Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Direct C-H Bond Heteroarylation by Acenaphthyl-based diimine Palladium Complexes: A General Access for bi(hetero)aryls under Aerobic Conditions

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Contents

1. Materials and Physical Measurements

1, 3, 5-tri-tert-butylbenzene, zinc powder, zinc chloride, acenaphthenequinone, palladium chloride, heteroarenes and heteroaryl bromides were purchased from Beijing HWEK Chem. Co., Ltd and Darui Chemical Reagent Factory. Solvents and bases were purchased from Guangzhou Chemical Reagent Factory and used without any further purification. The NMR spectra were recorded by using TMS as internal standard on a Bruker DMX 400 MHz spectrometer and the X-ray diffraction data of single crystal was obtained on a Bruker SMART 1000 CCD diffractometer.

2. Experimental Procedure

Synthesis of 1, 3, 5-tri-tert-butyl-2-nitrobenzene (n1): 1, 3, 5-tri-tert-butylbenzene (4.93g, 20 mmol) was dissolved in CH_2Cl_2 (84 mL), Ac_2O (56 mL), and AcOH (42 mL). The solution was cooled to 0 °C and fuming nitric acid (8.4 mL) was added dropwise for 1 h while keeping temperature between 0 and 5 °C. The resulting solution was stirred for an additional 5 h at 0 °C and then warmed to room temp. Next, water (100mL) and CH_2Cl_2 (60 mL) were added. The organic layer was separated and washed with cold aqueous NaOH (0.1 M) to remove acids as well as unreacted Ac_2O. The organic solution was then washed with brine, dried with $MgSO_4$, and filtered. The volatiles were removed under reduced pressure and the residue recrystallized from hot ethanol to provide 1, 3, 5-tri-tert-butyl-2-nitrobenzene (5.20 g, 89% yield) as white crystals.

Synthesis of 2, 4, 6-tri-tert-butylaniline(a1): 1, 3, 5-tri-tert-butylbenzene (4.66g, 16 mmol), Zn powder (8.37g, 128mmol) was combined in EtOAc/EtOH (80mL/80mL)

under a nitrogen atmosphere, and concentrated HCl/AcOH (16mL/16mL) was added dropwise for 0.5h. The mixture was heated to 70°C for 4h and evaporated under reduced pressure. The residue was added $NH_3 \cdot H_2O$ to adjust the reaction mixture to approximately pH 7~8 and extracted three times with CH_2Cl_2, the extract was washed with brine, dried with $MgSO_4$ and filtered. The solvent was removed under reduced pressure and purified by recrystallization from ethanol to give 2, 4, 6-tri-tert-butylaniline (3.05g, 73%yield) as white crystals.

Synthesis of N, N'-(acenaphthylene-1, 2-diylidene)bis(2, 4-di-tert-butylaniline) (L1): 40 ml of glacial acetic acid was added to a mixture of acenaphthenequinone (0.91g, 5 mmol), 2, 4, 6-tri-tert-butylaniline (2.61g, 10 mmol) and $ZnCl_2$ (1.36g, 10 mmol). The mixtures were heated to reflux for 5 h, and then cooled down to room temperature. Orange–red solids precipitated. These solids were filtered off, washed with acetic acid (3 × 50 ml) and hexane (3 × 50 ml), and dried in vacuum. And then suspending the orange–red solids in 200 ml of CH_2Cl_2, and solutions of $K_2C_2O_4$ (2.49g, 15 mmol) in water (60 ml) were added. The mixtures were vigorously stirred over night. White precipitates of ZnC_2O_4 could be seen suspended in the aqueous phases. Separating two phases and the organic layer was washed with water (3 × 30 ml), dried with MgSO4. After removal of the solvent, red-orange solids were isolated. These solids were further purified by recrystallization from a dilute solution in dichloromethane/ethanol (15mL/20mL). 1.89g, yields:68%.

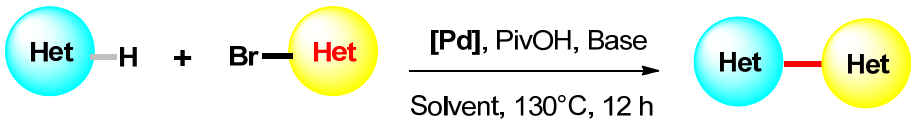
Synthesis of α-diimine palladium complexe(C1): The α-diimine ligand (0.556g, 1.0 mol) and palladium dichloride (0.177 g, 1.0 mmol) were mixed in 10 mL of methanol

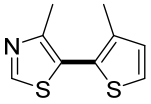
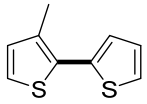
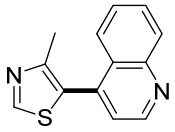
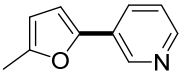
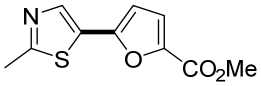
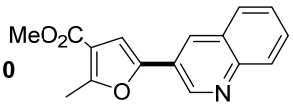
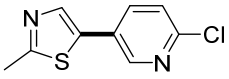
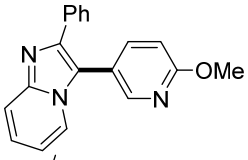
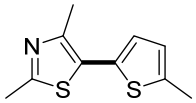
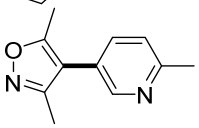
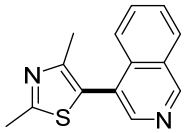
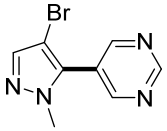
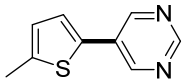
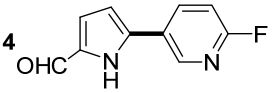
at room temperature. After the reaction mixture was heated to 70°C overnight, the methanol was removed under reduced pressure. The residue was dissolved in 5 mL of dichloromethane, and added into a short silica-gel column washing with substantial dichloromethane. Evaporating the filtrate, the solid was recrystallizated from a dilute solution in dichloromethane/ethanol (5mL/15mL). Drying in vacuum produced the saffron yellow palladium complex (0.616g, 84% yield).

