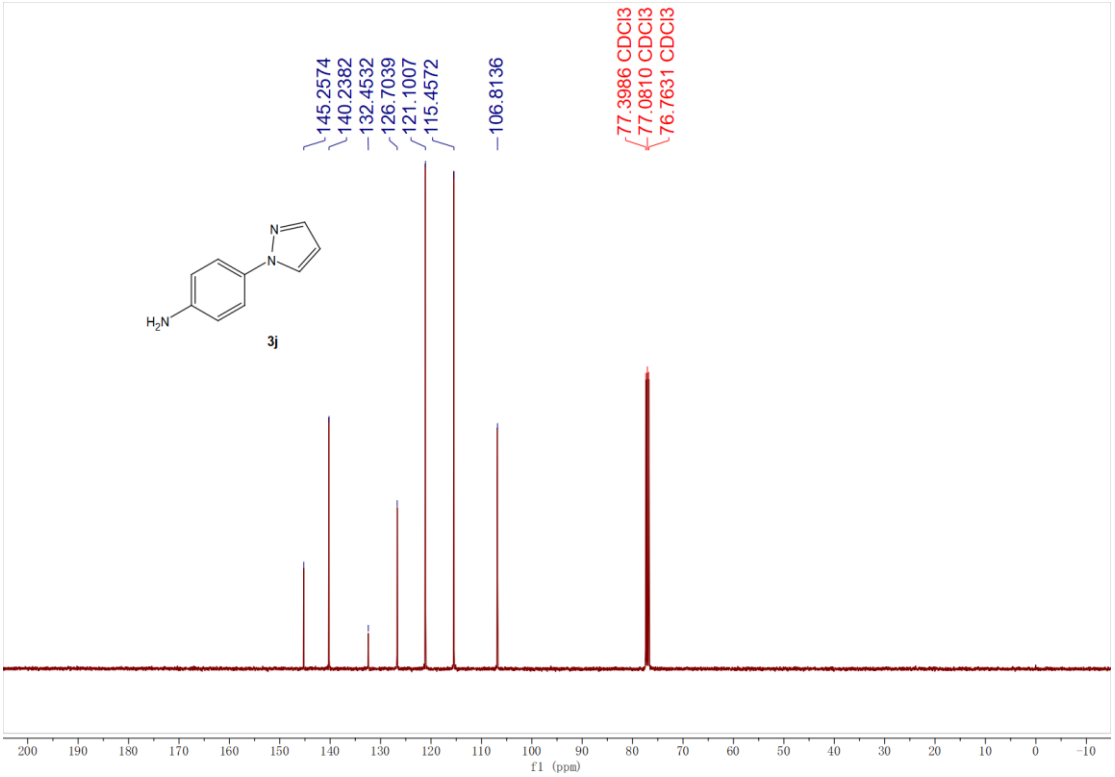
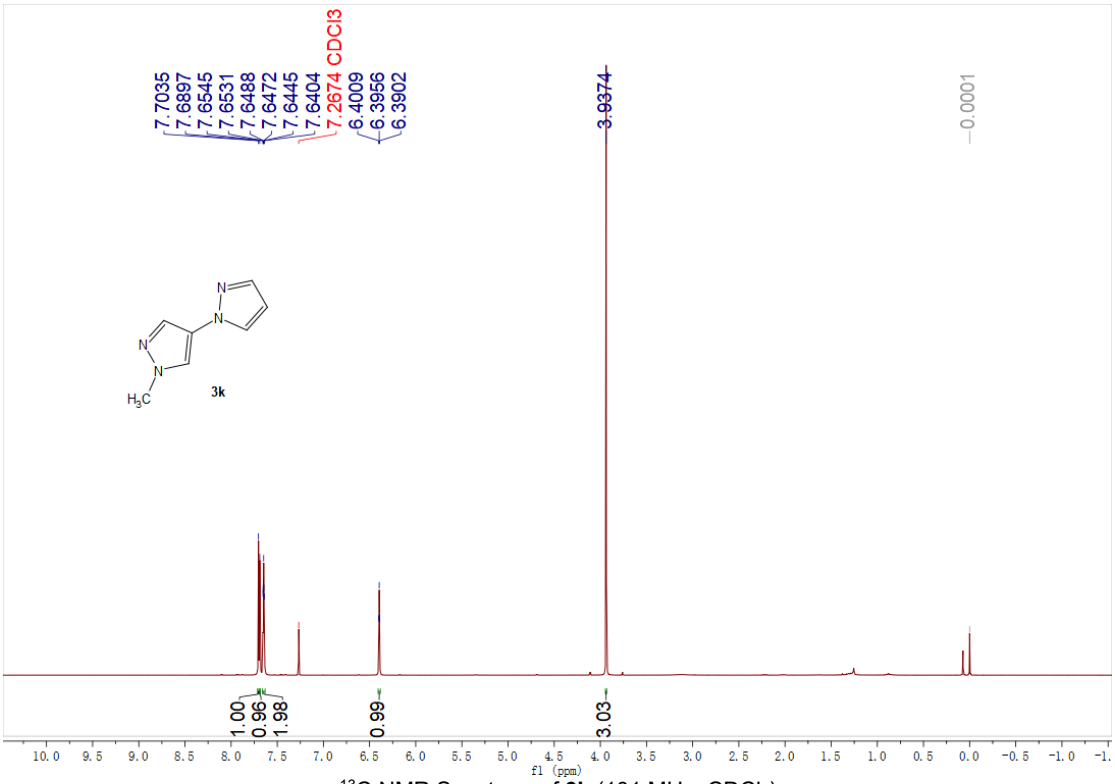
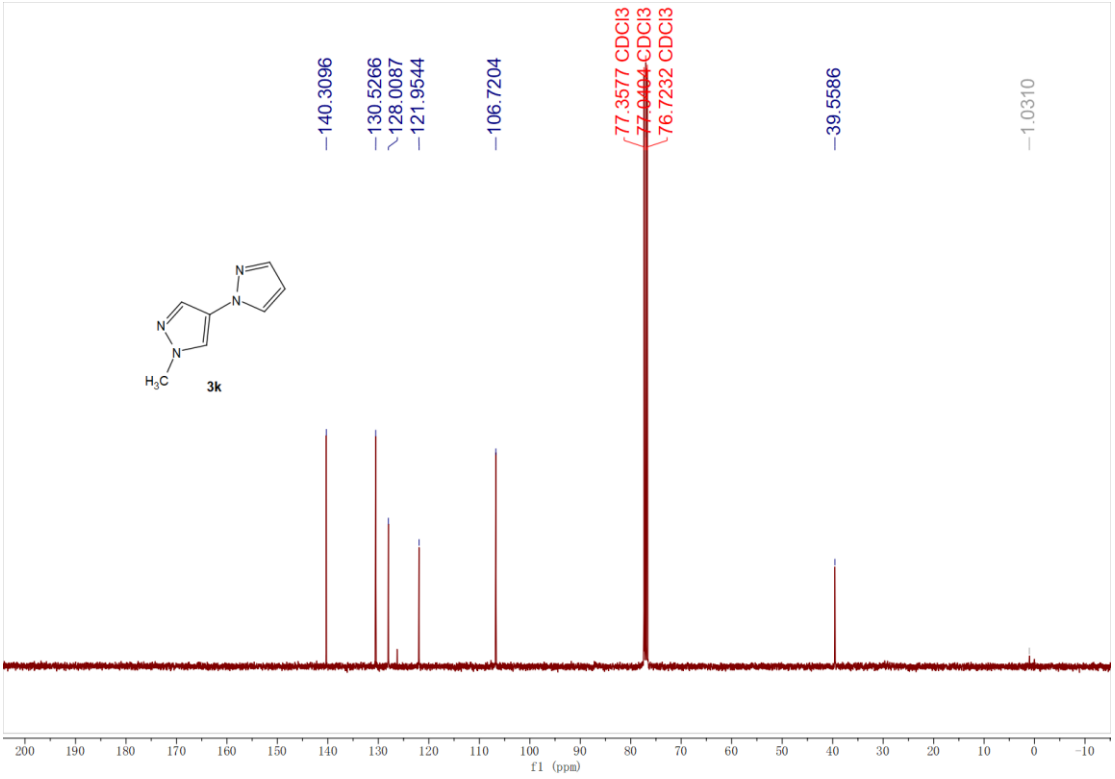


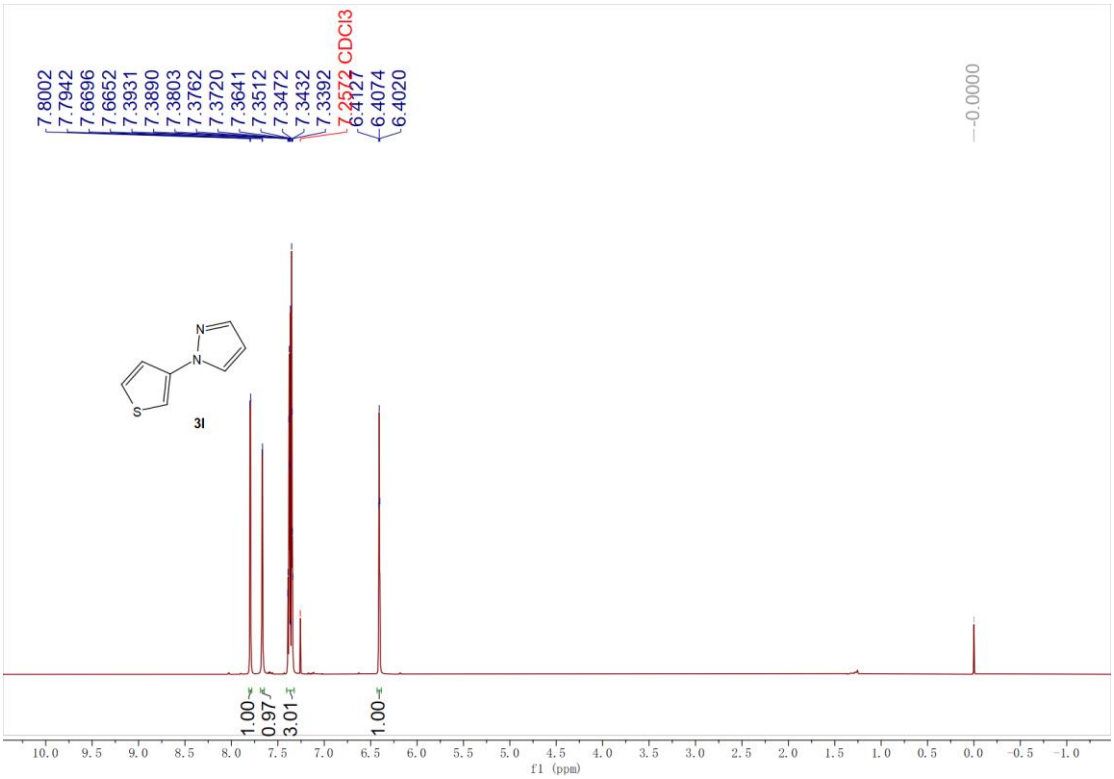
^{1}H NMR Spectrum of **3k** (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **3k** (101 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **3l** (400 MHz, $CDCl_3$)



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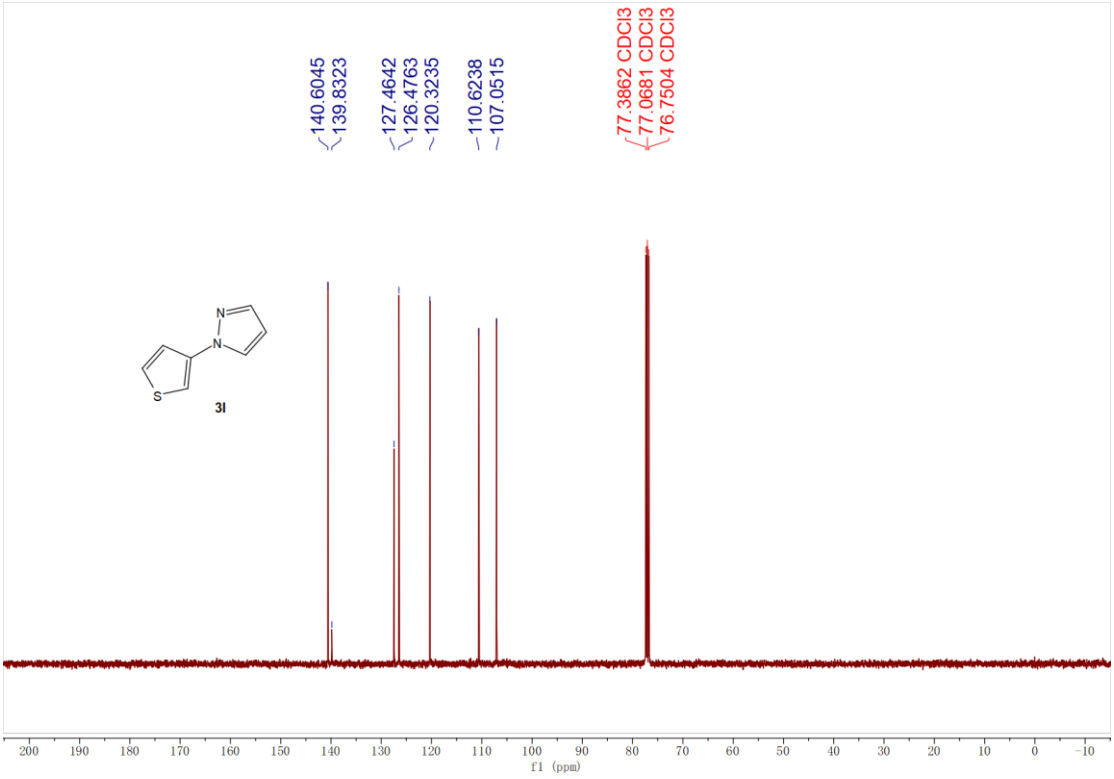

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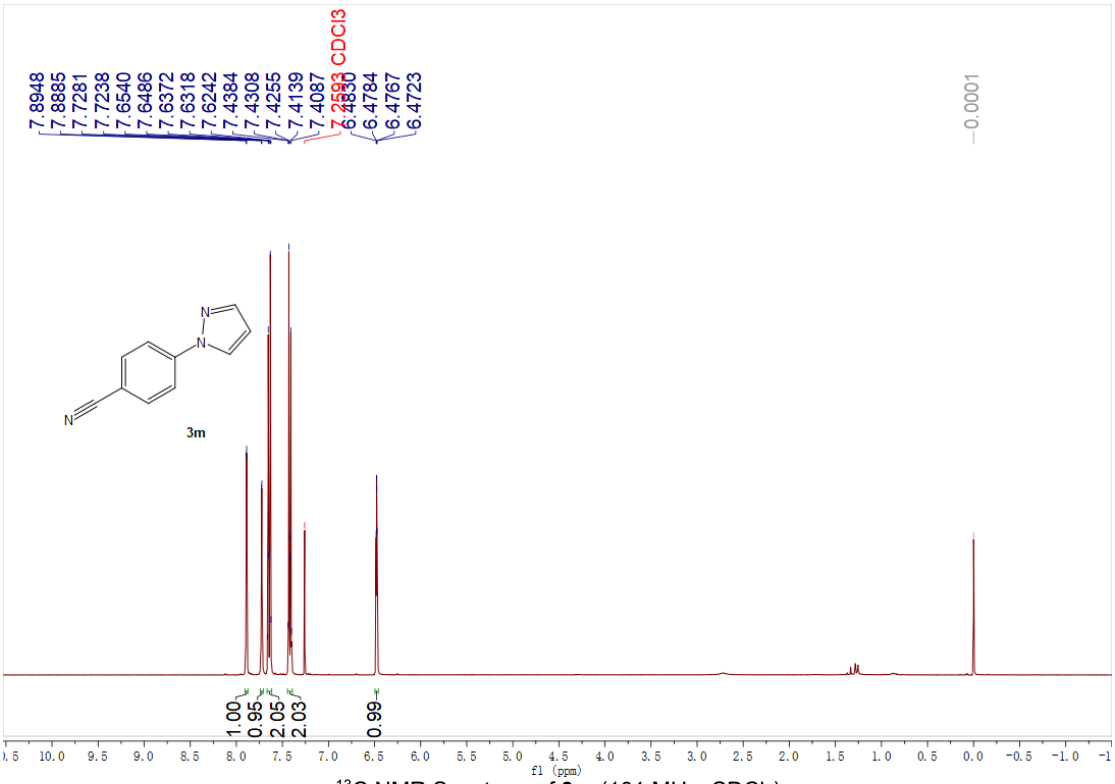
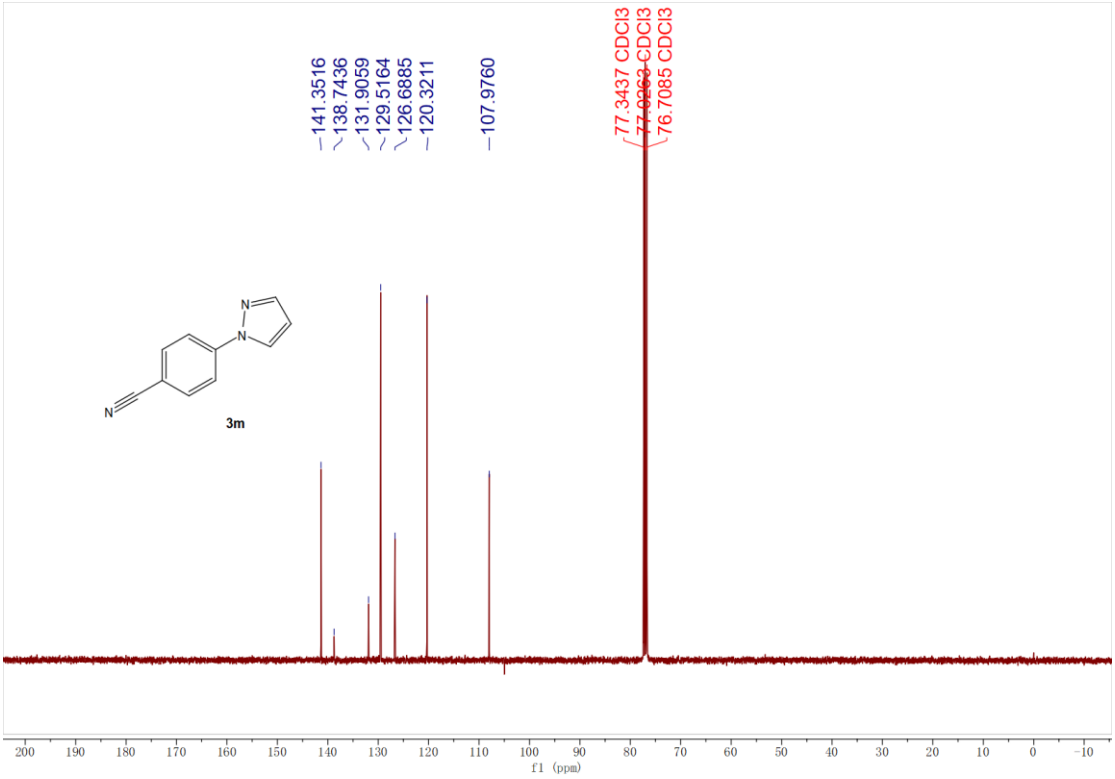
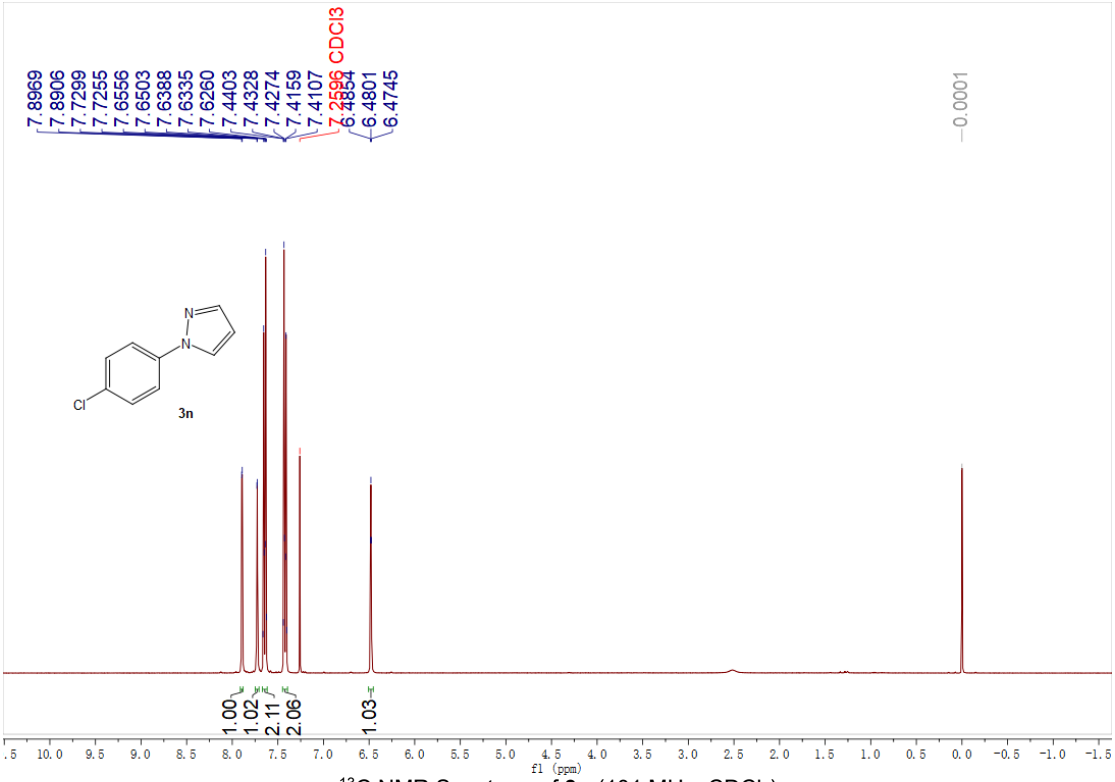


^{13}C NMR Spectrum of **3m** (101 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **3n** (400 MHz, $CDCl_3$)



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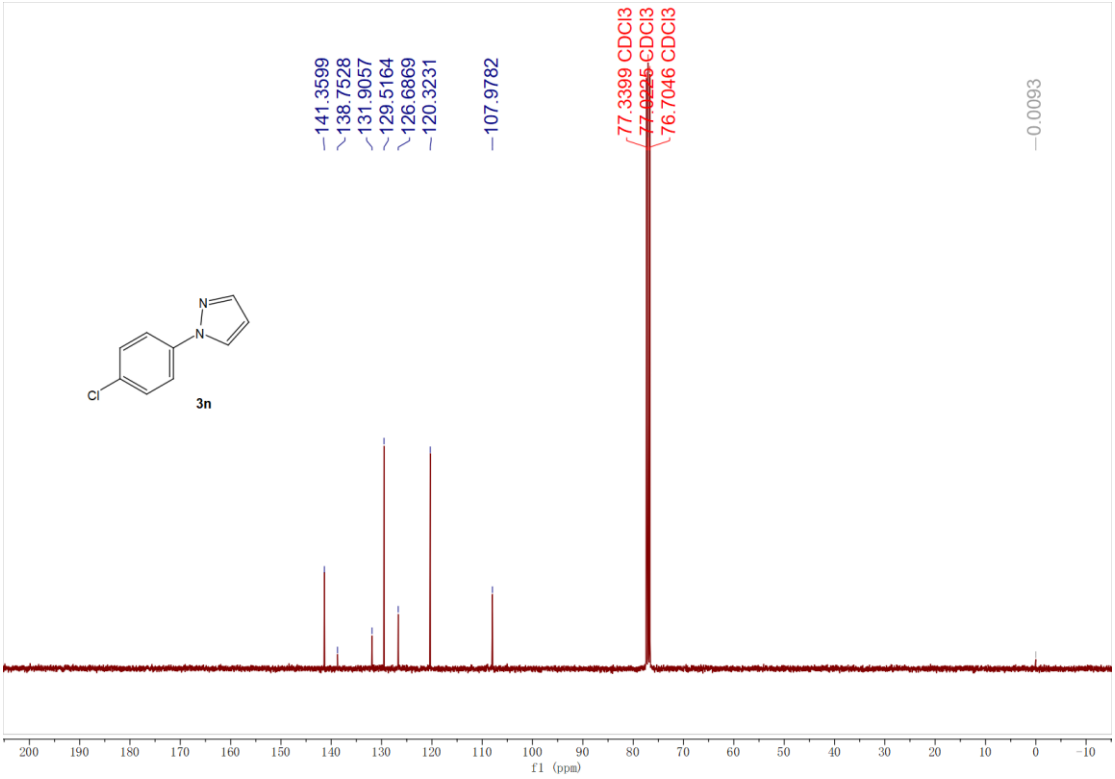

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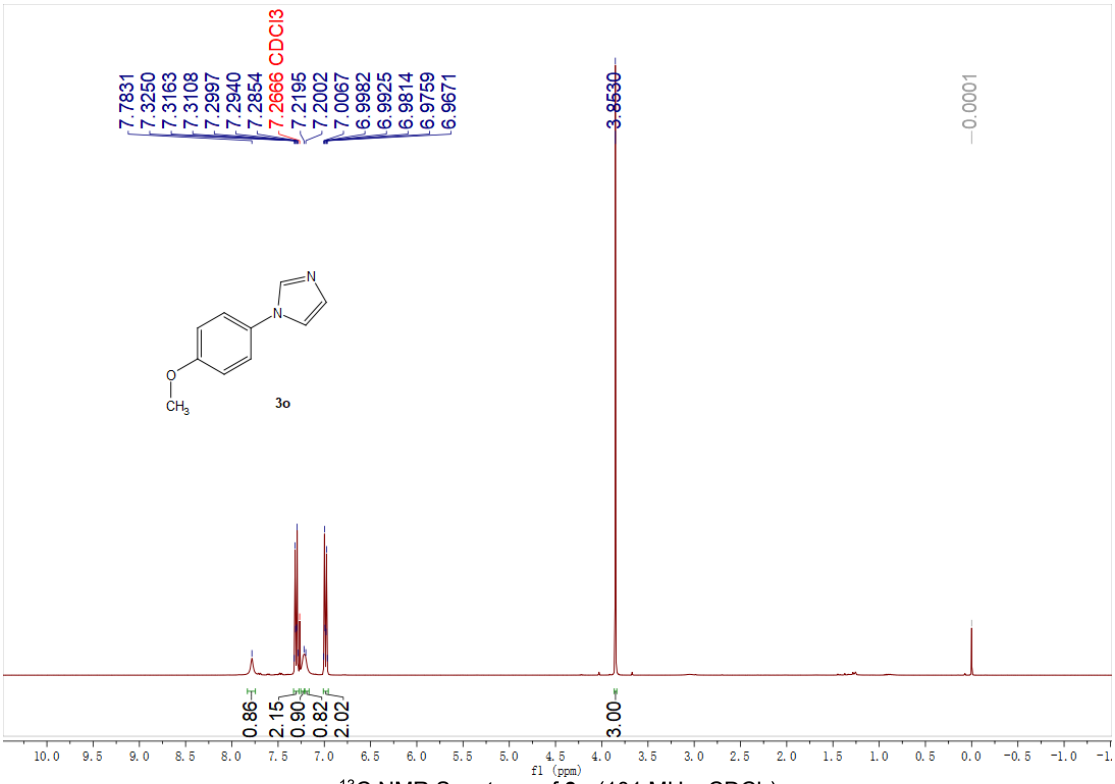
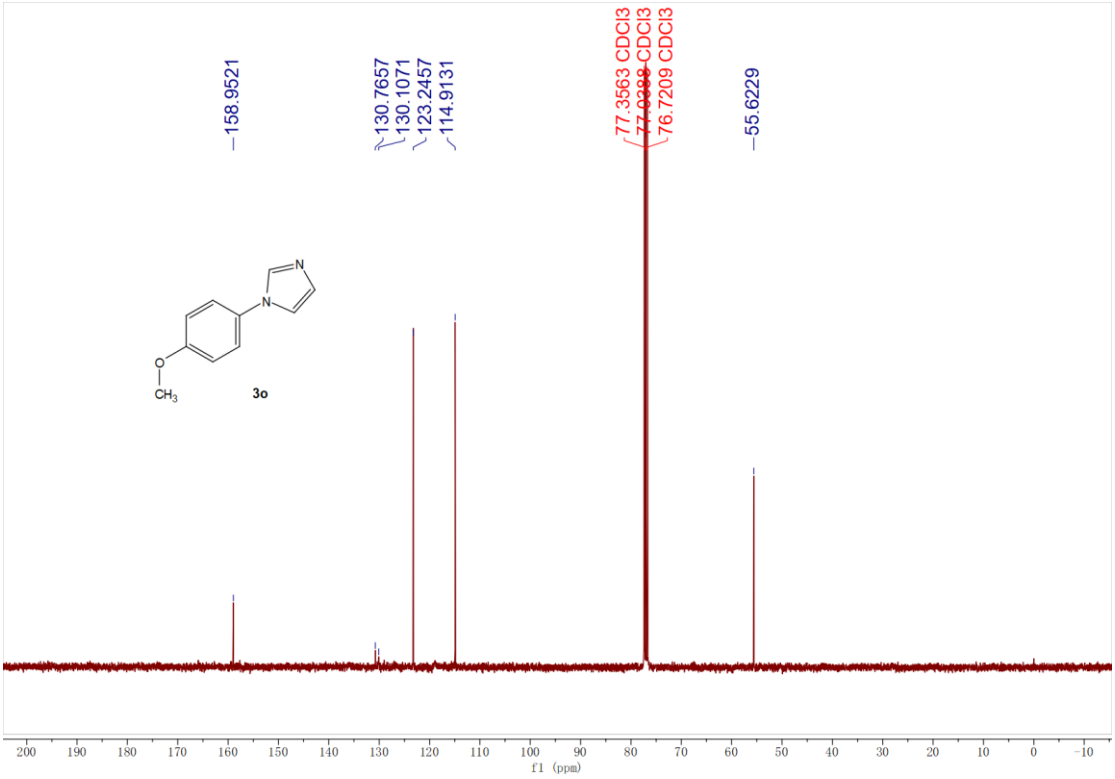
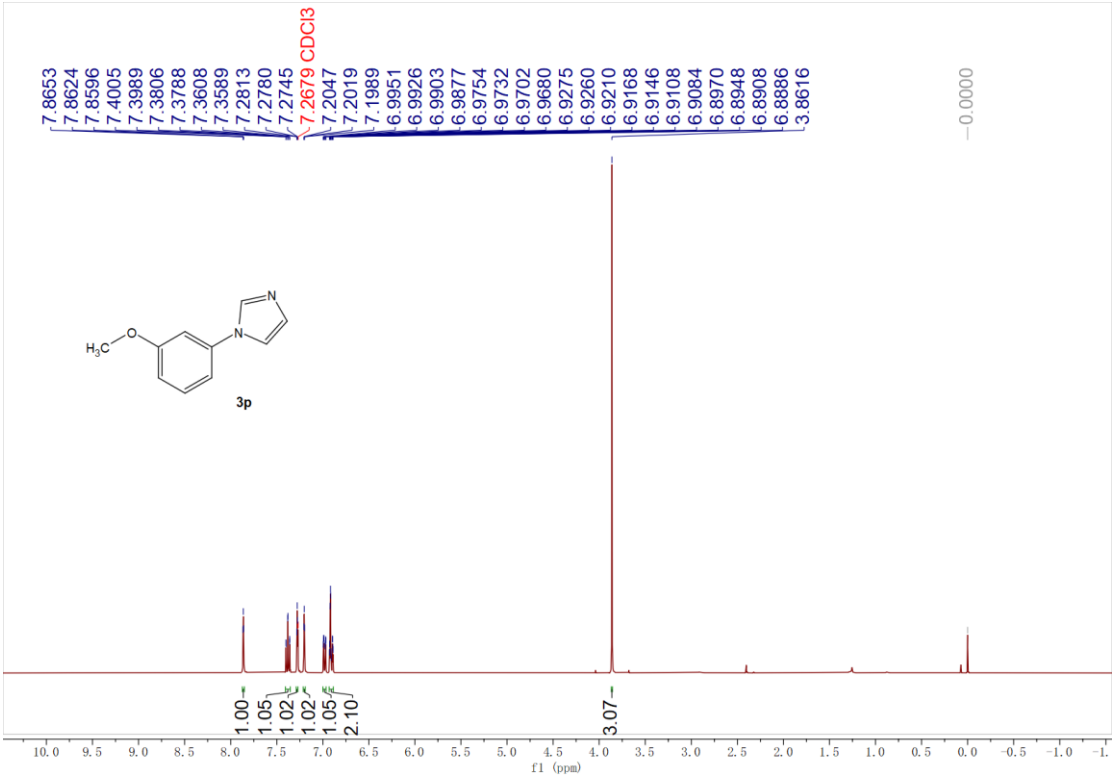


^{13}C NMR Spectrum of **3o** (101 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **3p** (400 MHz, $CDCl_3$)



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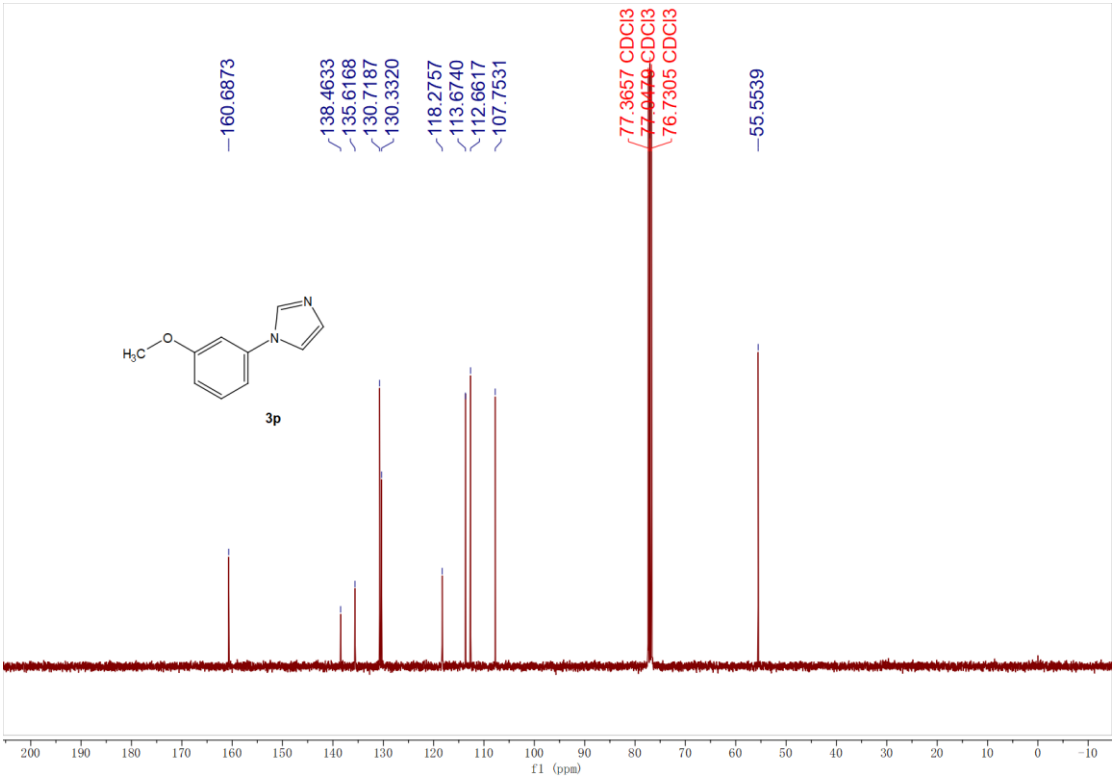

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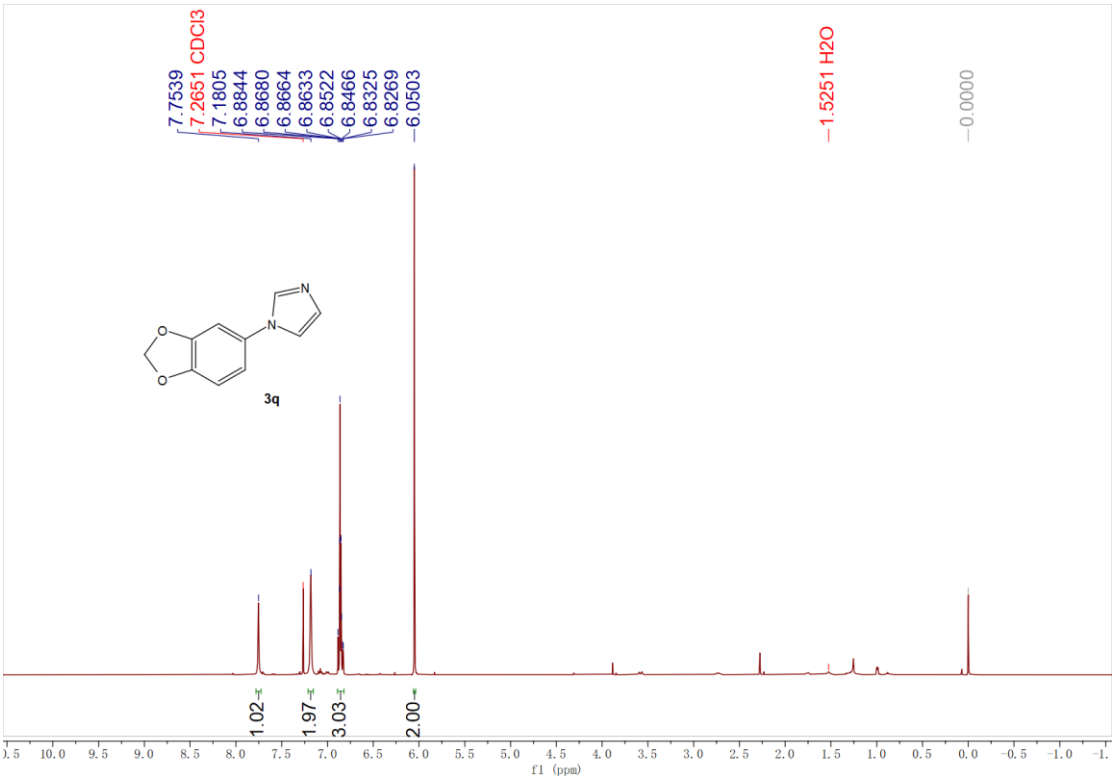
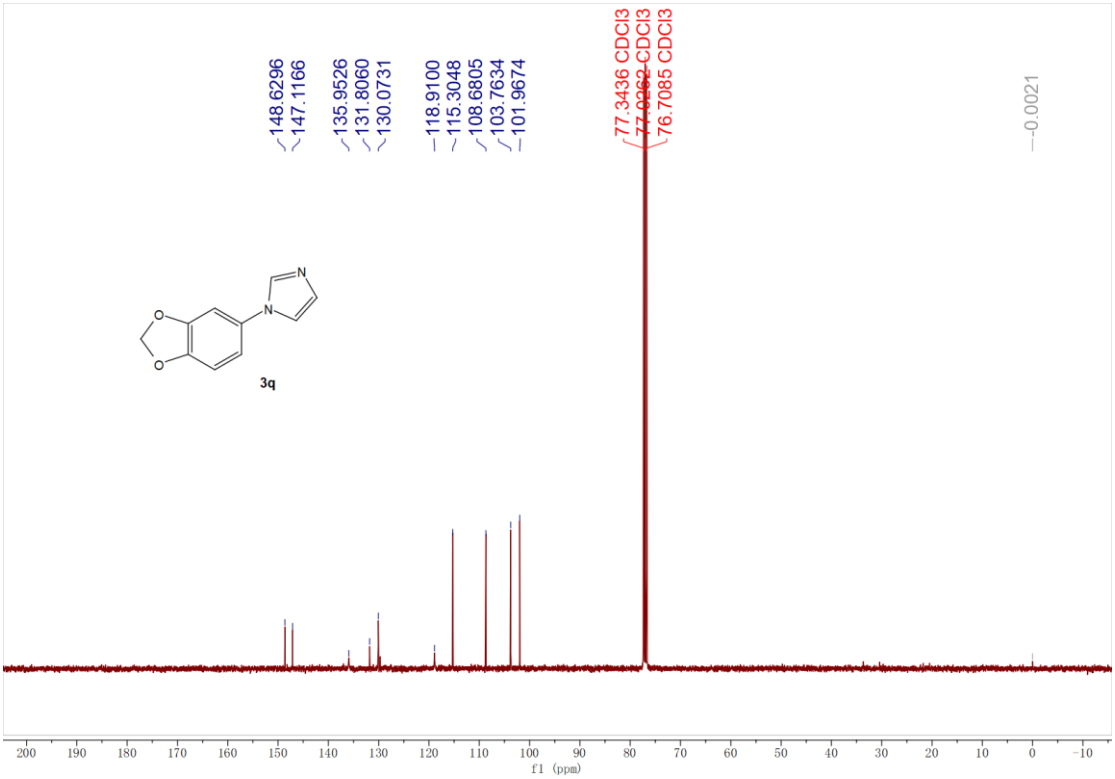
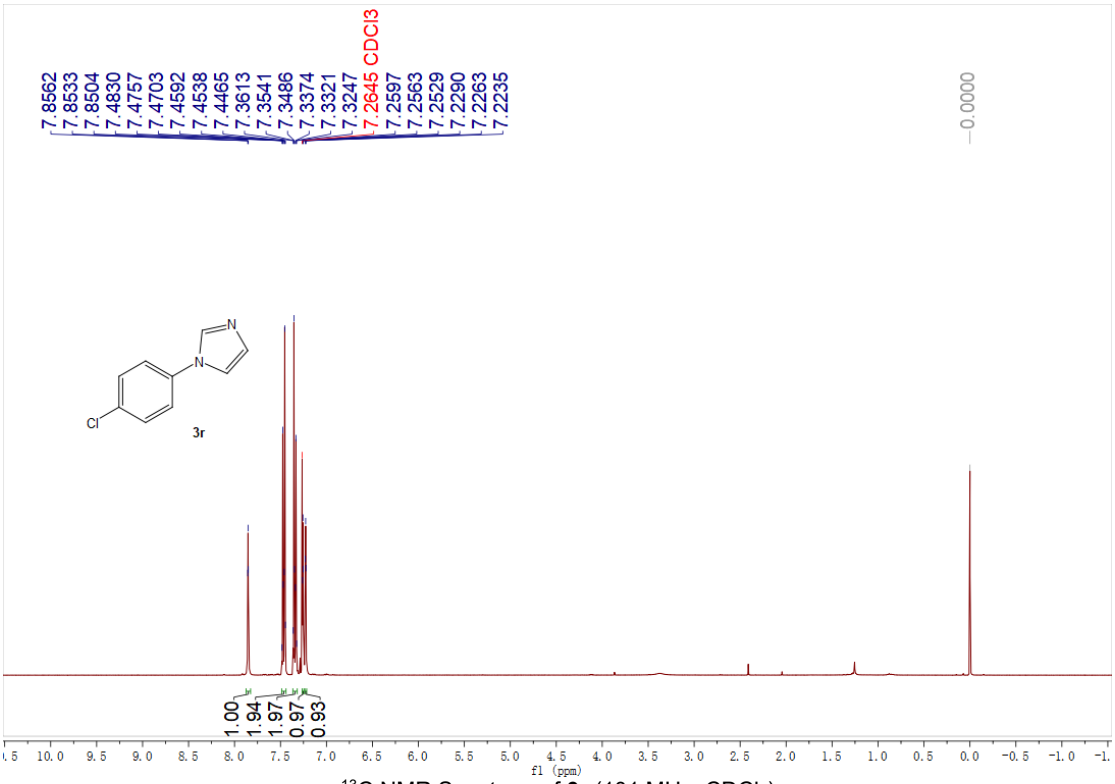


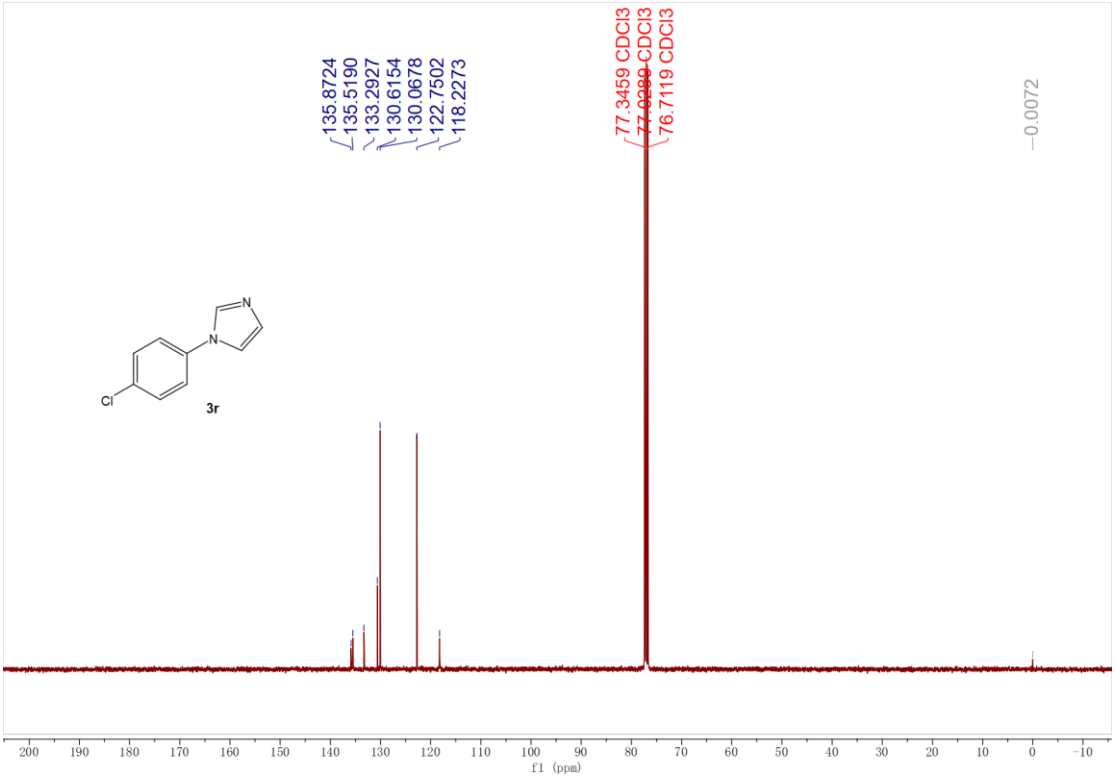
^{13}C NMR Spectrum of **3q** (101 MHz, $CDCl_3$)



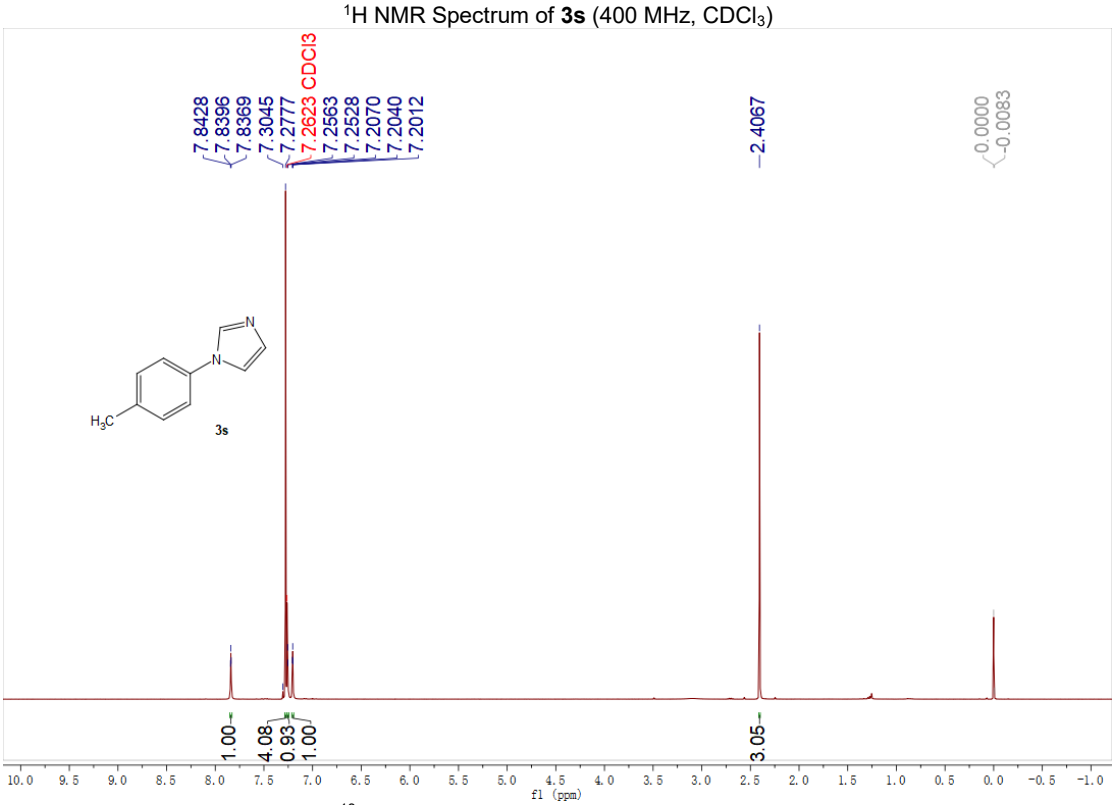
^{1}H NMR Spectrum of **3r** (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **3r** (101 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **3s** (400 MHz, $CDCl_3$)