General procedure for direct arylation promoted by palladium complexes: Unless otherwise noted, the direct C–H arylation reactions were carried out under aerobic conditions. All solvents were used as received and no further purification was needed. A parallel reactor containing a stirring bar was charged with Pd complexes (0.001–0.0005 mmol, extracted from a constant volume in the standard stock solution of DMAc), heteroarene (2.0 mmol), heteroaryl bromide (1.0 mmol), base (2.0 mmol), solvent (3 mL), 130 °C for 12 h. After completion of the reaction, the reaction mixture was cooled to ambient temperature and 10 mL of water was added. The mixture was diluted with dichloromethane (5 mL), followed by extraction three times (3 × 5 mL) with dichloromethane. The organic layer was dried with $MgSO_4$, filtered and evaporated under reduced pressure. The crude cross-coupling products were purified by silica-gel column chromatography using petroleum ether–dichloromethane (15/1) as an eluent. The isolated cross-coupling products were characterized by ^{1}H NMR and ^{13}C NMR, and the spectra can be found in the ESI.†

Comparative experiment of C1 and C2:

Table S1. Palladium-catalyzed direct arylation of heteroarenes with heteroaryl bromides[a]

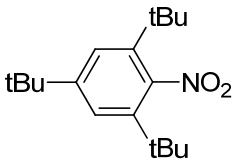


Run	Product	C1/(%)	C2/(%)	Run	Product	C1/(%)	C2/(%)
1		89	76	8		85	33
2		96	95	9		78	60
3		73	54	10		98	80
4		97	96	11		73	71
5		72	8	12		86	70
6		96	96	13		85	37
7		68	28	14		97	74

[a]Reaction conditions: palladium complex of **C1** or **C2** (0.001 mmol), heteroarenes (2 mmol), heteroaryl bromides (1 mmol), PivOH (0.3 mmol), K_2CO_3 (2 mmol), DMAc (3 mL), 130 °C for 12 h in an aerobic environment. Cross-coupling was performed in two parallel reactions and the isolated yield is given in average.

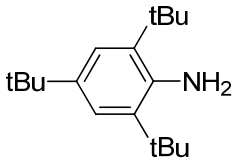
3. NMR data for the products

n1:1, 3, 5-tri-tert-butyl-2-nitrobenzene



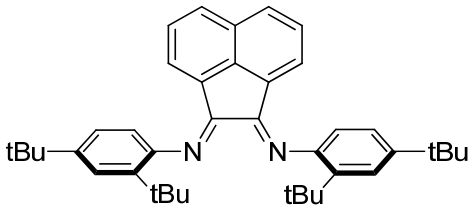
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, Ar-H, 2H), 4.07 (s, N-H, 2H), 1.51 (s, $C(CH_3)_3$, 18H), 1.33 (s, $C(CH_3)_3$, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 139.0, 133.4, 121.9, 34.8, 34.4, 31.7, 30.3.

a1: 2, 4, 6-tri-tert-butylaniline



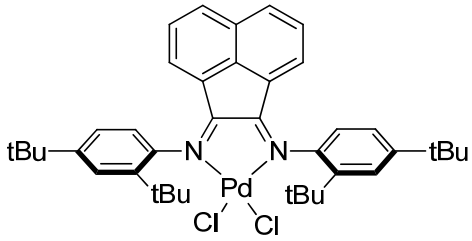
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, Ar-H, 2H), 4.07 (s, N-H, 2H), 1.51 (s, $C(CH_3)_3$, 18H), 1.33 (s, $C(CH_3)_3$, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 139.0, 133.4, 121.9, 34.8, 34.4, 31.7, 30.3.

L1: N, N'-(acenaphthylene-1, 2-diylidene)bis(2, 4-di-tert-butylaniline)



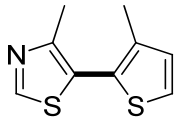
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, Ar-H, 2H), 7.53 (d, *J* = 2.0 Hz, Ar-H, 2H), 7.36 (dd, *J* = 8.1, 7.4 Hz, Ar-H, 2H), 7.23 (dd, *J* = 8.1, 2.1 Hz, Ar-H, 2H), 6.84 (t, *J* = 7.7 Hz, Ar-H, 4H), 1.40 (d, *J* = 8.4 Hz, $(CH_3)_3$, 36H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 147.9, 147.2, 141.6, 138.5, 131.1, 129.4, 128.4, 127.6, 123.7, 123.5, 123.3, 118.4, 35.7, 34.7, 31.7, 29.8. EIS-MS: 557.3 [**L1**+ H] $^{+}$.