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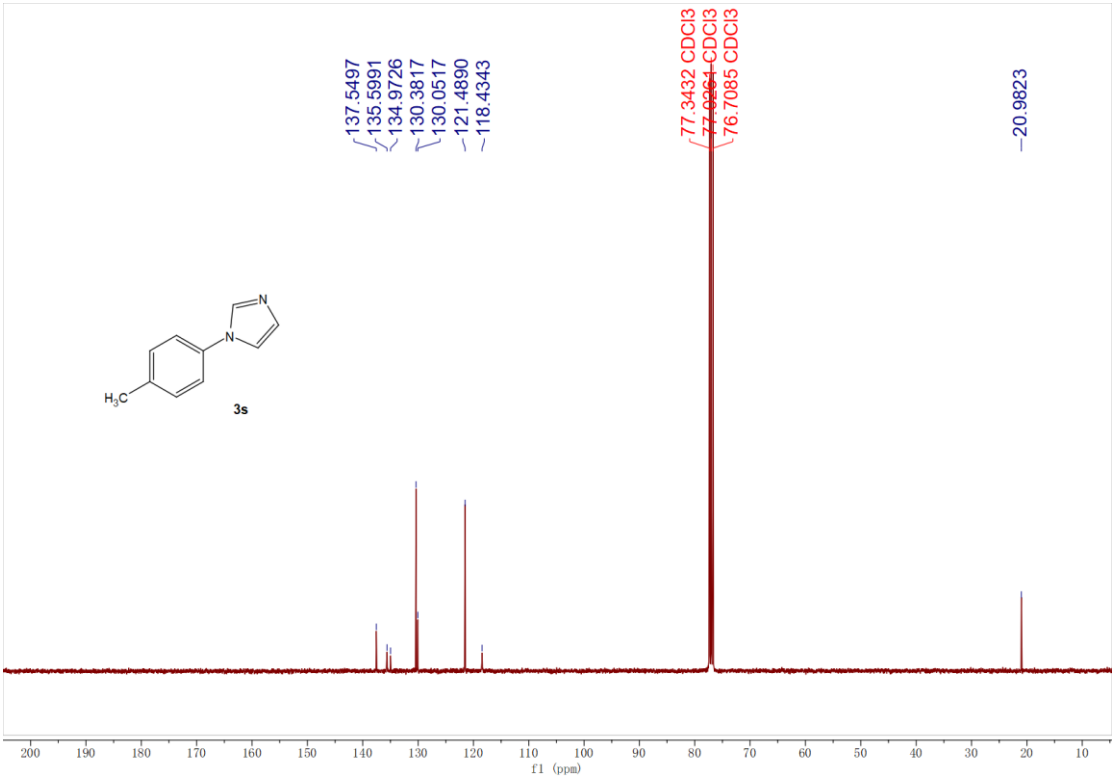
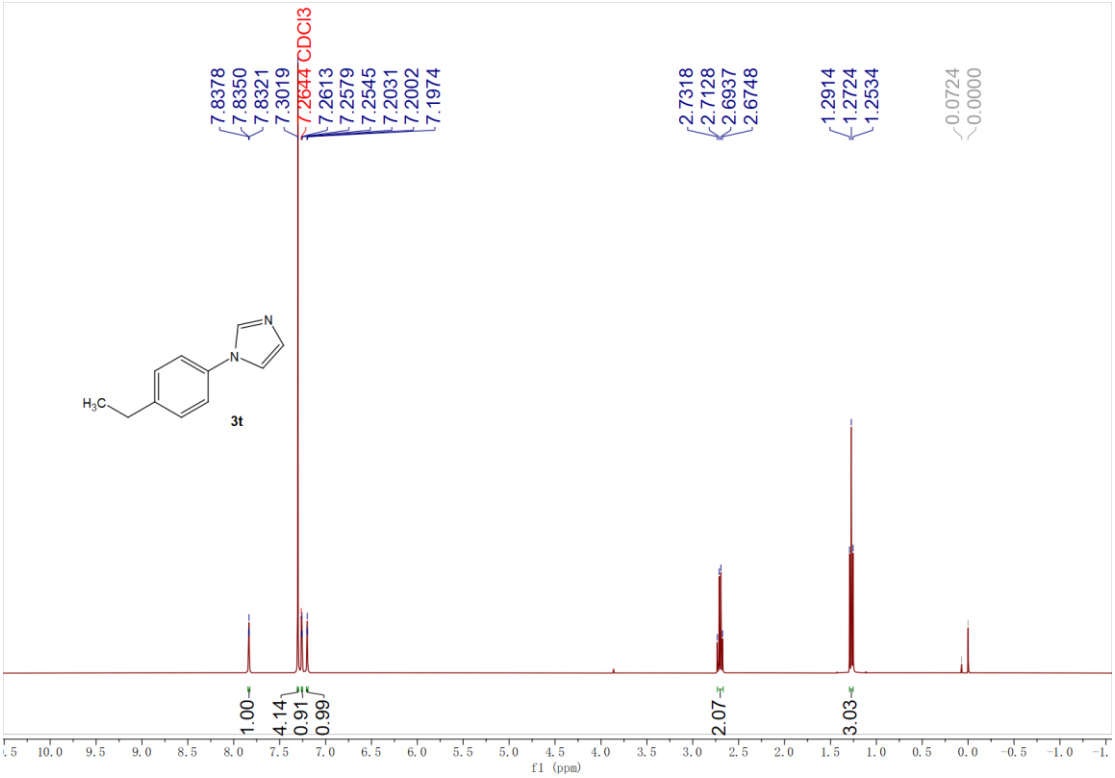


^{1}H NMR Spectrum of **3t** (400 MHz, $CDCl_3$)



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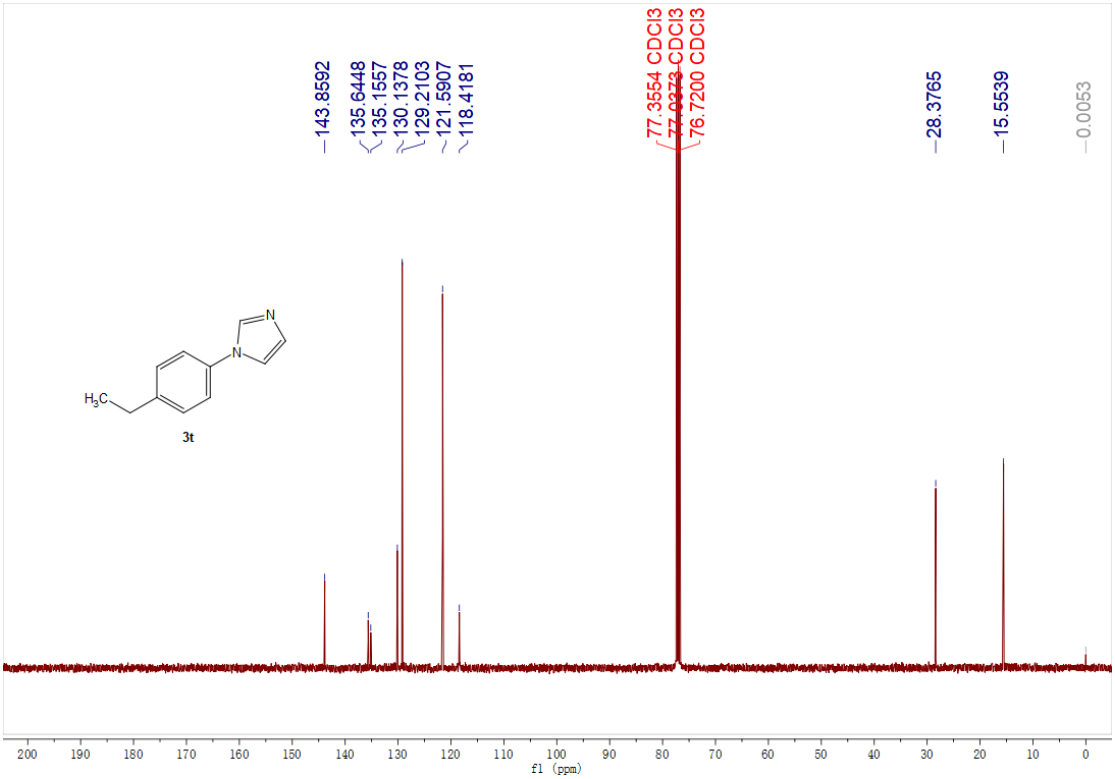
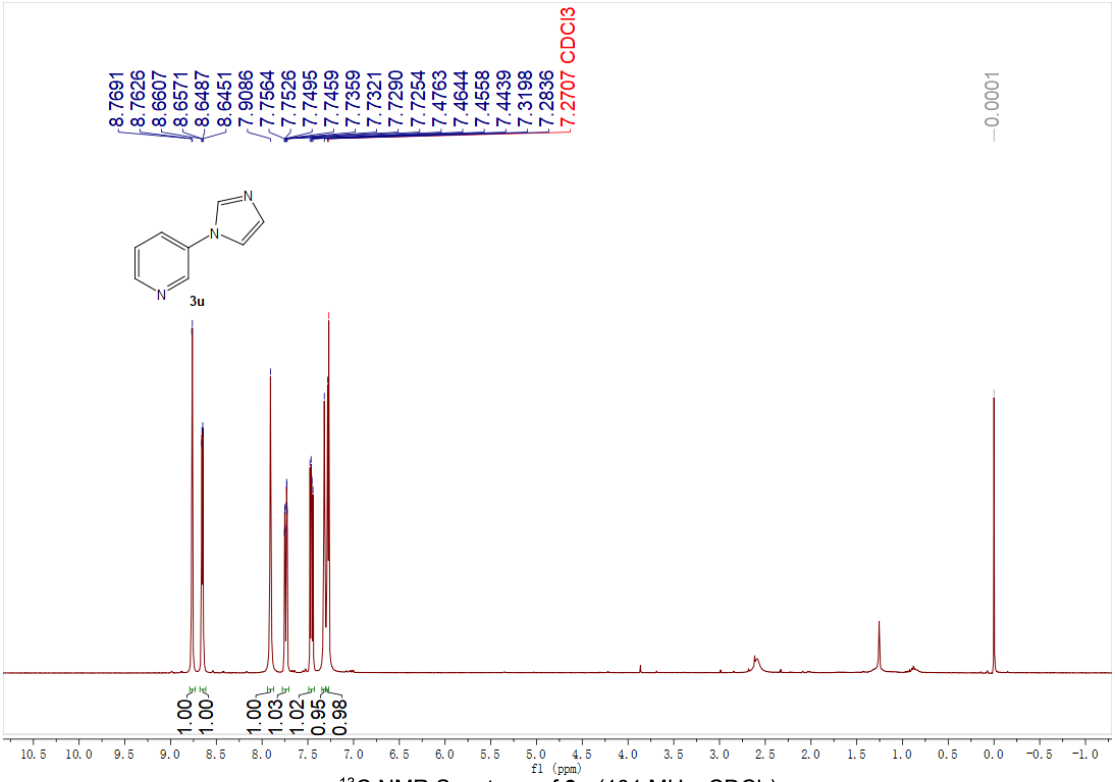
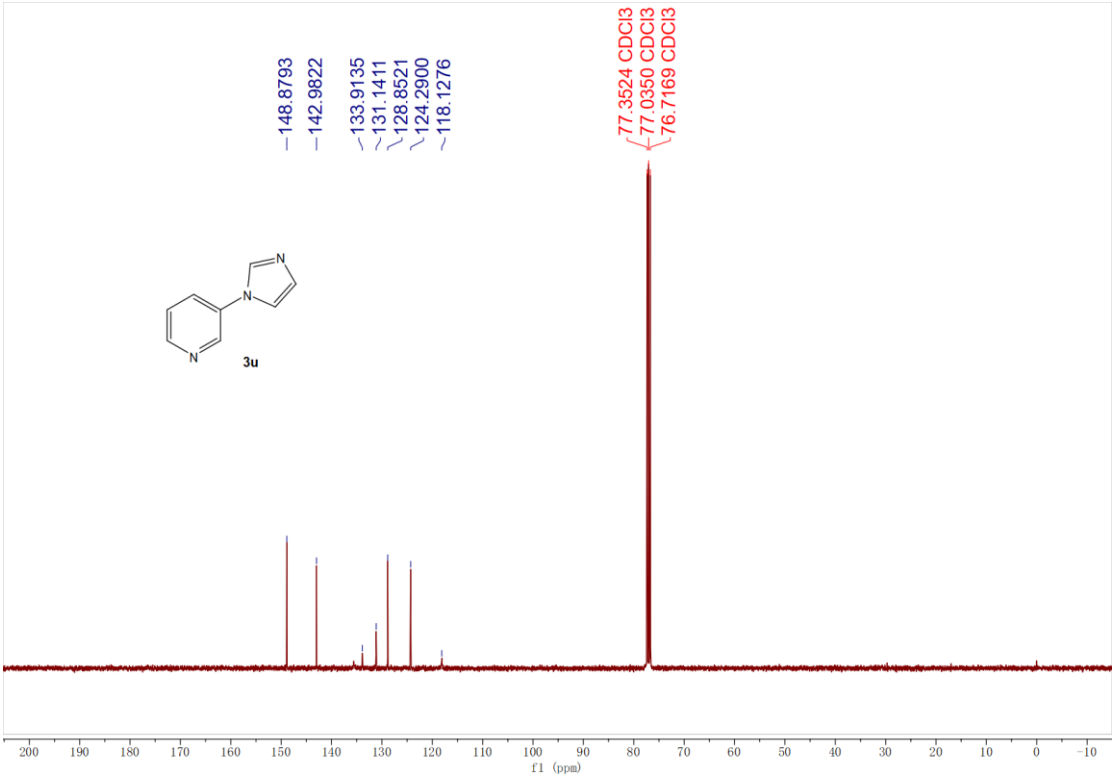


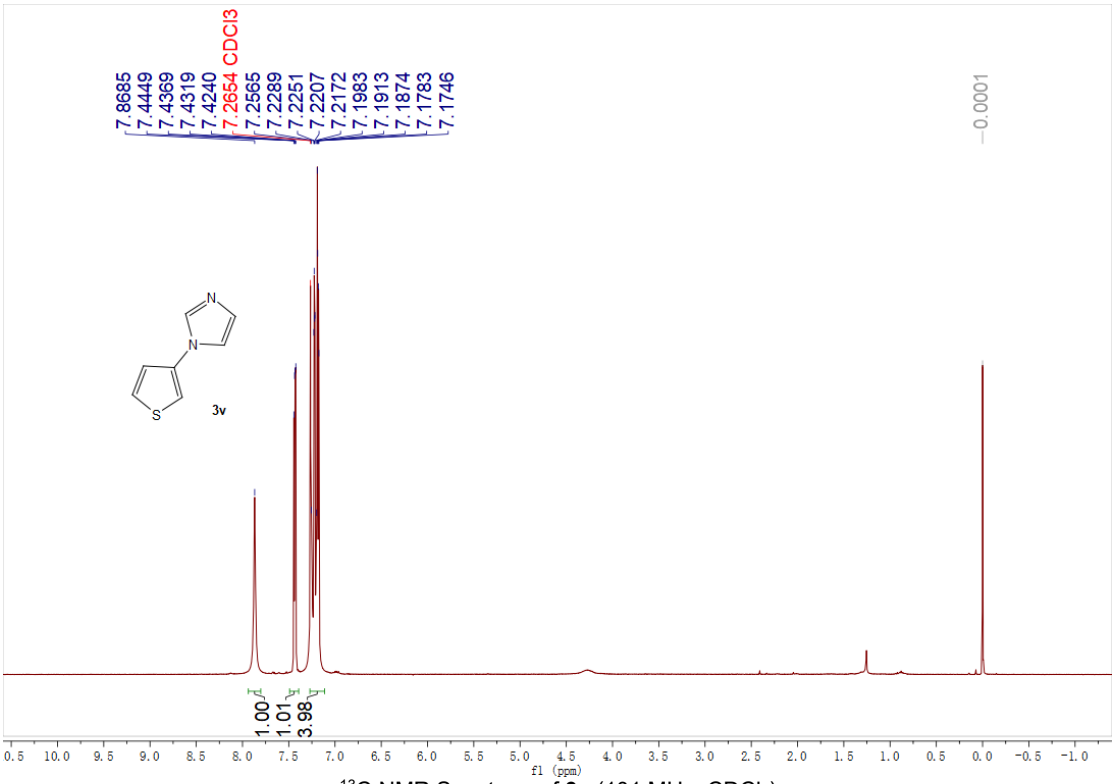
^{1}H NMR Spectrum of **3u** (400 MHz, $CDCl_3$)



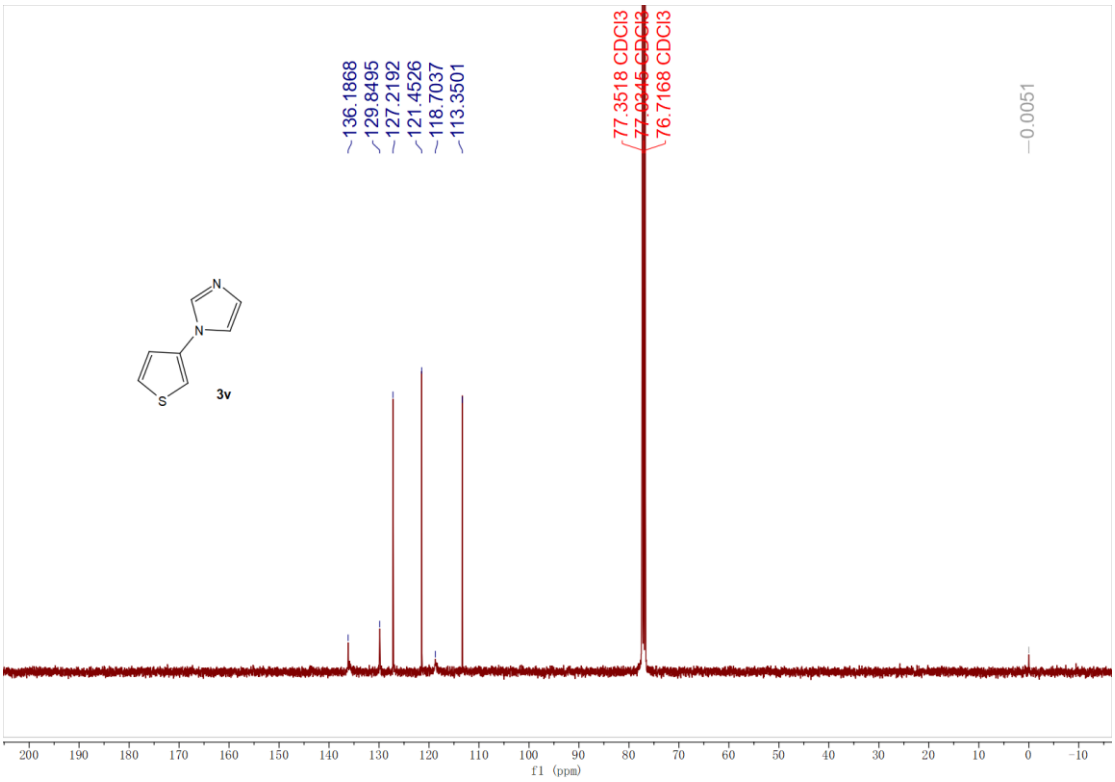
^{13}C NMR Spectrum of **3u** (101 MHz, $CDCl_3$)



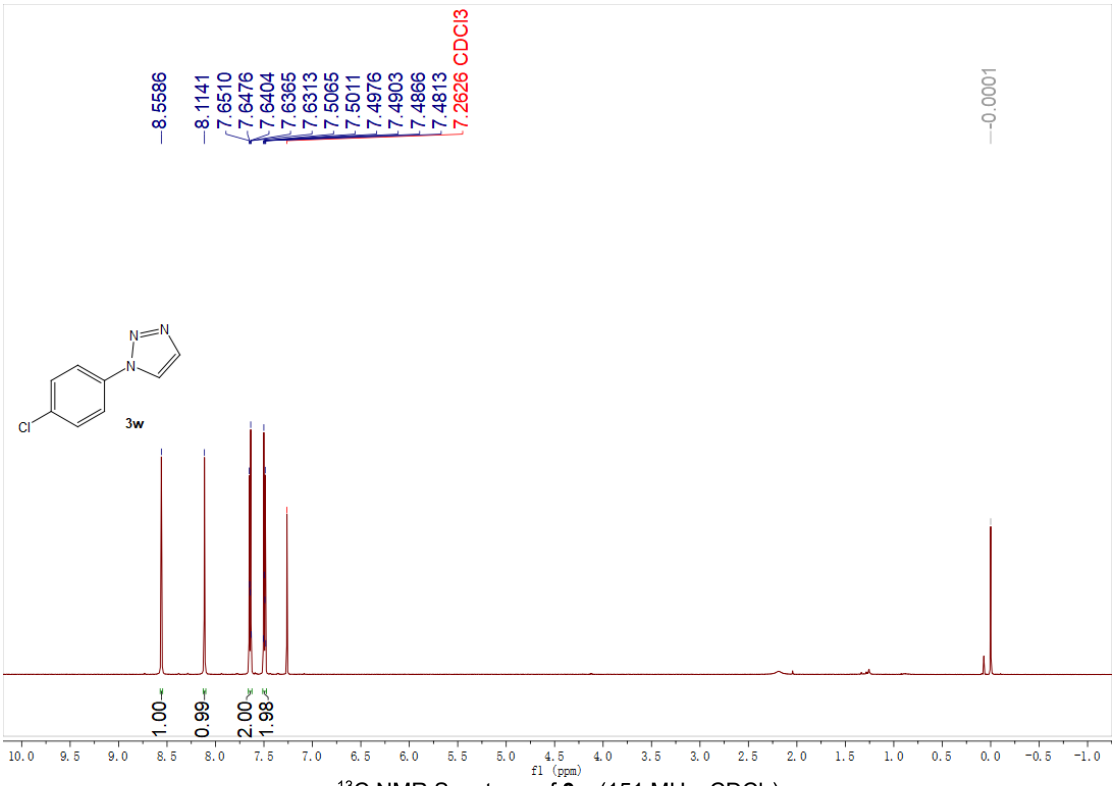
^{1}H NMR Spectrum of **3v** (400 MHz, $CDCl_3$)



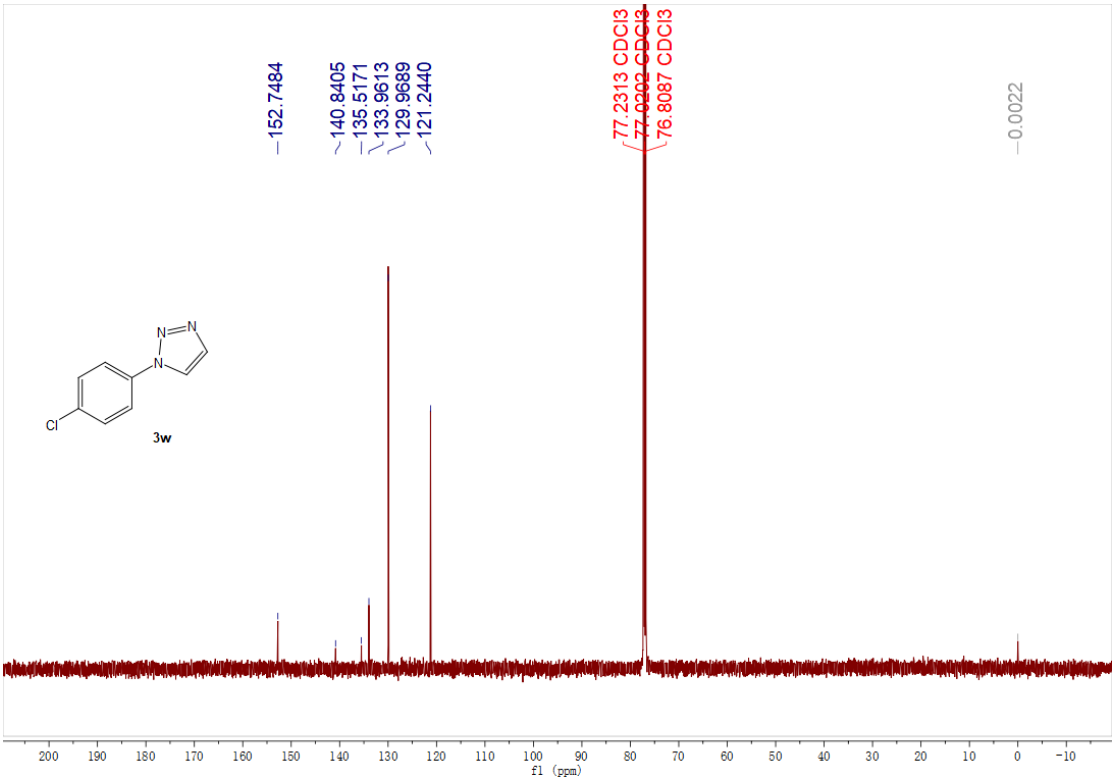
^{13}C NMR Spectrum of **3v** (101 MHz, $CDCl_3$)



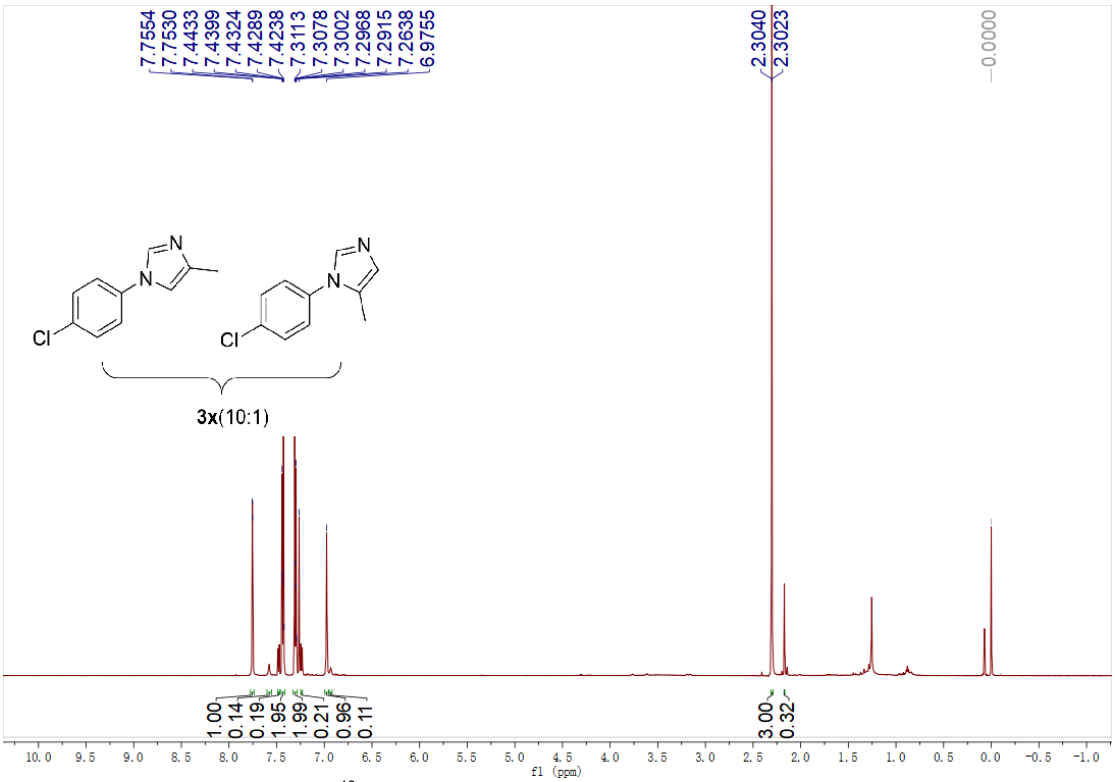
^{1}H NMR Spectrum of **3w** (600 MHz, $CDCl_3$)



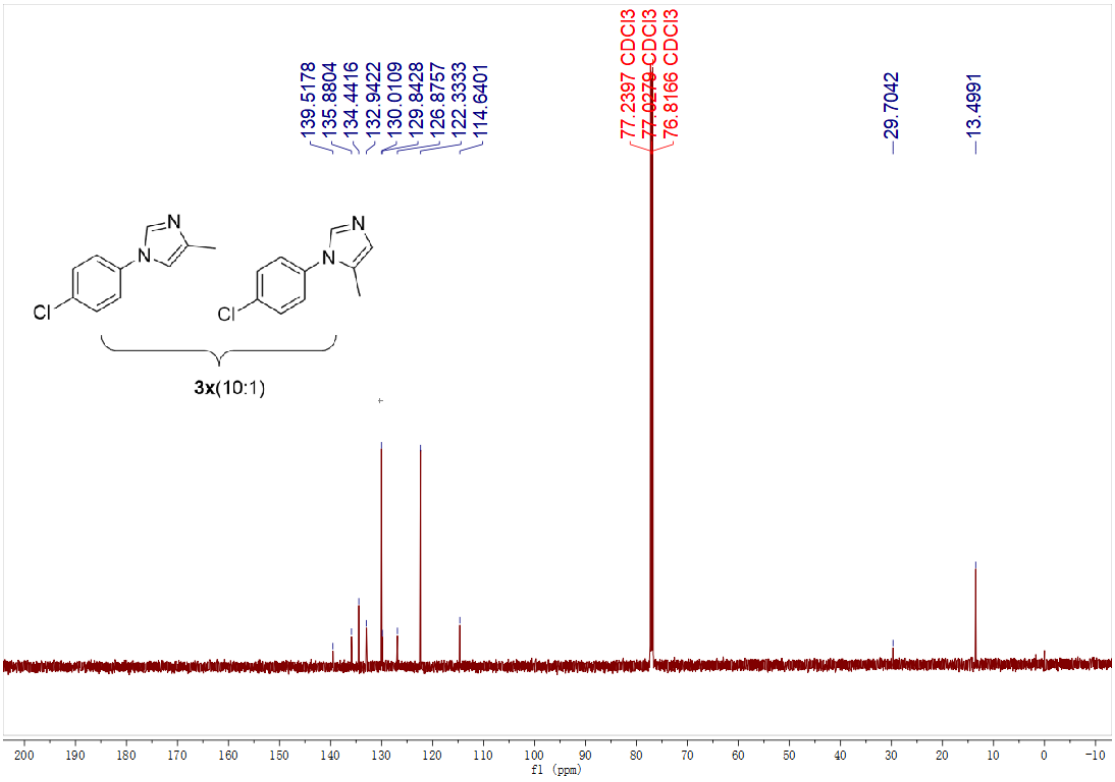
^{13}C NMR Spectrum of **3w** (151 MHz, $CDCl_3$)



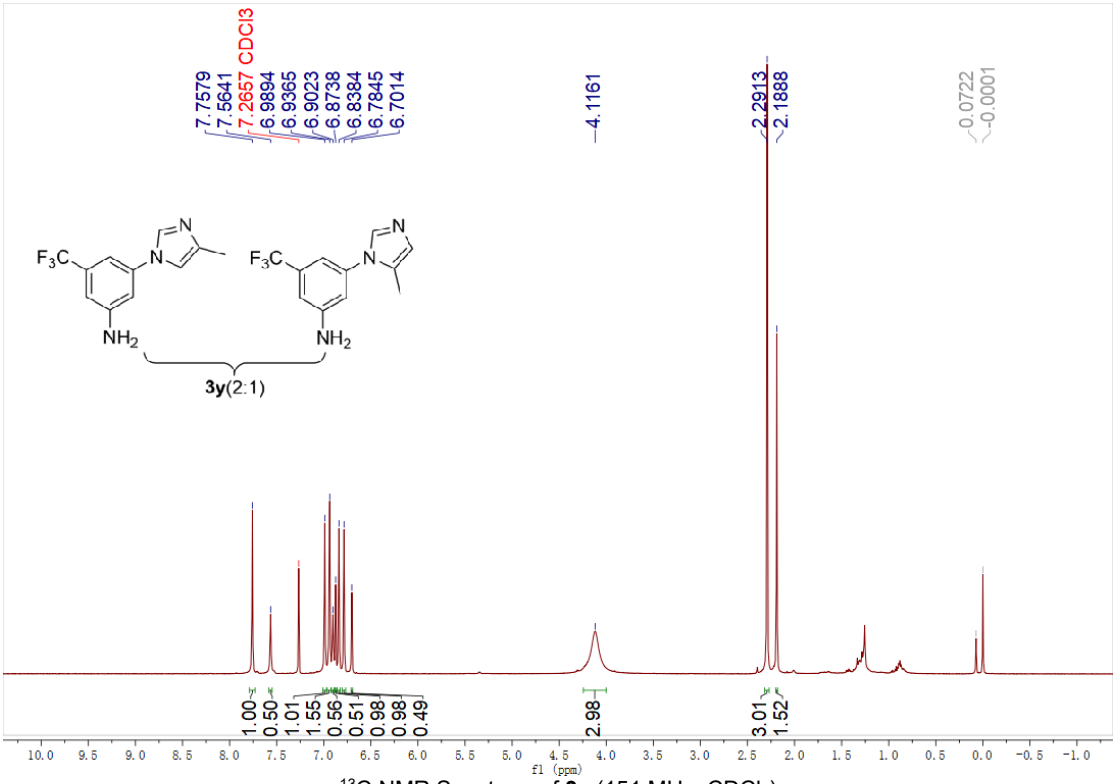
^{1}H NMR Spectrum of **3x** (600 MHz, $CDCl_3$)



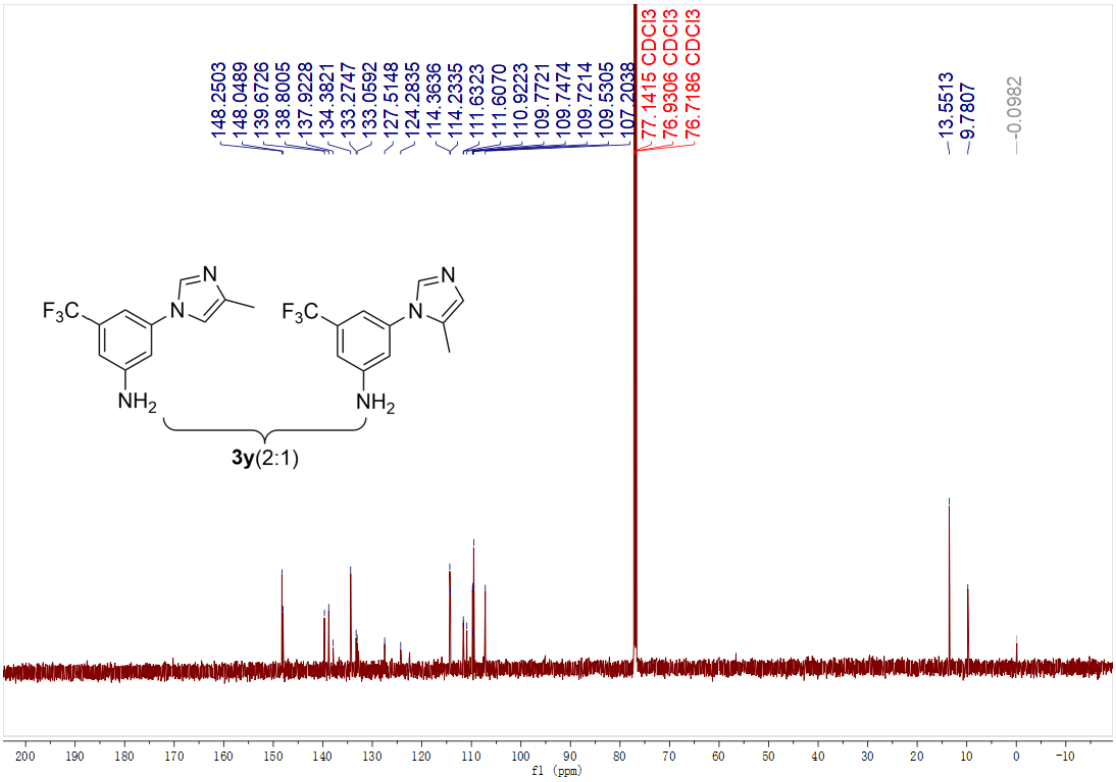
^{13}C NMR Spectrum of **3x** (151 MHz, $CDCl_3$)



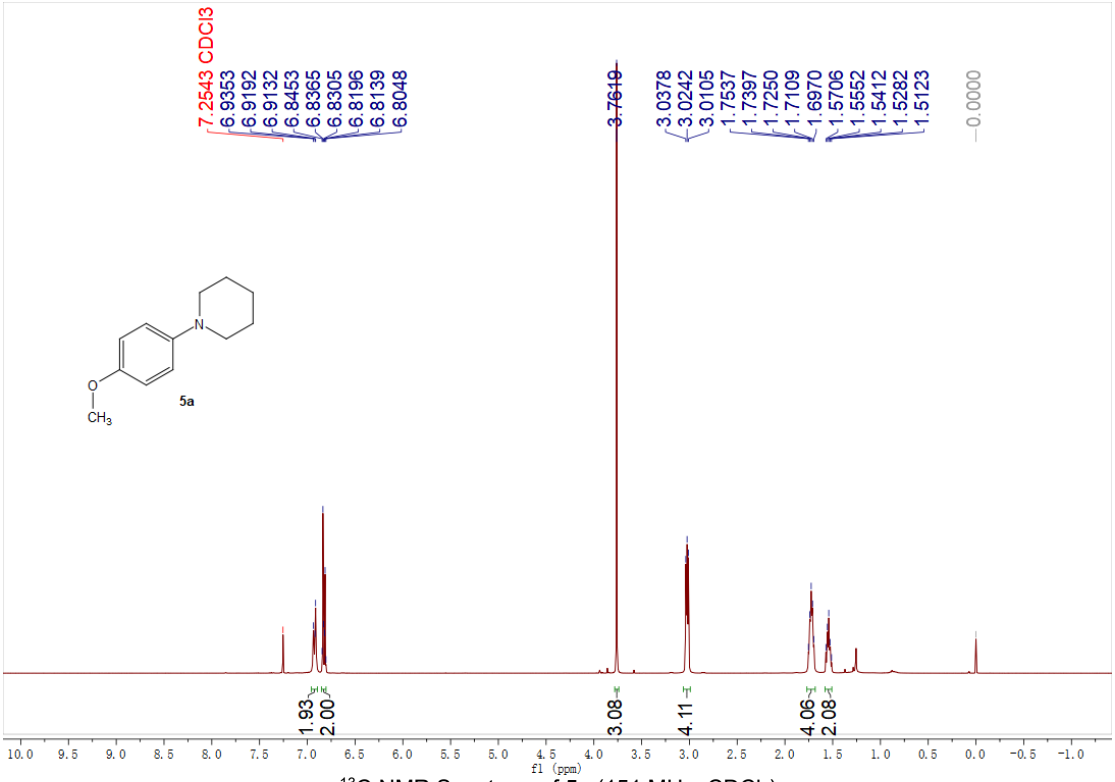
^{1}H NMR Spectrum of **3y** (600 MHz, $CDCl_3$)



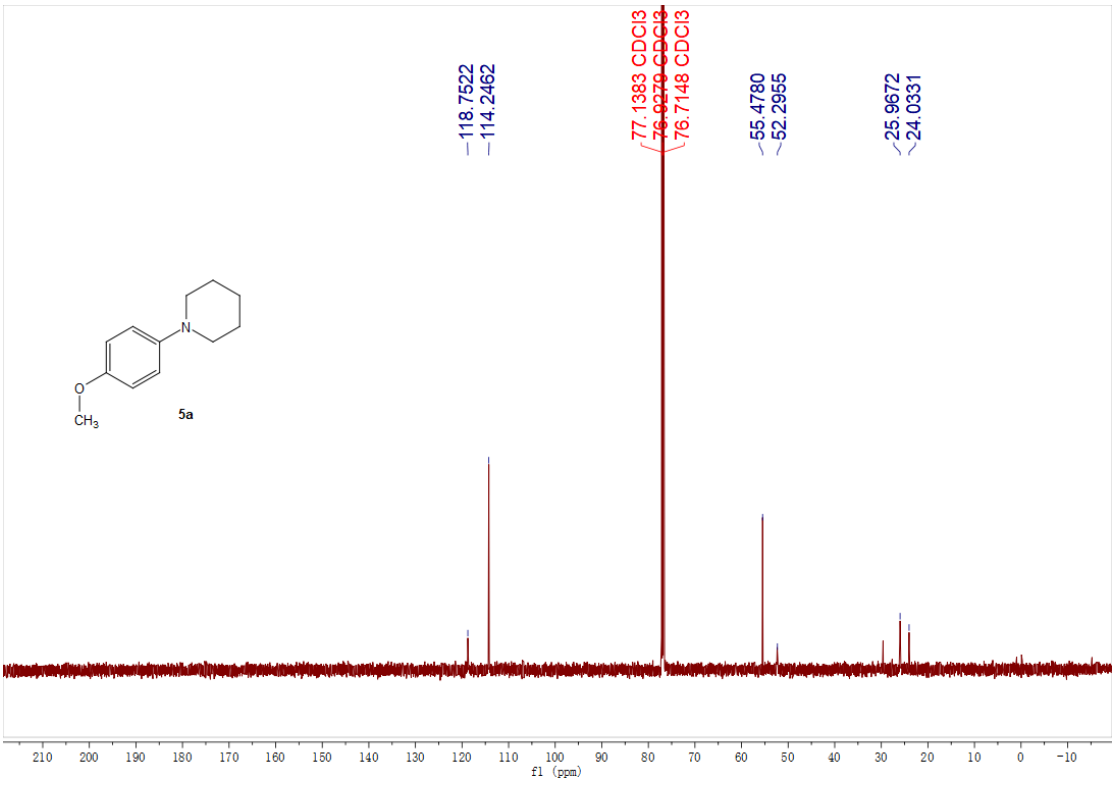
^{13}C NMR Spectrum of **3y** (151 MHz, $CDCl_3$)



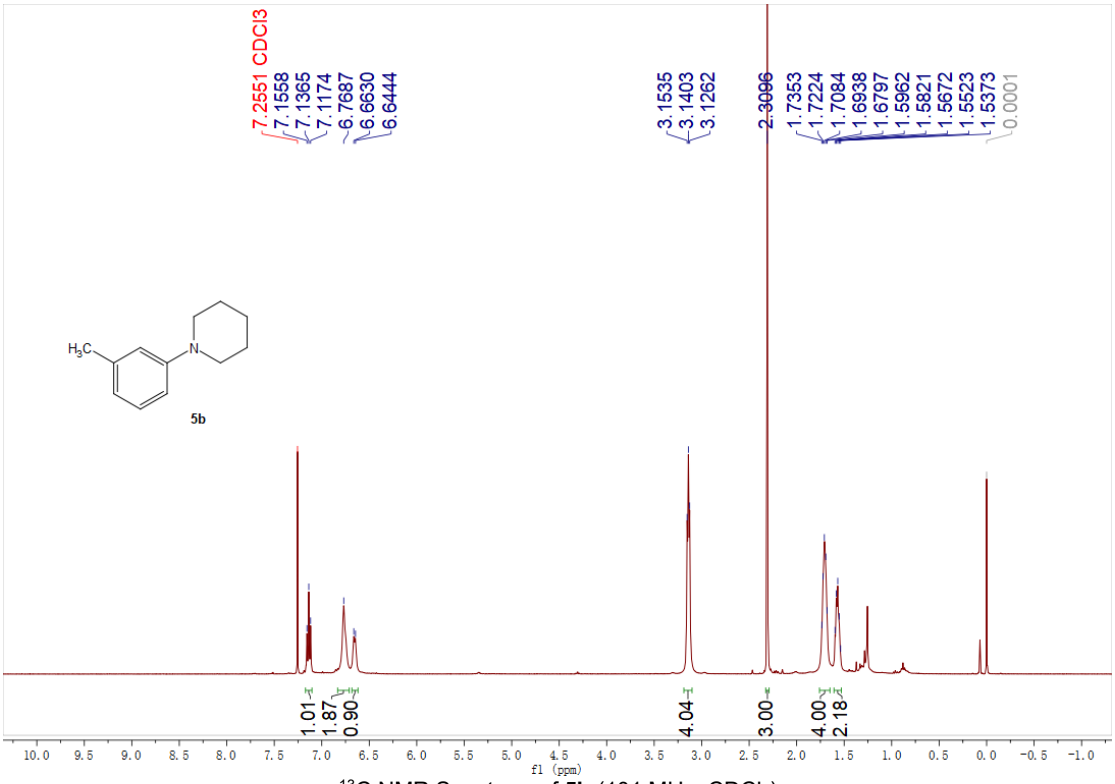
^{1}H NMR Spectrum of **5a** (400 MHz, $CDCl_3$)



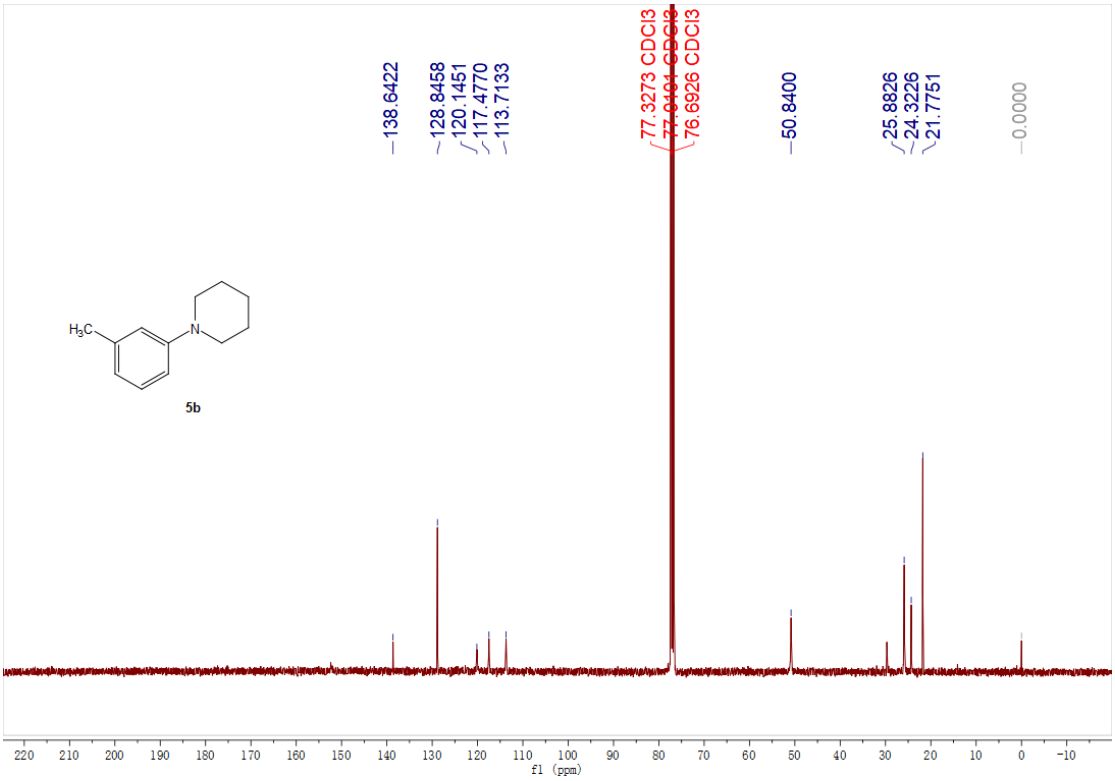
^{13}C NMR Spectrum of **5a** (151 MHz, $CDCl_3$)



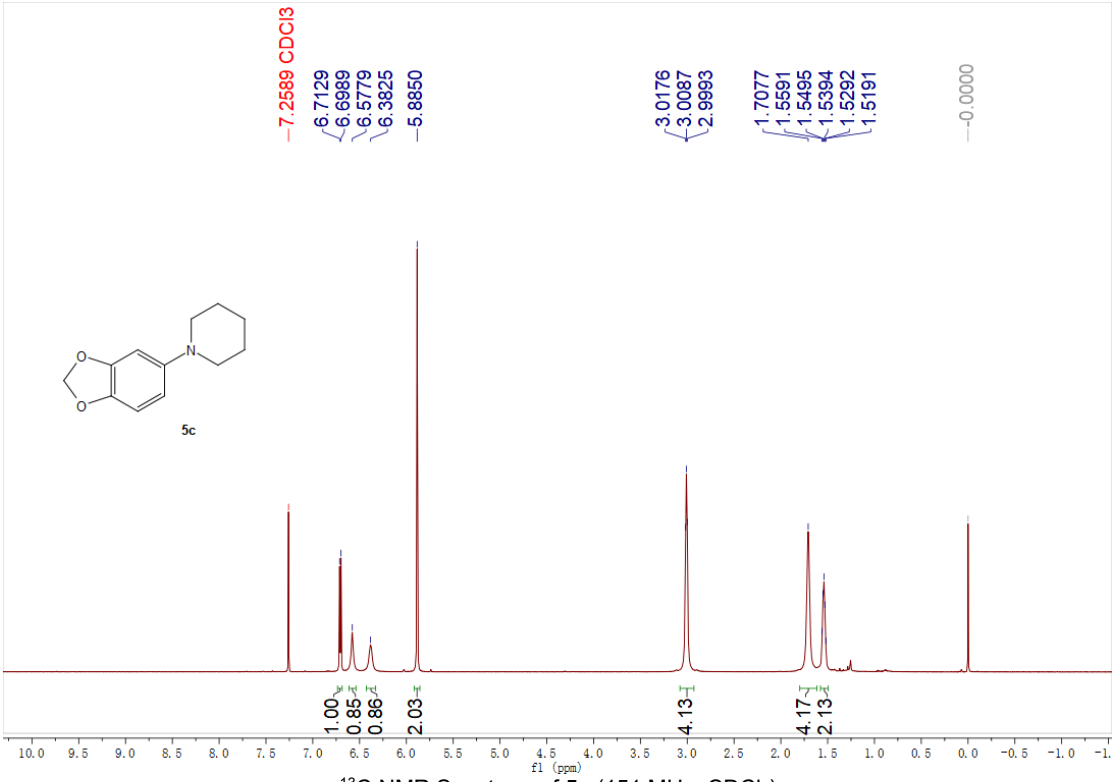
^{1}H NMR Spectrum of **5b** (400 MHz, $CDCl_3$)



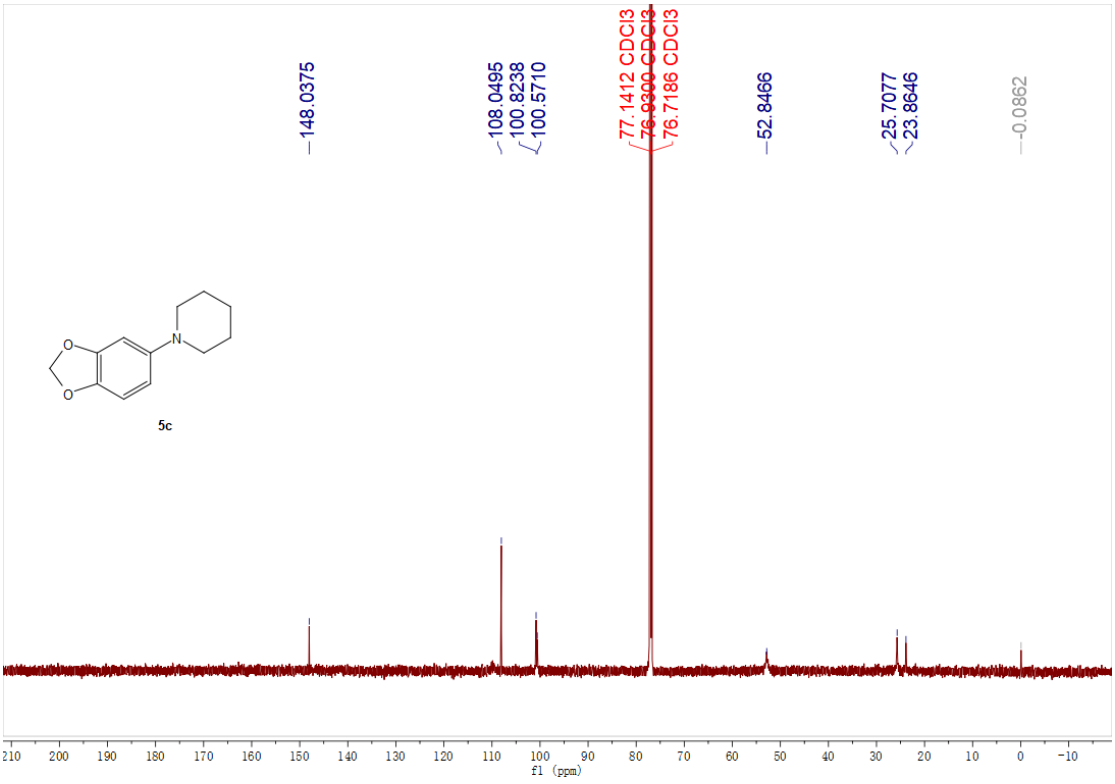
^{13}C NMR Spectrum of **5b** (101 MHz, $CDCl_3$)



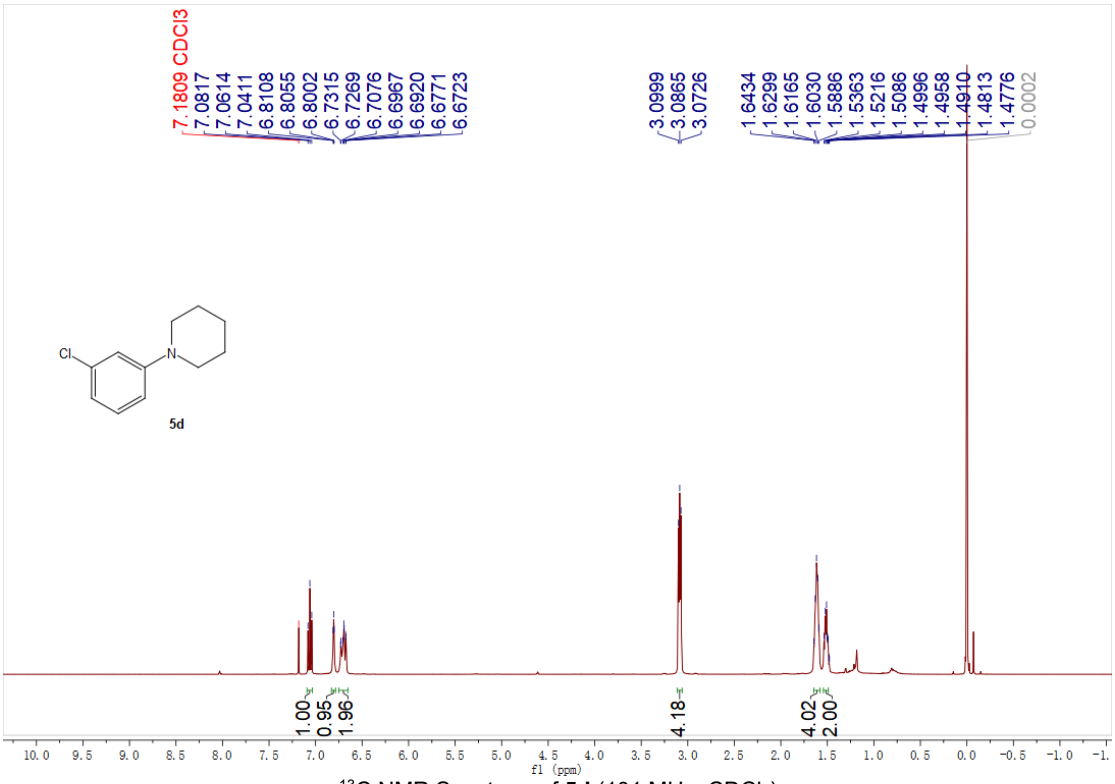
^{1}H NMR Spectrum of **5c** (600 MHz, $CDCl_3$)



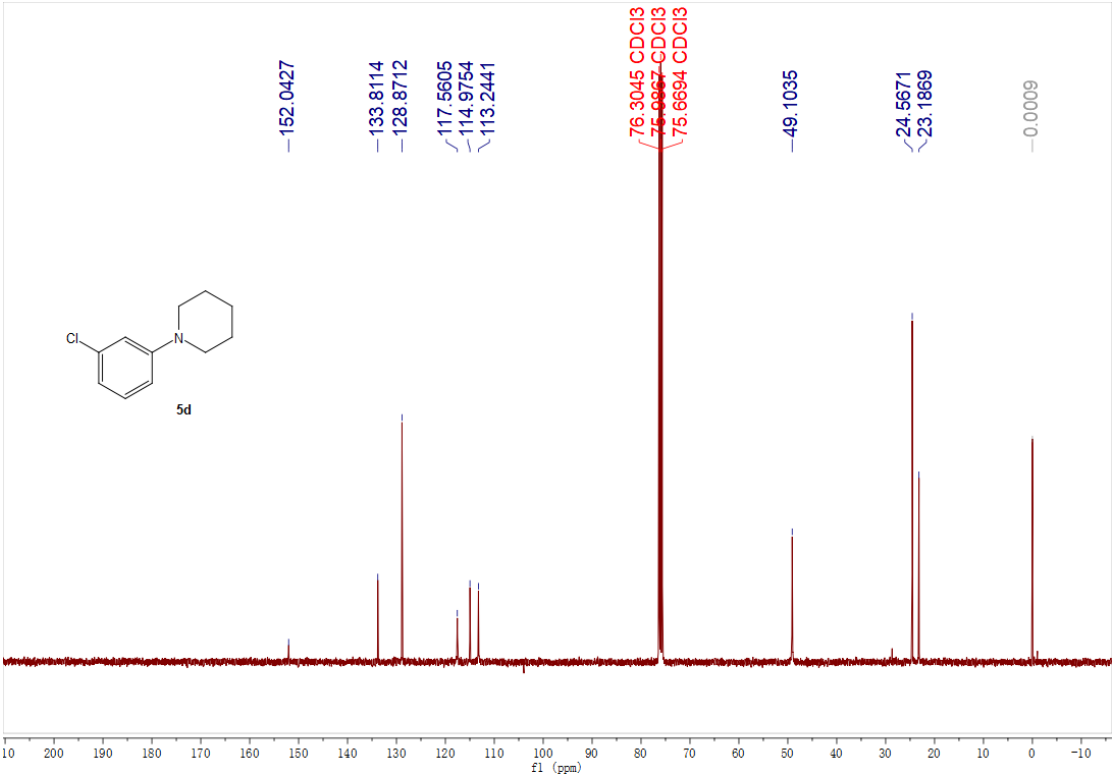
^{13}C NMR Spectrum of **5c** (151 MHz, $CDCl_3$)



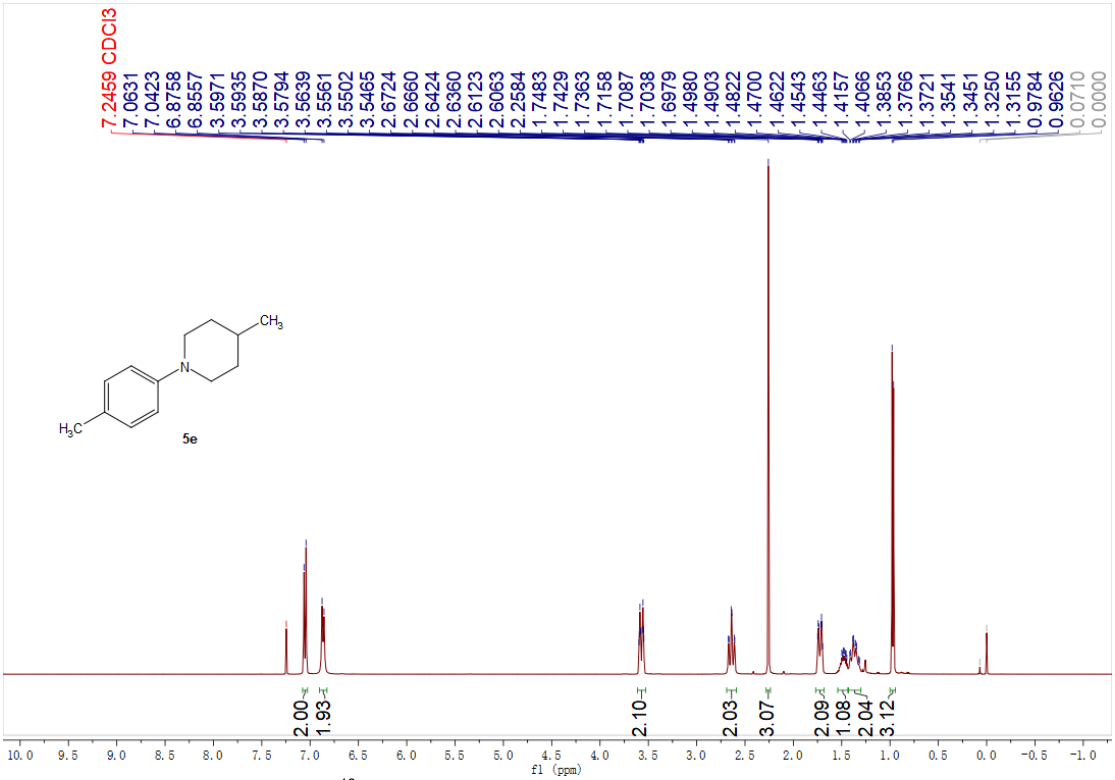
^{1}H NMR Spectrum of **5d** (400 MHz, $CDCl_3$)



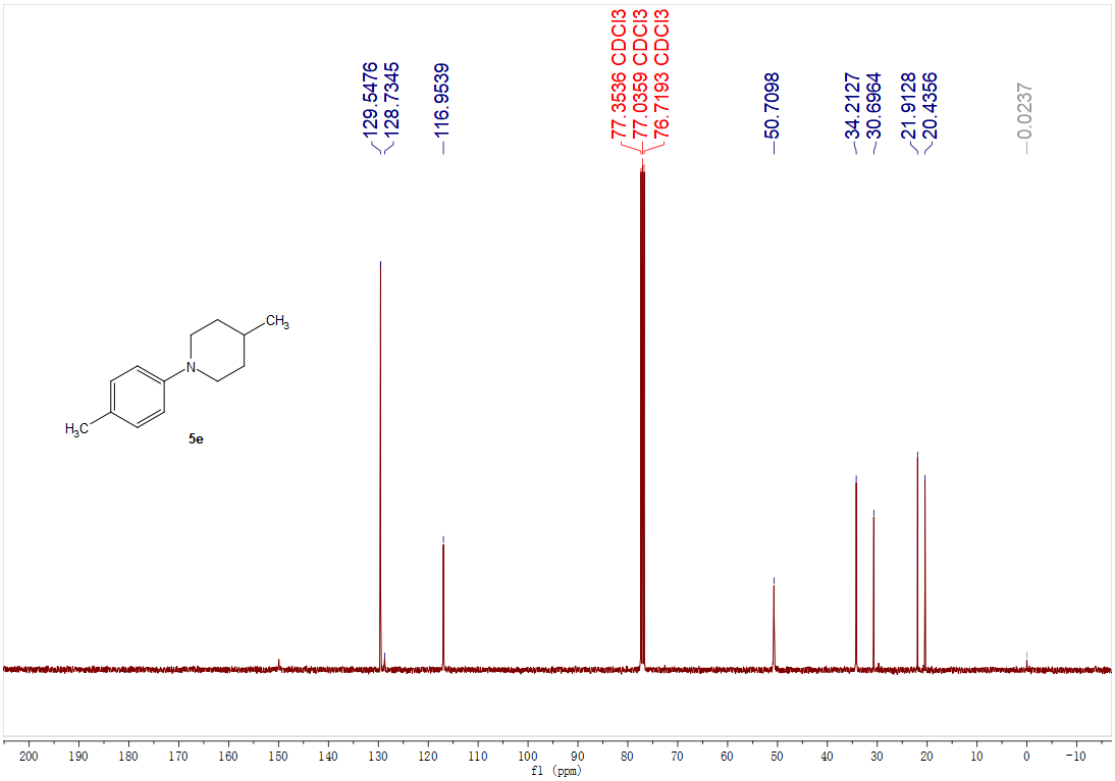
^{13}C NMR Spectrum of **5d** (101 MHz, $CDCl_3$)



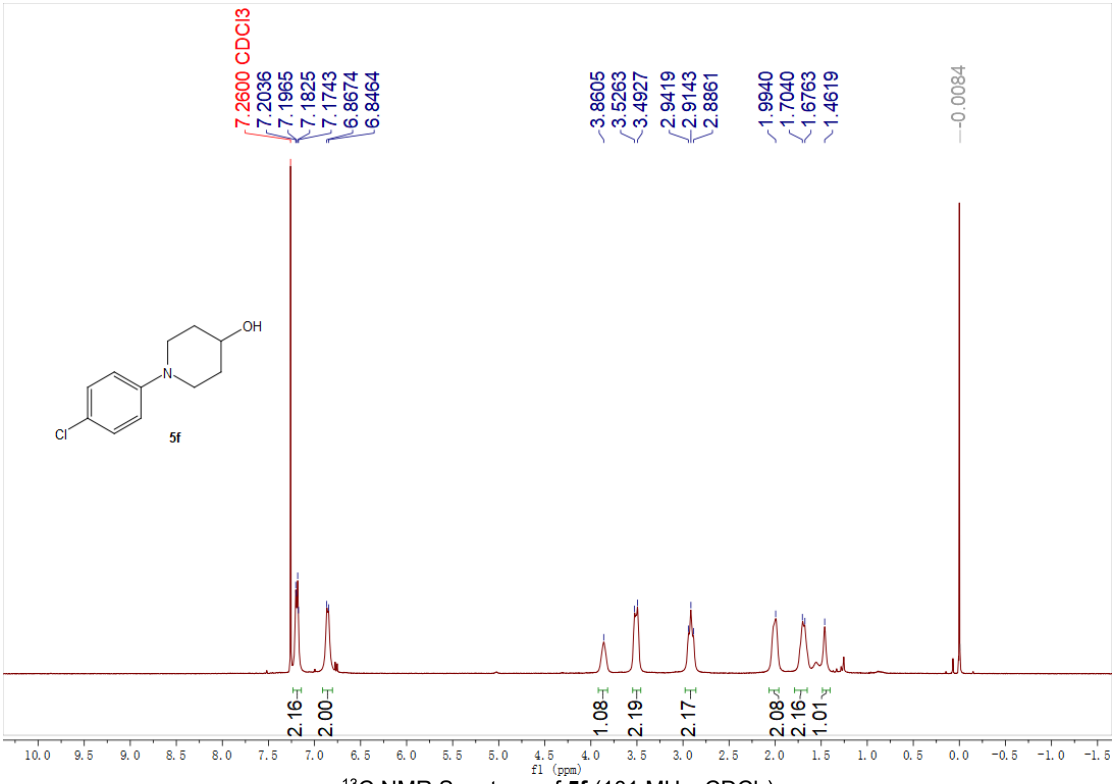
^{1}H NMR Spectrum of **5e** (400 MHz, $CDCl_3$)



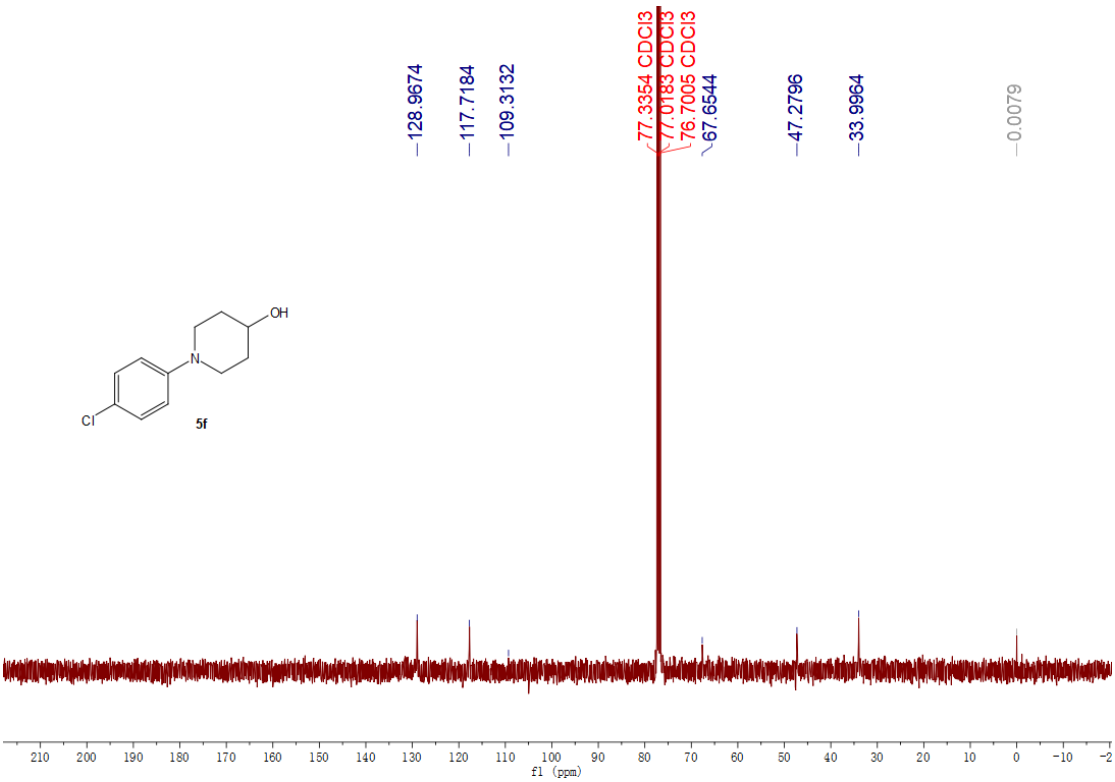
^{13}C NMR Spectrum of **5e** (101 MHz, $CDCl_3$)



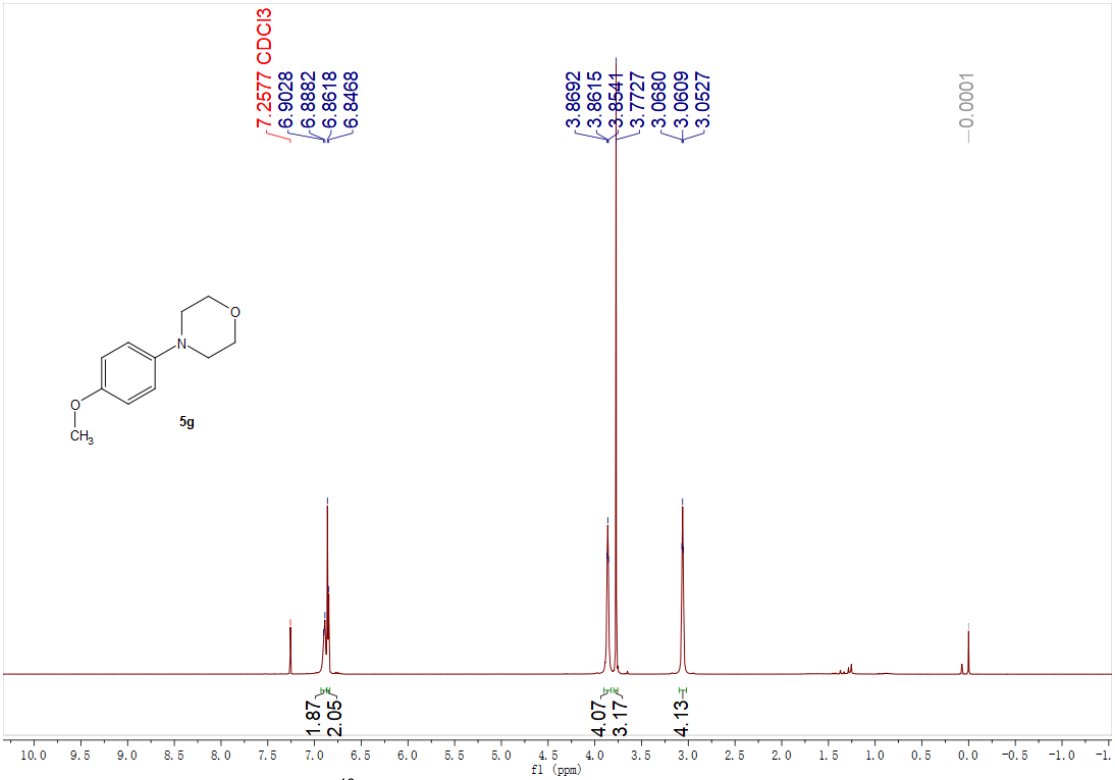
^{1}H NMR Spectrum of **5f** (400 MHz, $CDCl_3$)



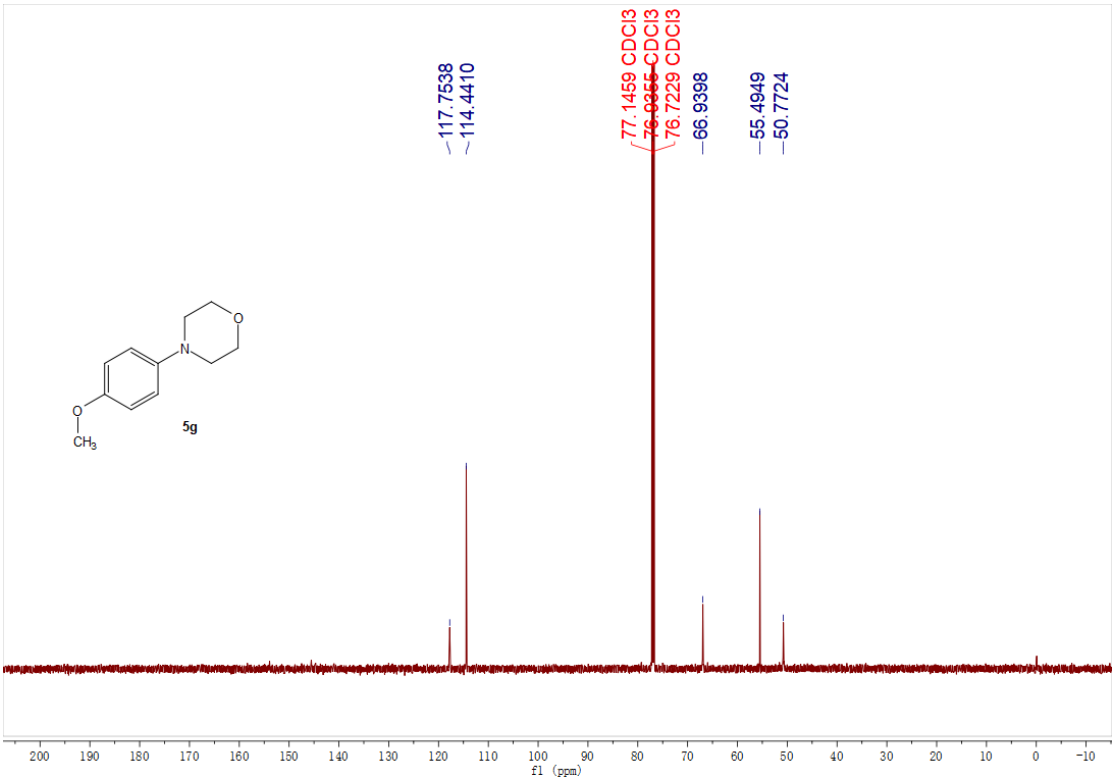
^{13}C NMR Spectrum of **5f** (101 MHz, $CDCl_3$)



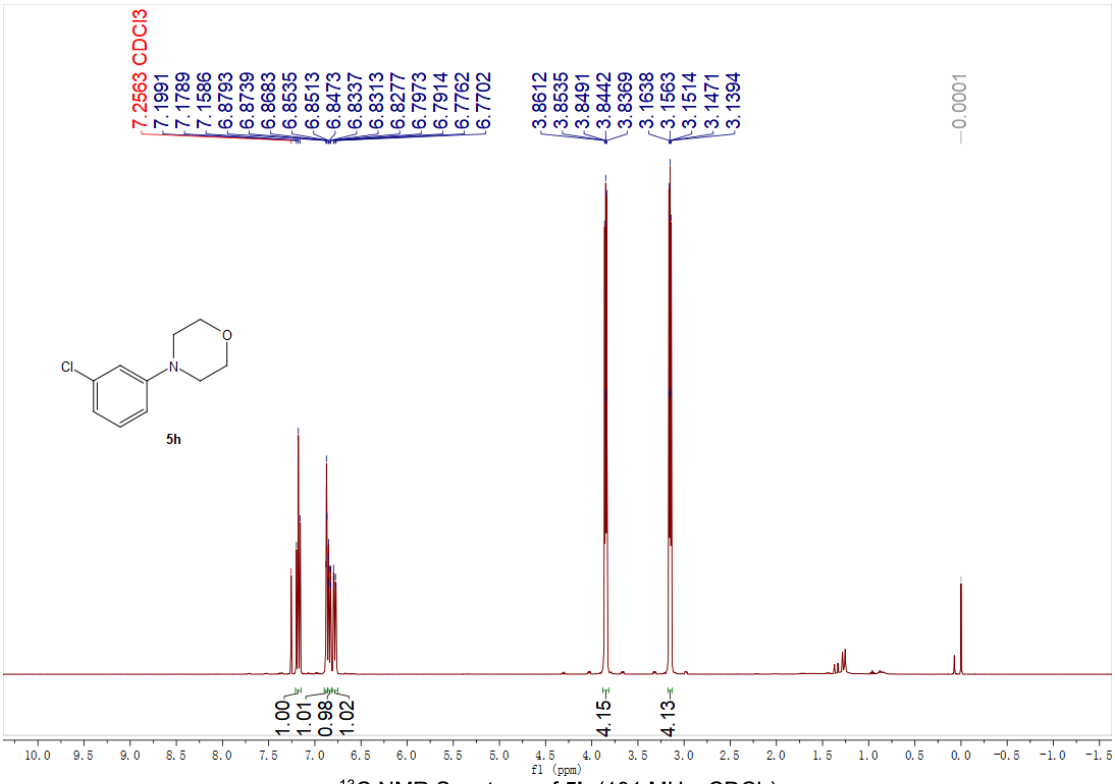
^{1}H NMR Spectrum of **5g** (600 MHz, $CDCl_3$)



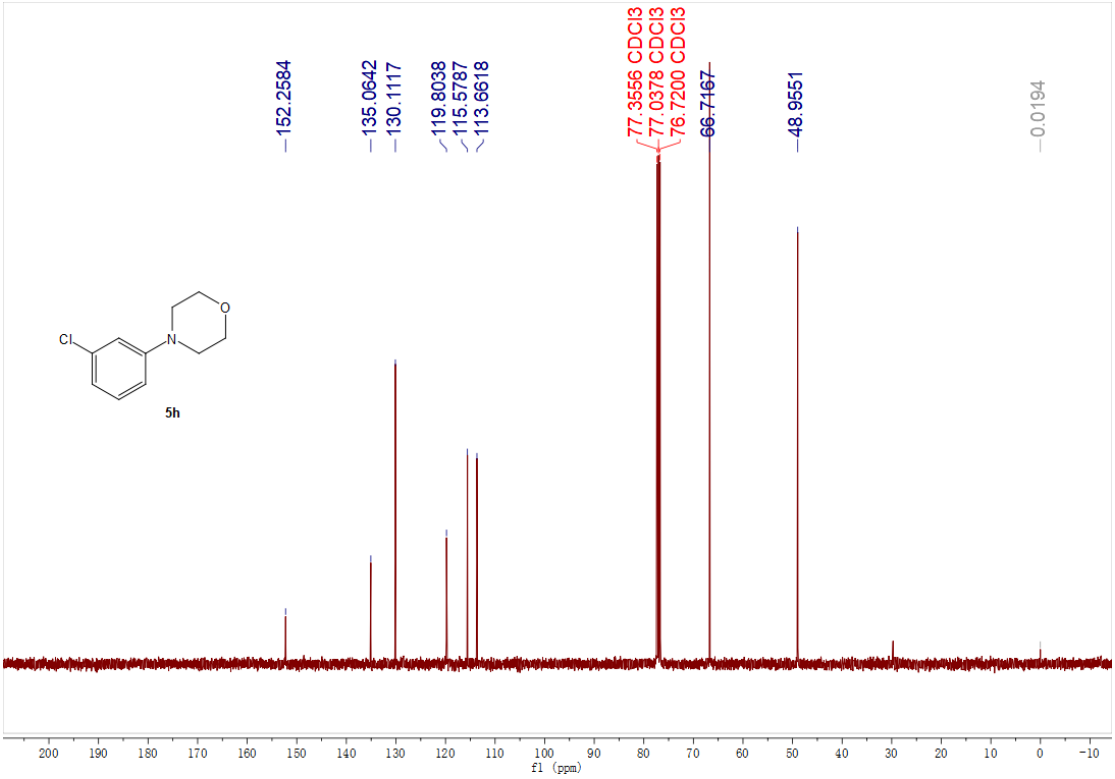
^{13}C NMR Spectrum of **5g** (151 MHz, $CDCl_3$)



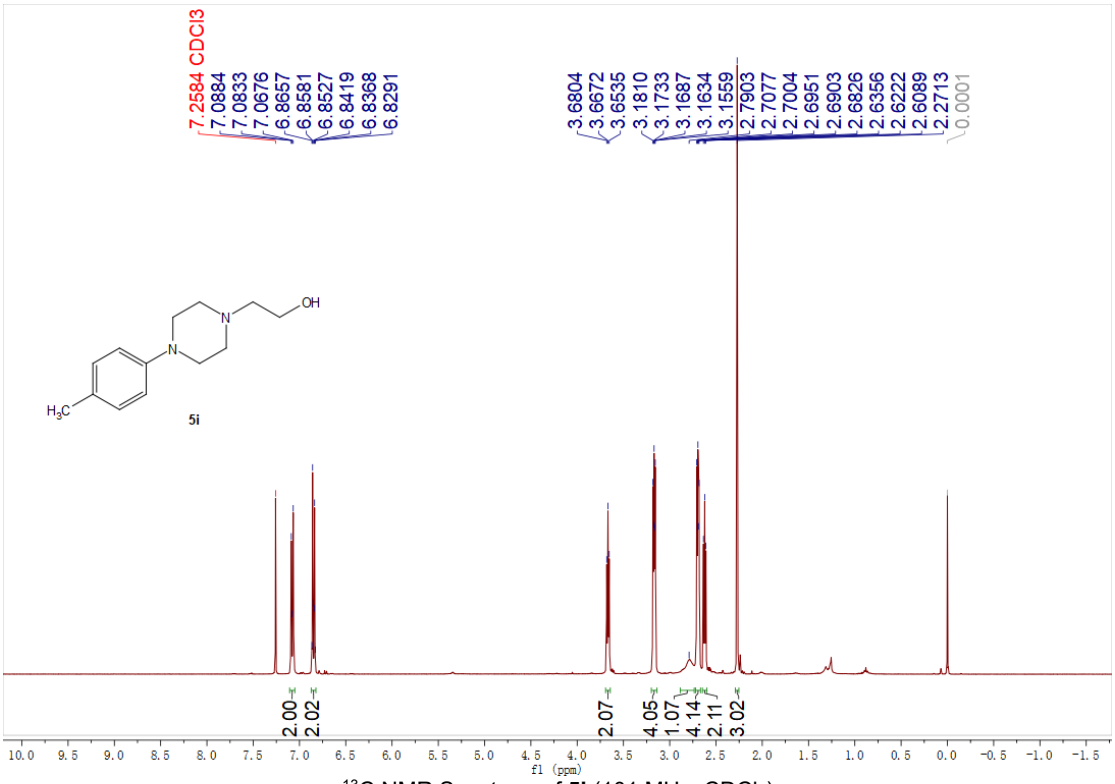
^{1}H NMR Spectrum of **5h** (400 MHz, $CDCl_3$)



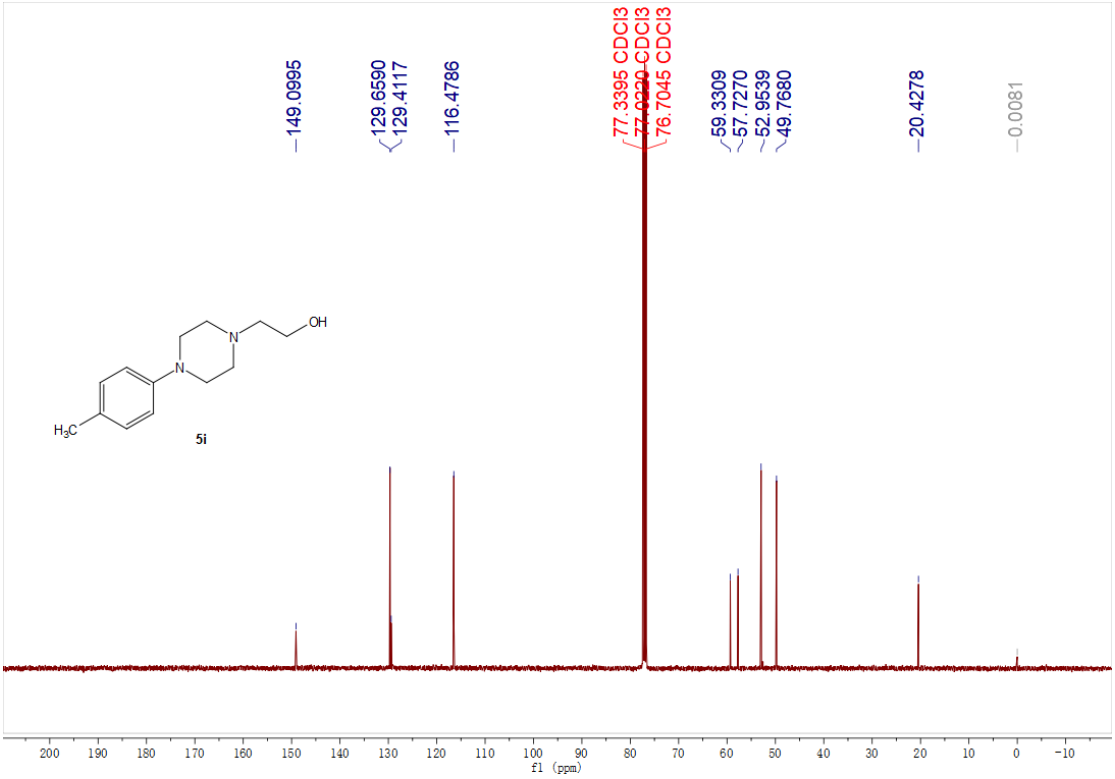
^{13}C NMR Spectrum of **5h** (101 MHz, $CDCl_3$)



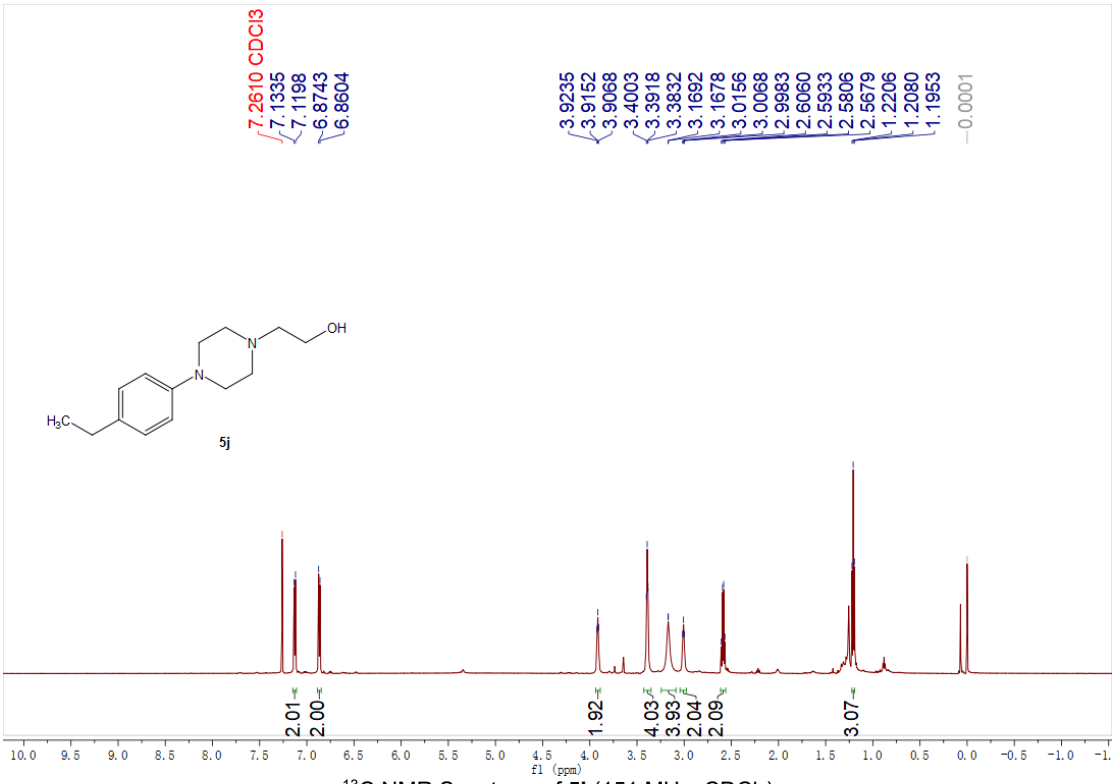
^{1}H NMR Spectrum of **5i** (400 MHz, $CDCl_3$)



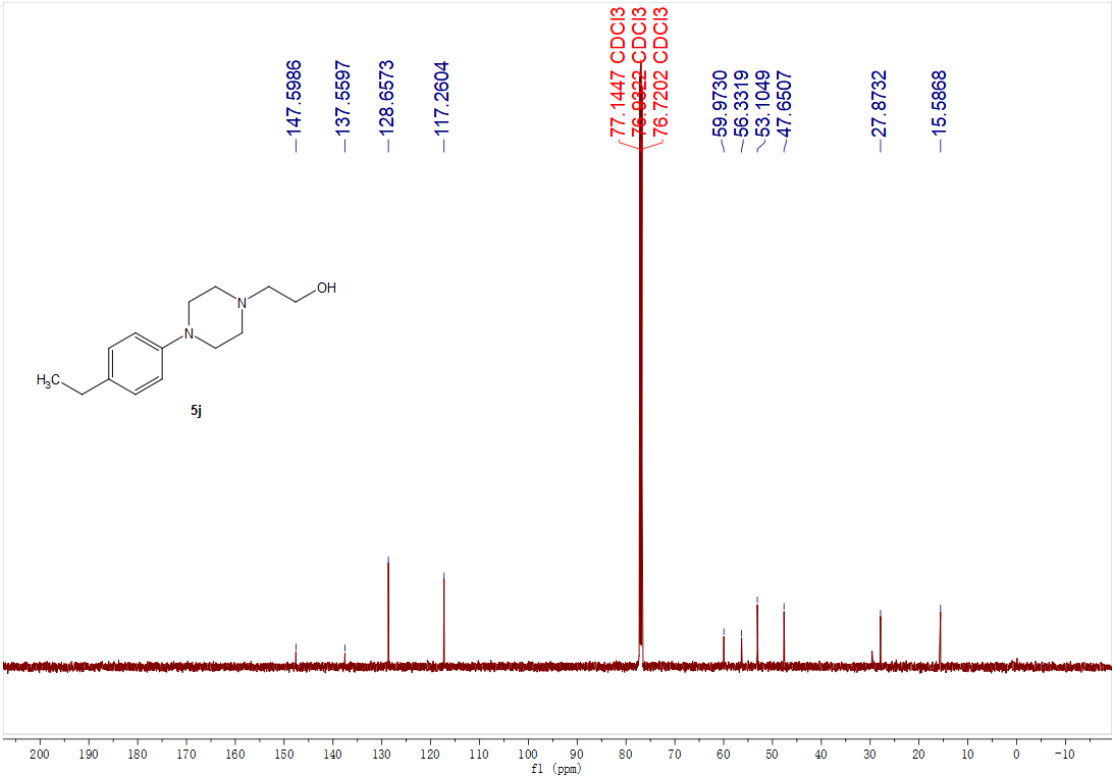
^{13}C NMR Spectrum of **5i** (101 MHz, $CDCl_3$)



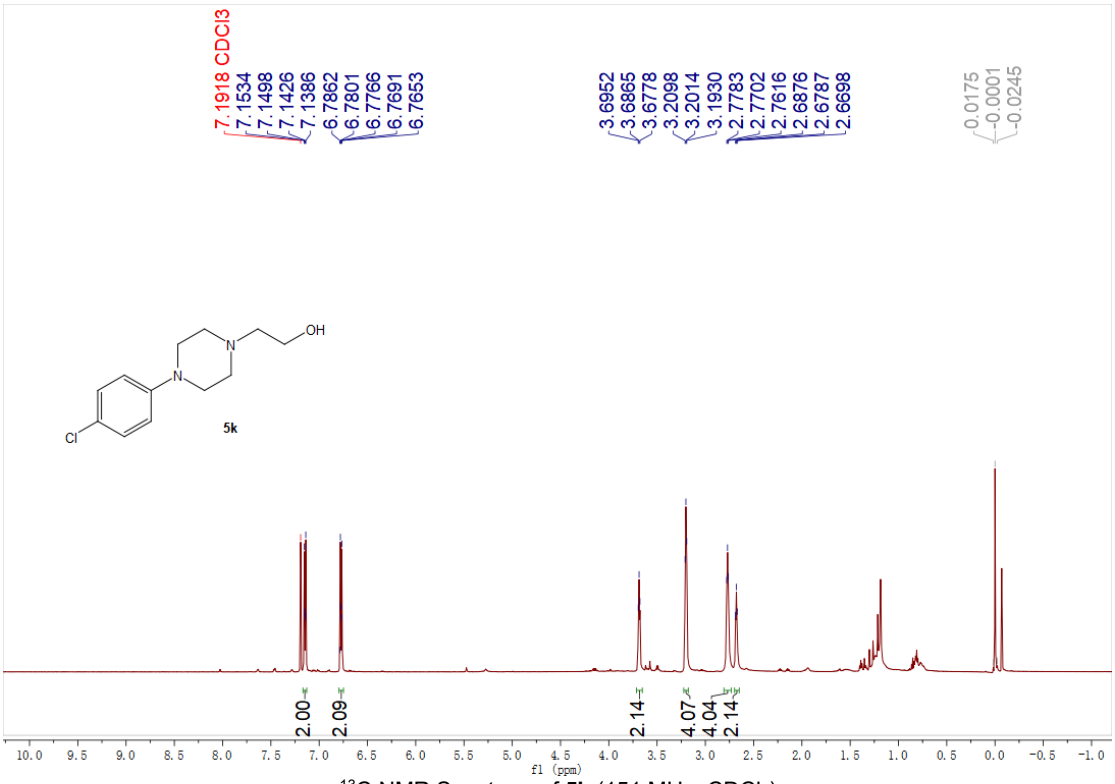
^{1}H NMR Spectrum of **5j** (600 MHz, $CDCl_3$)



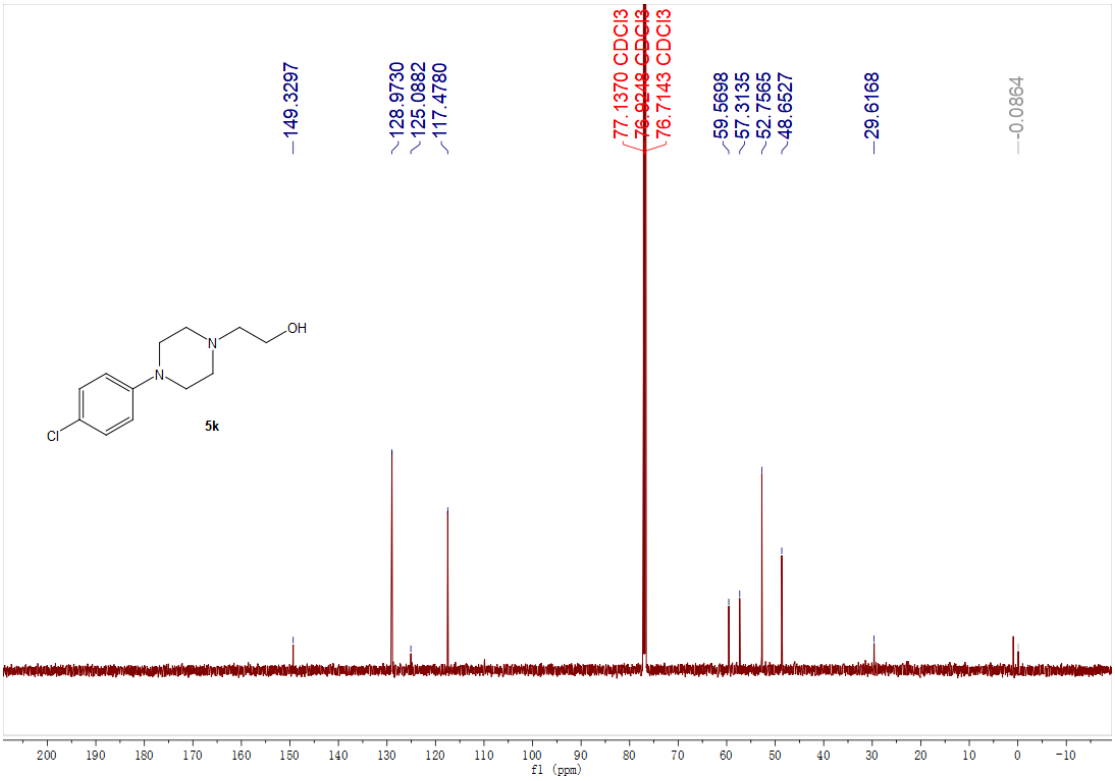
^{13}C NMR Spectrum of **5j** (151 MHz, $CDCl_3$)



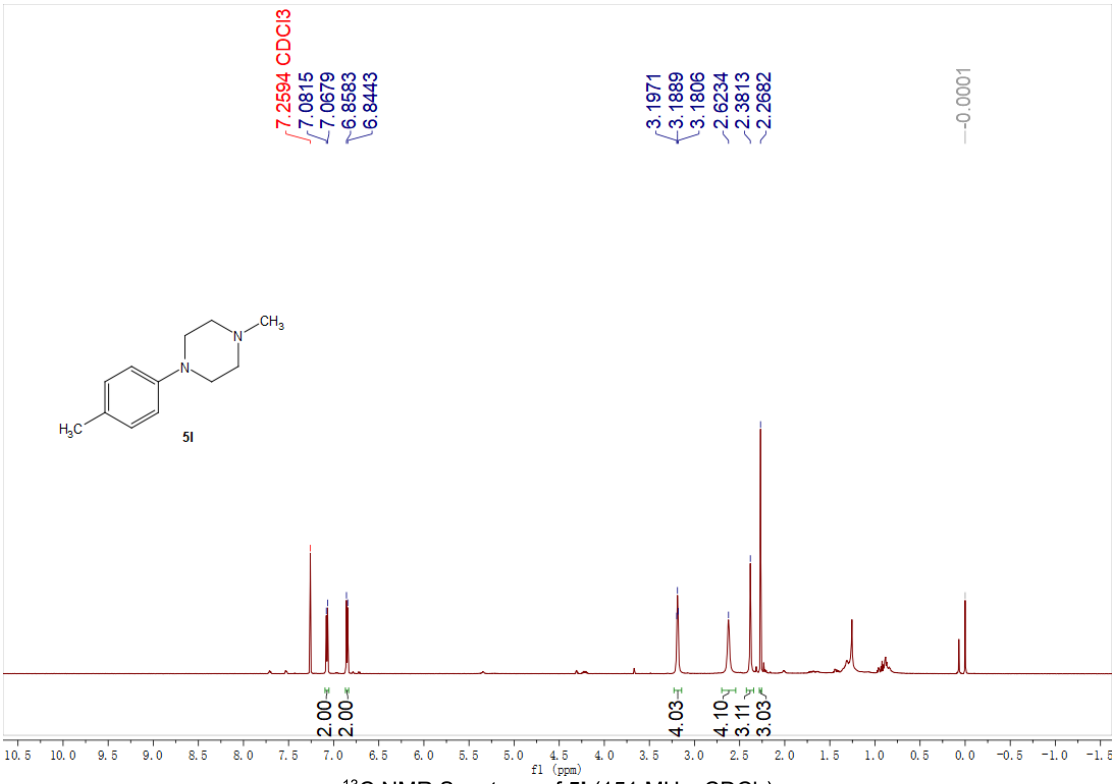
^{1}H NMR Spectrum of **5k** (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **5k** (151 MHz, $CDCl_3$)

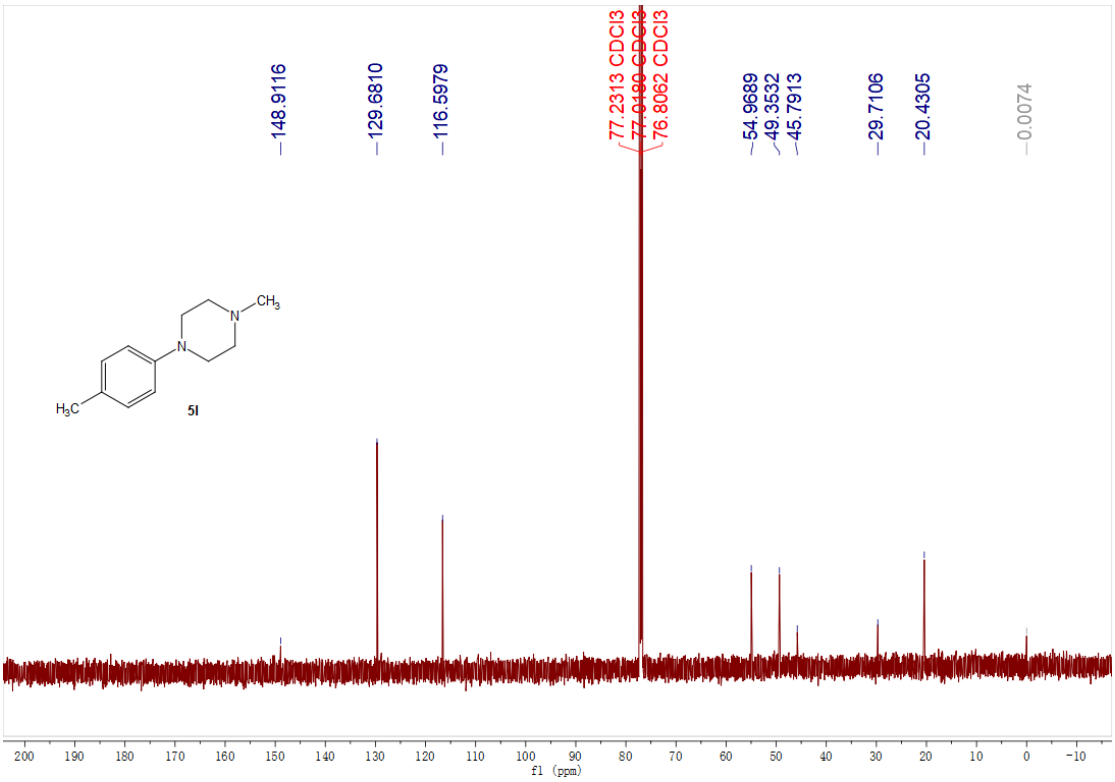


^{1}H NMR Spectrum of **5l** (600 MHz, $CDCl_3$)