C1: {N, N'-(acenaphthylene-1, 2-diylidene)bis(2, 4-di-tert-butylaniline)}dichloro -palladium



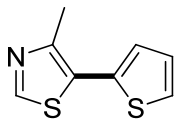
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, Ar-H, 2H), 7.63 (d, *J* = 1.5 Hz, Ar-H, 2H), 7.47 (t, *J* = 7.8 Hz, Ar-H, 2H), 7.37 (dd, *J* = 8.3, 1.7 Hz, Ar-H, 2H), 7.11 (d, *J* = 8.3 Hz, Ar-H, 2H), 6.28 (d, *J* = 7.3 Hz, Ar-H, 2H), 1.57 (s, $(CH_3)_3$, 18H), 1.41 (s, $(CH_3)_3$, 18H).^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 151.4, 144.6, 142.0, 140.5, 132.0, 131.2, 129.0, 126.4, 125.7, 125.5, 124.4, 123.3, 36.7, 35.0, 32.6, 31.4. EIS-MS: 737 [**C1** + H]$^+$; 702 [**L1** + PdCl]$^+$; 661 [**L1** + Pd]$^+$; 557 [**L1** + H]$^+$.

3a: 4-methyl-5-(3-methylthiophen-2-yl)thiazole



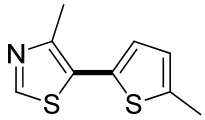
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (s, Ar-H, 1H), 7.30 (d, *J* = 5.2 Hz, Ar-H, 1H), 6.93 (d, *J* = 5.2 Hz, Ar-H, 1H), 2.40 (s, CH_3, 3H), 2.16 (s, CH_3, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9, 151.5, 137.5, 130.1, 126.0, 125.8, 123.6, 15.8, 14.6. EIS-MS: 196 [M + H] $^+$.

3b: 4-methyl-5-(thiophen-2-yl)thiazole



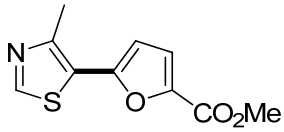
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (s, Ar-H, 1H), 7.34 (dd, *J* = 5.1, 1.2 Hz, Ar-H, 1H), 7.13 (dd, *J* = 3.6, 1.2 Hz, Ar-H, 1H), 7.07 (dd, *J* = 5.1, 3.6 Hz, Ar-H, 1H), 2.60 (s, CH_3, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9, 149.0, 133.1, 127.6, 127.1, 126.1, 125.5, 16.5.

3c: 4-methyl-5-(5-methylthiophen-2-yl)thiazole



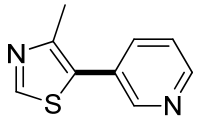
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, Ar-H, 1H), 6.93 (d, *J* = 3.5 Hz, Ar-H, 1H), 6.73 (d, *J* = 3.5 Hz, Ar-H, 1H), 2.59 (s, CH_3, 3H), 2.50(s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 148.4, 141.0, 130.7, 127.1, 125.9, 125.8, 16.4, 15.2.

3d: methyl5-(4-methylthiazol-5-yl)furan-2-carboxylate



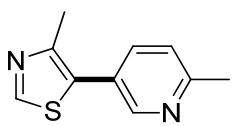
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, Ar-H, 1H), 7.26 (d, *J* = 2.6 Hz, Ar-H, 1H), 6.59 (d, *J* = 3.6 Hz, Ar-H, 1H), 3.91 (s, OCH_3, 3H), 2.68 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ158.9, 151.4, 151.2, 150.6, 143.8, 121.3, 119.8, 109.5, 52.0, 17.0. EIS-MS: 224 $[M + H]^+$.

3e: 4-methyl-5-(pyridin-3-yl)thiazole



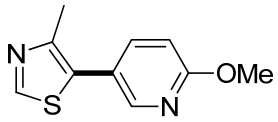
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, Ar-H, 1H), 8.65 (dd, *J* = 2.3, 0.7 Hz, Ar-H, 1H), 8.54 (dd, *J* = 4.9, 1.6 Hz, Ar-H, 1H), 7.72 – 7.68 (m, Ar-H, 1H), 7.34 – 7.30 (m, Ar-H, 1H), 2.49 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 149.6, 149.6, 148.8, 136.3, 128.1, 127.9, 123.3, 15.8.

3f: 4-methyl-5-(6-methylpyridin-3-yl)thiazole



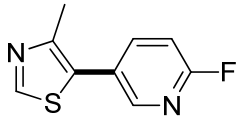
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, Ar-H, 1H), 8.56 (d, *J* = 1.3 Hz, Ar-H, 1H), 7.61 (dd, *J* = 8.0, 2.0 Hz, Ar-H, 1H), 7.20 (d, *J* = 8.0 Hz, Ar-H, 1H), 2.57 (s, CH_3, 3H), 2.50 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 150.8, 149.4, 148.9, 136.7, 128.2, 125.1, 123.0, 24.1, 15.9. EIS-MS: 191 $[M + H]^+$.

3g: 5-(6-methoxypyridin-3-yl)-4-methylthiazole



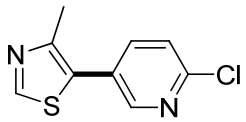
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, Ar-H, 1H), 8.23 (dd, *J* = 2.5, 0.6 Hz, Ar-H, 1H), 7.62 (dd, *J* = 8.6, 2.5 Hz, Ar-H, 1H), 6.81 (dd, *J* = 8.6, 0.7 Hz, Ar-H, 1H), 3.97 (s, CH_3, 3H), 2.49 (s, CH_3, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 150.5, 149.0, 147.0, 139.4, 128.3, 121.1, 111.0, 53.7, 15.9. EIS-MS: 207 $[M + H]^+$.