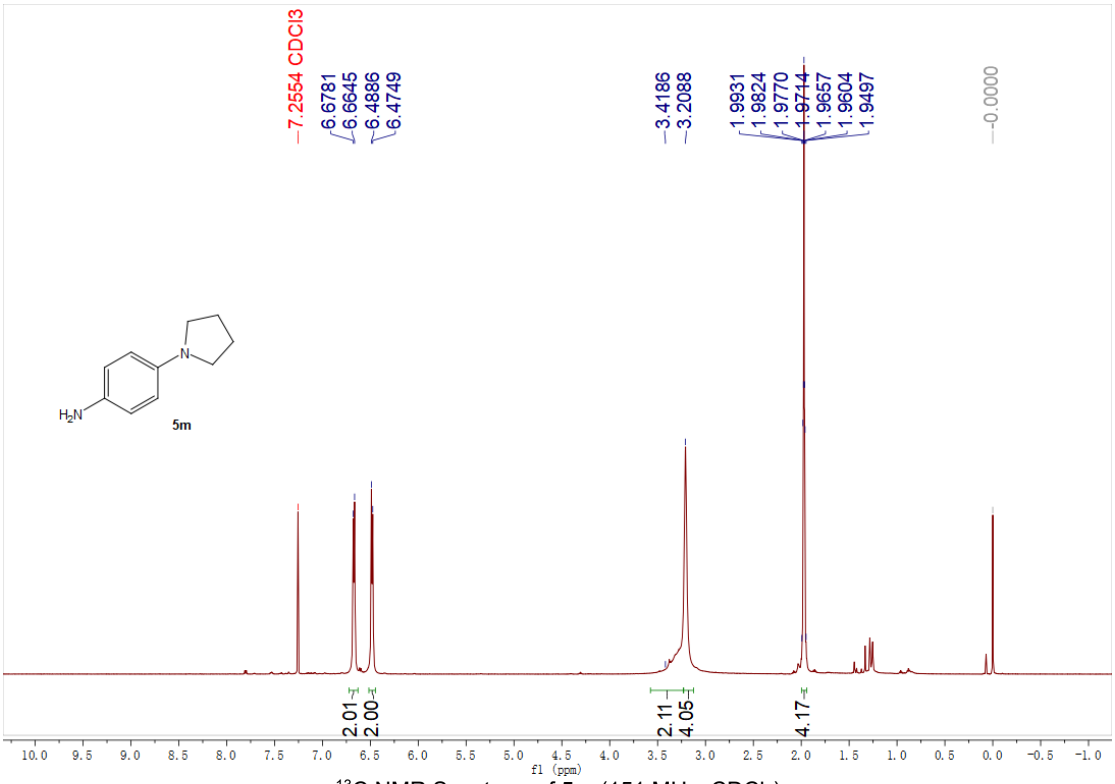
5l

^{13}C NMR Spectrum of **5l** (151 MHz, $CDCl_3$)

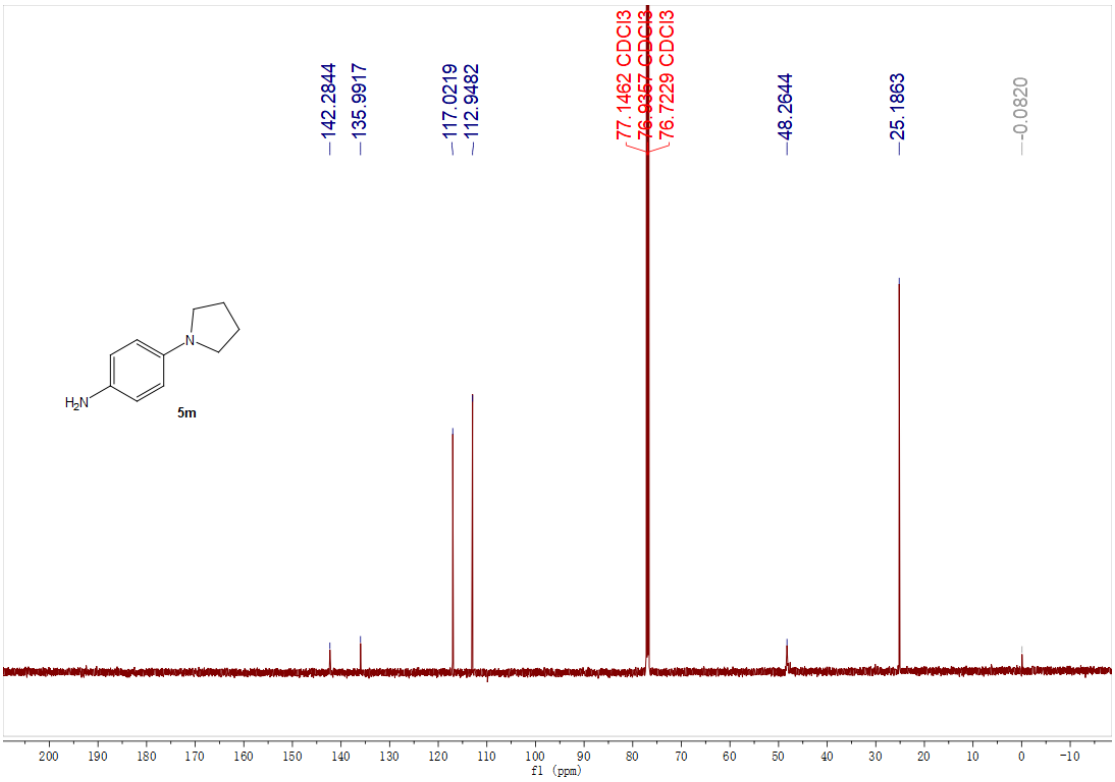


5l

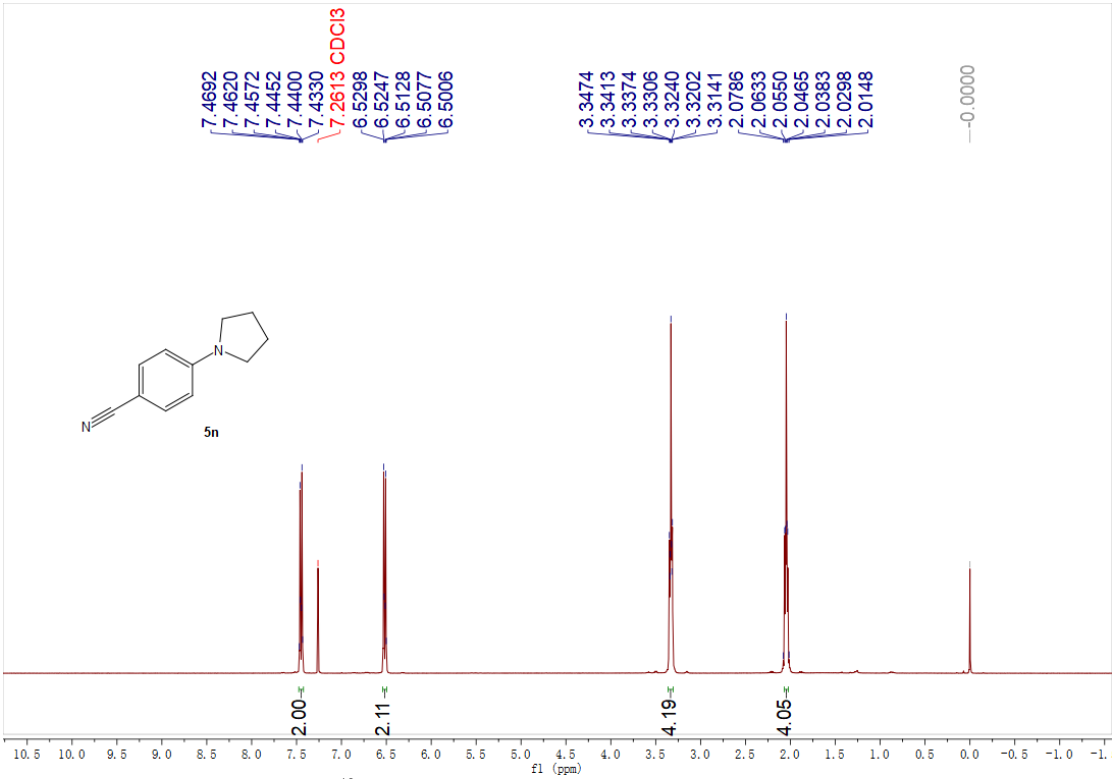
^{1}H NMR Spectrum of **5m** (600 MHz, $CDCl_3$)



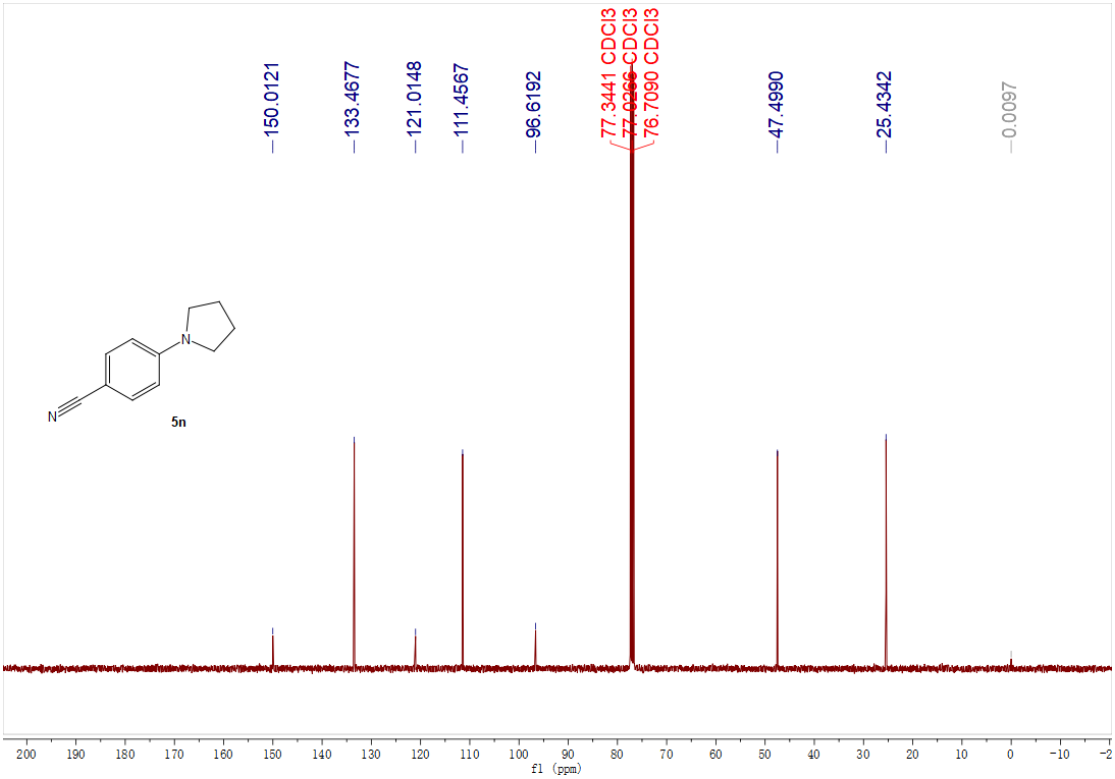
^{13}C NMR Spectrum of **5m** (151 MHz, $CDCl_3$)



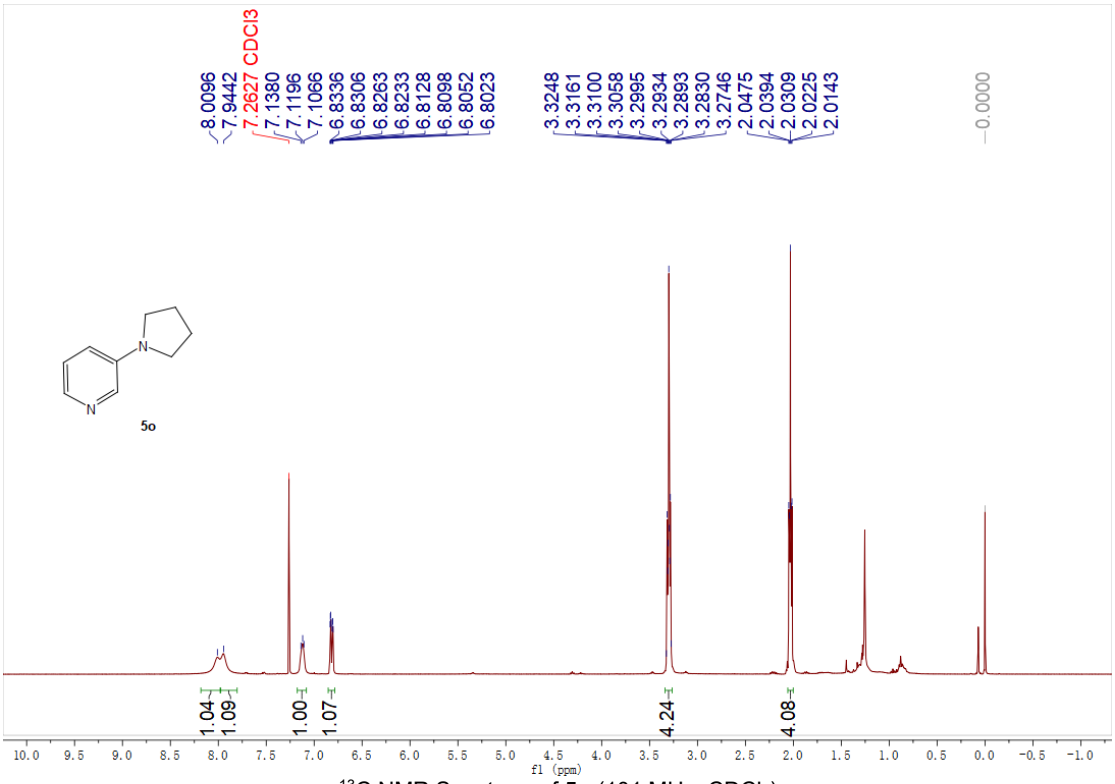
^{1}H NMR Spectrum of **5n** (400 MHz, $CDCl_3$)



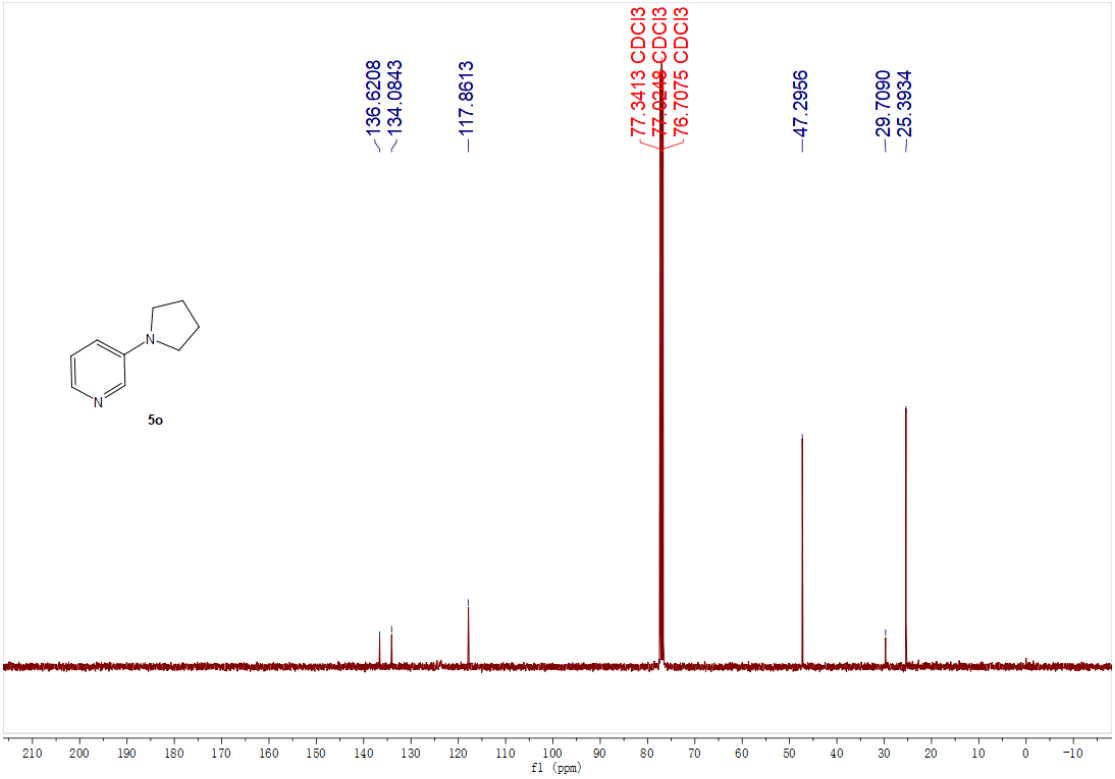
^{13}C NMR Spectrum of **5n** (101 MHz, $CDCl_3$)



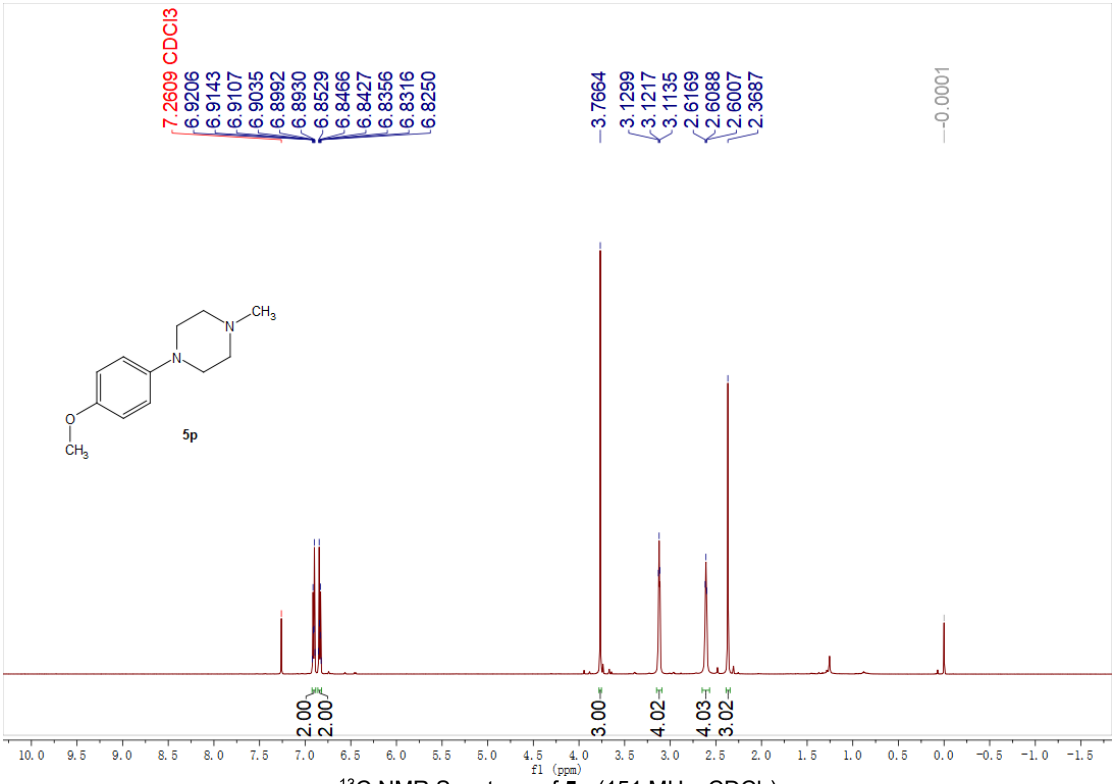
^{1}H NMR Spectrum of **5o** (400 MHz, $CDCl_3$)



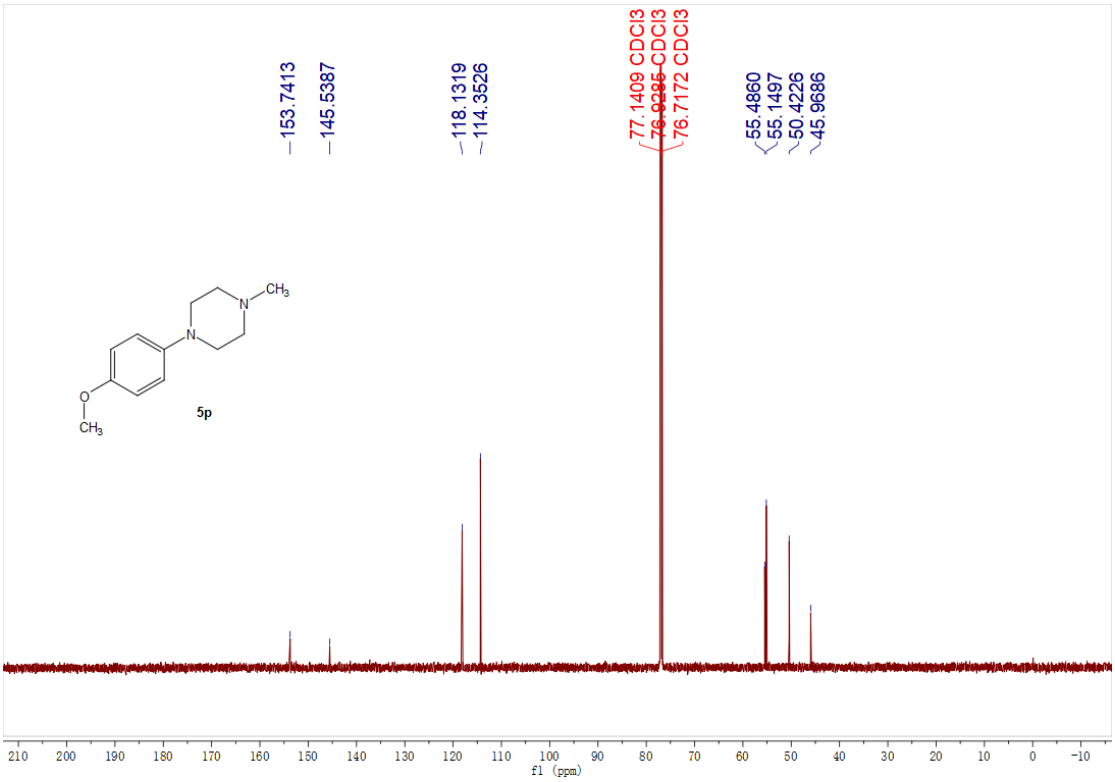
^{13}C NMR Spectrum of **5o** (101 MHz, $CDCl_3$)



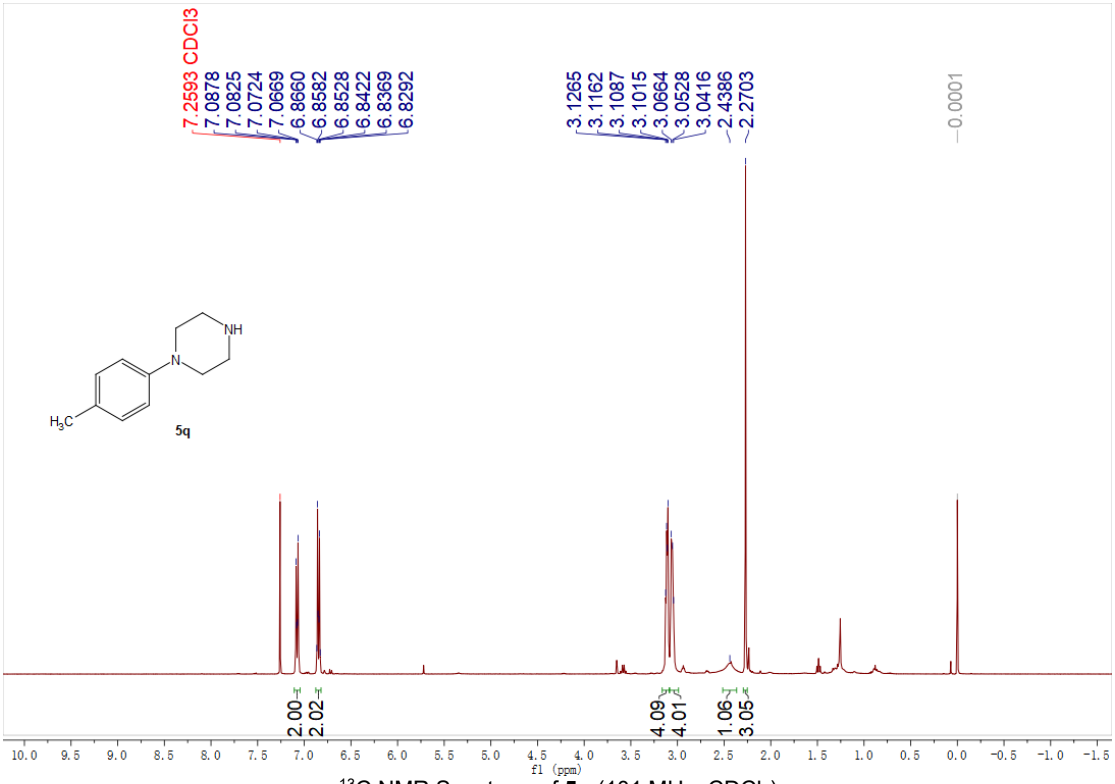
^{1}H NMR Spectrum of **5p** (600 MHz, $CDCl_3$)



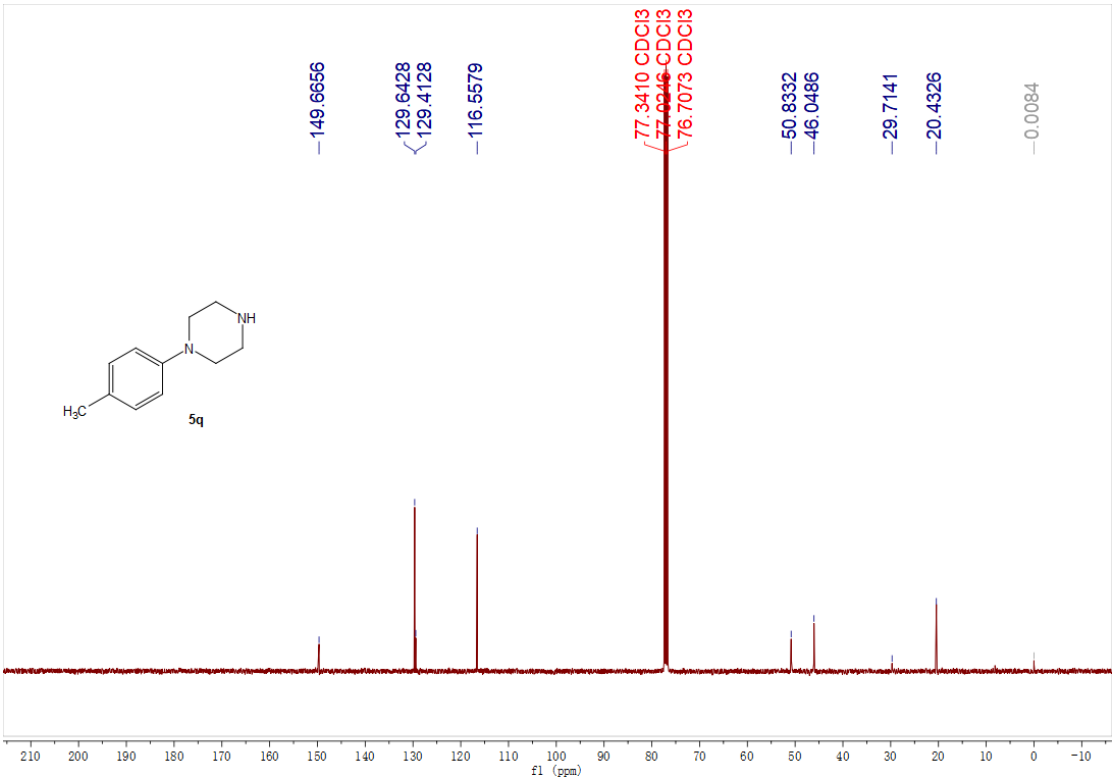
^{13}C NMR Spectrum of **5p** (151 MHz, $CDCl_3$)



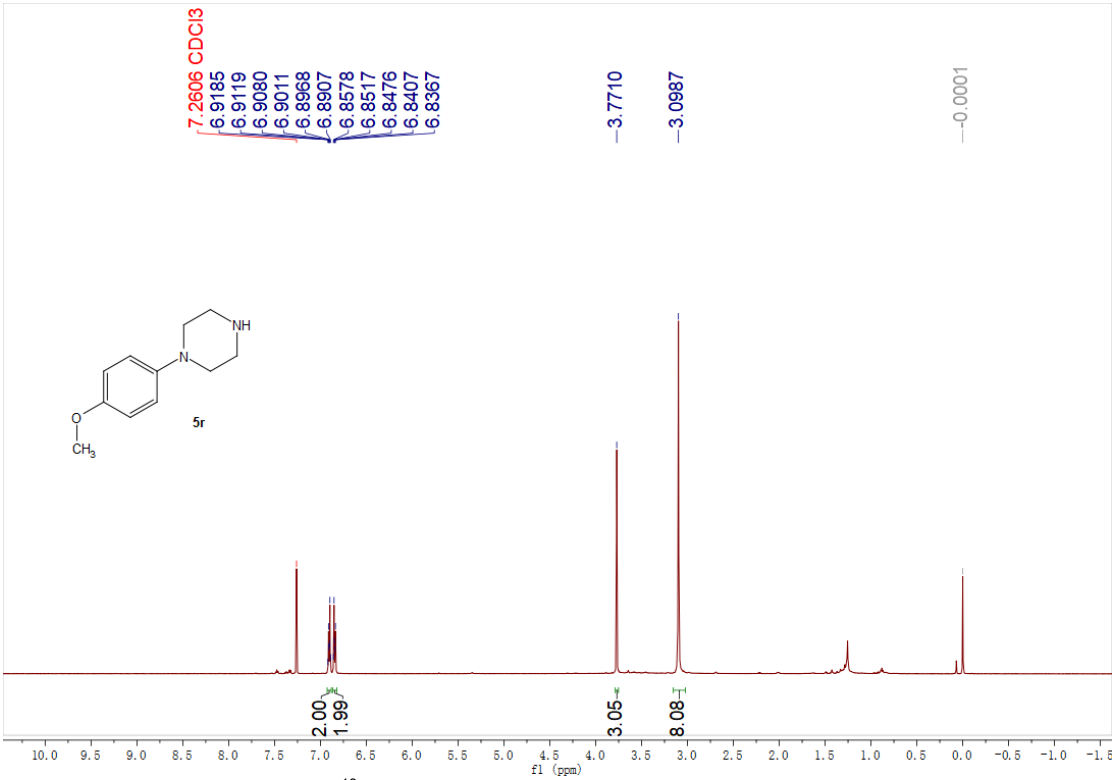
^{1}H NMR Spectrum of **5q** (400 MHz, $CDCl_3$)



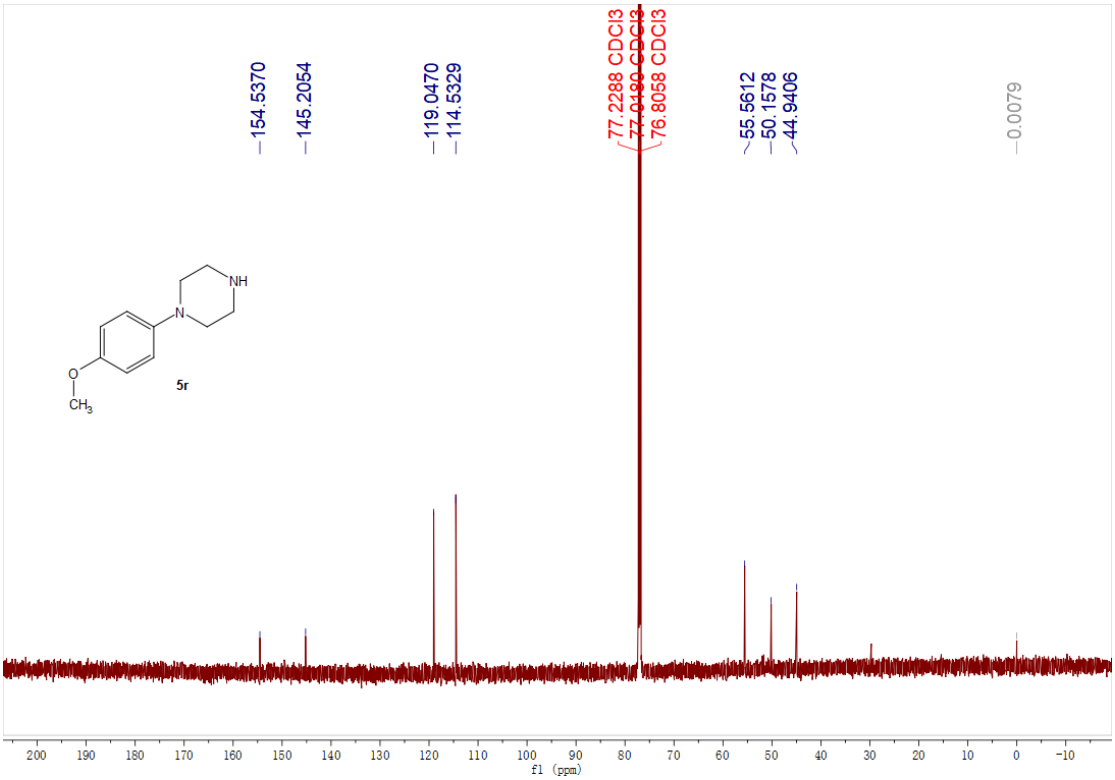
^{13}C NMR Spectrum of **5q** (101 MHz, $CDCl_3$)



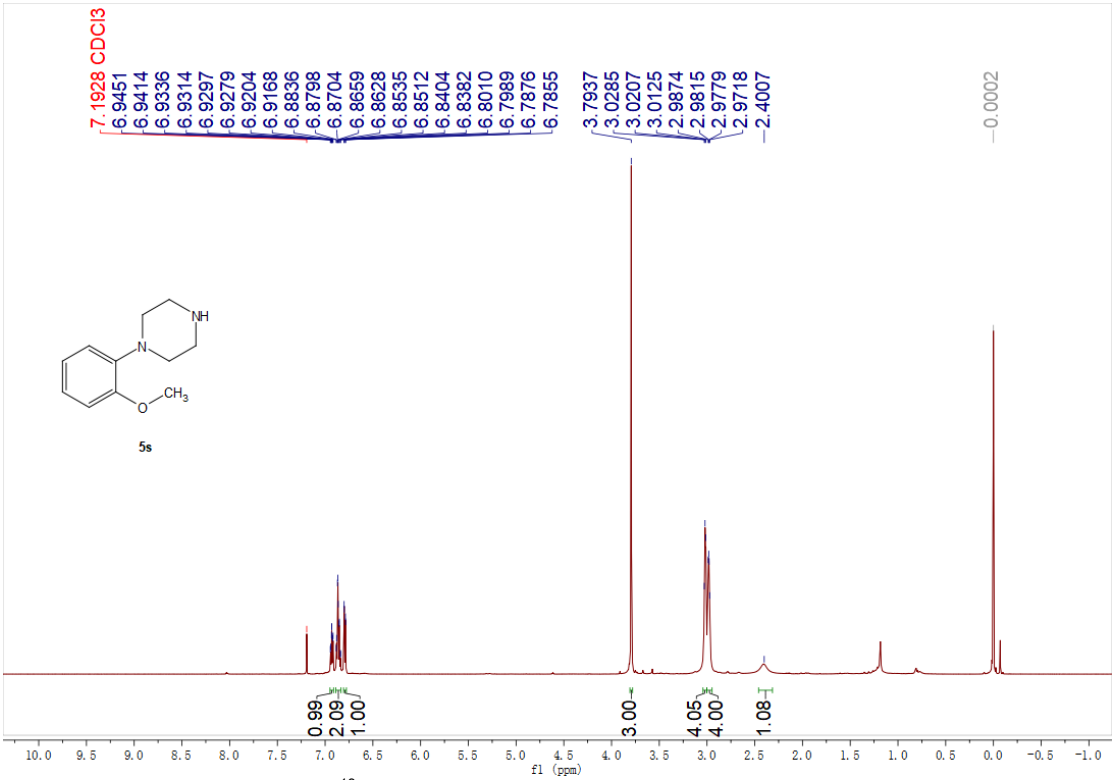
^{1}H NMR Spectrum of **5r** (600 MHz, $CDCl_3$)



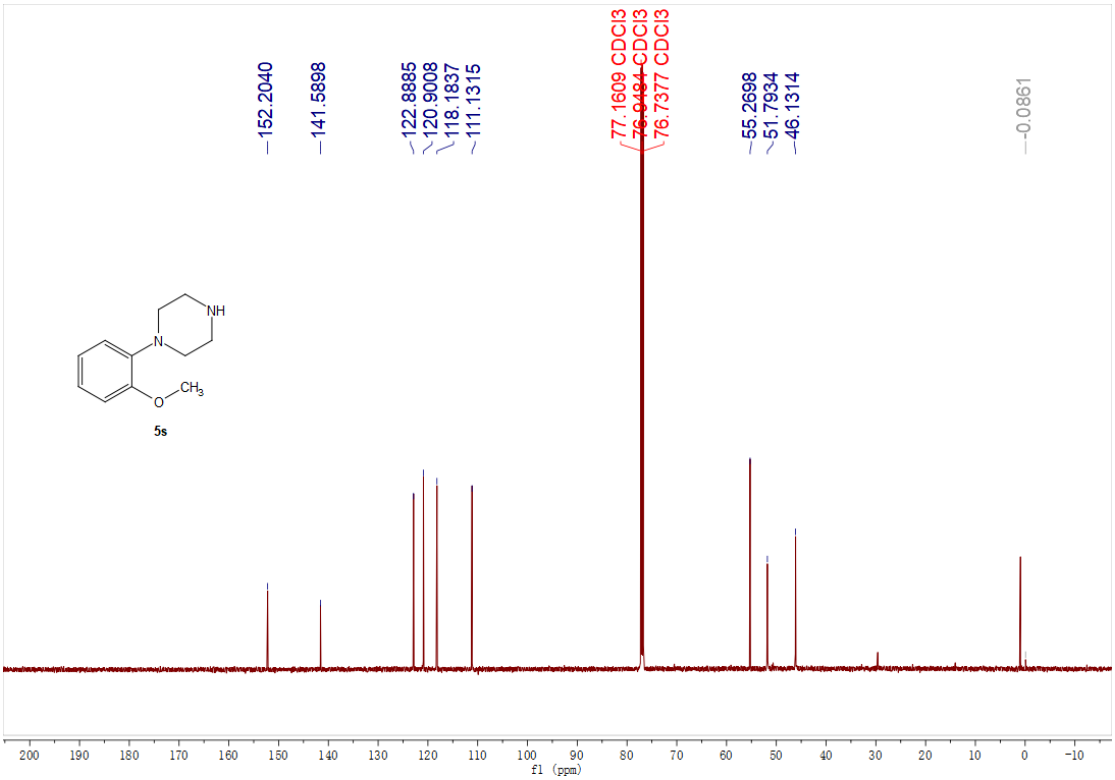
^{13}C NMR Spectrum of **5r** (151 MHz, $CDCl_3$)



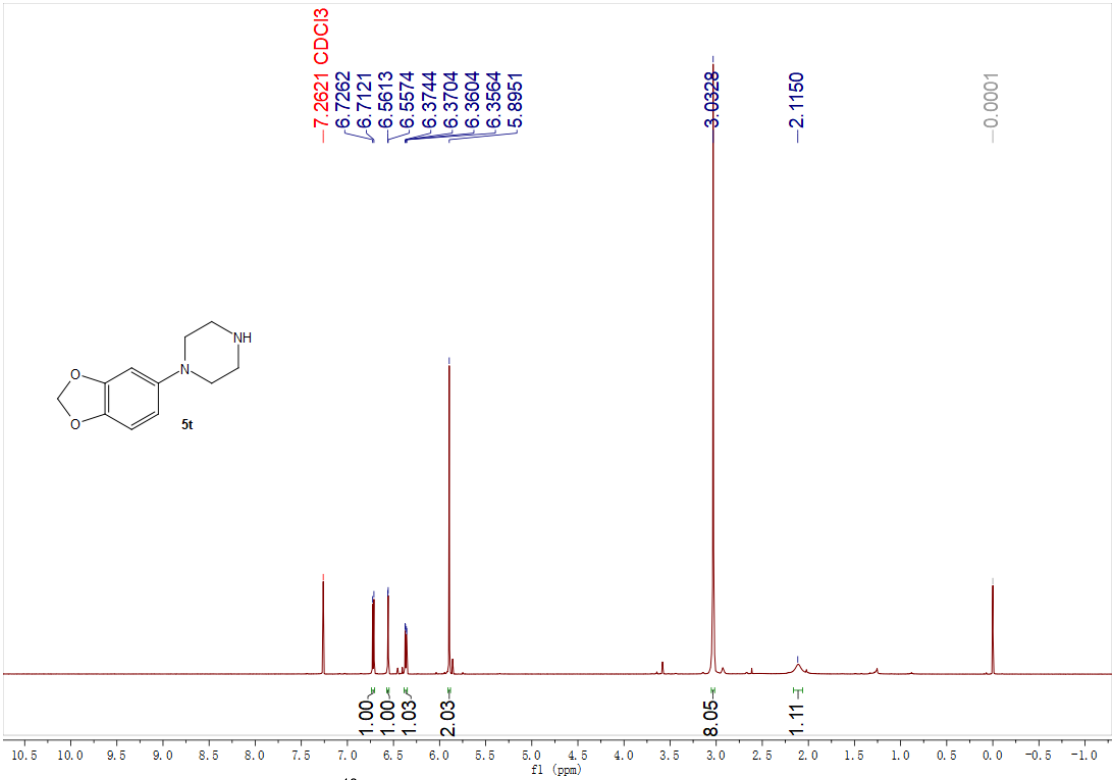
^{1}H NMR Spectrum of **5s** (600 MHz, $CDCl_3$)



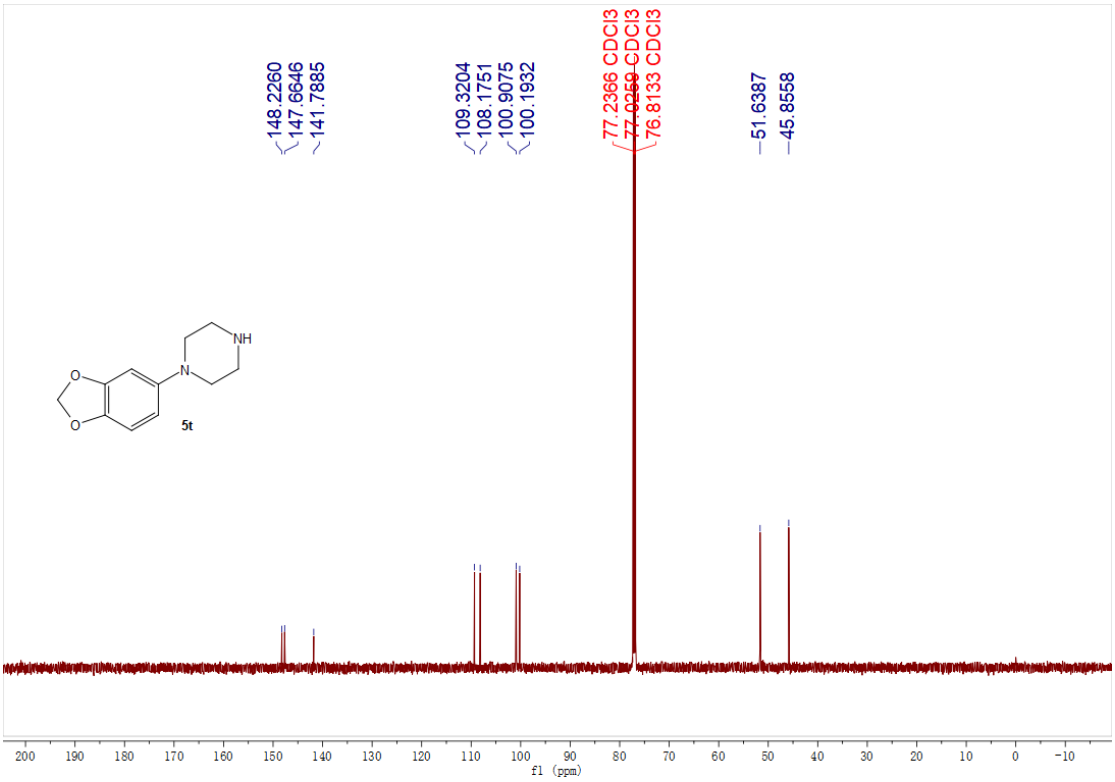
^{13}C NMR Spectrum of **5s** (151 MHz, $CDCl_3$)



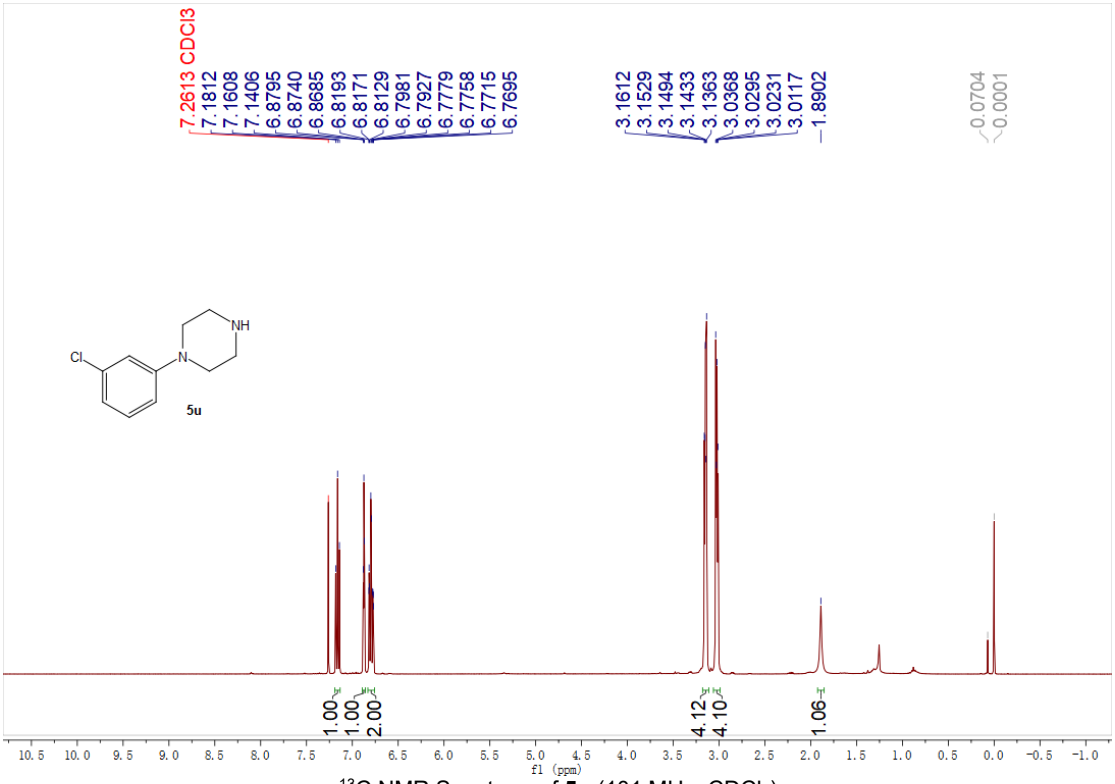
^{1}H NMR Spectrum of **5t** (600 MHz, $CDCl_3$)



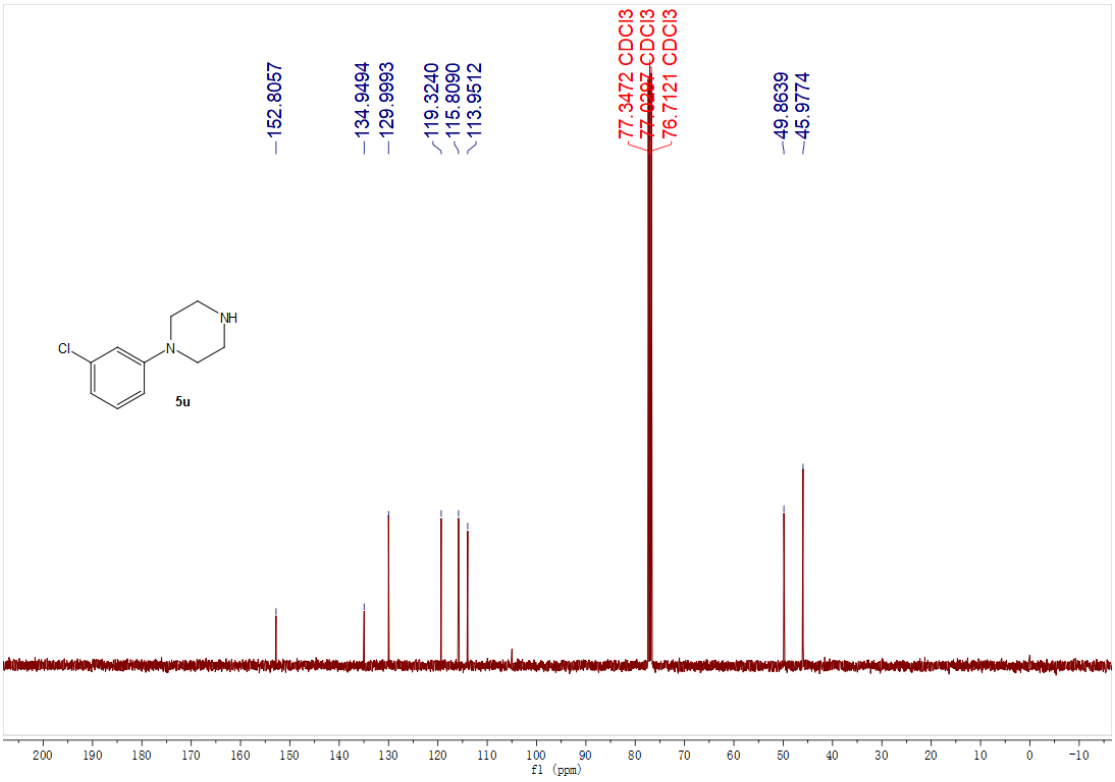
^{13}C NMR Spectrum of **5t** (151 MHz, $CDCl_3$)