3h: 5-(6-fluoropyridin-3-yl)-4-methylthiazole



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, Ar-H, 1H), 8.29 (dd, *J* = 1.7, 0.8 Hz, Ar-H, 1H), 7.86 – 7.81 (m, Ar-H, 1H), 7.03 – 7.00 (m, Ar-H, 1H), 2.50 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 241.4 Hz), 151.3, 149.9, 147.7 (d, *J* = 15.0 Hz), 141.7 (d, *J* = 8.2 Hz), 126.7, 126.1 (d, *J* = 4.8 Hz), 109.6 (d, *J* = 37.7 Hz), 15.8. EIS-MS: 195 $[M + H]^+$.

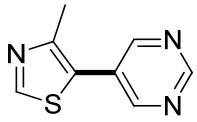
3i: 5-(6-chloropyridin-3-yl)-4-methylthiazole



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, Ar-H, 1H), 8.47 (s, Ar-H, 1H), 7.70 (dd, *J* = 8.2, 2.1 Hz, Ar-H, 1H), 7.40 (d, *J* = 8.2 Hz, Ar-H, 1H), 2.52 (s, CH_3, H).^{13}C NMR

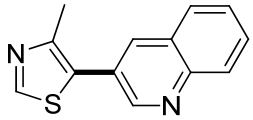
(101 MHz, $CDCl_3$) δ 151.5, 150.8, 150.2, 149.4, 139.0, 127.2, 126.7, 124.2, 16.0. EIS-MS: 211 $[M + H]^+$.

3j: 4-methyl-5-(pyrimidin-5-yl)thiazole



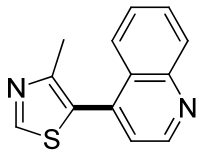
^1H NMR (400 MHz, $CDCl_3$): δ 9.20(s, Ar-H, 1H), 8.84 (s, Ar-H, 2H), 8.82 (s, Ar-H, 1H), 2.57 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ 157.7, 156.4, 152.3, 151.1, 127.0, 124.3, 16.0.

3k: 4-methyl-5-(quinolin-3-yl)thiazole



^1H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 2.3 Hz, Ar-H, 1H), 8.70 (s, Ar-H, 1H), 8.06 (dd, *J* = 8.2, 5.4 Hz, Ar-H, 2H), 7.74 (dd, *J* = 8.1, 1.2 Hz, Ar-H, 1H), 7.64 (ddd, *J* = 8.4, 6.9, 1.4 Hz, Ar-H, 1H), 7.48 (ddd, *J* = 8.1, 7.0, 1.1 Hz, Ar-H, 1H), 2.52 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 150.2, 149.7, 146.9, 135.3, 129.8, 129.1, 128.0, 127.6, 127.2, 127.1, 125.1, 15.9.

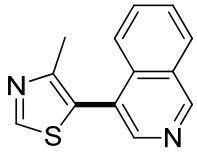
3l: 4-methyl-5-(quinolin-4-yl)thiazole



^1H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 4.4 Hz, Ar-H,1H), 8.88 (s, Ar-H, 1H), 8.17 (d, *J* = 8.5 Hz, Ar-H, 1H), 7.75 – 7.69 (m, Ar-H, 2H), 7.53 (ddd, *J* = 8.2, 6.9, 1.1 Hz, Ar-H, 1H), 7.35 (d, *J* = 4.4 Hz, Ar-H, 1H), 2.30 (s, CH_3, 3H).^{13}C NMR (126 MHz,

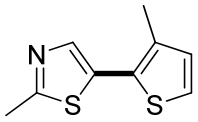
$CDCl_3$) δ 152.3, 151.5, 149.6, 148.5, 138.2, 130.0, 129.7, 127.2, 127.2, 126.1, 125.3, 123.3, 15.8. EIS-MS: 227 $[M + H]^+$.

3m: 5-(isoquinolin-4-yl)-4-methylthiazole



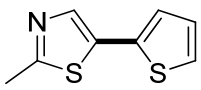
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, Ar-H, 1H), 8.82 (s, Ar-H, 1H), 8.45 (s, Ar-H, 1H), 7.97 (d, *J* = 7.9 Hz, Ar-H, 1H), 7.66 – 7.53 (m, Ar-H, 3H), 2.24 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 152.1, 151.6, 144.6, 134.7, 131.0, 128.0, 127.8, 127.4, 125.1, 124.1, 122.7, 15.6. EIS-MS: 227 $[M + H]^+$.

4a: 2-methyl-5-(3-methylthiophen-2-yl)thiazole



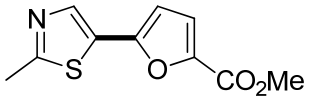
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (s, Ar-H, 1H), 7.114 (d, *J* = 5.1 Hz, Ar-H, 1H), 6.88 (d, *J* = 5.1 Hz, Ar-H, 1H), 2.73 (s, CH_3, 3H), 2.34 (s, CH_3, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ171.1, 165.4, 139.5, 135.4, 131.5 129.3, 123.4, 19.2, 15.4. EIS-MS: 195 $[M]^+$.

4b: 2-methyl-5-(thiophen-2-yl)thiazole



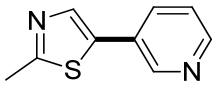
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, Ar-H, 1H), 7.5 (dd, *J* = 5.2, 1.0 Hz, Ar-H, 1H), 7.12 (dd, *J* = 3.5, 0.9 Hz, Ar-H, 1H), 7.02 (dd, *J* = 5.1, 3.6 Hz, Ar-H, 1H), 2.70 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 137.9, 133.3, 132.0, 127.8, 125.3, 125.1, 19.2. EIS-MS: 182$[M + H]^+$.