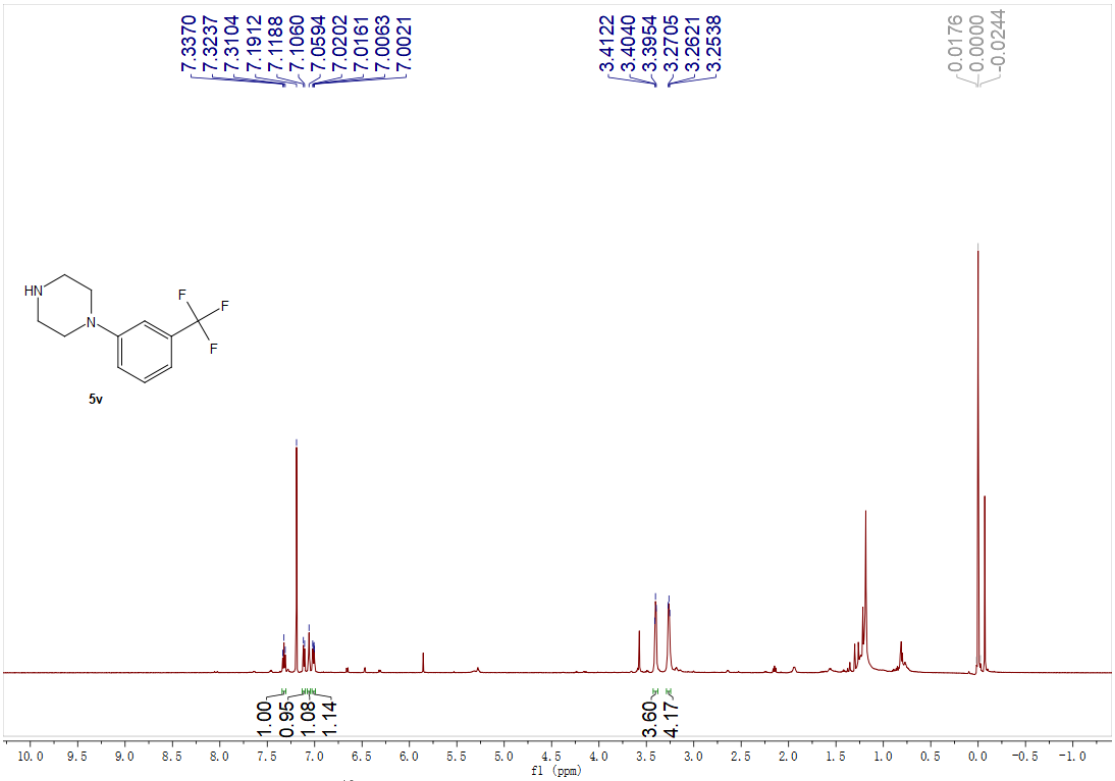
^{1}H NMR Spectrum of **5u** (400 MHz, $CDCl_3$)



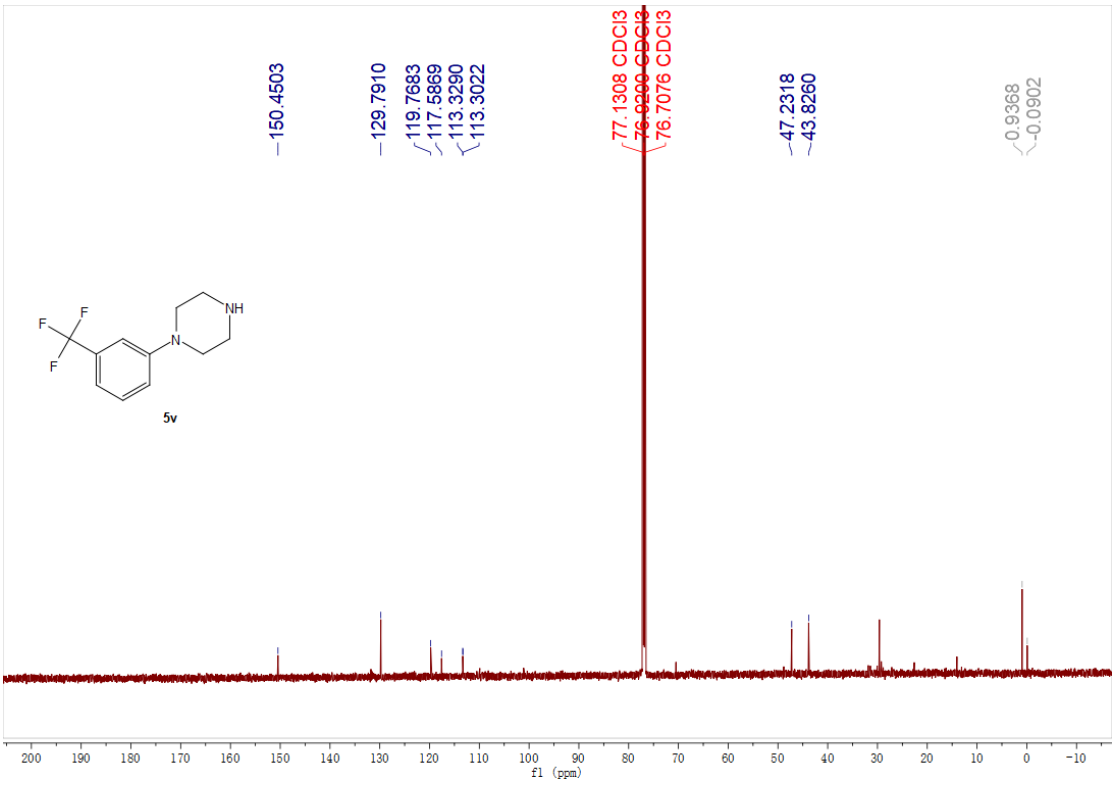
^{13}C NMR Spectrum of **5u** (101 MHz, $CDCl_3$)



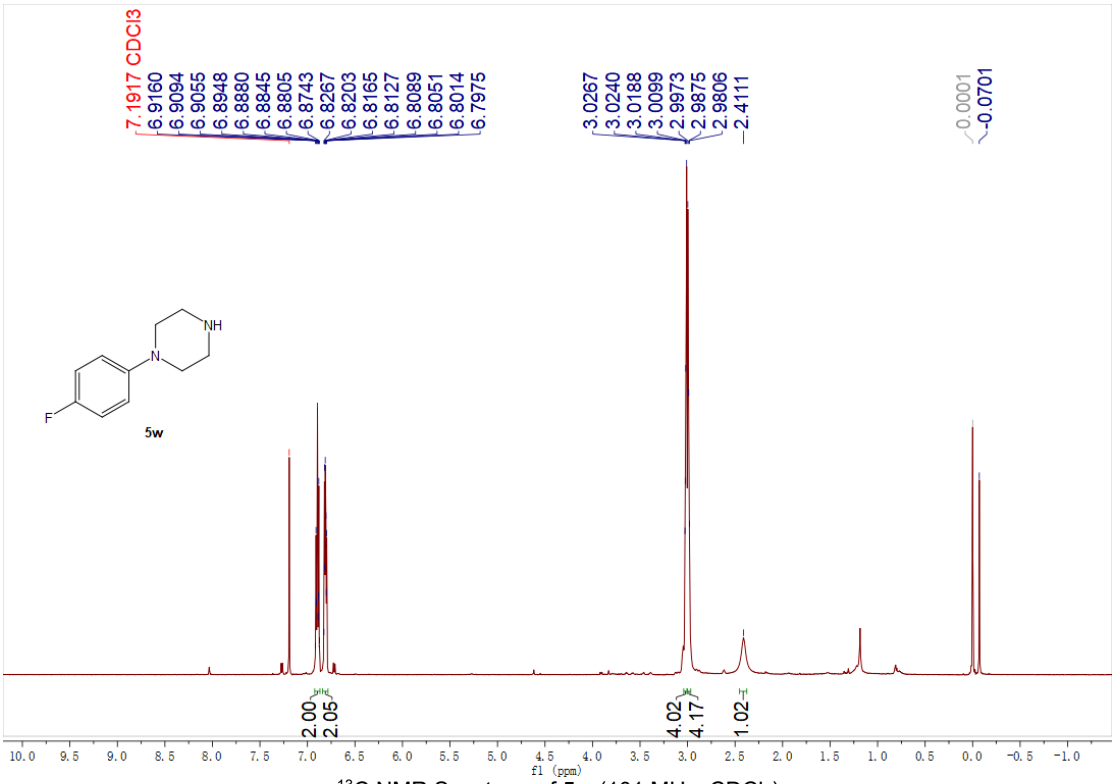
^{1}H NMR Spectrum of **5v** (600 MHz, $CDCl_3$)



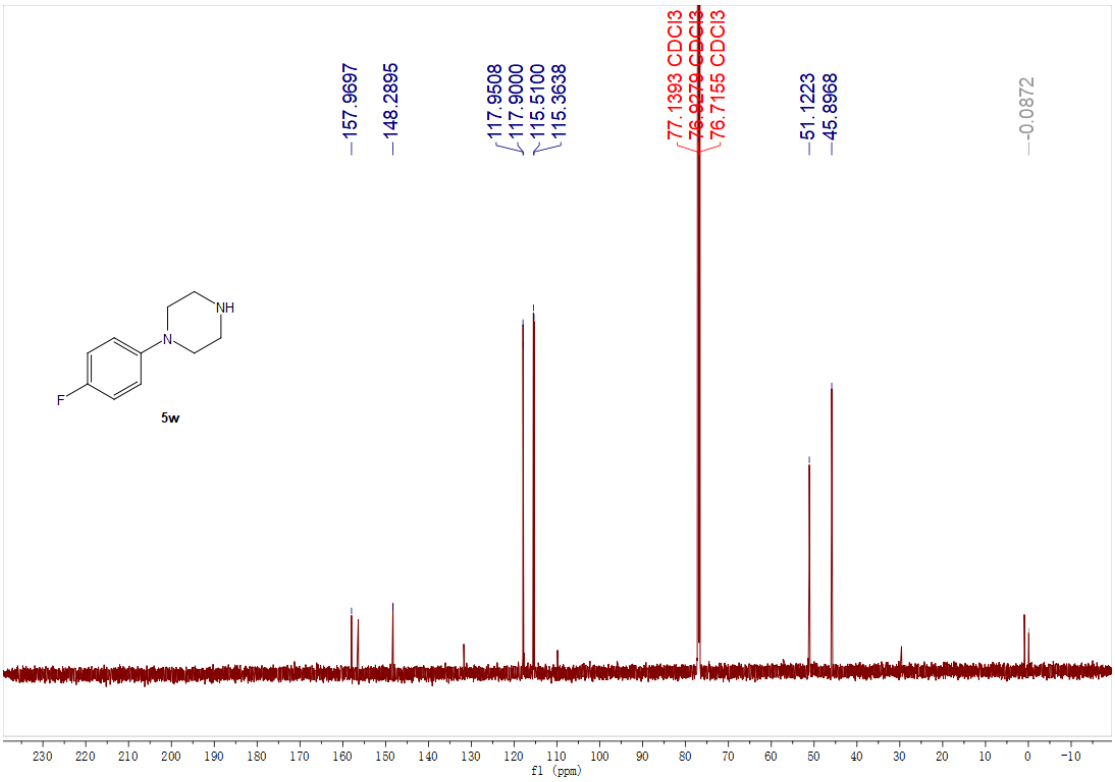
^{13}C NMR Spectrum of **5v** (151 MHz, $CDCl_3$)



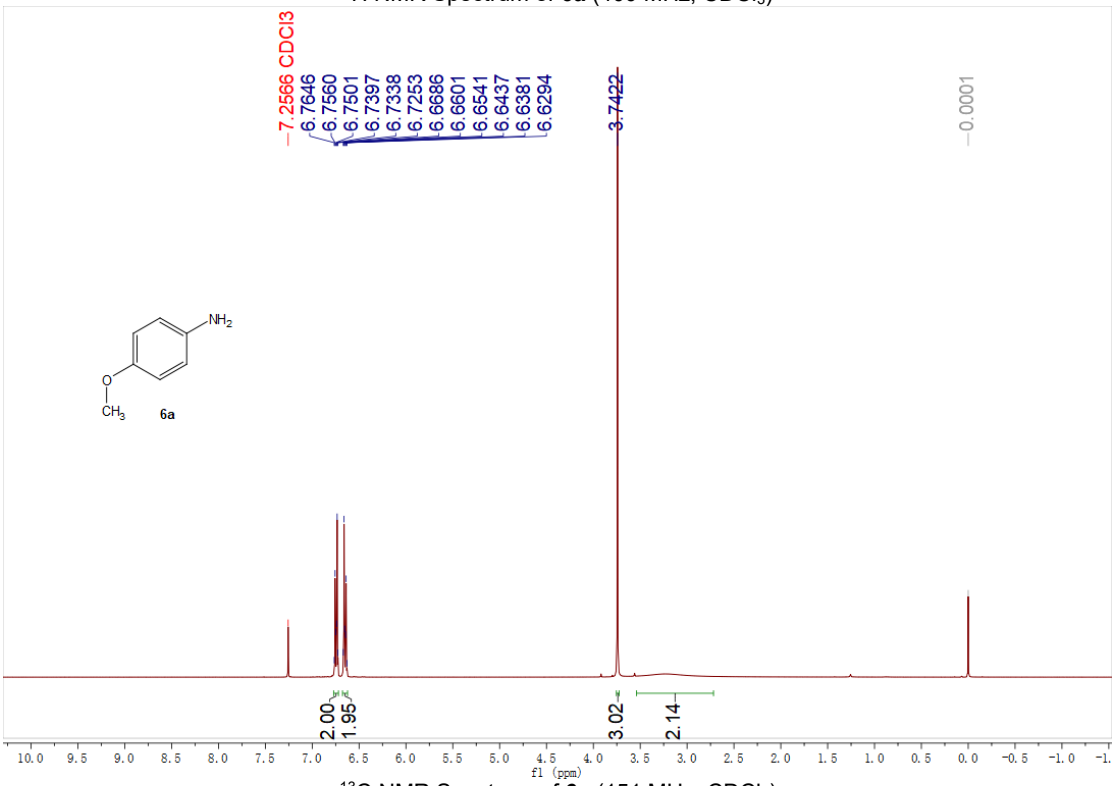
^{1}H NMR Spectrum of **5w** (600 MHz, $CDCl_3$)



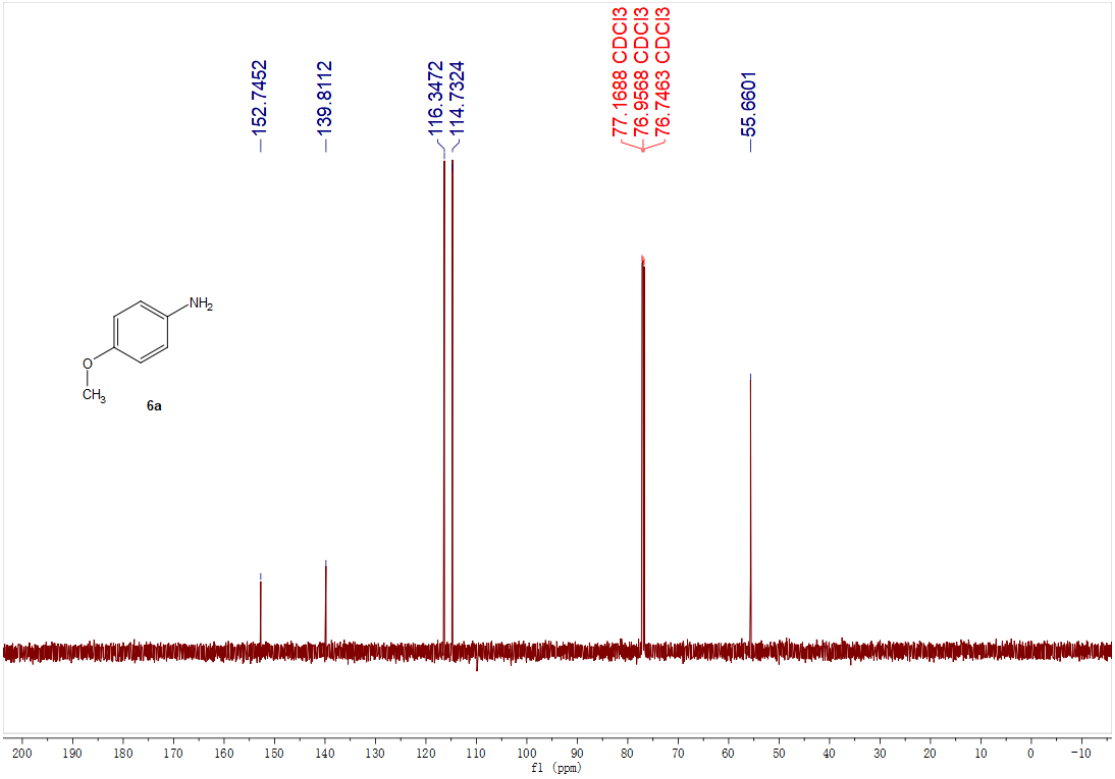
^{13}C NMR Spectrum of **5w** (101 MHz, $CDCl_3$)



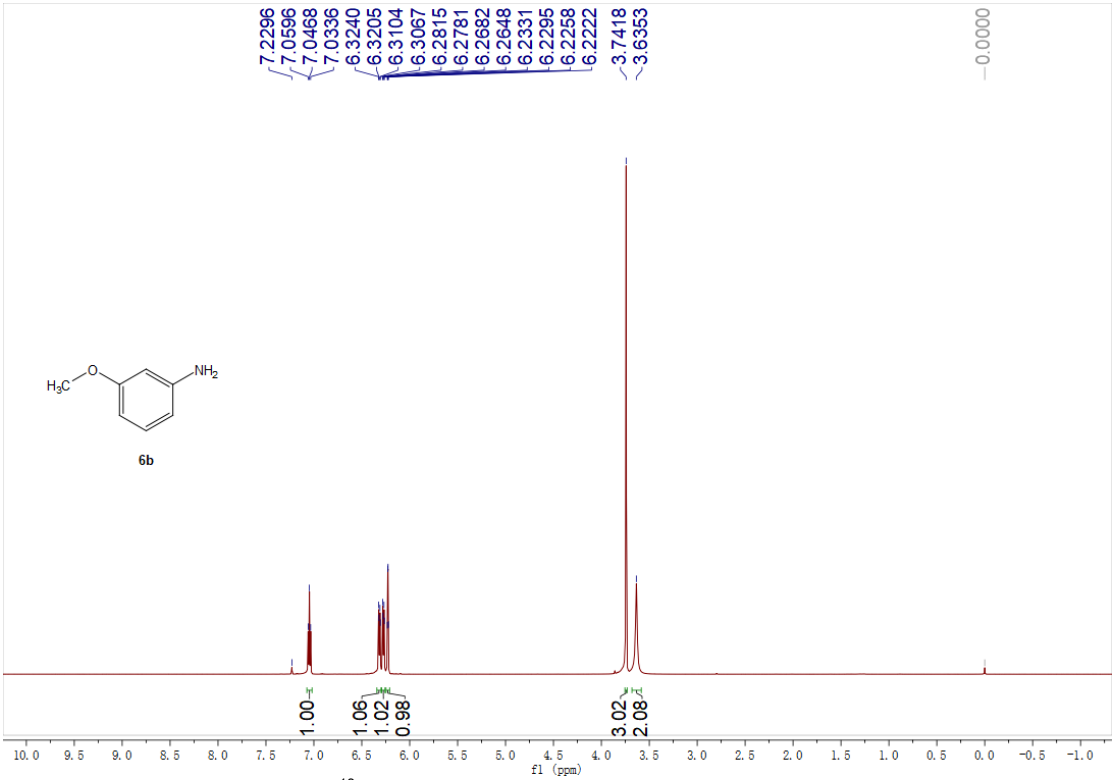
^{1}H NMR Spectrum of **6a** (400 MHz, $CDCl_3$)



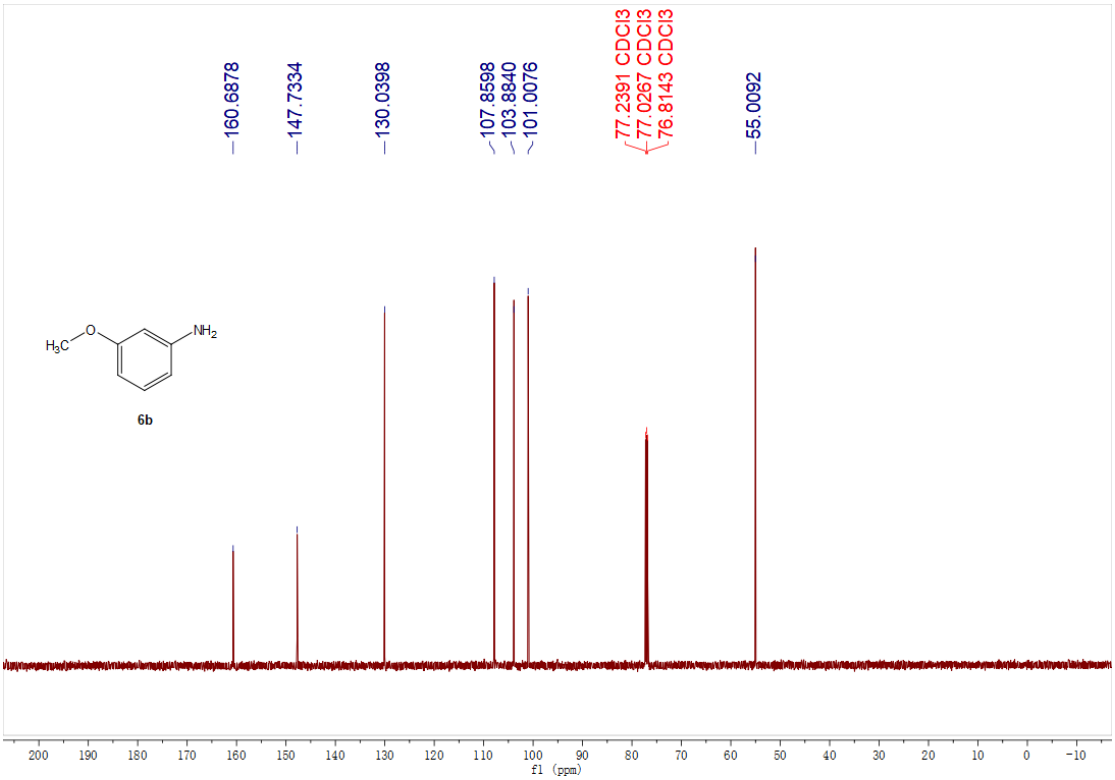
^{13}C NMR Spectrum of **6a** (151 MHz, $CDCl_3$)



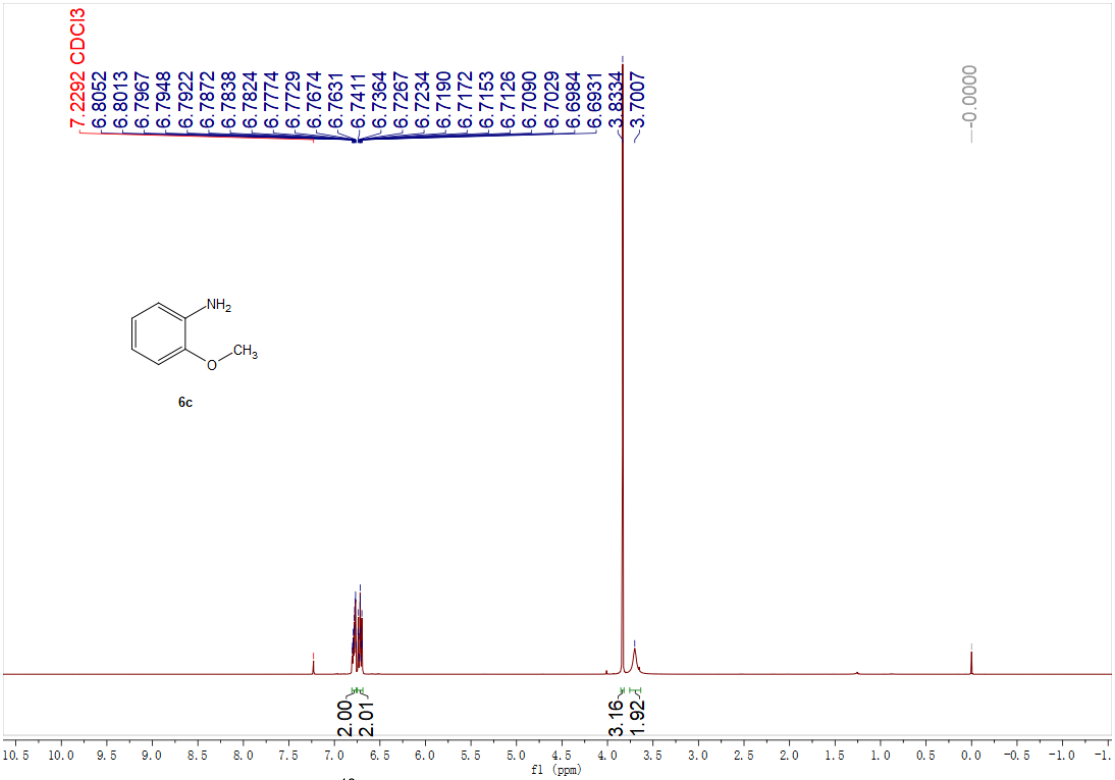
^{1}H NMR Spectrum of **6b** (600 MHz, $CDCl_3$)



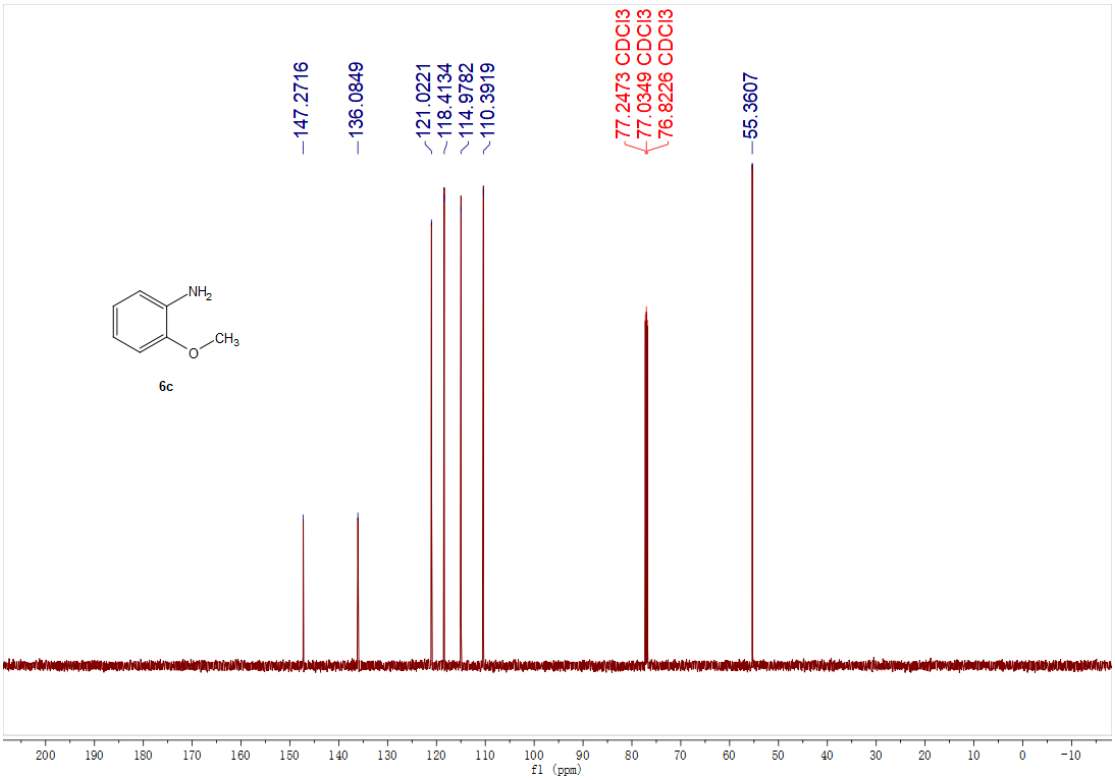
^{13}C NMR Spectrum of **6b** (151 MHz, $CDCl_3$)



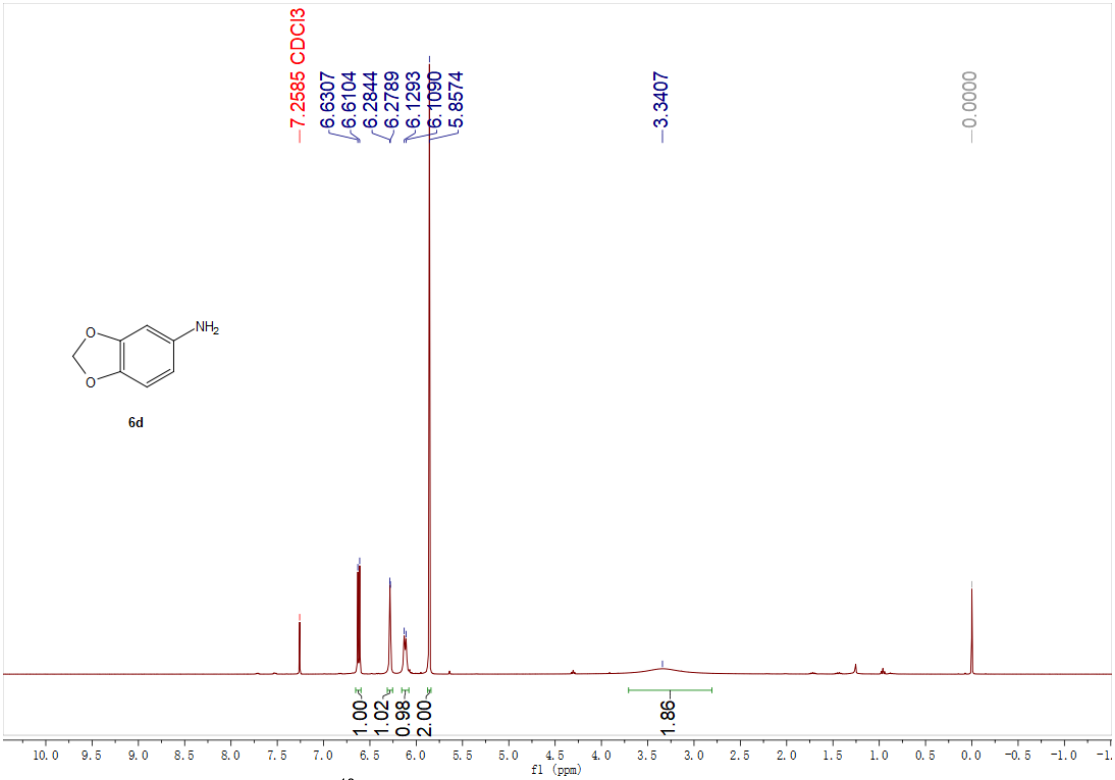
^{1}H NMR Spectrum of **6c** (600 MHz, $CDCl_3$)



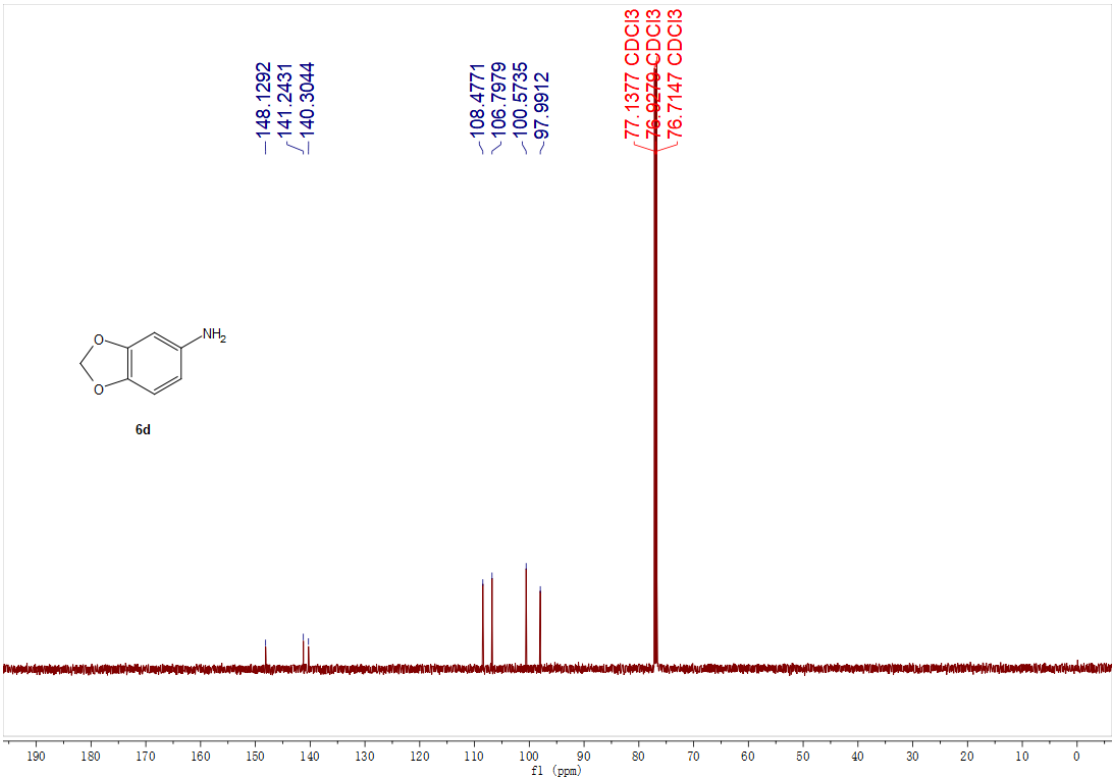
^{13}C NMR Spectrum of **6c** (151 MHz, $CDCl_3$)



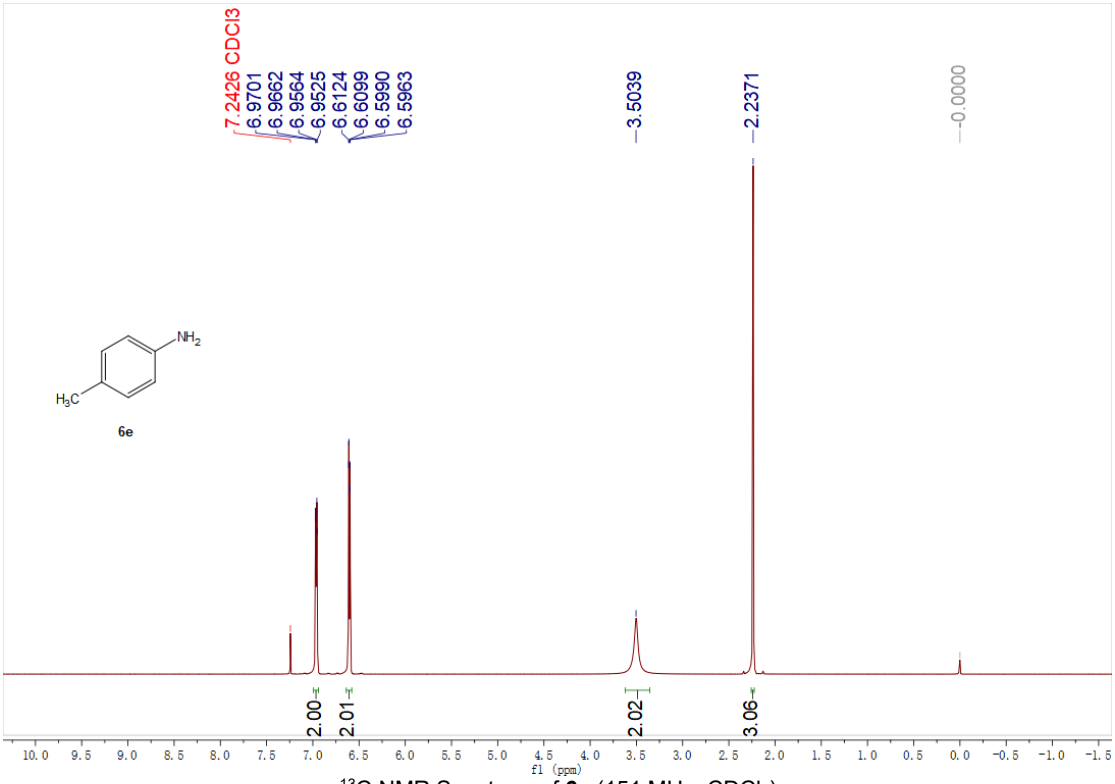
^{1}H NMR Spectrum of **6d** (400 MHz, $CDCl_3$)



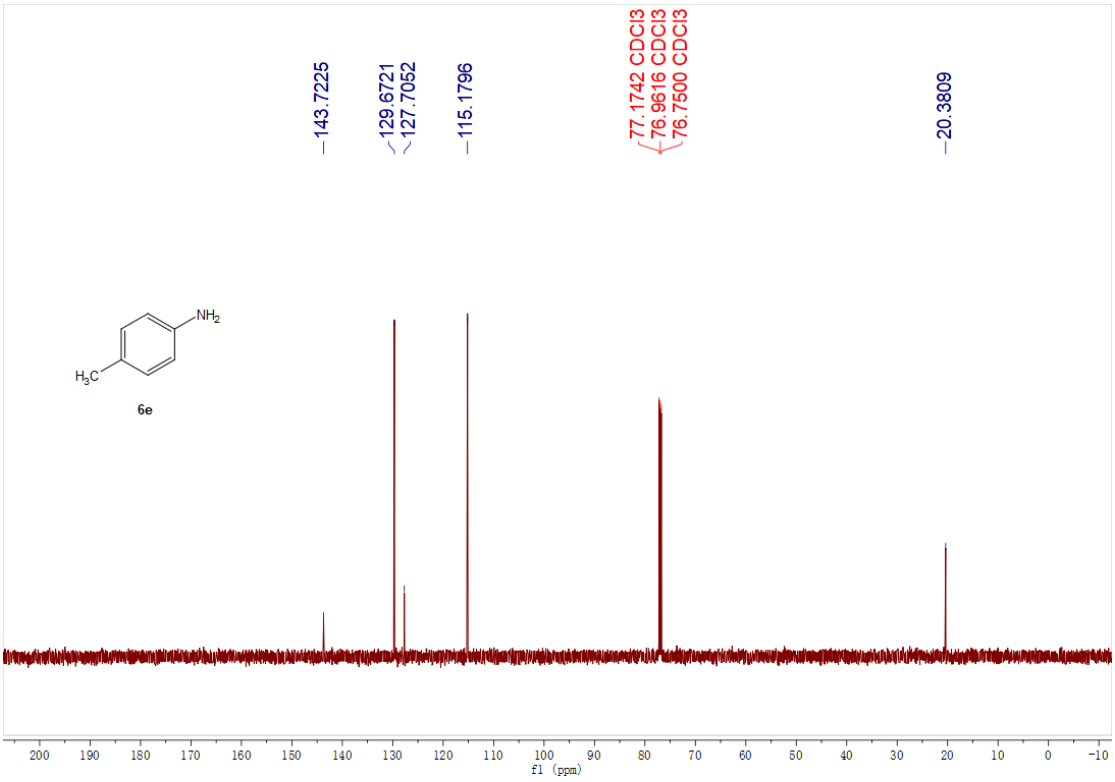
^{13}C NMR Spectrum of **6d** (151 MHz, $CDCl_3$)



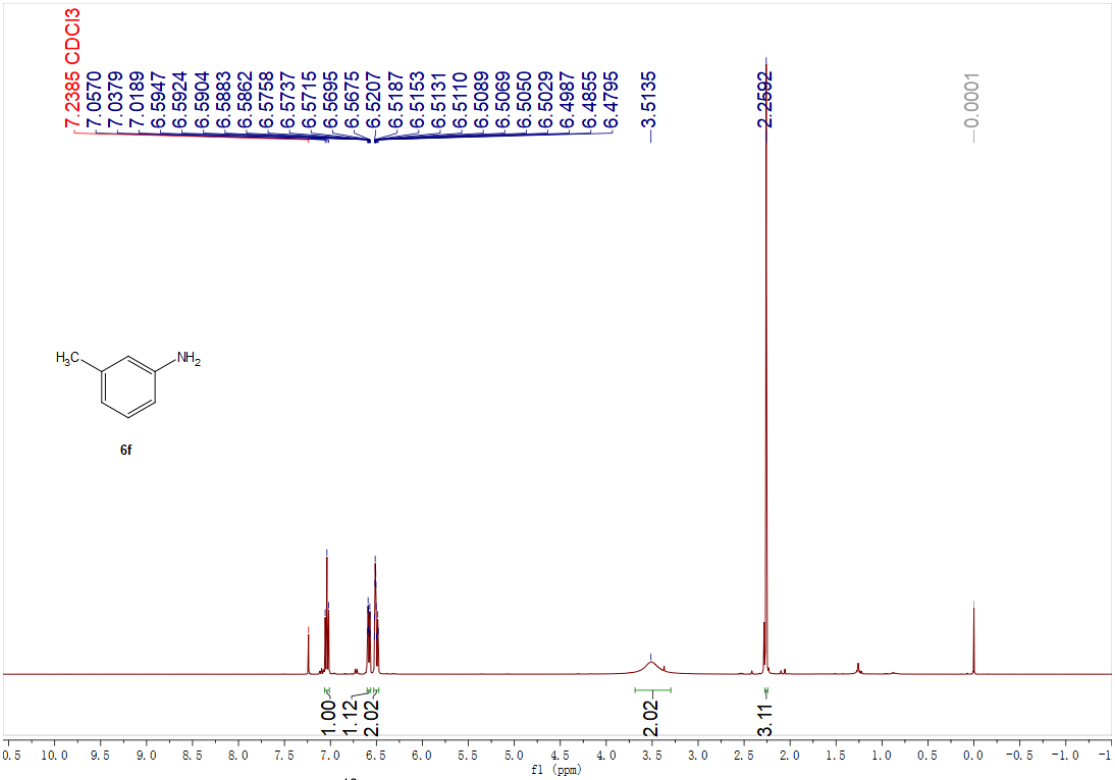
^{1}H NMR Spectrum of **6e** (600 MHz, $CDCl_3$)



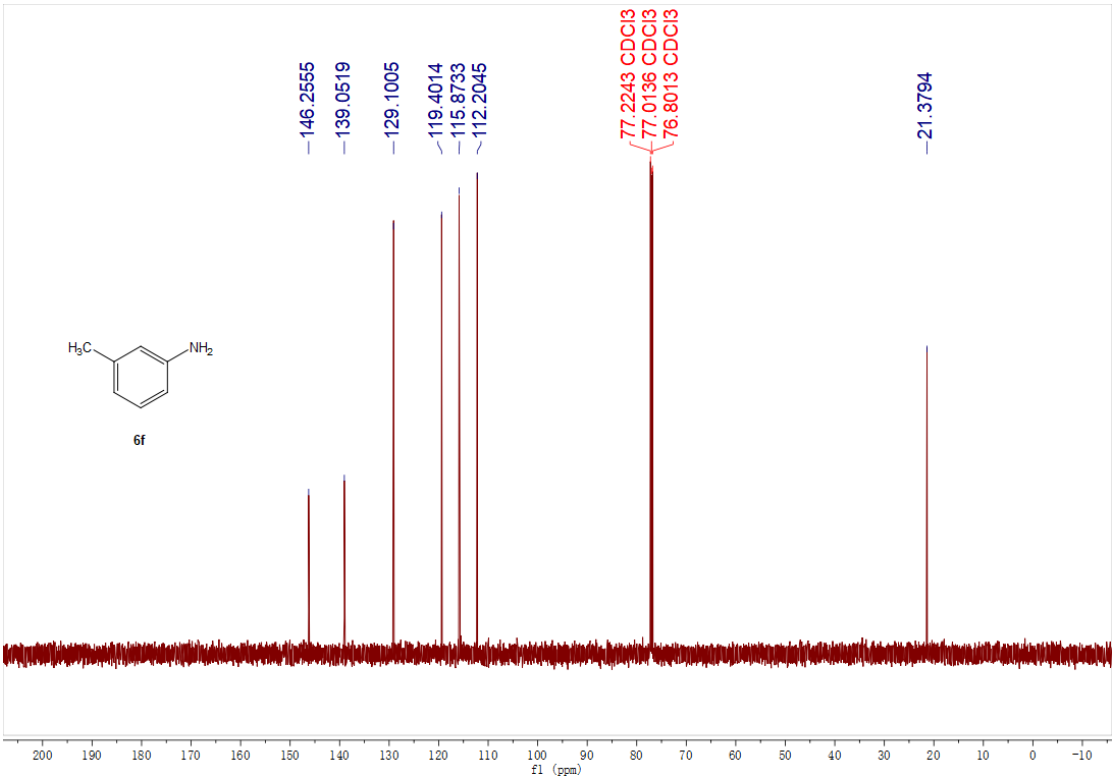
^{13}C NMR Spectrum of **6e** (151 MHz, $CDCl_3$)



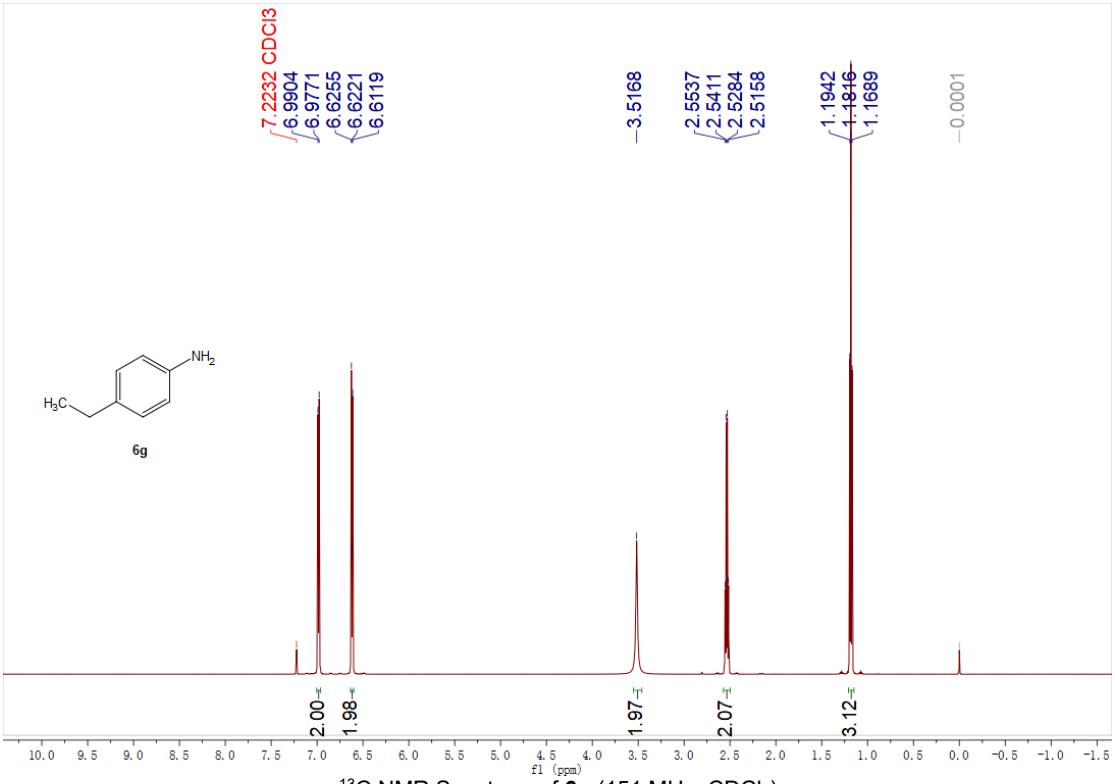
^{1}H NMR Spectrum of **6f** (400 MHz, $CDCl_3$)



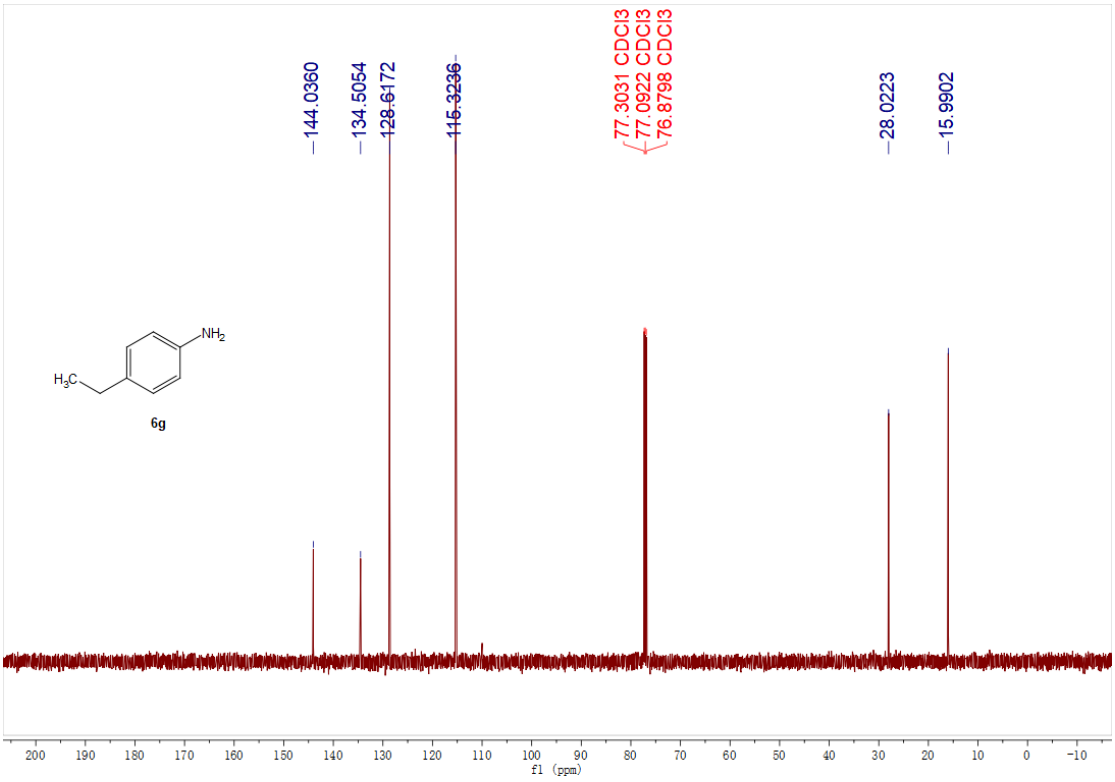
^{13}C NMR Spectrum of **6f** (151 MHz, $CDCl_3$)