4d: methyl 5-(2-methylthiazol-5-yl)furan-2-carboxylate



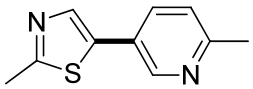
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, Ar-H, 1H), 7.21 (d, *J* = 3.5 Hz, Ar-H, 1H), 6.56 (d, *J* = 3.4 Hz, Ar-H, 1H), 3.91 (s, OCH_3, 3H), 2.74 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 158.8, 150.1, 143.7, 139.8, 127.1, 119.9, 108.3, 52.0, 19.3. EIS-MS: 224 $[M + H]^+$.

4e: 2-methyl-5-(pyridin-3-yl)thiazole



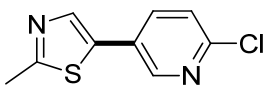
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 – 8.72 (m, Ar-H, 1H), 8.54 (dd, *J* = 4.8, 1.6 Hz, Ar-H , 1H), 8.06 – 7.66 (m, Ar-H , 2H), 7.58 – 7.12 (m, Ar-H , 1H), 2.75 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 148.8, 147.3, 138.6, 134.8, 133.4, 127.6, 123.5, 19.2.

4f: 2-methyl-5-(6-methylpyridin-3-yl) thiazole



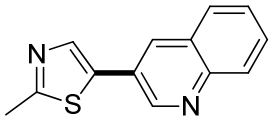
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, Ar-H, 1H), 7.77 (s, Ar-H, 1H), 7.67 (dd, *J* = 7.8, 2.3 Hz, Ar-H, 1H), 7.16 (d, *J* = 7.7 Hz, Ar-H, 1H), 2.72 (s, CH_3, 3H), 2.56 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 158.0, 146.7, 138.2, 135.2, 133.9, 124.9, 123.2, 24.2, 19.4. EIS-MS: 191 $[M + H]^+$.

4i: 5-(6-chloropyridin-3-yl)-2-methylthiazole



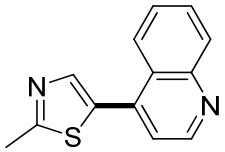
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 2.5, 0.5 Hz, Ar-H, 1H), 7.82 (s, Ar-H, 1H), 7.76 (dd, *J* = 8.3, 2.6 Hz, Ar-H, 1H), 7.36 (dd, *J* = 8.3, 0.6 Hz, Ar-H, 1H), 2.75 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 150.6, 147.0, 139.1, 136.2, 133.6, 126.8, 124.5, 19.5. EIS-MS: 221 $[M + H]^+$.

4k: 2-methyl-5-(quinolin-3-yl)thiazole



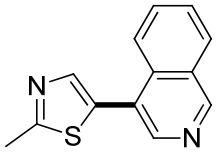
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 1.7 Hz, Ar-H, 1H), 8.19 (s, Ar-H, 1H), 8.10 (d, *J* = 8.4 Hz, Ar-H, 1H), 7.97 (s, Ar-H, 1H), 7.83 (d, *J* = 8.1 Hz, Ar-H, 1H), 7.71 (t, *J* = 7.6 Hz, Ar-H, 1H), 7.57 (t, *J* = 7.5 Hz, Ar-H, 1H), 2.78 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 148.6, 147.5, 138.9, 135.4, 132.4, 129.7, 129.4, 127.8, 127.4, 125.0, 19.5. EIS-MS: 227 $[M + H]^+$.

4l: 2-methyl-5-(quinolin-4-yl)thiazole



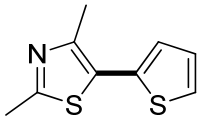
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.4 Hz, Ar-H, 1H), 8.25 – 8.00 (m, Ar-H, 2H), 7.82 (s, Ar-H, 1H), 7.72 (ddd, *J* = 8.4, 6.9, 1.3 Hz, Ar-H, 1H), 7.55 (ddd, *J* = 8.2, 6.9, 1.3 Hz, Ar-H, 1H), 7.36 (d, *J* = 4.4 Hz, Ar-H, 1H), 2.79 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 149.7, 148.6, 142.1, 137.5, 133.0, 130.0, 129.7, 127.2, 126.2, 124.9, 121.9, 19.2. EIS-MS: 227 $[M + H]^+$.

4m: 5-(isoquinolin-4-yl)-2-methylthiazole



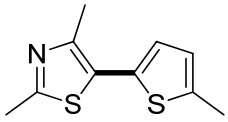
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, Ar-H, 1H), 8.57 (s, Ar-H, 1H), 8.12 (dd, *J* = 8.5, 0.8 Hz, Ar-H, 1H), 8.05 (d, *J* = 8.1 Hz, Ar-H, 1H), 7.79 – 7.73 (m, Ar-H, 2H), 7.70 – 7.65 (m, Ar-H, 1H), 2.82 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 153.1, 143.8, 141.8, 134.3, 132.1, 131.3, 128.3, 128.1, 127.7, 124.2, 123.0, 19.4. EIS-MS: 227 $[M + H]^+$.

5b: 2, 4-dimethyl-5-(thiophen-2-yl)thiazole



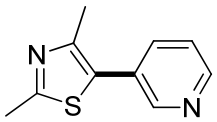
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 4.9, 1.4 Hz, Ar-H, 1H), 7.07 – 7.02 (m, Ar-H, 2H), 2.64 (s, CH_3, 3H), 2.51 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 147.7, 133.6, 127.4, 126.5, 125.6, 124.8, 19.0, 16.4.

5c: 2, 4-dimethyl-5-(5-methylthiophen-2-yl)thiazole



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, *J* = 3.5 Hz, Ar-H, 1H), 6.70(dd, *J* = 3.5, 1.1 Hz, Ar-H, 1H), 2.64 (s, CH_3, 3H), 2.49 (s, CH_3, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 147.1, 140.4, 131.2, 126.5, 125.6, 125.2, 19.0, 16.3, 15.2. EIS-MS: 210 $[M + H]^+$.

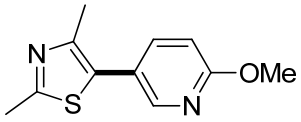
5e: 2, 4-dimethyl-5-(pyridin-3-yl)thiazole



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 1.7 Hz, Ar-H, 1H), 8.56 (dd, *J* = 4.8, 1.6 Hz, Ar-H, 1H), 7.74 – 7.69 (m, Ar-H, 1H), 7.37 – 7.34 (m, Ar-H, 1H), 2.71 (s, CH_3,

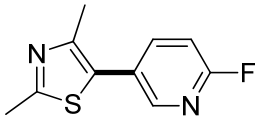
3H), 2.47 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 149.6, 148.5, 148.4, 136.2, 128.6, 127.4, 123.4, 19.1, 15.9.

5g: 5-(6-methoxypyridin-3-yl)-2, 4-dimethylthiazole



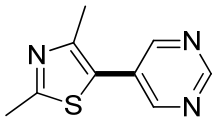
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, Ar-H, 1H), 7.56 (d, *J* = 8.5 Hz, Ar-H, 1H), 6.76 (d, *J* = 8.5 Hz, Ar-H, 1H), 3.94 (s, OCH_3, 3H), 2.66 (s, CH_3, 3H), 2.39 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 147.5, 146.7, 139.2, 127.5, 121.4, 110.8, 99.9, 53.5, 19.1, 15.7. EIS-MS: 221 $[M + H]^+$.

5h: 5-(6-fluoropyridin-3-yl)-2,4-dimethylthiazole



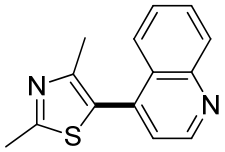
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 2.4 Hz, Ar-H, 1H), 7.76 (ddd, *J* = 8.4, 7.6, 2.6 Hz, Ar-H, 1H), 6.98 – 6.91 (m, Ar-H, 1H), 2.65 (s, CH_3, 3H), 2.37 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 162.7 (d, *J* = 240.9 Hz), 148.4, 147.4 (d, *J* = 14.9 Hz), 141.4 (d, *J* = 8.1 Hz), 126.4 (d, *J* = 4.8 Hz), 126.0, 109.4 (d, *J* = 37.7 Hz),19.0, 15.7. EIS-MS: 208 $[M]^+$.

5i: 2,4-dimethyl-5-(pyrimidin-5-yl)thiazole



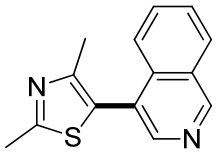
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (s, Ar-H, 1H), 8.79 (s, Ar-H, 2H), 2.72 (s, CH_3, 3H), 2.48 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ 165.5, 157.3, 156.1, 149.7, 127.2, 123.5, 19.2, 16.0.

5l: 2,4-dimethyl-5-(quinolin-4-yl)thiazole



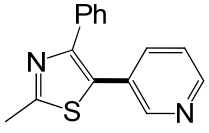
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 3.7 Hz, Ar-H, 1H), 8.16 (d, *J* = 5.3 Hz, Ar-H, 1H), 7.84 – 7.67 (m, Ar-H, 2H), 7.54 (d, *J* = 5.4 Hz, Ar-H, 1H), 7.38 – 7.28 (m, Ar-H, 1H), 2.80 – 2.68 (m, CH_3, 3H), 2.23 (dd, *J* = 6.8, 1.6 Hz, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 150.2, 149.7, 148.6, 138.5, 130.0, 129.7, 127.3, 127.1, 125.5, 123.2, 19.1, 16.0.

5m: 5-(isoquinolin-4-yl)-2, 4-dimethylthiazole



^{1}H NMR (400 MHz,) δ 9.20 (s, Ar-H, 1H), 8.44 (s, Ar-H, 1H), 7.96 (d, *J* = 8.1 Hz, Ar-H, 1H), 7.70 (d, *J* = 8.4 Hz, Ar-H, 1H), 7.66 – 7.61 (m, Ar-H, 1H), 7.58 – 7.53 (m, Ar-H, 1H), 2.69 (s, CH_3, 3H), 2.16 (s, CH_3, 3H).^{13}C NMR (101 MHz,) δ 165.3, 153.0, 150.4, 144.8, 135.0, 131.0, 128.3, 128.0, 127.5, 124.6, 124.5, 123.3, 19.2, 15.8. EIS-MS: 241 $[M + H]^{+}$.

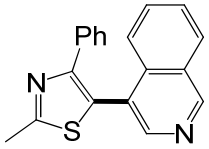
6e: 2-methyl-4-phenyl-5-(pyridin-3-yl)thiazole



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 1.6 Hz, Ar-H, 1H), 8.50 (dd, *J* = 4.8, 1.6 Hz, Ar-H, 1H), 7.60 – 7.55 (m, Ar-H, 1H), 7.49 – 7.42 (m, Ar-H, 2H), 7.32 – 7.25 (m, Ar-H, 3H), 7.22 – 7.17 (m, Ar-H, 1H), 2.76 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$)

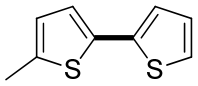
δ 164.7, 150.7, 149.7, 148.6, 136.4, 134.0, 128.7, 128.4, 128.3, 128.0, 127.9, 123.1, 19.1.