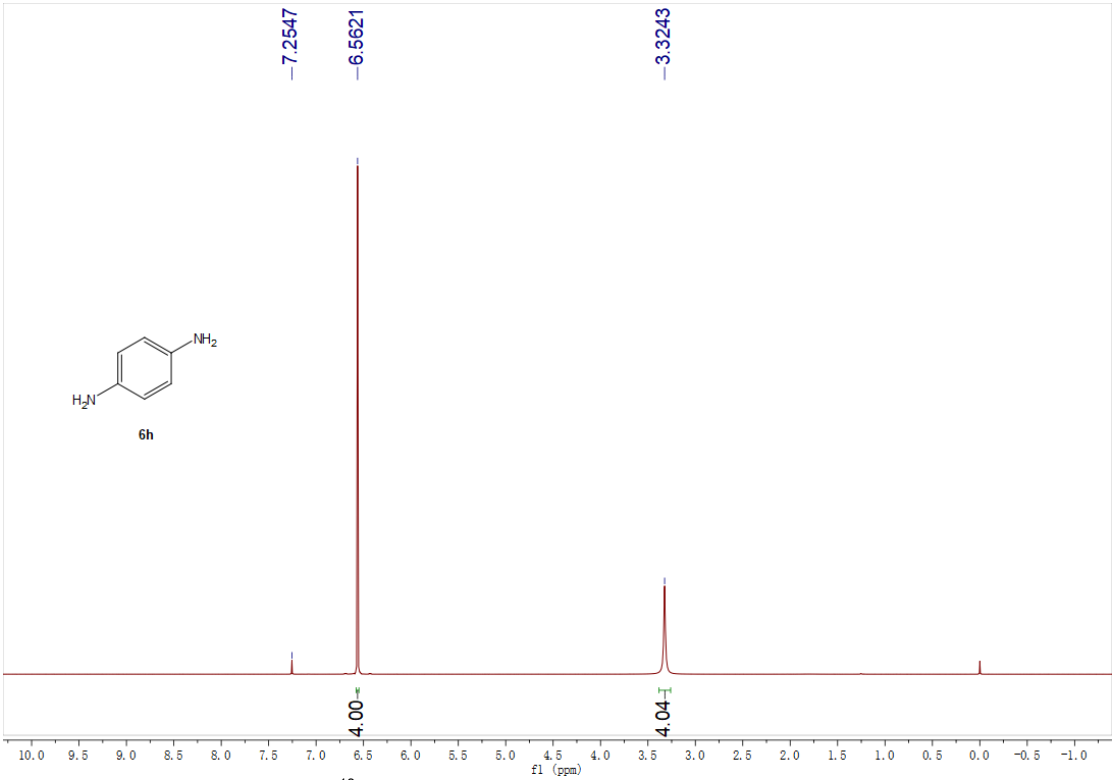
^{1}H NMR Spectrum of **6g** (600 MHz, $CDCl_3$)



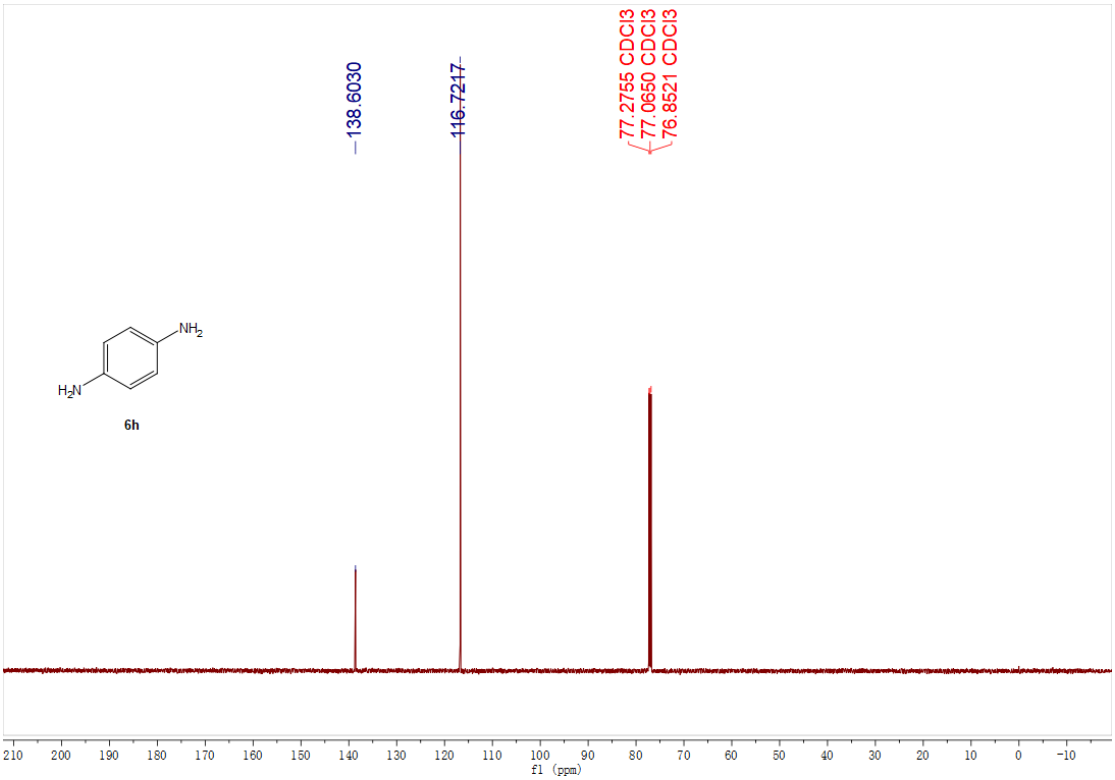
^{13}C NMR Spectrum of **6g** (151 MHz, $CDCl_3$)



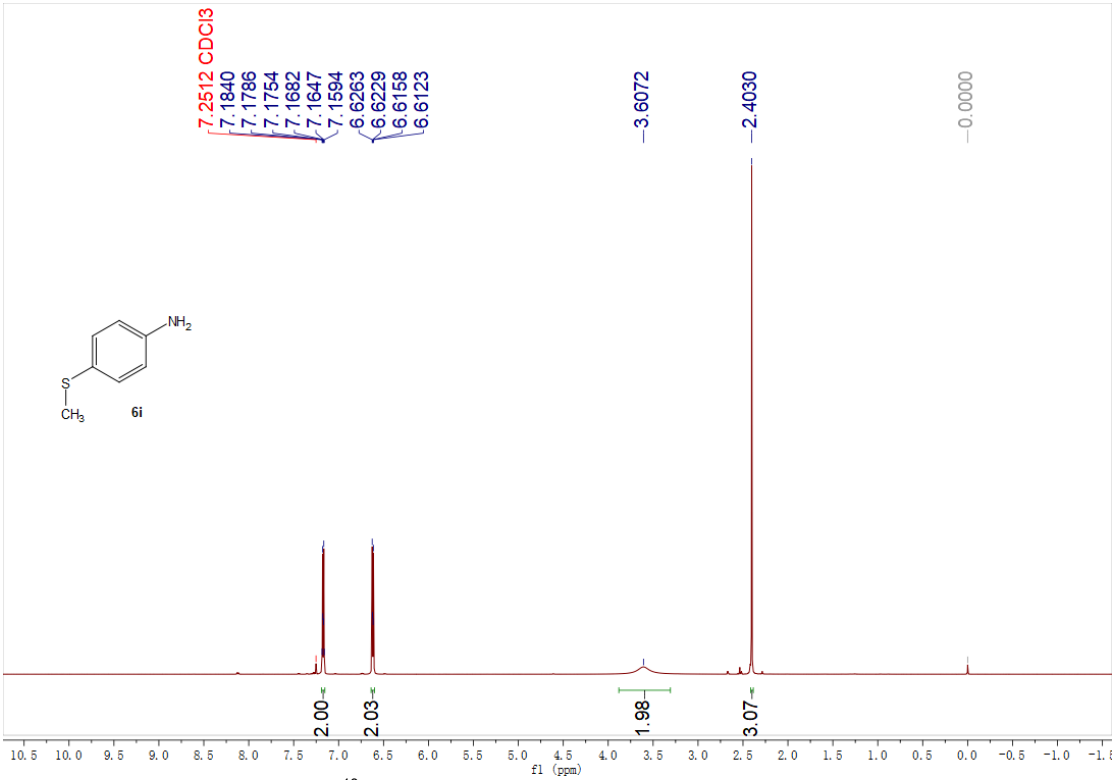
^{1}H NMR Spectrum of **6h** (600 MHz, $CDCl_3$)



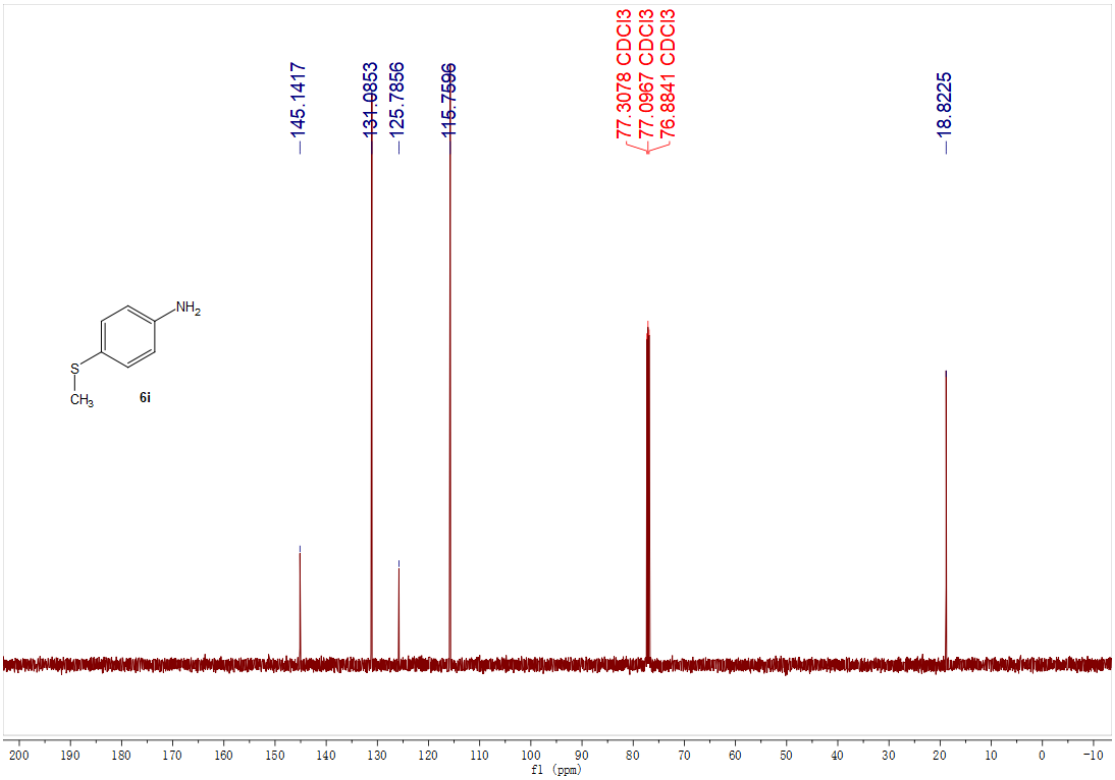
^{13}C NMR Spectrum of **6h** (151 MHz, $CDCl_3$)



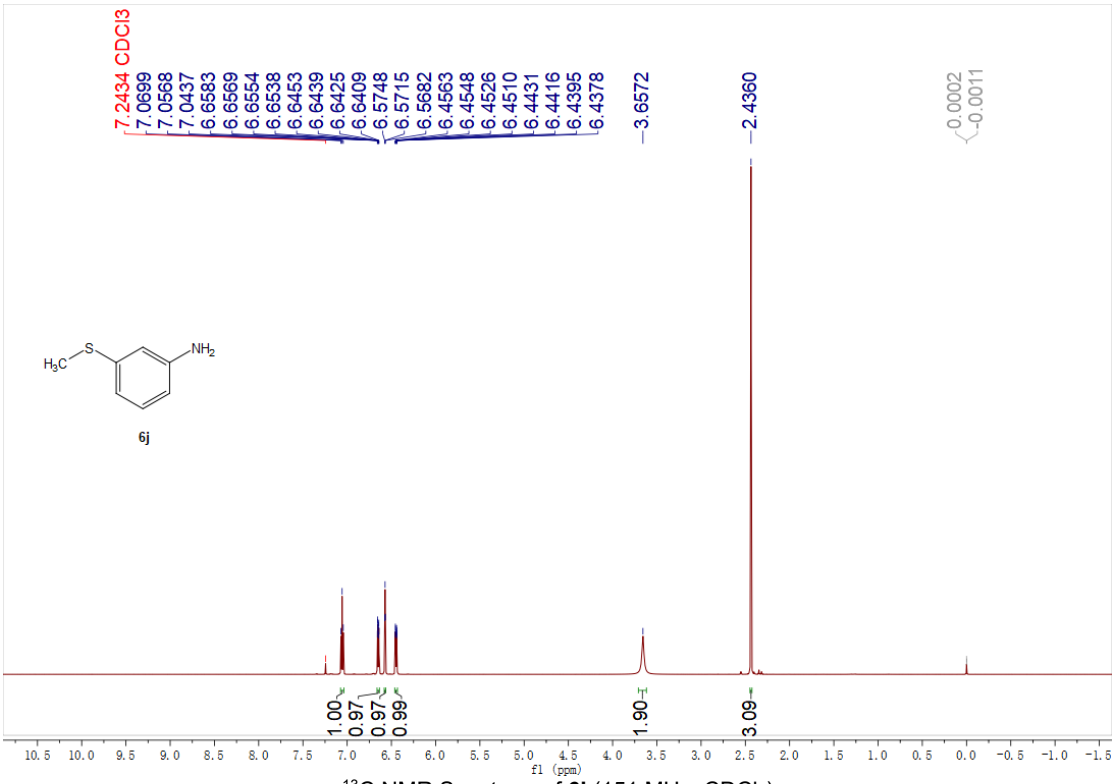
^{1}H NMR Spectrum of **6i** (600 MHz, $CDCl_3$)



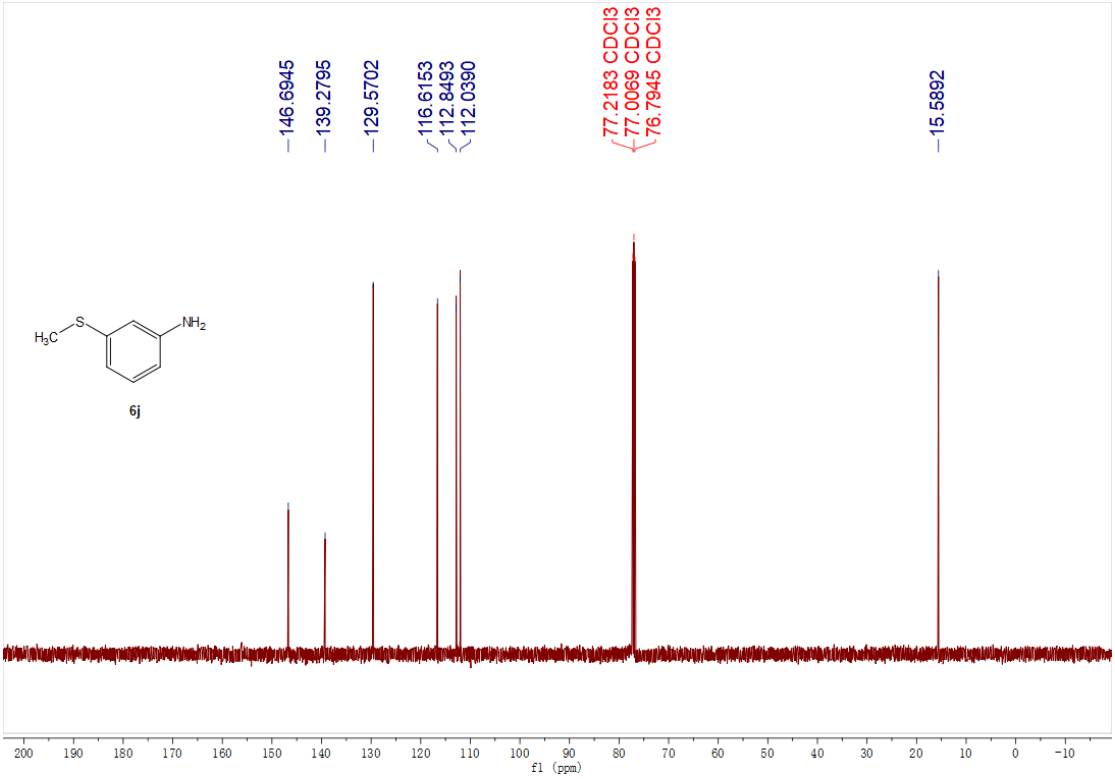
^{13}C NMR Spectrum of **6i** (151 MHz, $CDCl_3$)



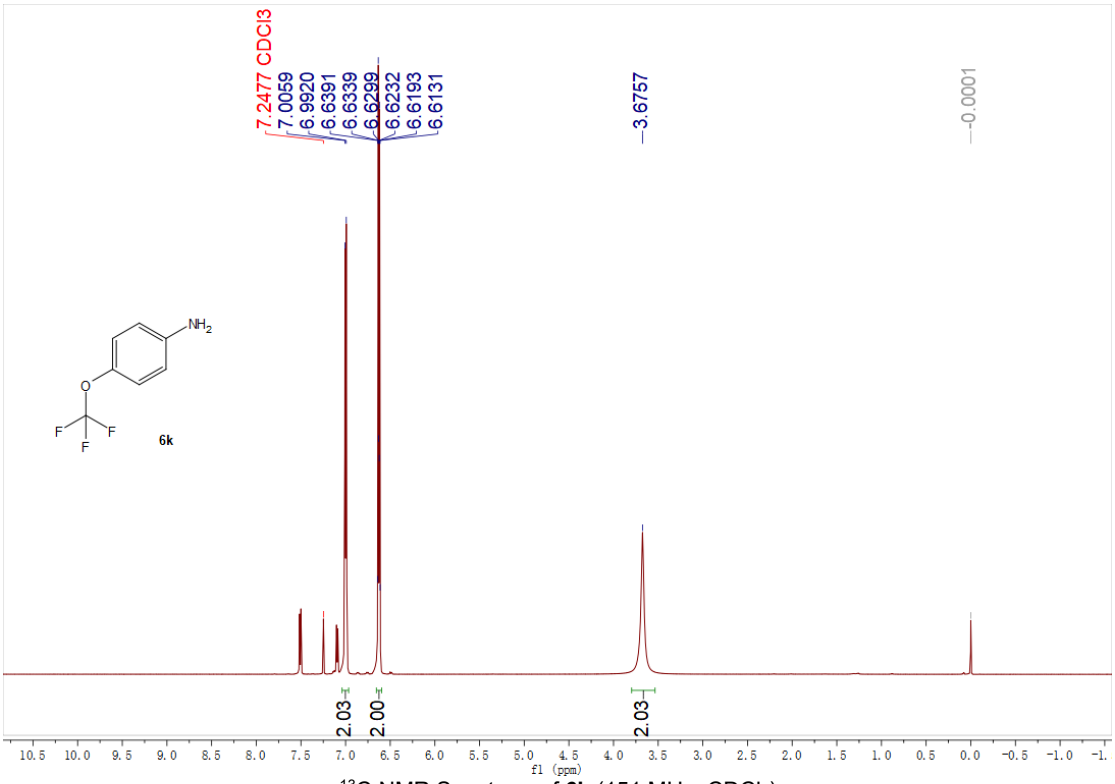
^{1}H NMR Spectrum of **6j** (600 MHz, $CDCl_3$)



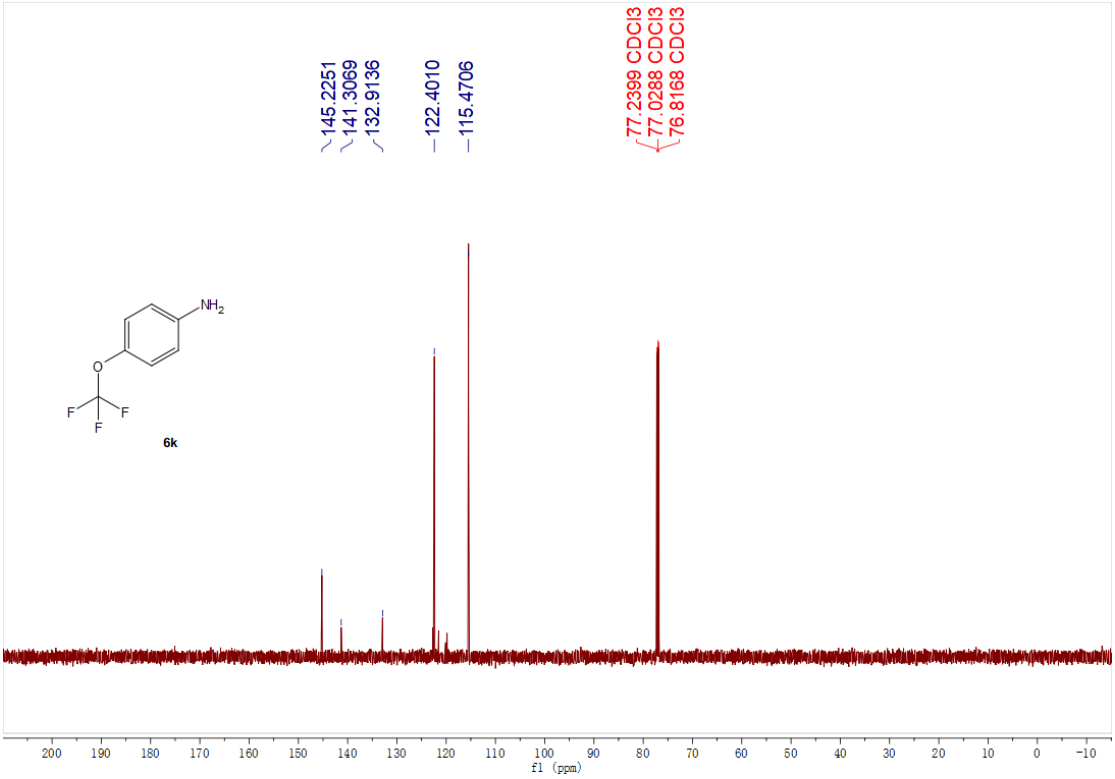
^{13}C NMR Spectrum of **6j** (151 MHz, $CDCl_3$)



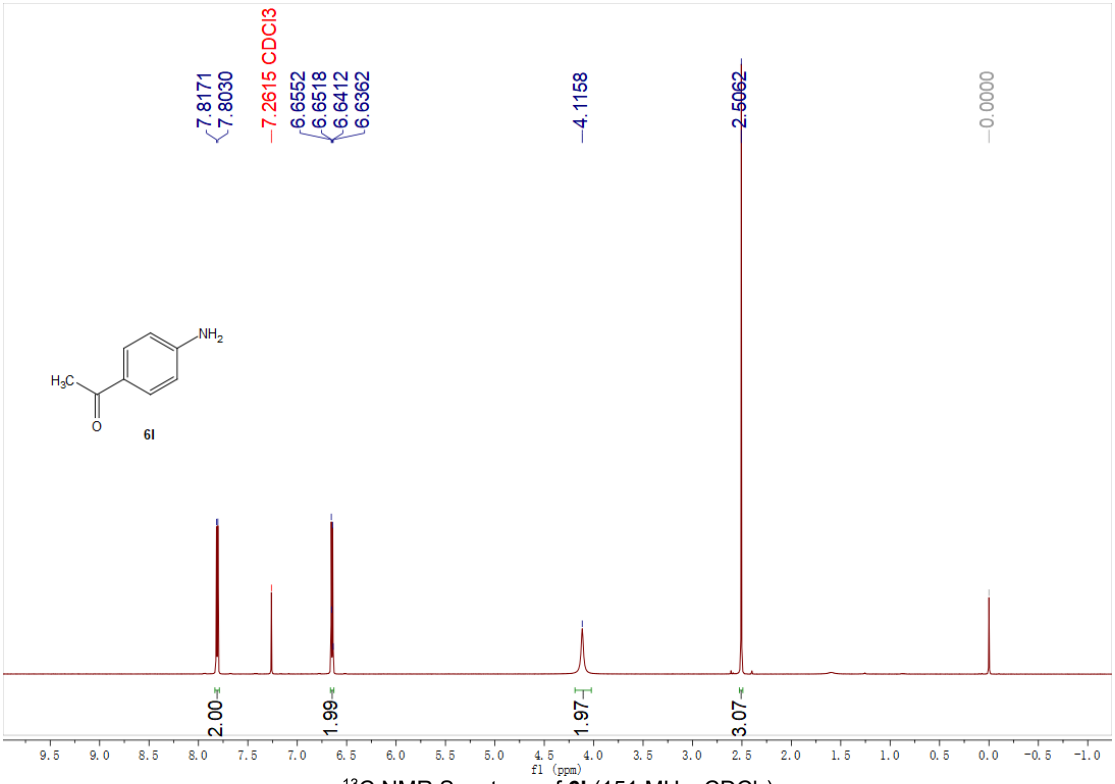
^{1}H NMR Spectrum of **6k** (600 MHz, $CDCl_3$)



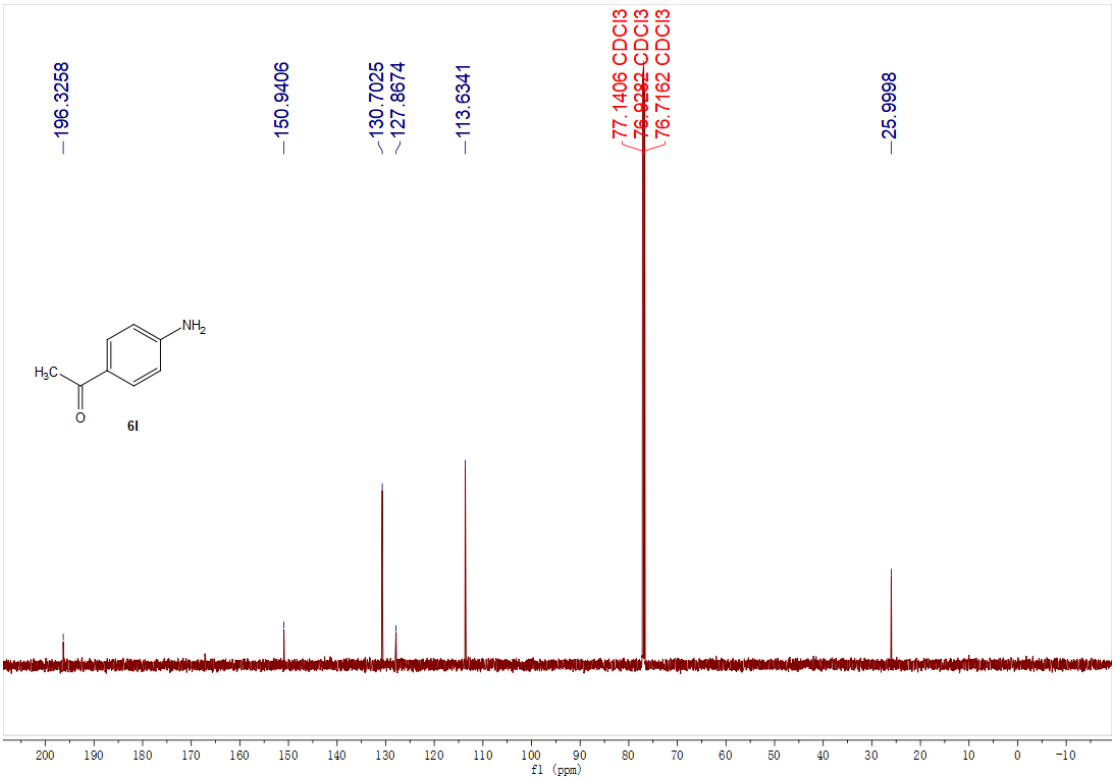
^{13}C NMR Spectrum of **6k** (151 MHz, $CDCl_3$)



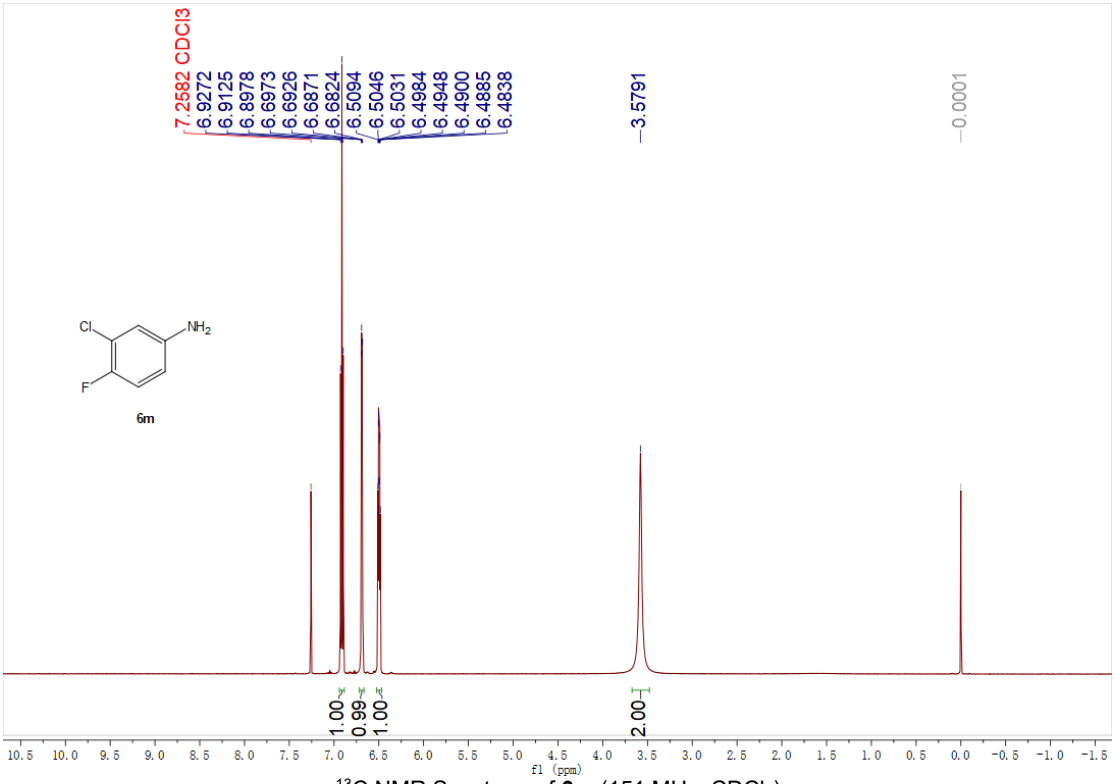
^{1}H NMR Spectrum of **6l** (600 MHz, $CDCl_3$)

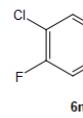


^{13}C NMR Spectrum of **6l** (151 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **6m** (600 MHz, $CDCl_3$)



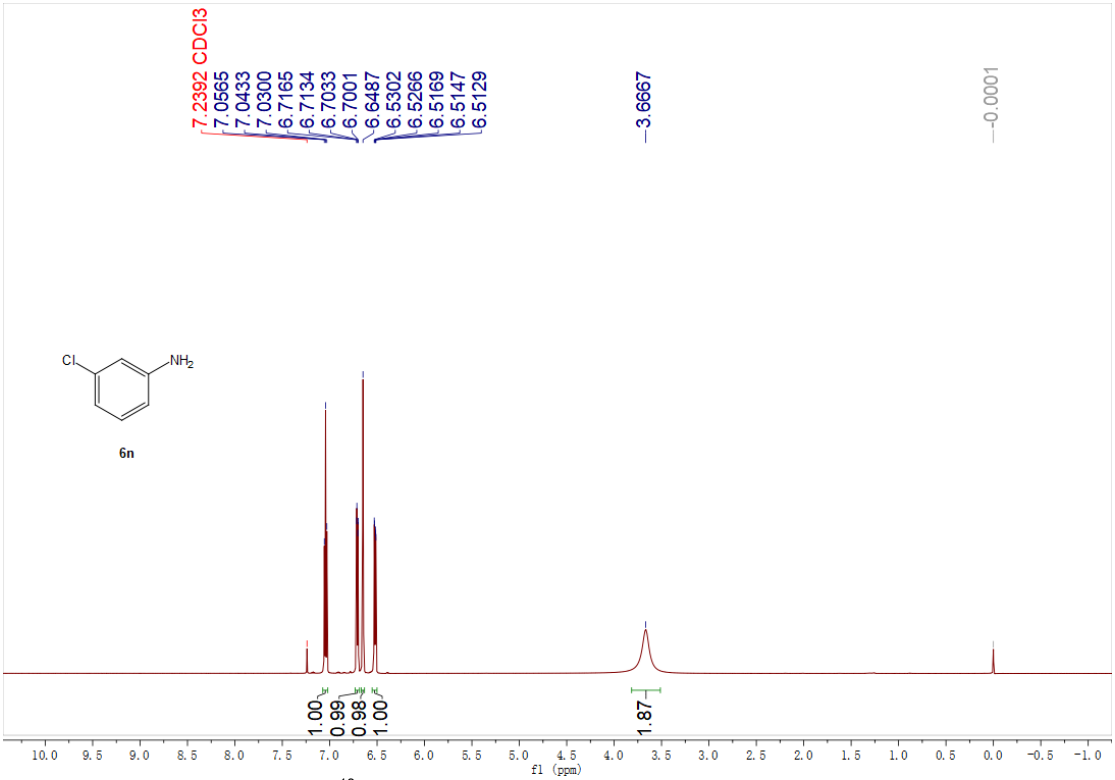


6m

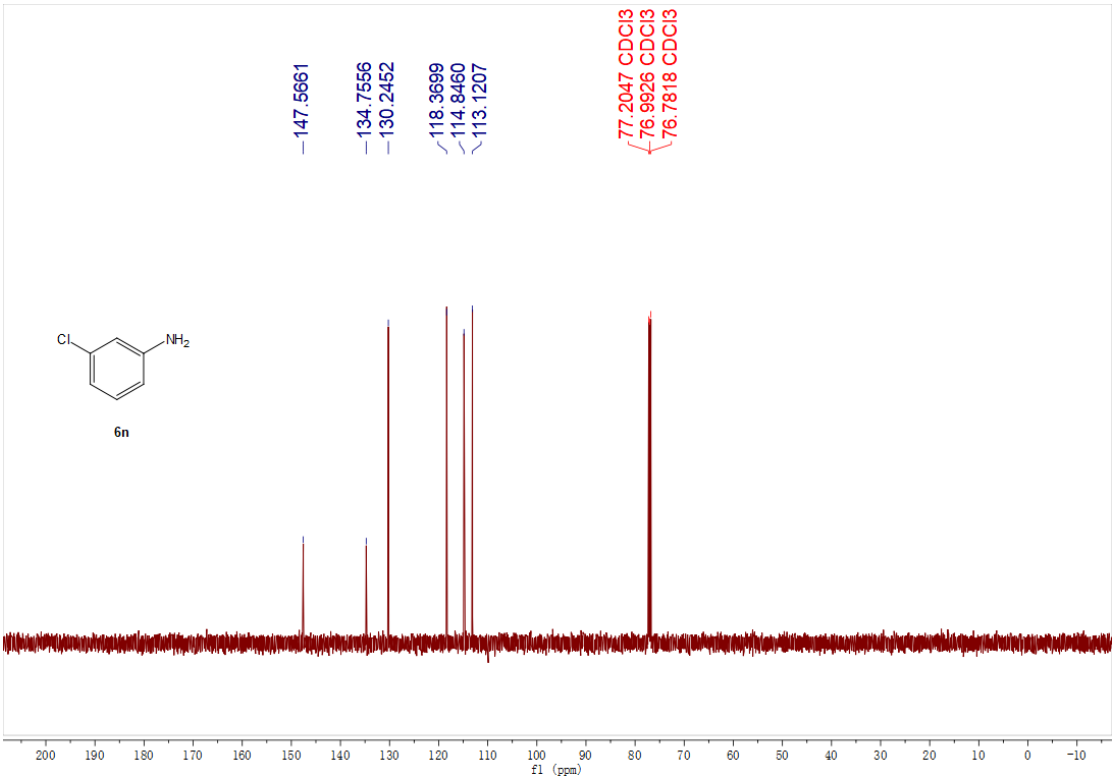
^{13}C NMR Spectrum of **6m** (151 MHz, $CDCl_3$)

6m

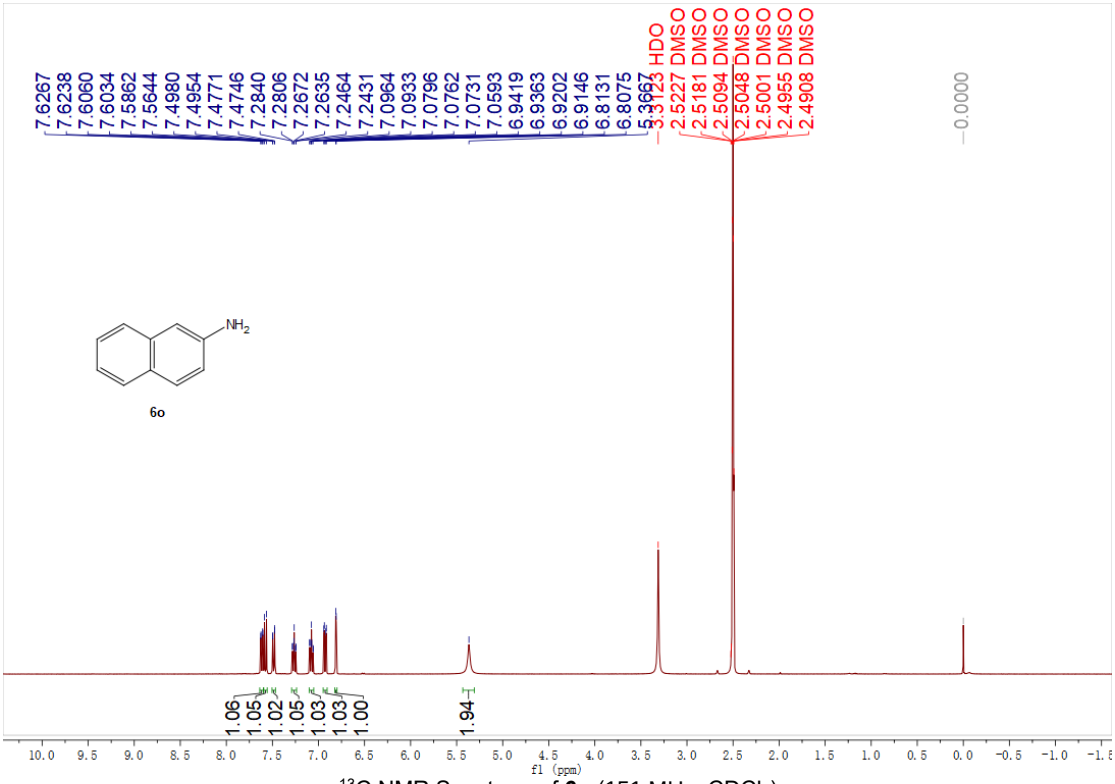
^{1}H NMR Spectrum of **6n** (600 MHz, $CDCl_3$)



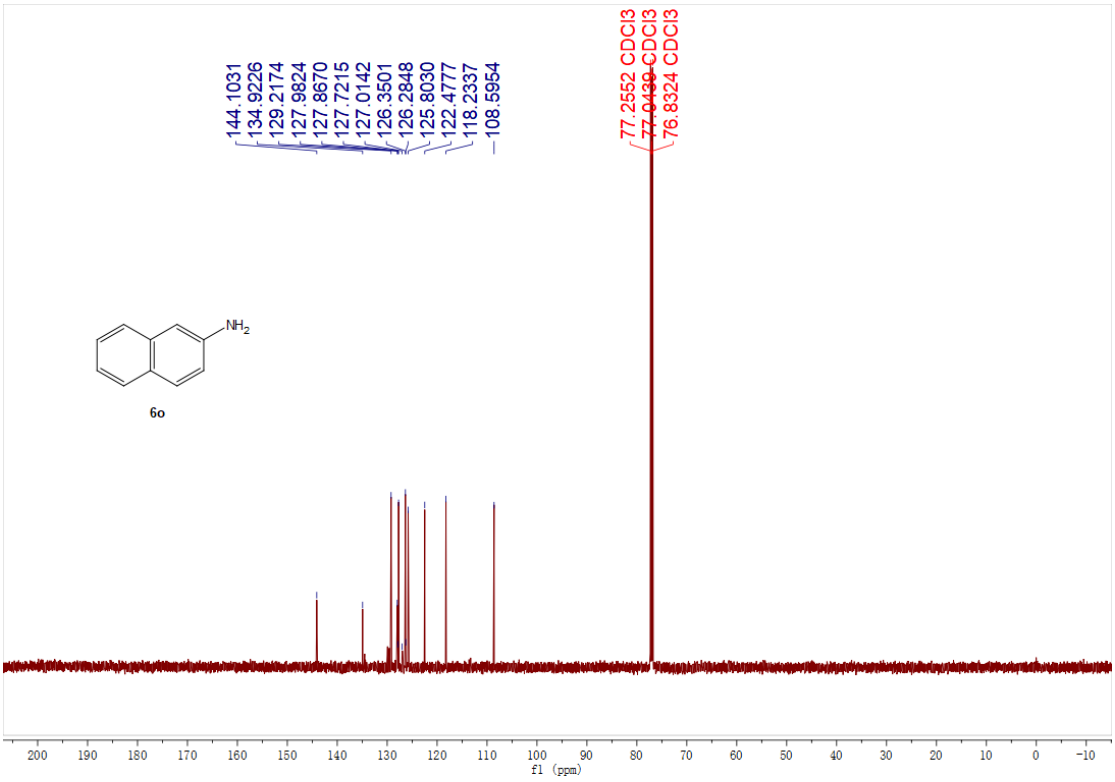
^{13}C NMR Spectrum of **6n** (151 MHz, $CDCl_3$)



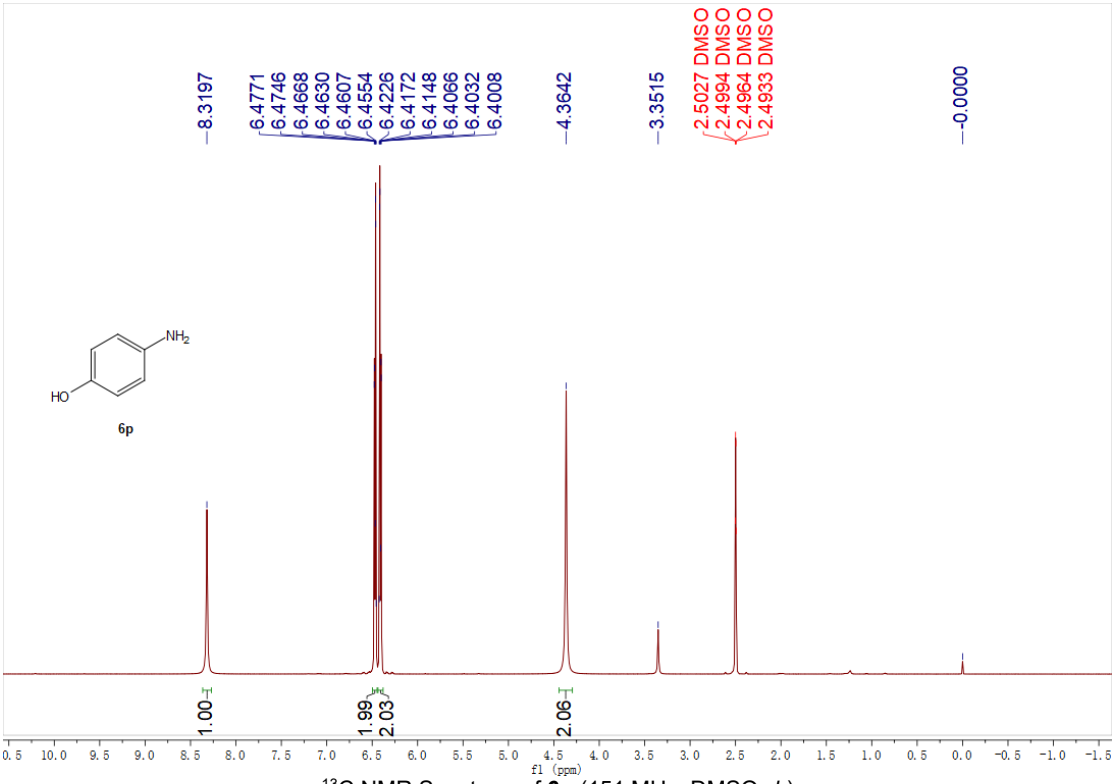
^{1}H NMR Spectrum of **6o** (400 MHz, DMSO-d_6)



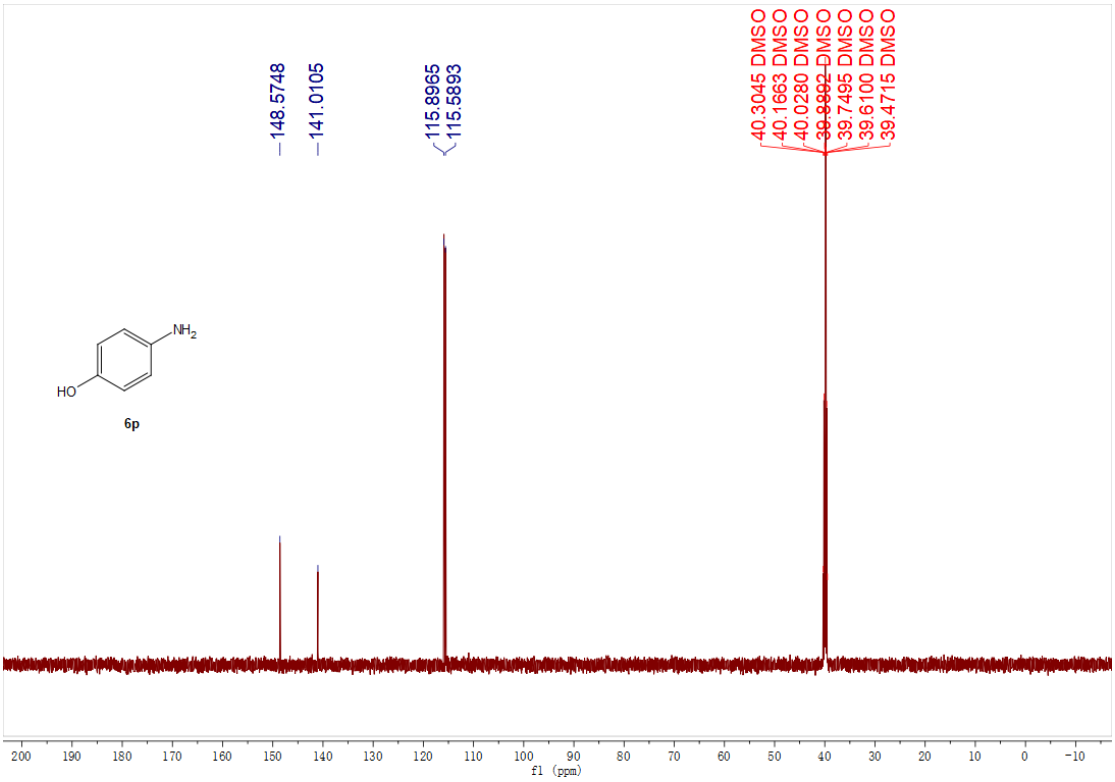
^{13}C NMR Spectrum of **6o** (151 MHz, $CDCl_3$)



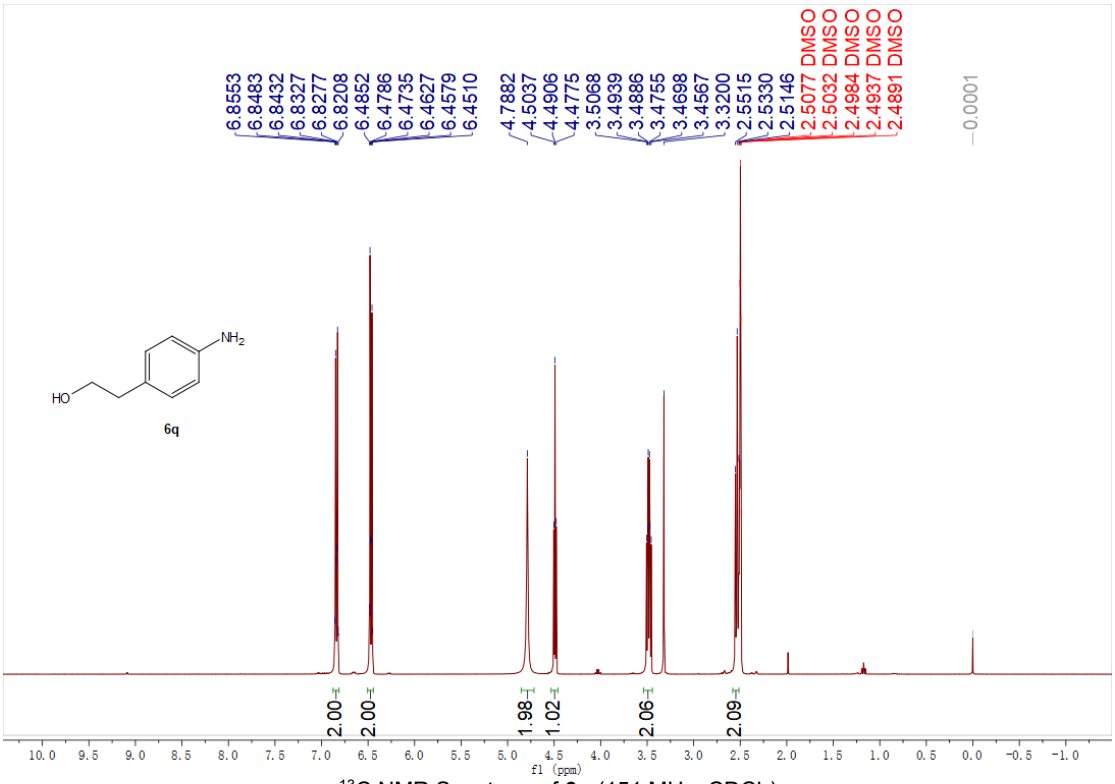
^{1}H NMR Spectrum of **6p** (600 MHz, DMSO-d_6)