6m: 5-(isoquinolin-4-yl)-2-methyl-4-phenylthiazole



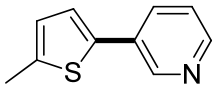
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, Ar-H, 1H), 8.51 (s, Ar-H, 1H), 8.08 – 7.97 (m, Ar-H, 1H), 7.74 (dd, *J* = 6.0, 3.5 Hz, Ar-H, 1H), 7.60 (dd, *J* = 6.2, 3.3 Hz, Ar-H, 2H), 7.45 – 7.33 (m, Ar-H, 2H), 7.18 – 7.05 (m, Ar-H, 3H), 2.84 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 153.2, 152.2, 144.9, 134.8, 134.2, 131.1, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 125.5, 124.6, 123.8, 19.3. EIS-MS: 303 $[M + H]^+$.

7b: 5-methyl-2, 2'-bithiophene



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 5.1, 1.2 Hz, Ar-H, 1H), 7.09 (dd, *J* = 3.6, 1.1 Hz, Ar-H, 1H), 7.00 – 6.96 (m, Ar-H, 2H), 6.68 – 6.65 (m, Ar-H, 1H), 2.48 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 137.8, 135.0, 127.6, 125.9, 123.7, 123.6, 123.0, 15.3.

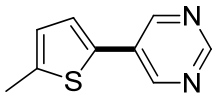
7e: 3-(5-methylthiophen-2-yl)pyridine



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81 (d, *J* = 1.8 Hz, Ar-H, 1H), 8.46 (dd, *J* = 4.8, 1.5 Hz, Ar-H, 1H), 7.81 – 7.76 (m, Ar-H, 1H), 7.28 – 7.24 (m, Ar-H, 1H), 7.15 (d, *J* = 3.5

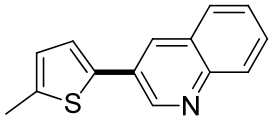
Hz, Ar-H, 1H), 6.79 – 6.71 (m, Ar-H, 1H), 2.51 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 146.5, 140.8, 137.8, 132.4, 130.6, 126.4, 124.0, 123.5, 15.4.

7i: 5-(5-methylthiophen-2-yl)pyrimidine



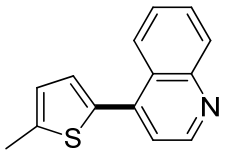
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, Ar-H, 1H), 8.90 (s, Ar-H, 2H), 7.23 (d, *J* = 3.6 Hz, Ar-H, 1H), 6.84 – 6.81 (m, Ar-H, 1H), 2.55 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 152.9, 142.3, 133.7, 128.9, 126.8, 125.2, 15.4.

7k: 3-(5-methylthiophen-2-yl)quinolone



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 2.0 Hz, Ar-H, 1H), 8.16 (s, Ar-H, 1H), 8.07 (d, *J* = 8.4 Hz, Ar-H, 1H), 7.79 (d, *J* = 8.1 Hz, Ar-H,1H), 7.65 (t, *J* = 7.6 Hz, Ar-H, 1H), 7.52 (t, *J* = 7.3 Hz, Ar-H, 1H), 7.28 (d, *J* = 3.4 Hz, Ar-H, 1H), 6.79 (d, *J* = 2.4 Hz, Ar-H, 1H), 2.54 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 147.0, 141.0, 138.2, 130.5, 129.2, 129.0, 128.0, 127.8, 127.7, 127.1, 126.6, 124.3, 15.5.

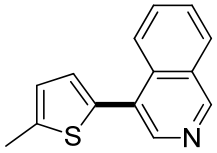
7l: 4-(5-methylthiophen-2-yl)quinolone



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 4.3 Hz, Ar-H, 1H), 8.35 (d, *J* = 8.5 Hz, Ar-H, 1H), 8.15 (d, *J* = 8.4 Hz, Ar-H, 1H), 7.73 (t, *J* = 7.6 Hz, Ar-H, 1H), 7.55 (t, *J* = 7.6 Hz, Ar-H, 1H), 7.40 (d, *J* = 4.3 Hz, Ar-H, 1H), 7.19 (d, *J* = 2.9 Hz, Ar-H, 1H), 6.91 – 6.84 (m, Ar-H, 1H), 2.58 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4,

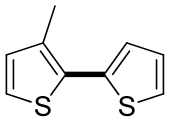
147.0, 141.0, 138.3, 130.5, 129.2, 129.0, 128.0, 127.8, 127.7,127.1, 126.6,124.3, 15.5. EIS-MS: 226 $[M + H]^+$.

7m: 4-(5-methylthiophen-2-yl)isoquinoline



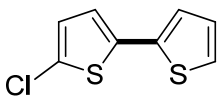
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, Ar-H, 1H), 8.58 (s, Ar-H, 1H), 8.26 (d, *J* = 8.5 Hz, Ar-H, 1H), 7.97 (d, *J* = 8.0 Hz, Ar-H, 1H), 7.72 – 7.65 (m, Ar-H, 1H), 7.60 (dd, *J* = 12.7, 5.4 Hz, Ar-H, 1H), 7.12 – 7.03 (m, Ar-H, 1H), 6.85 (d, *J* = 1.1 Hz, Ar-H, 1H), 2.56 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 143.1, 141.2, 135.2, 134.0, 130.7, 128.2, 127.9, 127.8, 127.2, 126.4, 125.8, 124.5, 15.2.