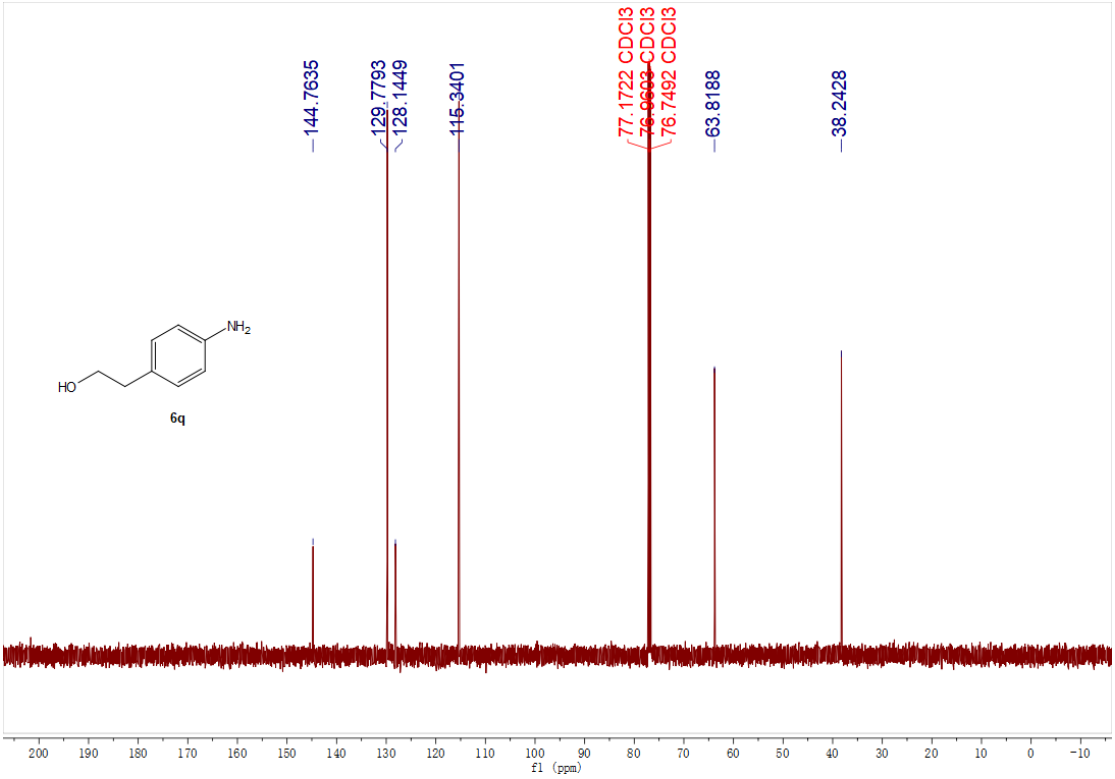
^{13}C NMR Spectrum of **6p** (151 MHz, DMSO-d_6)



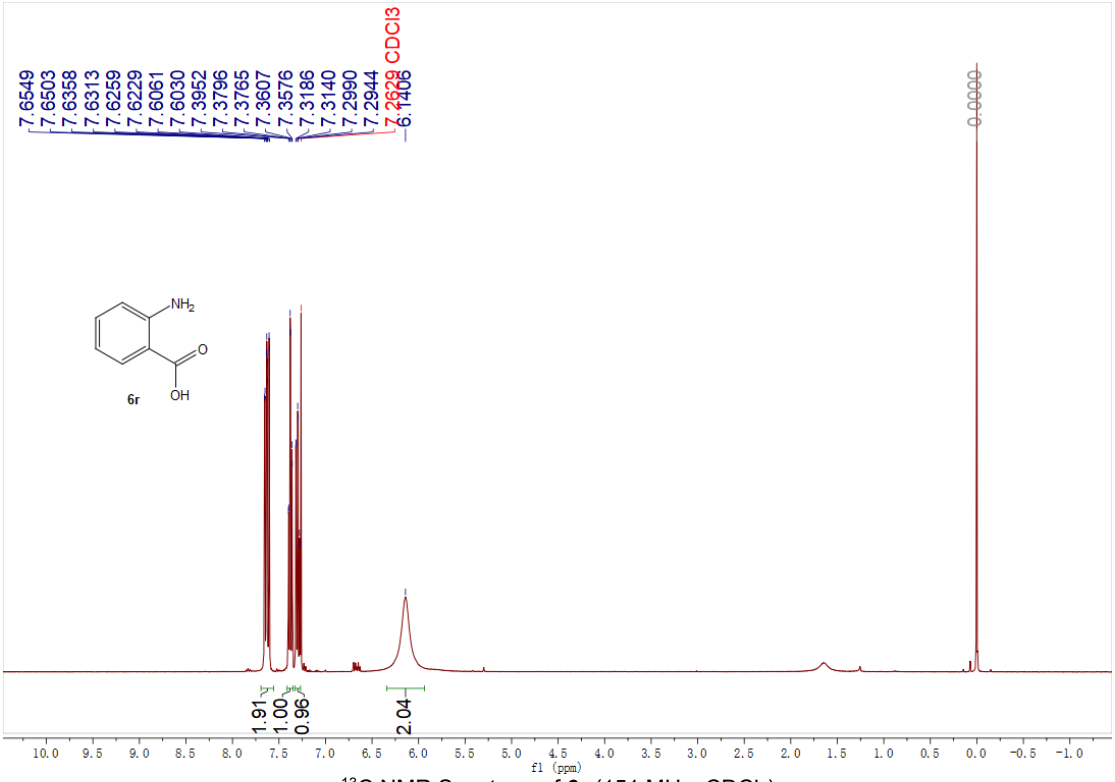
^{1}H NMR Spectrum of **6q** (400 MHz, $CDCl_3$)



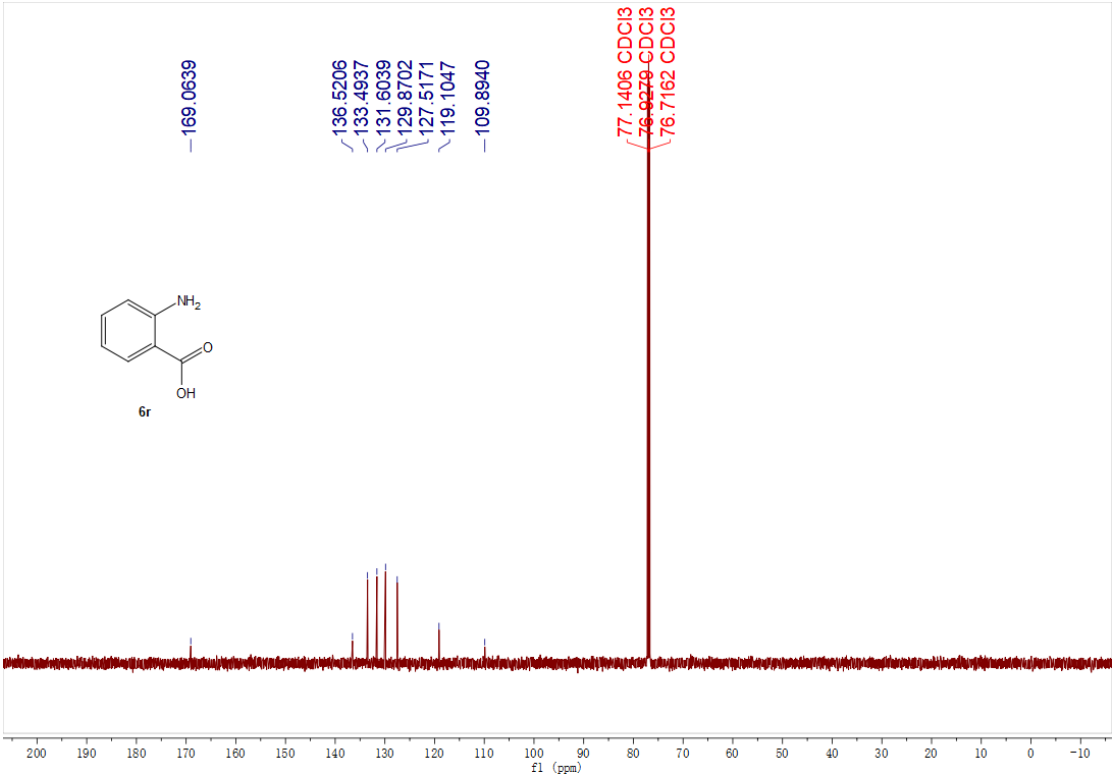
^{13}C NMR Spectrum of **6q** (151 MHz, $CDCl_3$)



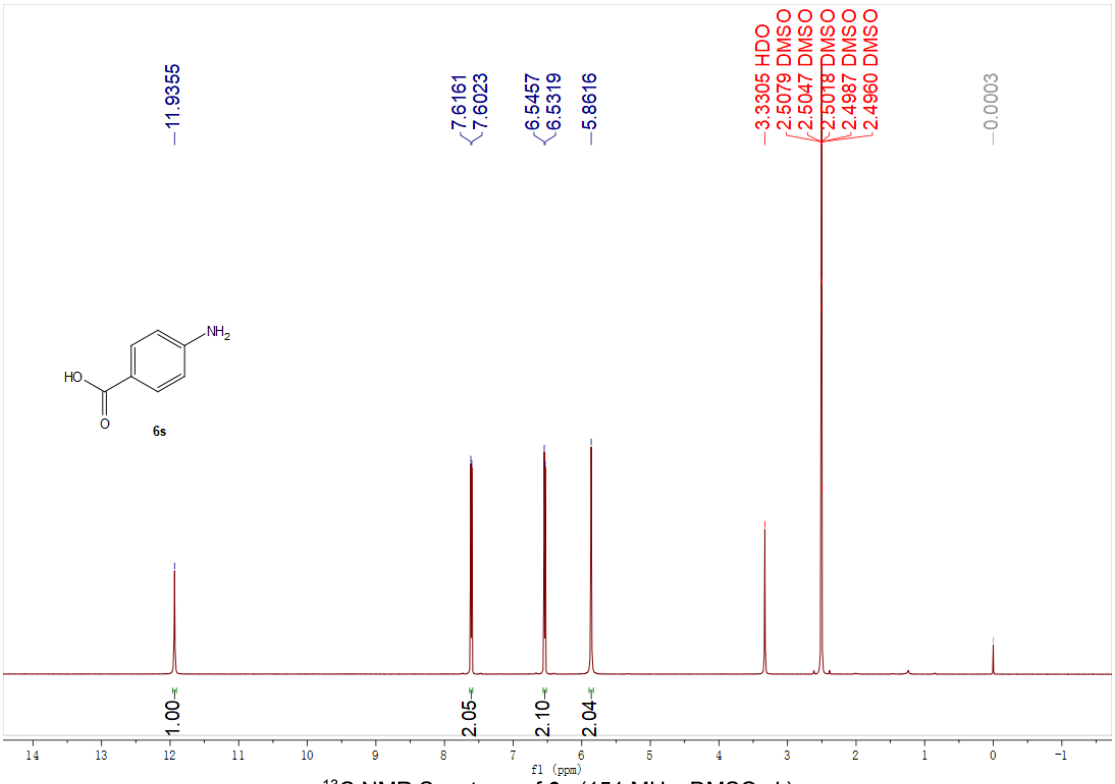
^{1}H NMR Spectrum of **6r** (400 MHz, $CDCl_3$)



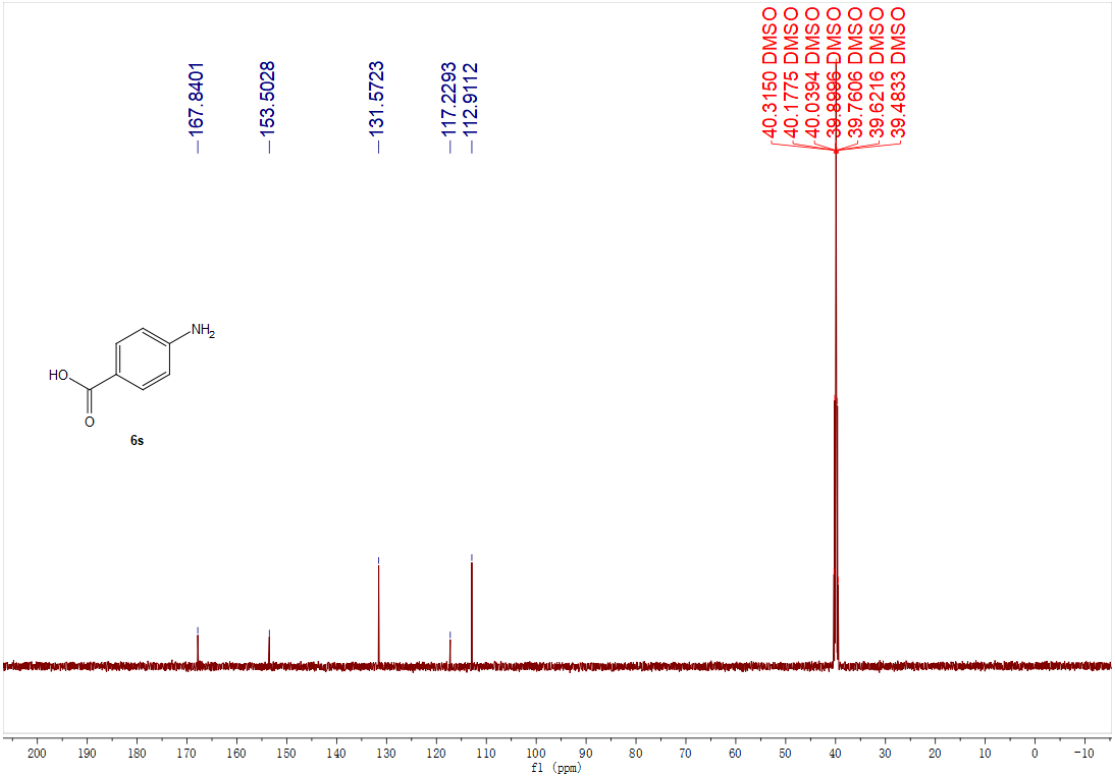
^{13}C NMR Spectrum of **6r** (151 MHz, $CDCl_3$)



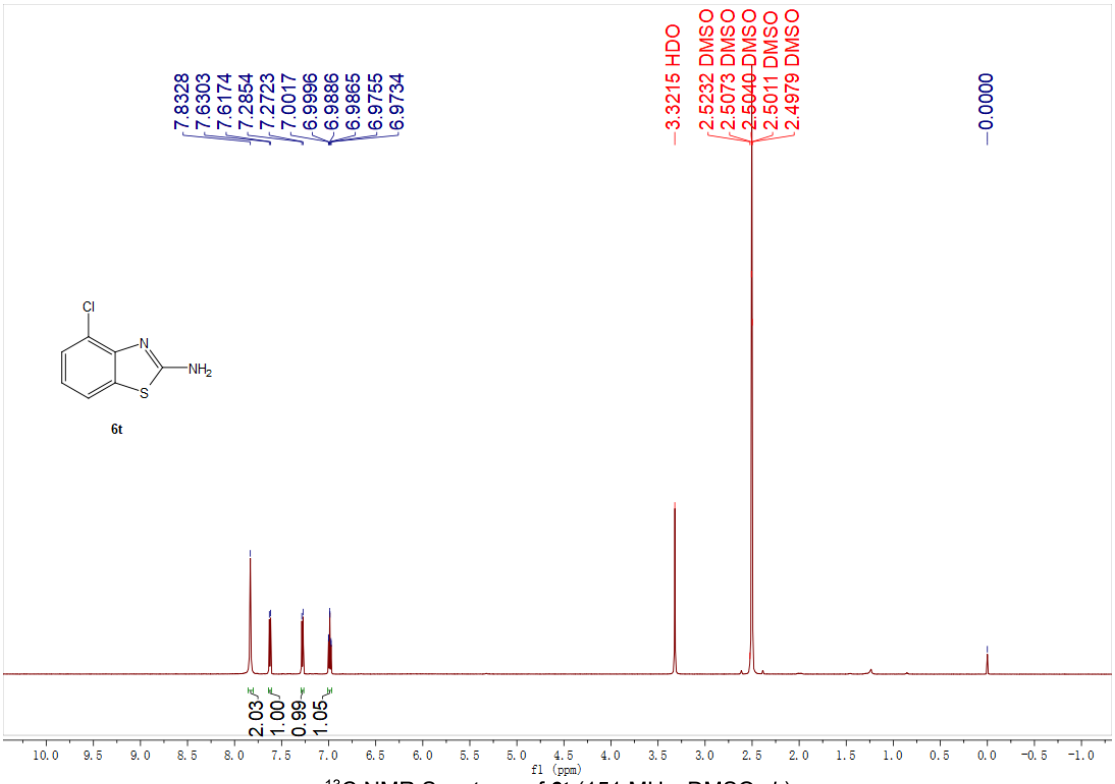
^{1}H NMR Spectrum of **6s** (600 MHz, DMSO-d_6)



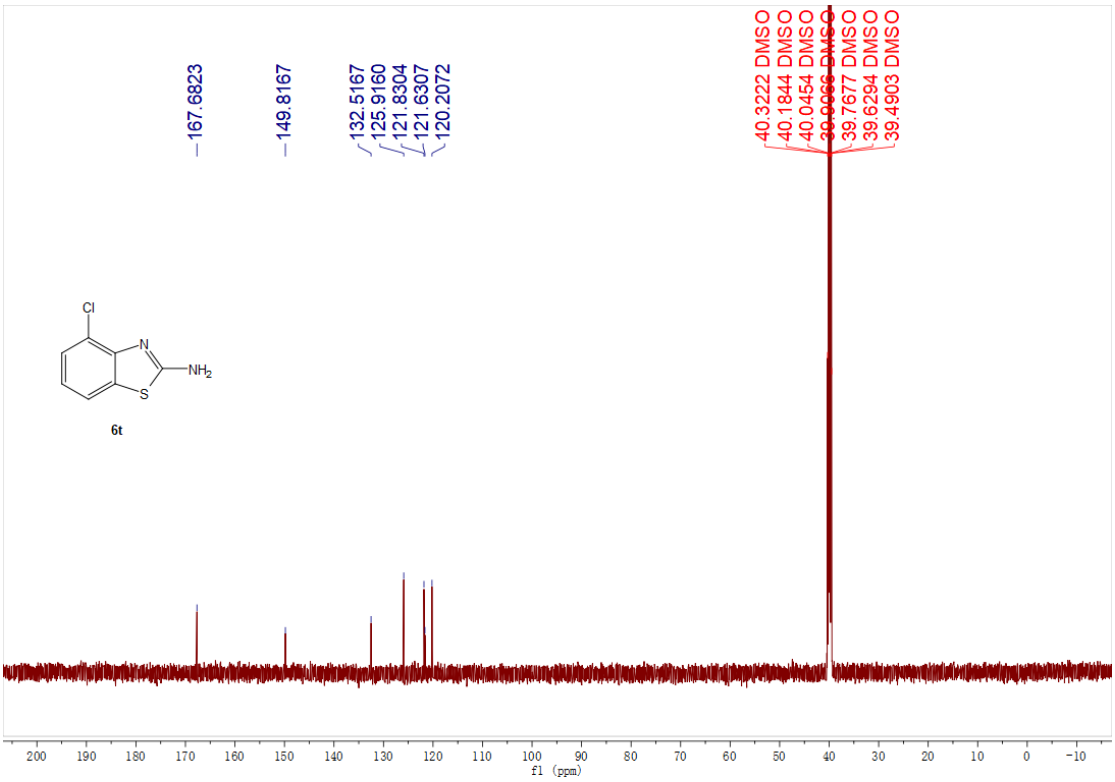
^{13}C NMR Spectrum of **6s** (151 MHz, DMSO-d_6)



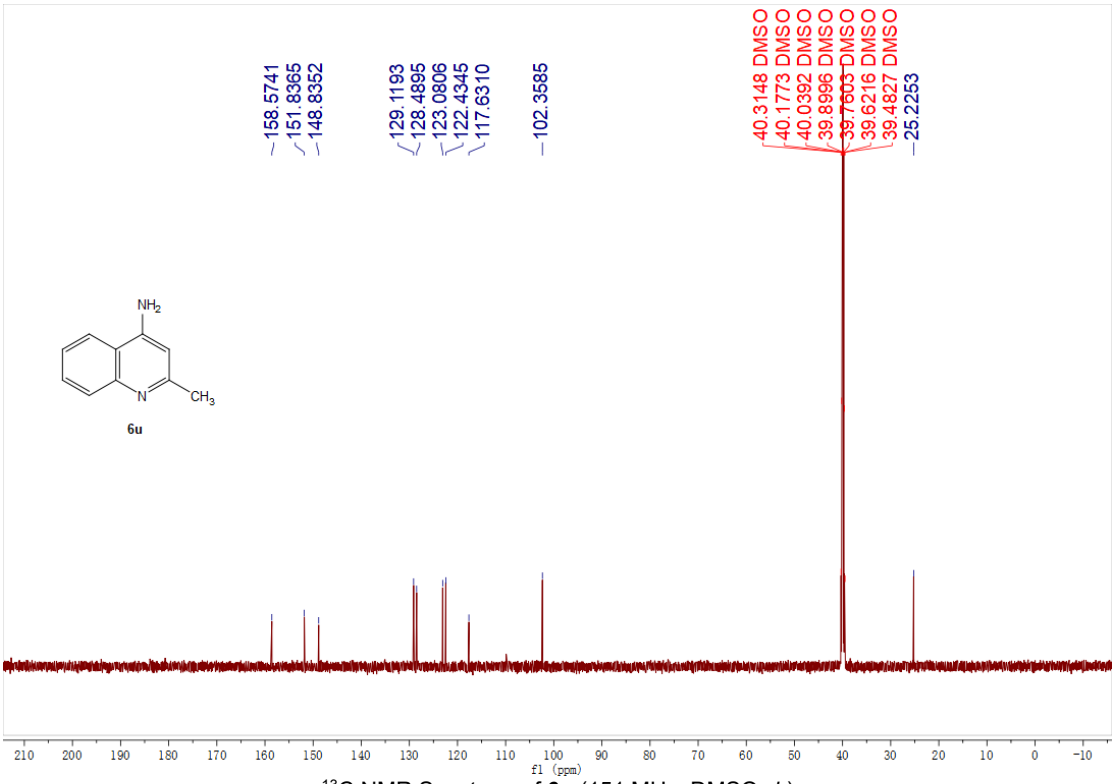
^{1}H NMR Spectrum of **6t** (600 MHz, DMSO-d_6)



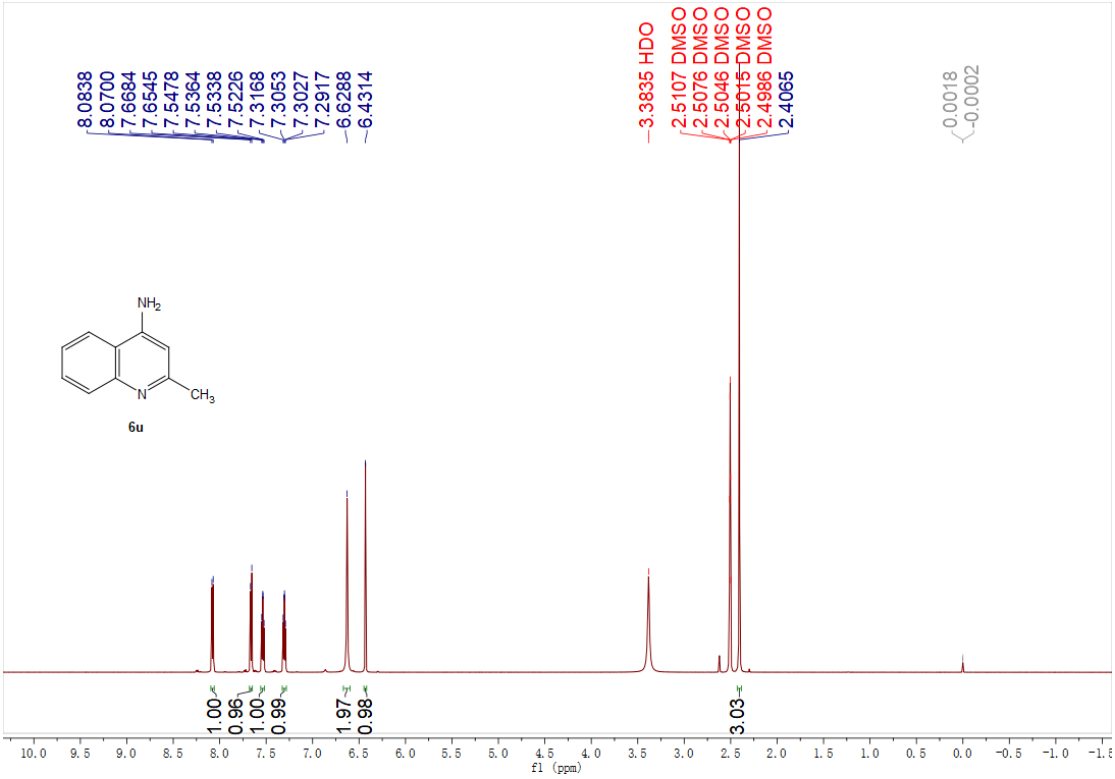
^{13}C NMR Spectrum of **6t** (151 MHz, DMSO-d_6)



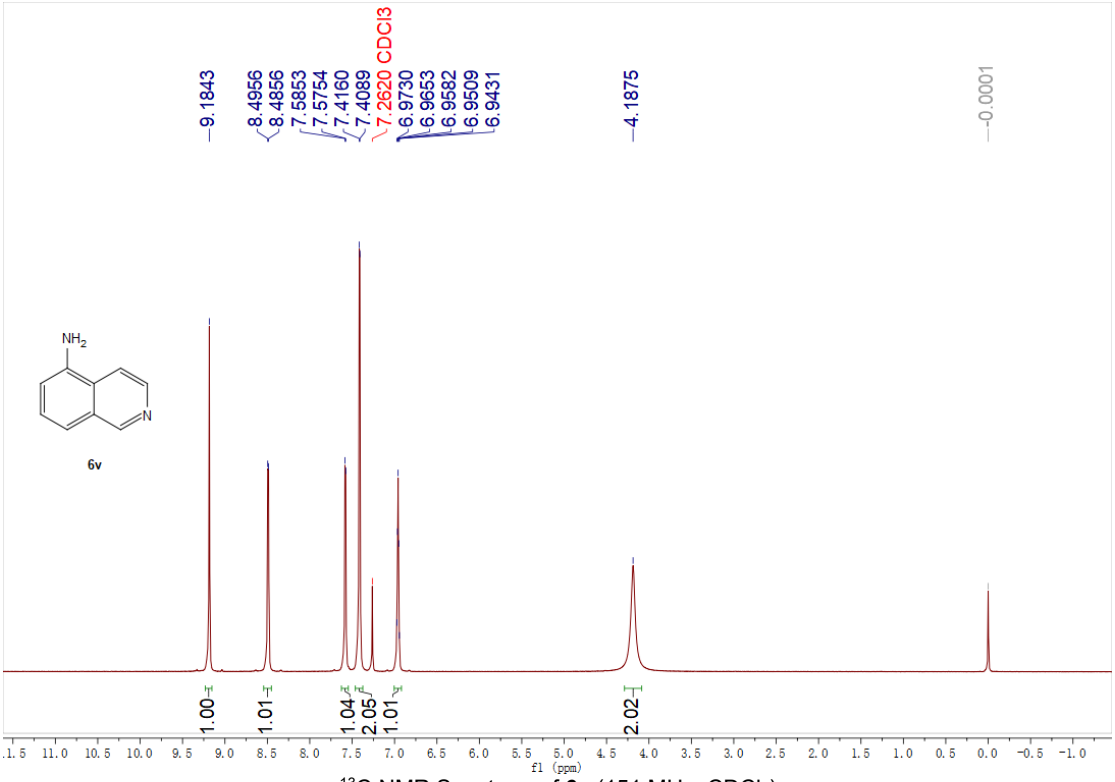
^{1}H NMR Spectrum of **6u** (600 MHz, DMSO-d_6)



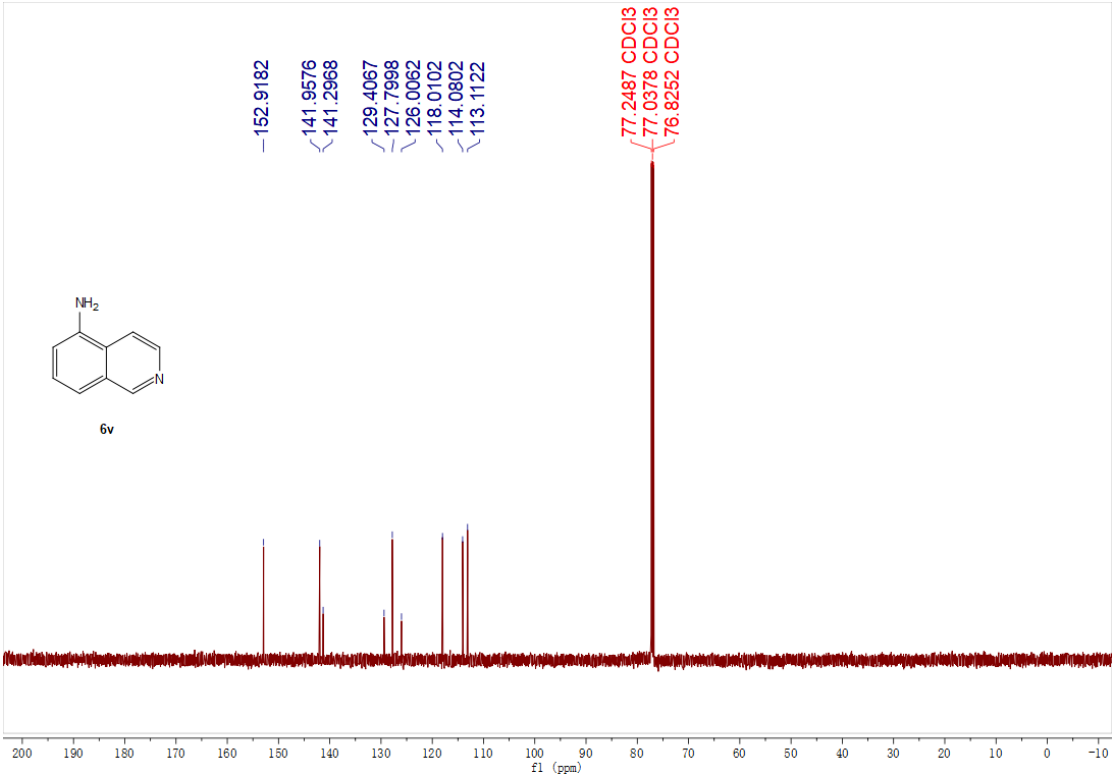
^{13}C NMR Spectrum of **6u** (151 MHz, DMSO-d_6)



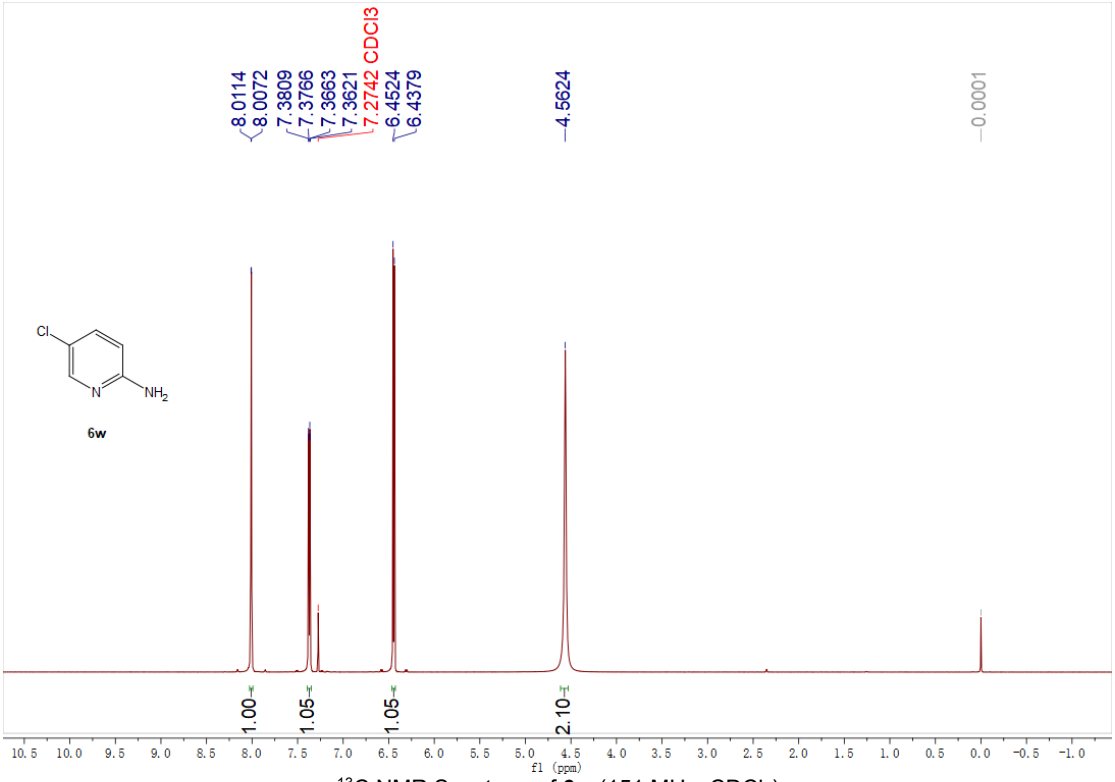
^{1}H NMR Spectrum of **6v** (600 MHz, $CDCl_3$)



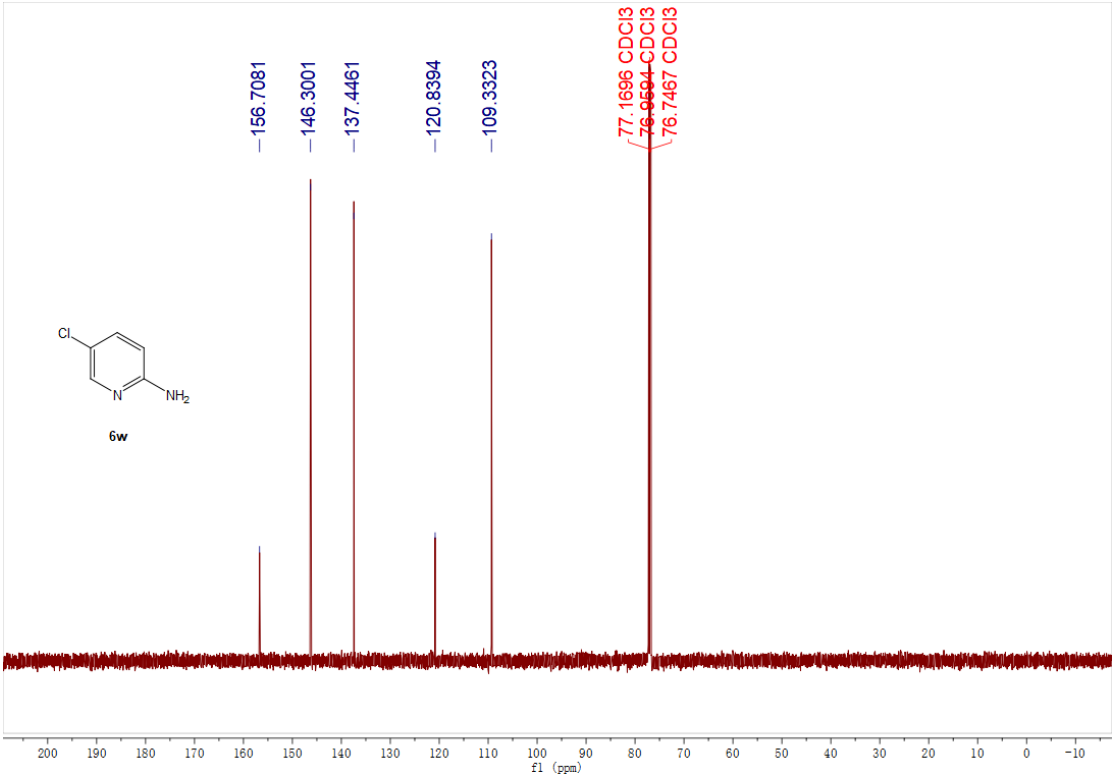
^{13}C NMR Spectrum of **6v** (151 MHz, $CDCl_3$)



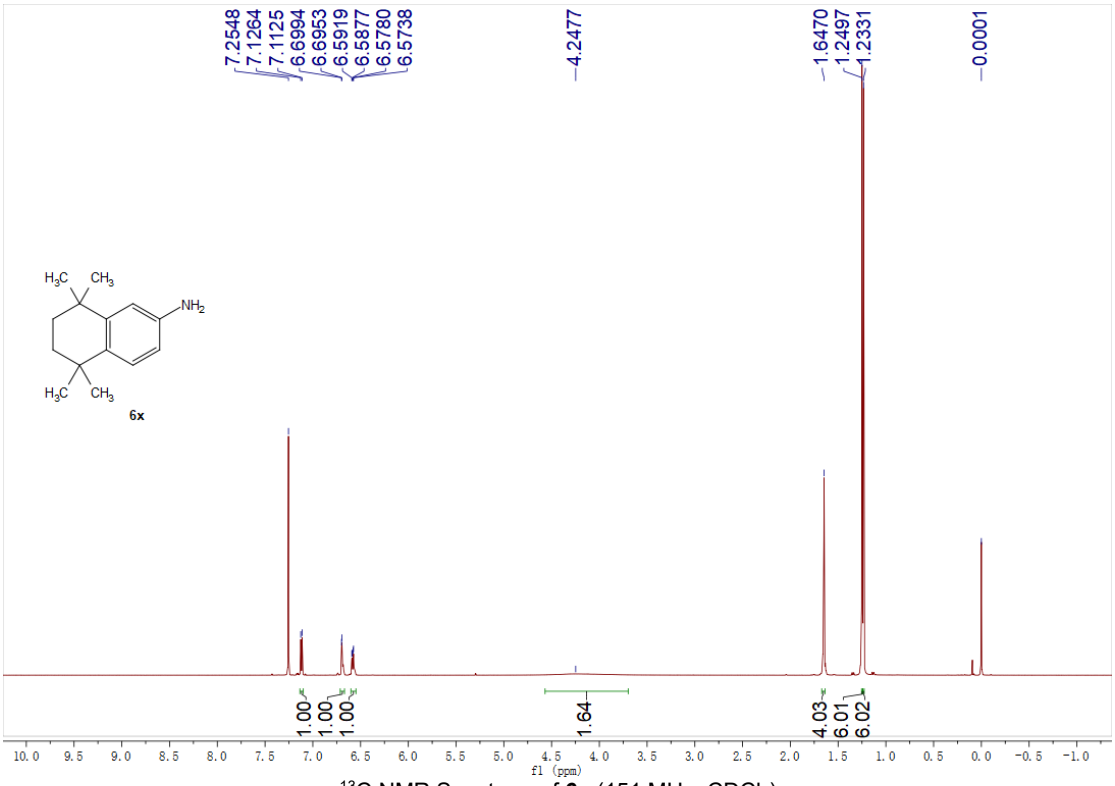
^{1}H NMR Spectrum of **6w** (600 MHz, $CDCl_3$)



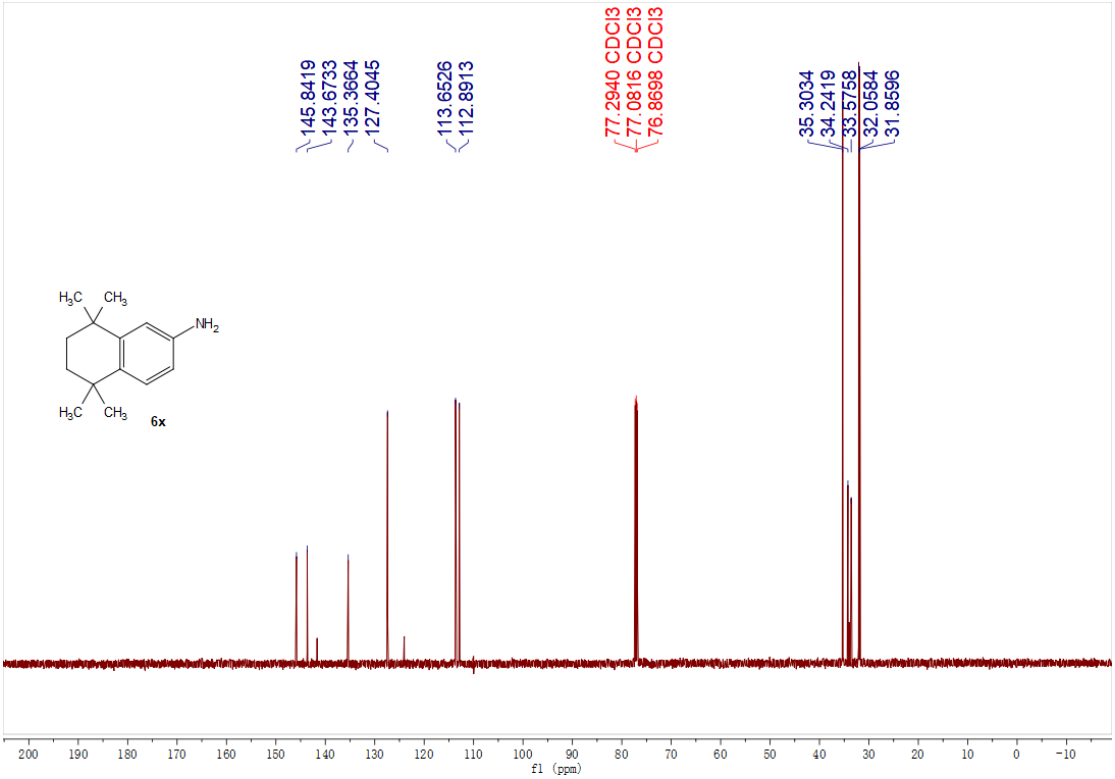
^{13}C NMR Spectrum of **6w** (151 MHz, $CDCl_3$)



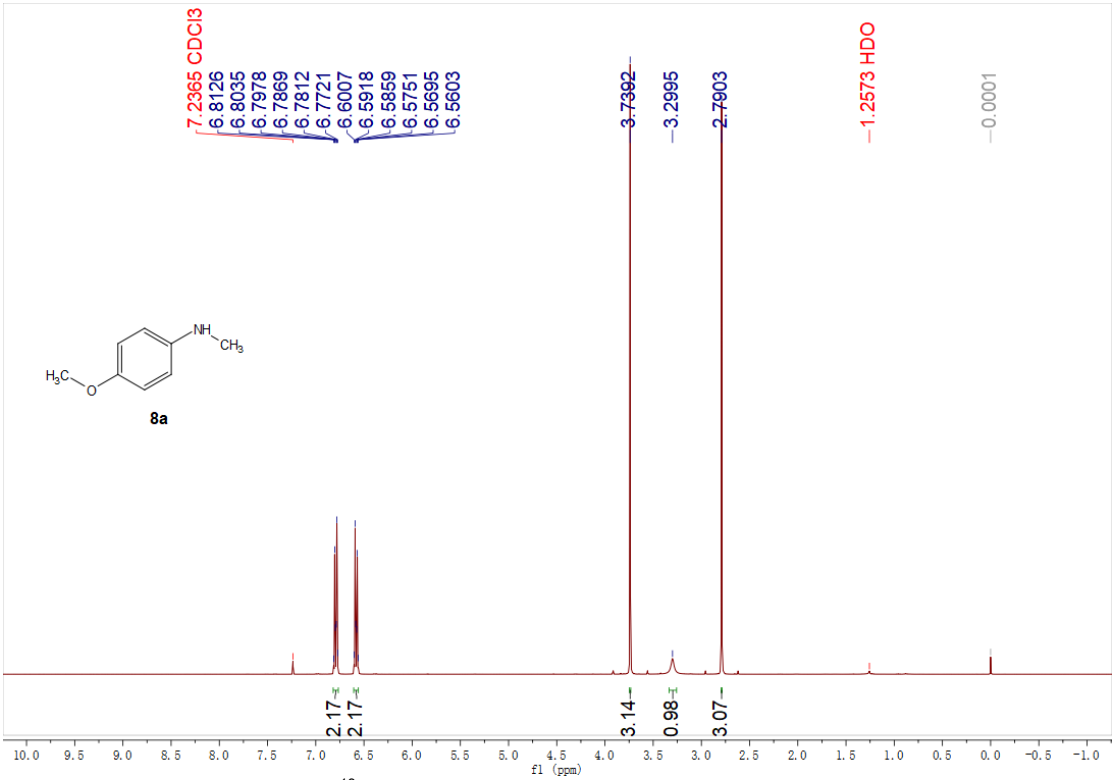
^{1}H NMR Spectrum of **6x** (600 MHz, $CDCl_3$)



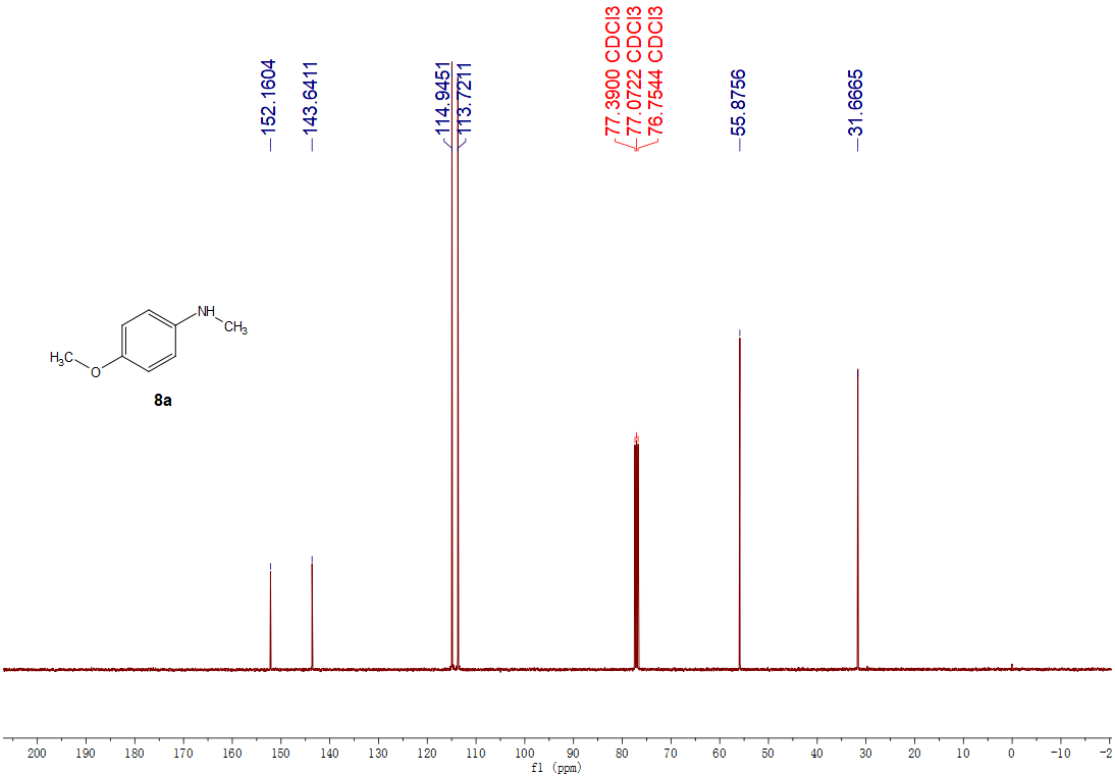
^{13}C NMR Spectrum of **6x** (151 MHz, $CDCl_3$)



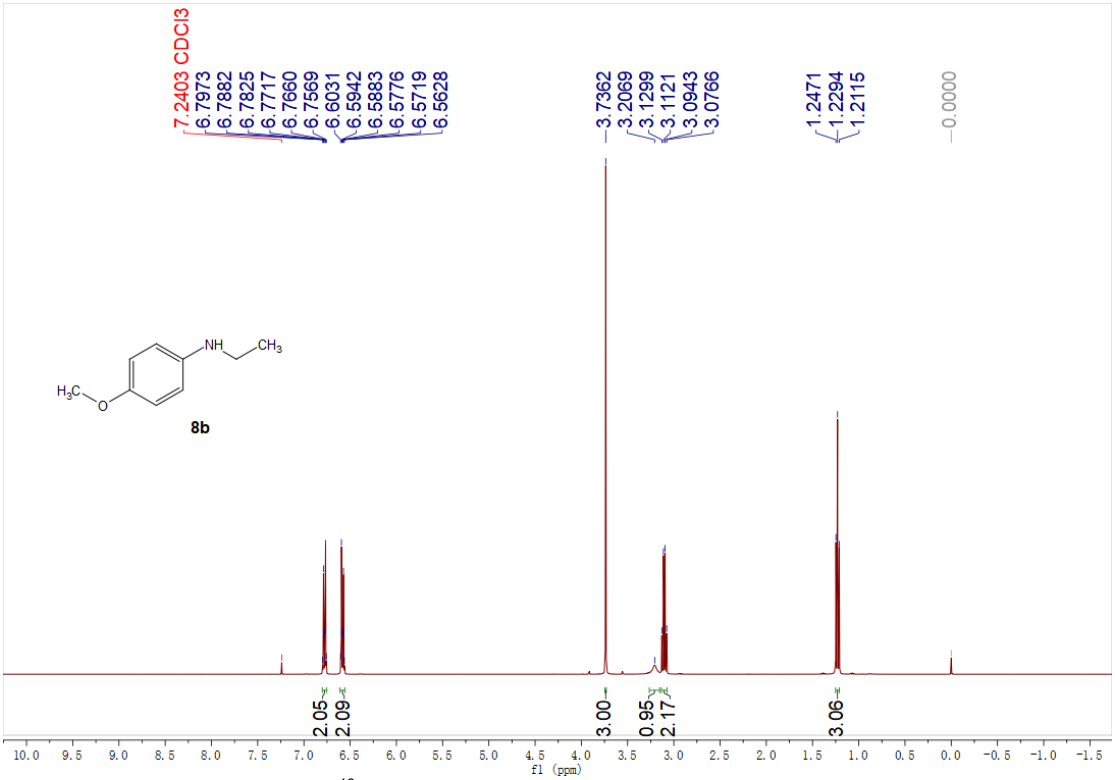
^{1}H NMR Spectrum of **8a** (400 MHz, $CDCl_3$)



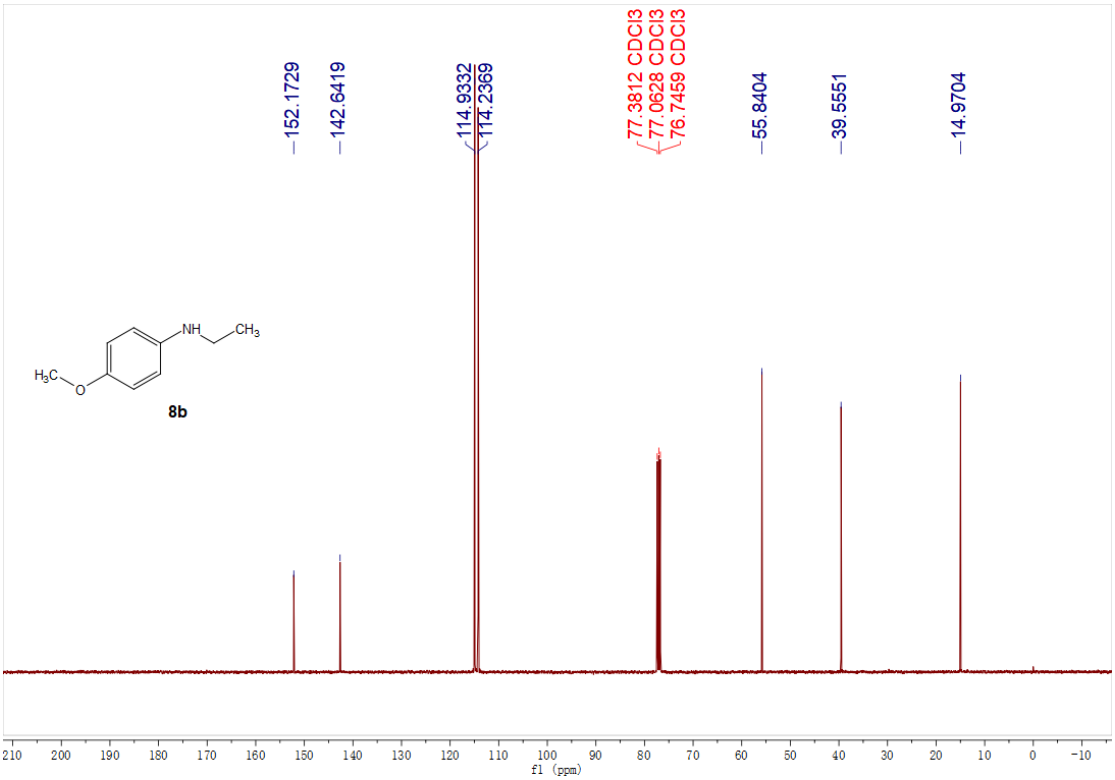
^{13}C NMR Spectrum of **8a** (101 MHz, $CDCl_3$)



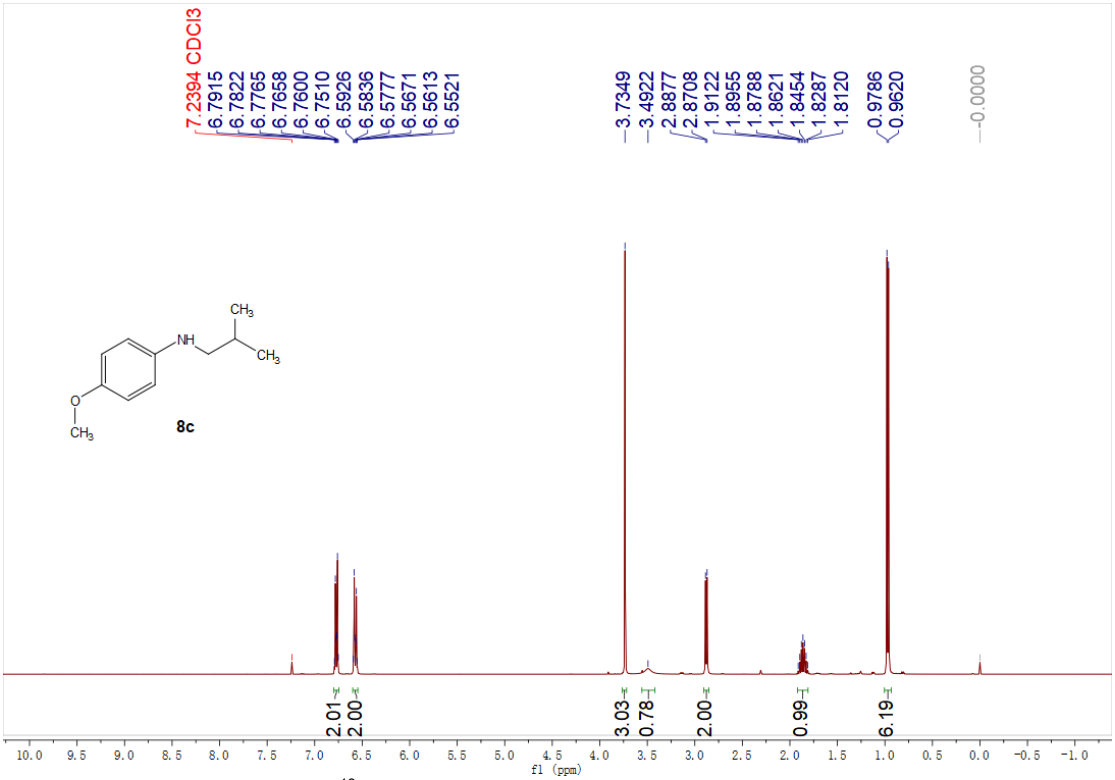
^{1}H NMR Spectrum of **8b** (400 MHz, $CDCl_3$)



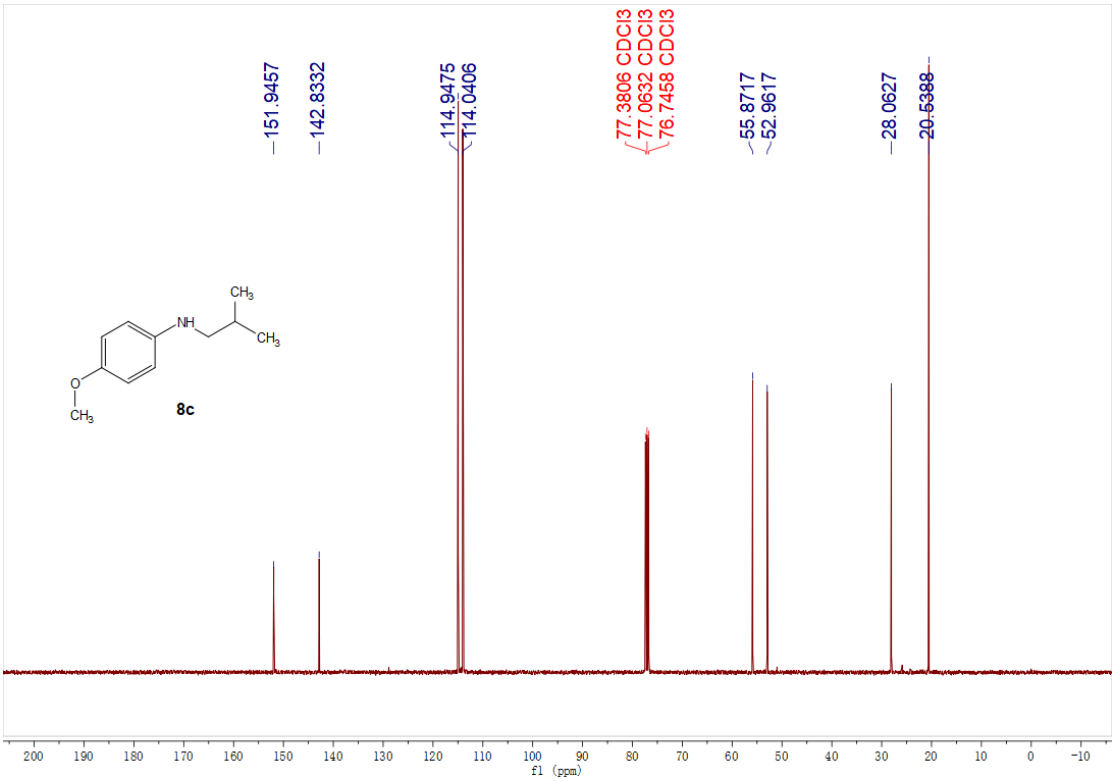
^{13}C NMR Spectrum of **8b** (101 MHz, $CDCl_3$)



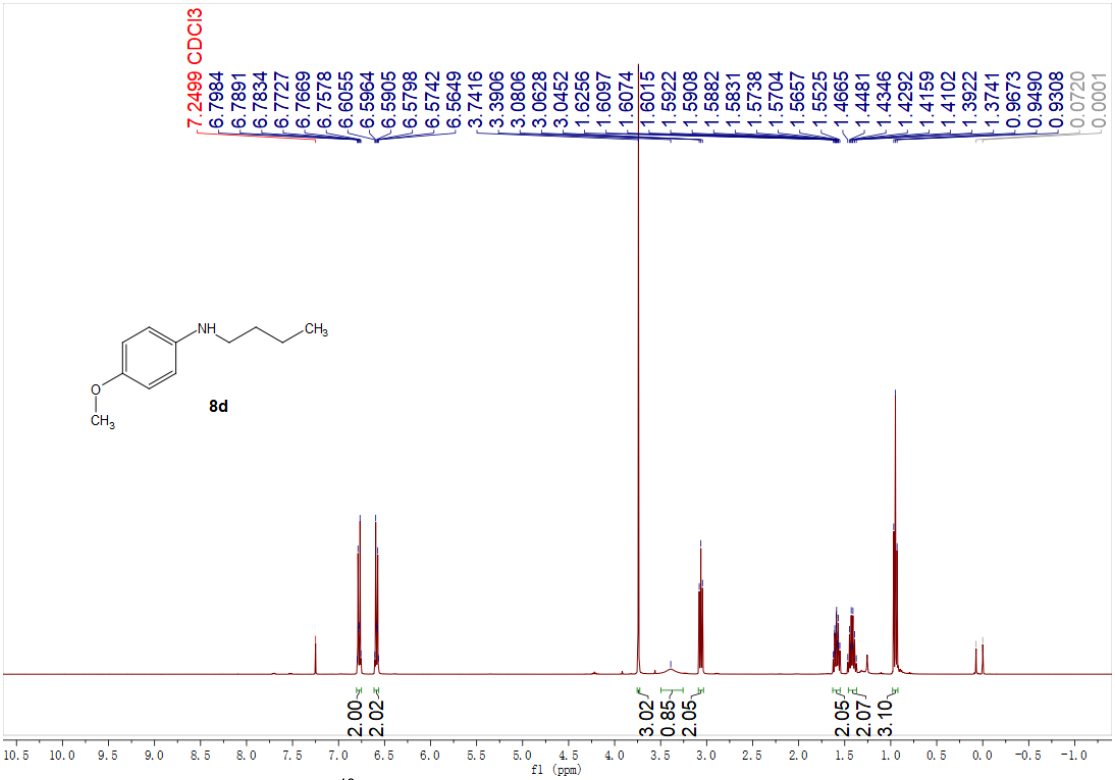
^{1}H NMR Spectrum of **8c** (400 MHz, $CDCl_3$)



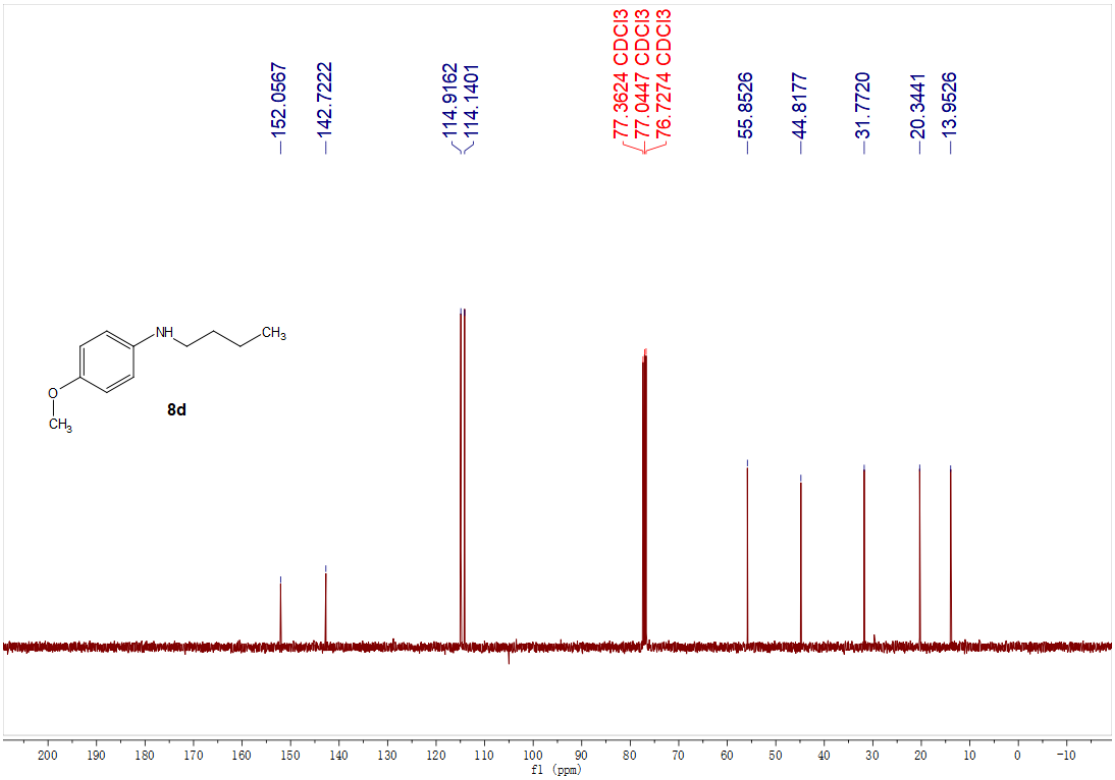
^{13}C NMR Spectrum of **8c** (101 MHz, $CDCl_3$)



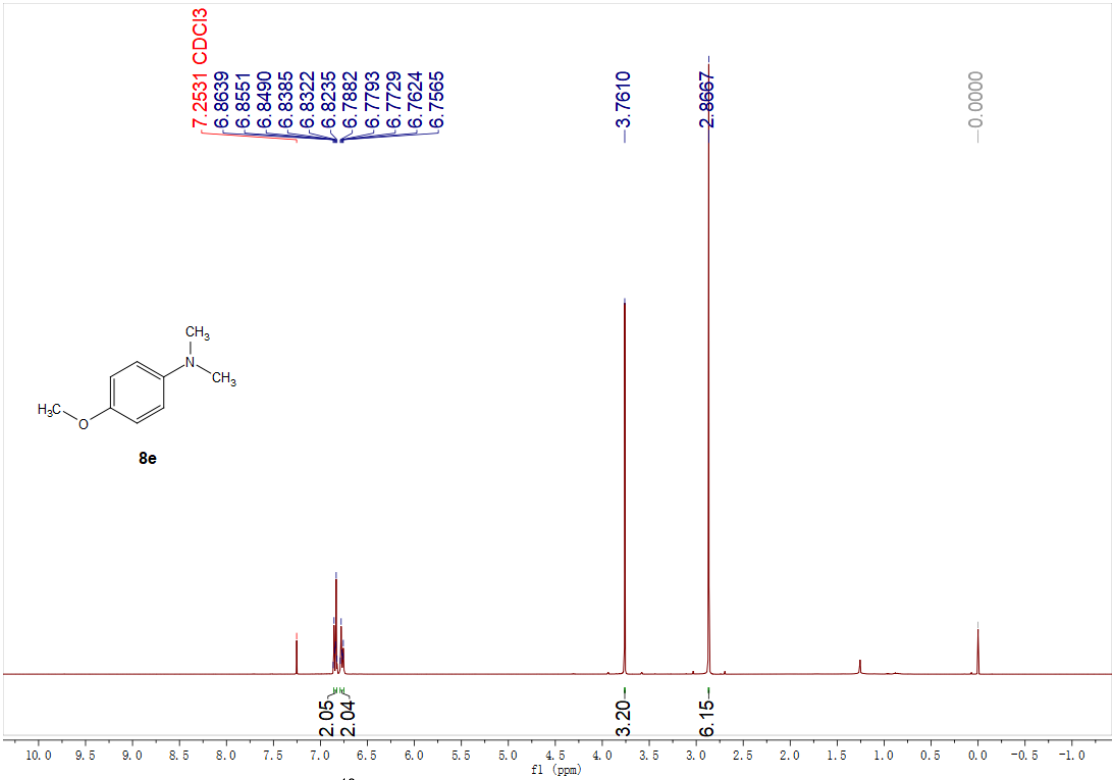
^{1}H NMR Spectrum of **8d** (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **8d** (101 MHz, $CDCl_3$)

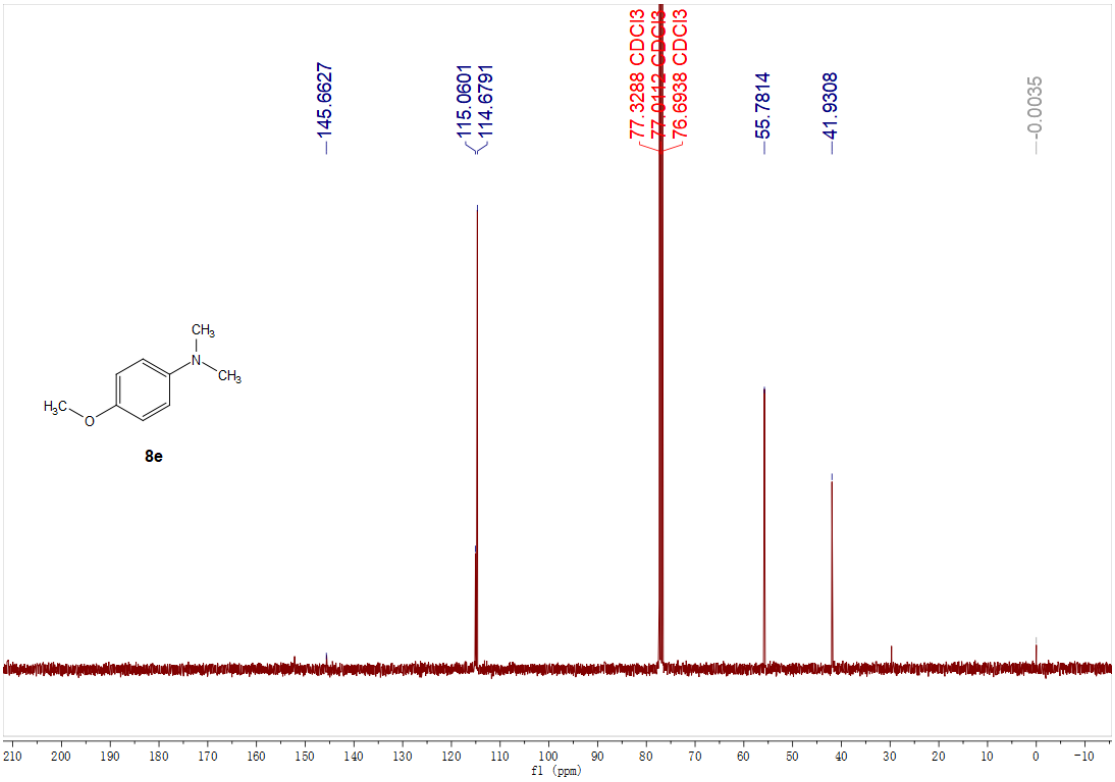


^{1}H NMR Spectrum of **8e** (400 MHz, $CDCl_3$)



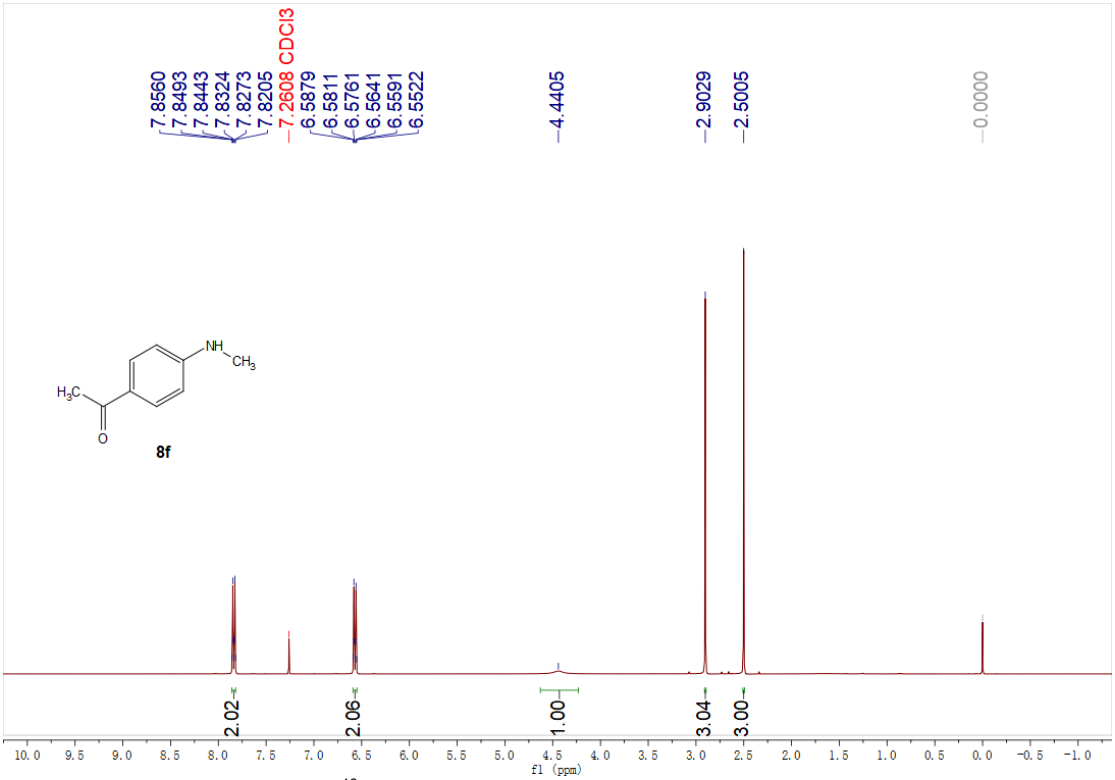
8e

^{13}C NMR Spectrum of **8e** (101 MHz, $CDCl_3$)

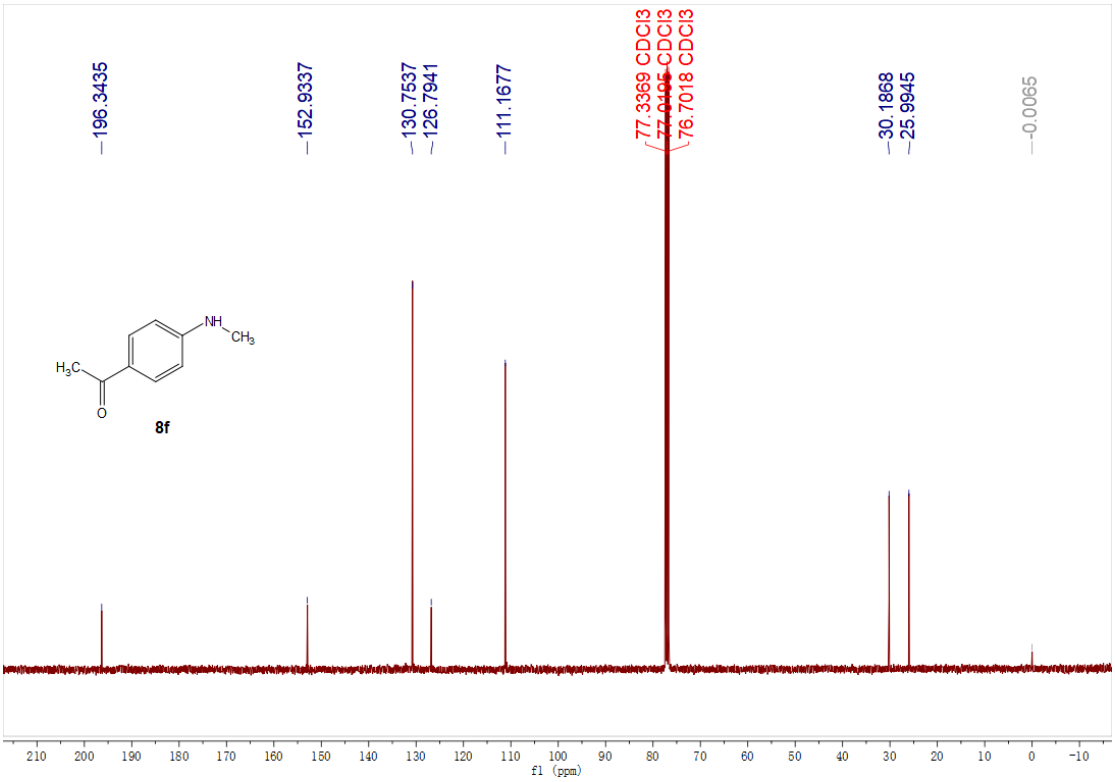


8e

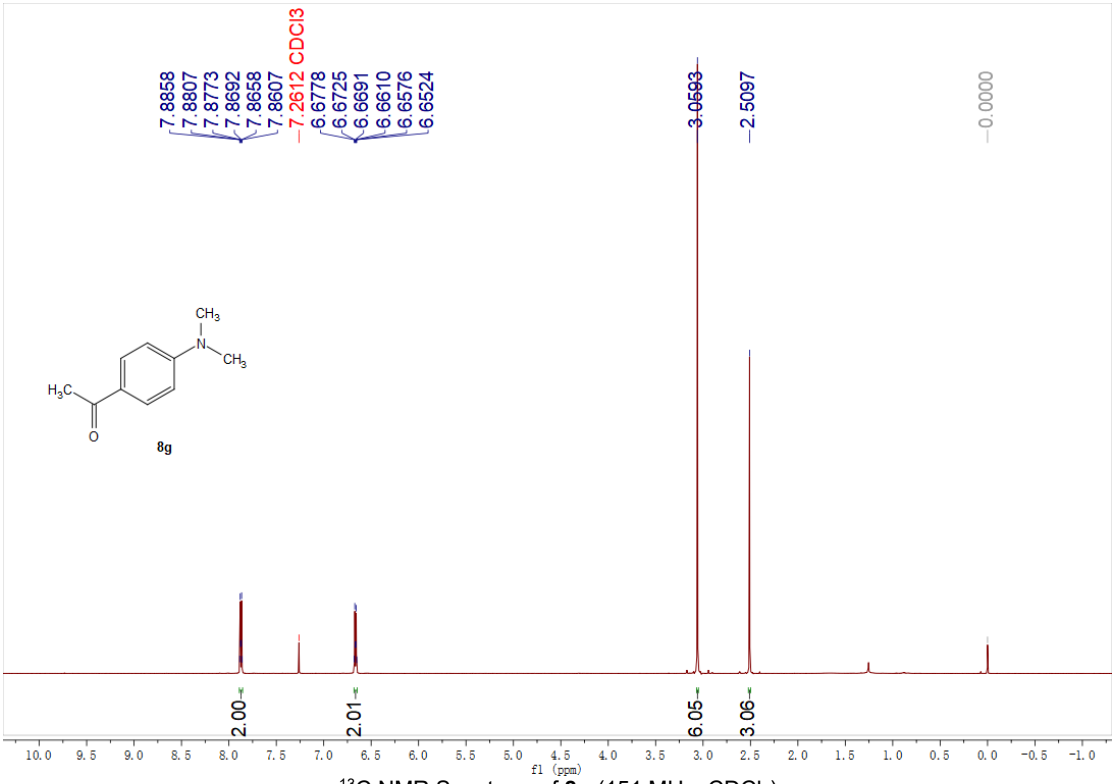
^{1}H NMR Spectrum of **8f** (400 MHz, $CDCl_3$)



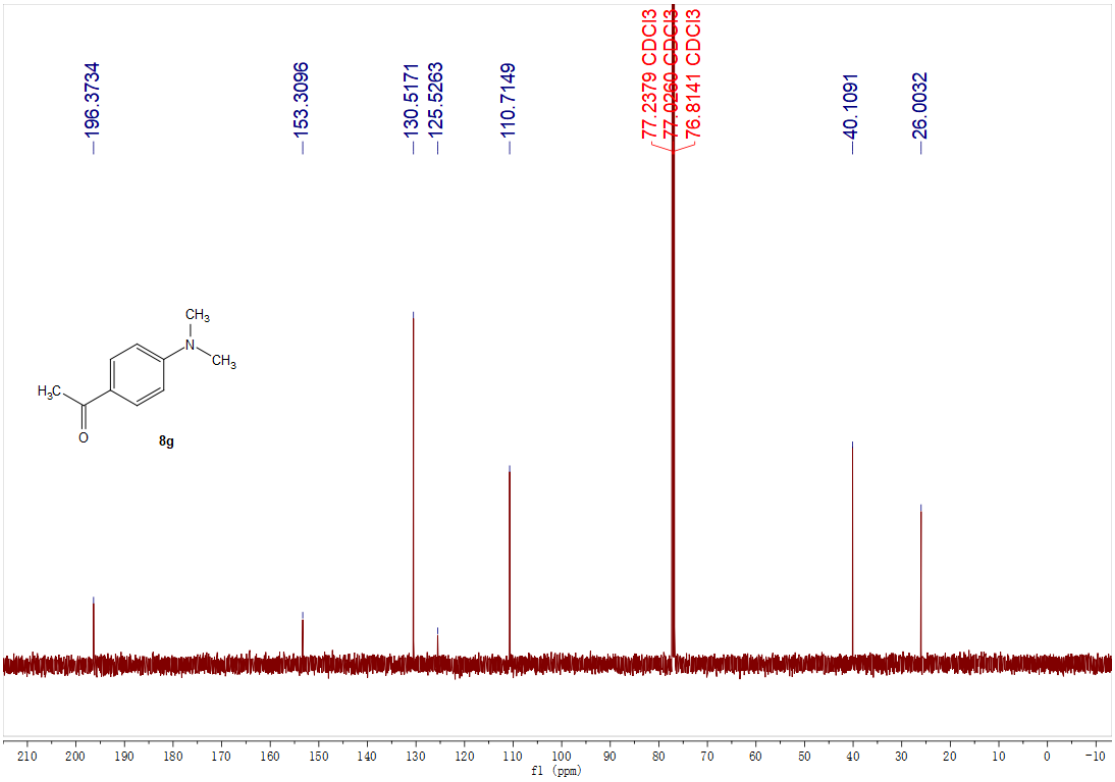
^{13}C NMR Spectrum of **8f** (101 MHz, $CDCl_3$)



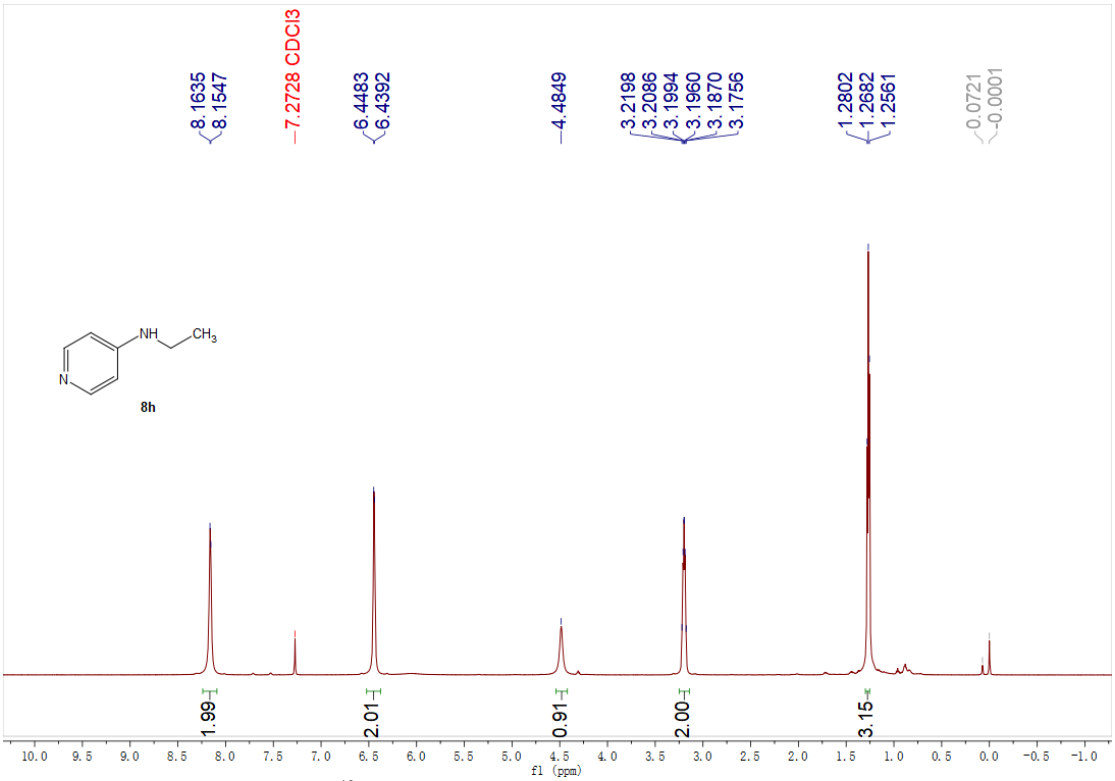
^{1}H NMR Spectrum of **8g** (600 MHz, $CDCl_3$)



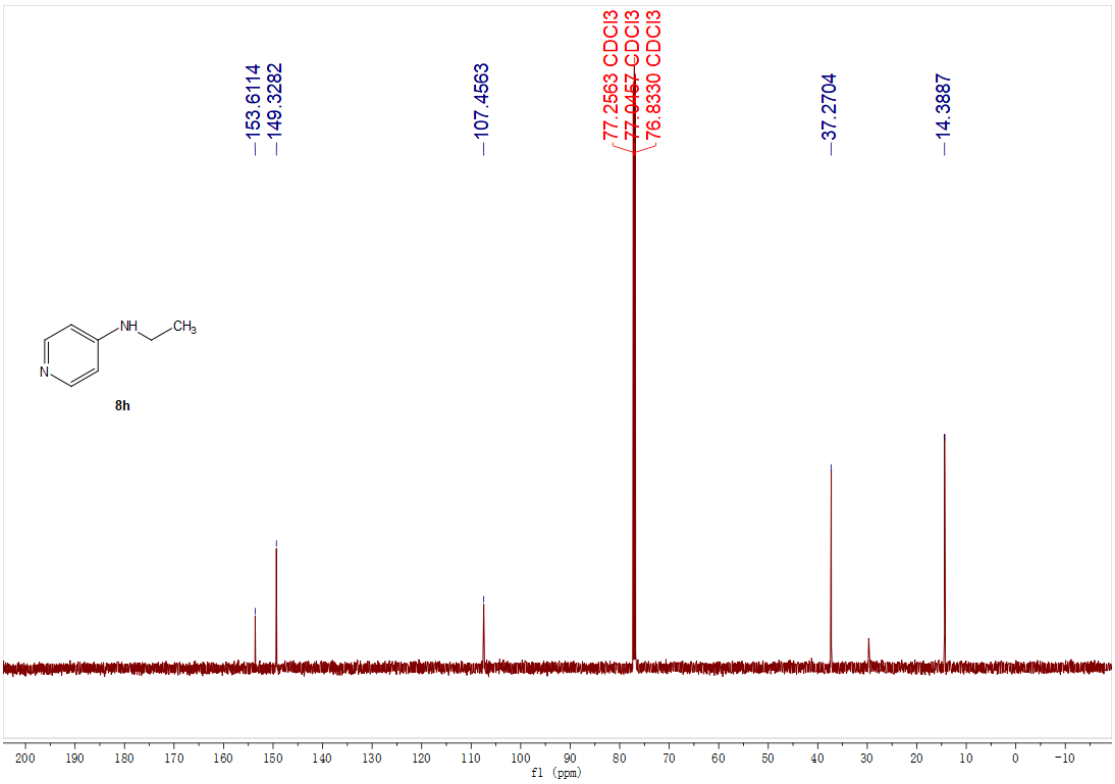
^{13}C NMR Spectrum of **8g** (151 MHz, $CDCl_3$)



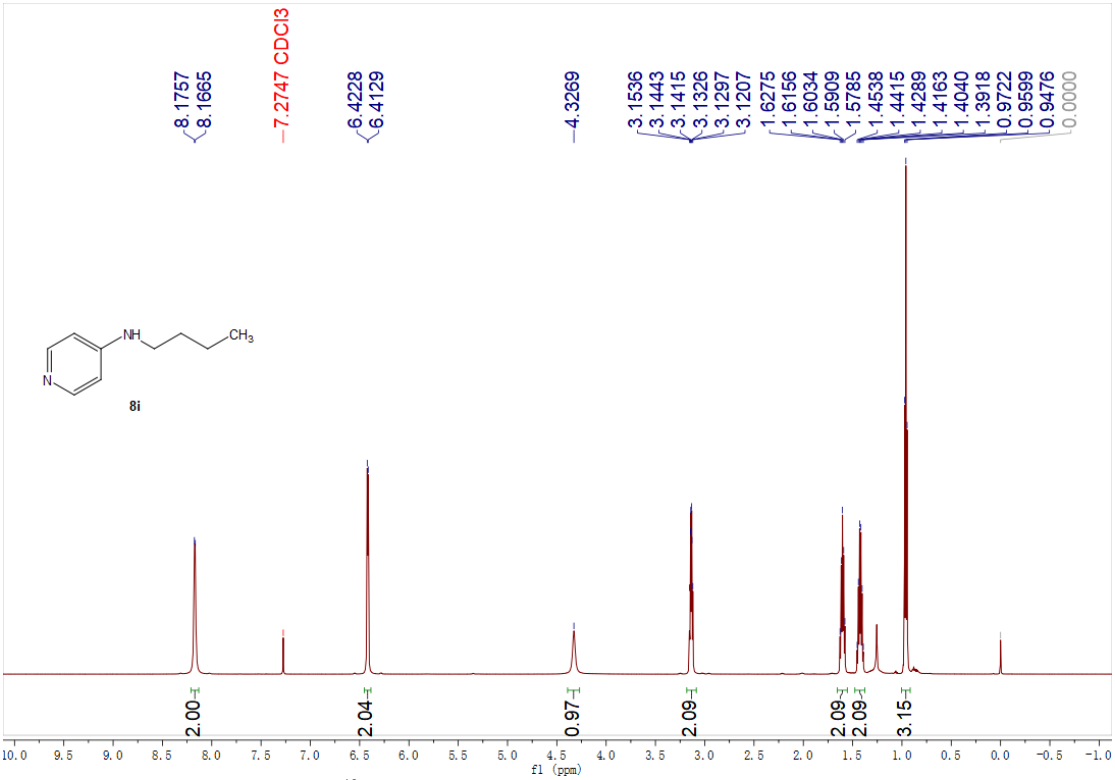
^{1}H NMR Spectrum of **8h** (600 MHz, $CDCl_3$)



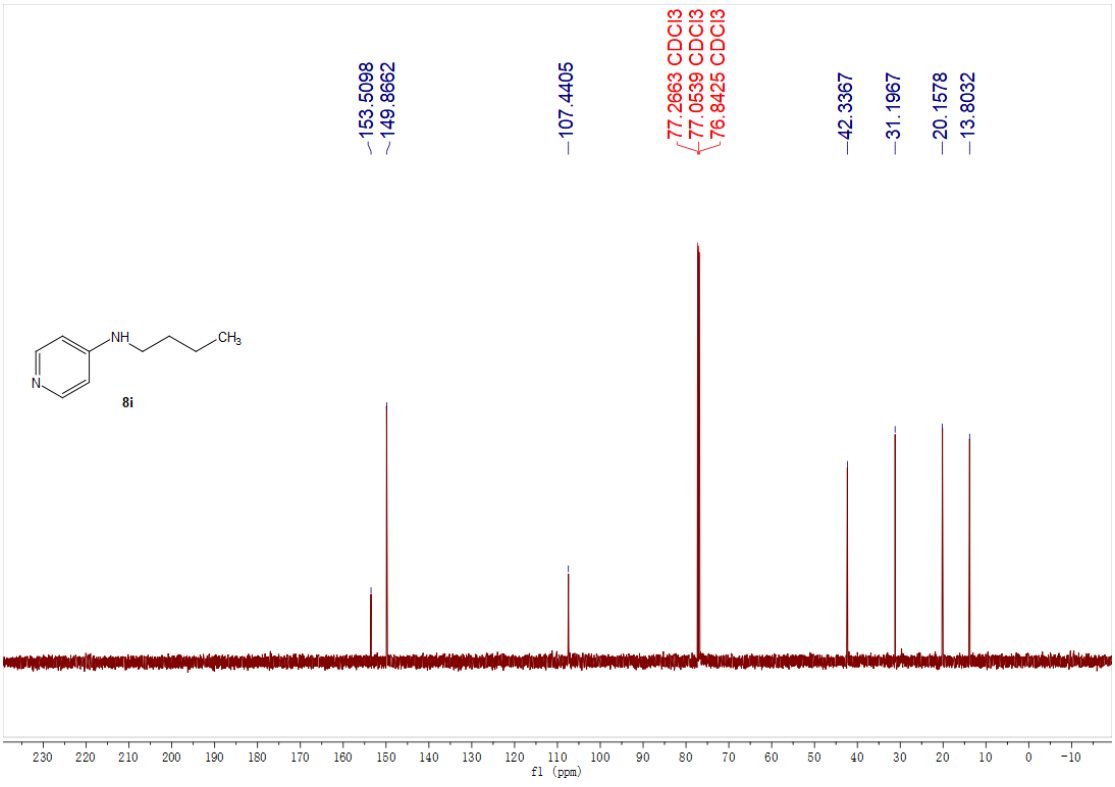
^{13}C NMR Spectrum of **8h** (151 MHz, $CDCl_3$)



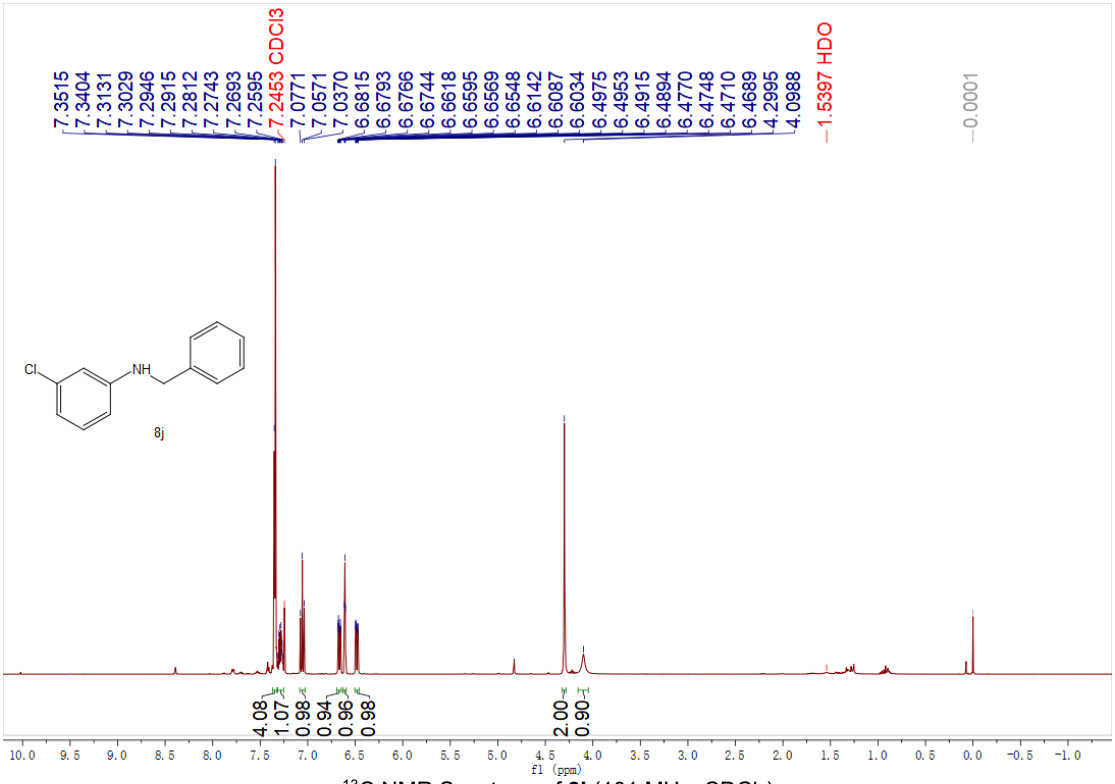
^{1}H NMR Spectrum of **8i** (600 MHz, $CDCl_3$)



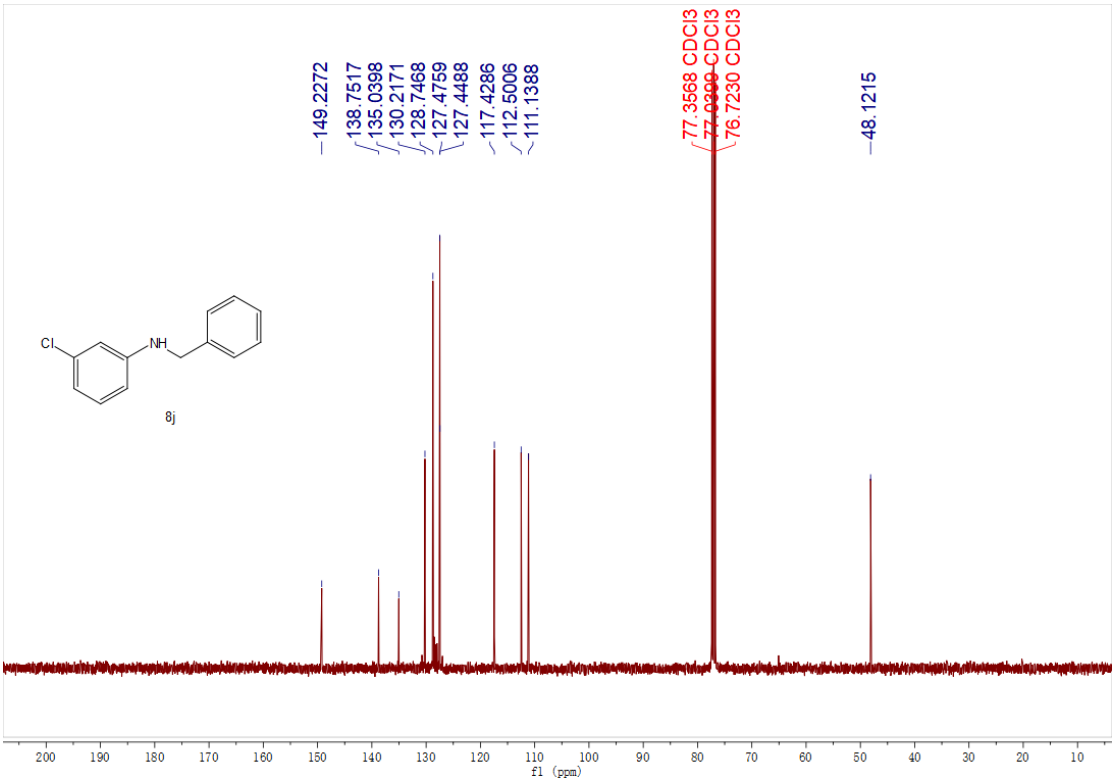
^{13}C NMR Spectrum of **8i** (151 MHz, $CDCl_3$)



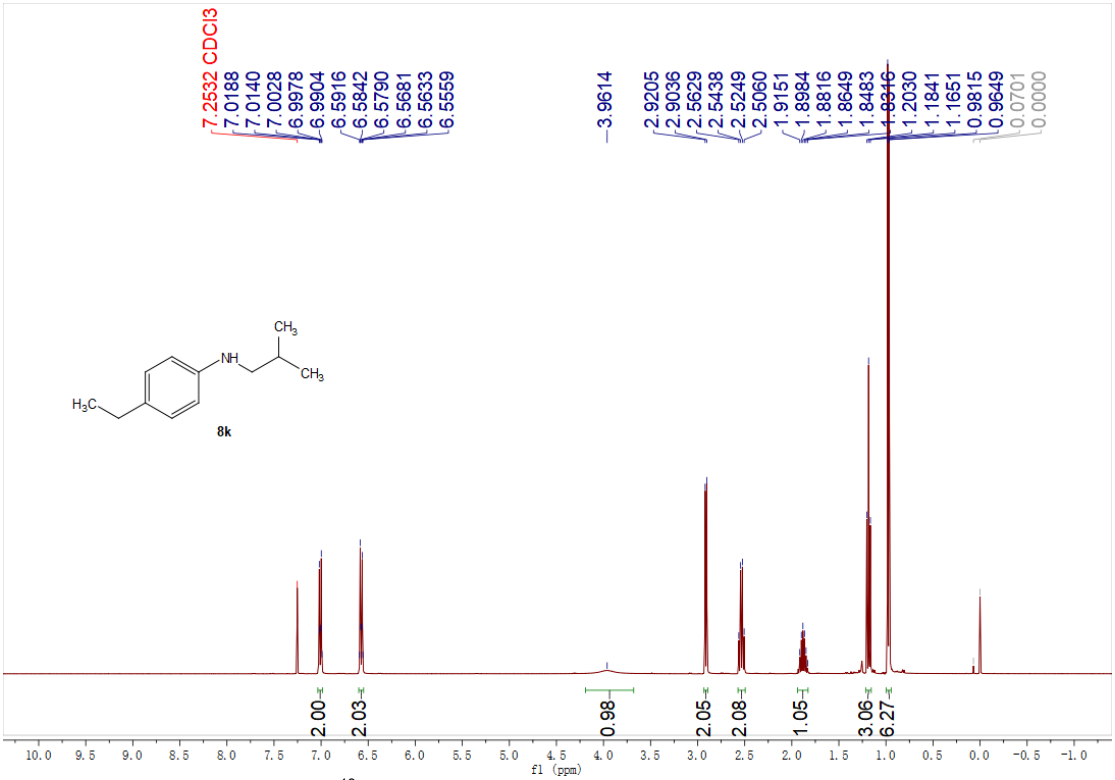
^{1}H NMR Spectrum of **8j** (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **8j** (101 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **8k** (400 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **8k** (101 MHz, $CDCl_3$)