8b: 3-methyl-2, 2'-bithiophene



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 5.1, 1.2 Hz, Ar-H, 1H), 7.16 – 7.13 (m, Ar-H, 2H), 7.07 (dd, *J* = 5.1, 3.6 Hz, Ar-H, 1H), 6.89(d, *J* = 5.1 Hz, Ar-H, 1H), 2.40(s, CH_3, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 136.6, 133.9, 131.3, 127.4, 125.5, 125.0, 123.4, 123.2, 15.3.

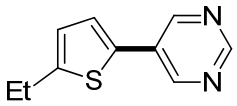
9b: 5-chloro-2, 2'-bithiophene



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 5.1, 1.1 Hz, Ar-H, 1H), 7.10 (dd, *J* = 3.6, 1.1 Hz, Ar-H, 1H), 7.01 (dd, *J* = 5.1, 3.6 Hz, Ar-H, 1H), 6.93 (d, *J* = 3.9 Hz, Ar-H,

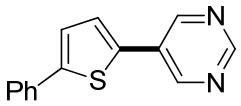
1H), 6.83 (d, J = 3.9 Hz, Ar-H, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 136.0, 128.6, 127.8, 126.8, 124.7, 1239, 122.8.

10j: 5-(5-ethylthiophen-2-yl)pyrimidine



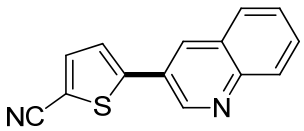
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, Ar-H, 1H), 8.88 (s, Ar-H, 2H), 7.23 (d, J = 3.5 Hz, Ar-H, 1H), 6.83 (d, J = 3.3 Hz, Ar-H, 1H), 2.89 (q, J = 7.5 Hz, CH_2, 2H), 1.34 (t, J = 7.5 Hz, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 152.9, 150.1, 133.3, 128.9, 125.0, 125.0, 23.6, 15.8.

11j: 5-(5-phenylthiophen-2-yl)pyrimidine



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, Ar-H, 1H), 8.96 (s, Ar-H, 2H), 7.64 (dd, J = 7.3, 1.2 Hz, Ar-H, 2H), 7.44 – 7.39 (m, Ar-H, 3H), 7.35 (dd, J = 5.6, 3.7 Hz, Ar-H, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 153.1, 146.5, 135.1, 133.5, 129.1, 128.7, 128.3, 126.2, 125.9, 124.4.

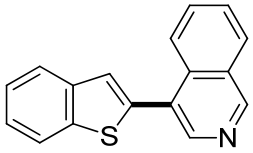
12k: 5-(quinolin-3-yl)thiophene-2-carbonitrile



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, J = 2.4 Hz, Ar-H, 1H), 8.32 (d, J = 2.2 Hz, Ar-H, 1H), 8.13 (d, J = 8.5 Hz, Ar-H, 1H), 7.88 (dd, J = 8.1, 1.3 Hz, Ar-H, 1H), 7.77 (ddd, J = 8.4, 6.9, 1.4 Hz, Ar-H, 1H), 7.68 (d, J = 3.9 Hz, Ar-H, 1H), 7.62 (ddd, J = 8.1, 7.0, 1.1 Hz, Ar-H, 1H), 7.47 (d, J = 3.9 Hz, Ar-H, 1H).^{13}C NMR (101 MHz,

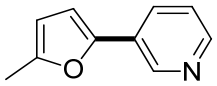
$CDCl_3$) δ 148.0, 148.0, 147.9, 138.6, 132.9, 130.5, 129.4, 128.1, 127.8, 127.5, 125.4, 124.4, 114.0, 109.5. EIS-MS: 237 $[M + H]^+$.

13m: 4-(benzo[b]thiophen-2-yl)isoquinoline



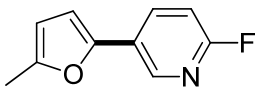
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, Ar-H, 1H), 8.73 (s, Ar-H, 1H), 8.29 (d, *J* = 8.4 Hz, Ar-H, 1H), 8.03 – 7.97 (m, Ar-H, 1H), 7.88 (dd, *J* = 16.5, 7.4 Hz, Ar-H, 2H), 7.70 (dd, *J* = 11.0, 4.0 Hz, Ar-H, 1H), 7.66 – 7.58 (m, Ar-H, 1H), 7.51 (d, *J* = 11.8 Hz, Ar-H, 1H), 7.46 –7.35 (m, Ar-H, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 143.5, 140.2, 139.8, 137.9, 133.9, 130.9, 128.0, 127.8, 127.3, 126.1, 124.6, 124.4, 124.4, 124.2, 123.5, 121.9.

14e: 3-(5-methylfuran-2-yl)pyridine



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, Ar-H, 1H), 8.43 (d, *J* = 3.6 Hz, Ar-H, 1H), 7.88 (d, *J* = 8.0 Hz, Ar-H, 1H), 7.28 (t, *J* = 6.3 Hz, Ar-H, 1H), 6.63 (d, *J* = 2.9 Hz, Ar-H, 1H), 6.08 (d, *J* = 1.9 Hz, Ar-H, 1H), 2.37 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 149.0, 147.3, 144.6, 130.3, 127.2, 123.5, 107.9, 107.4, 13.6.

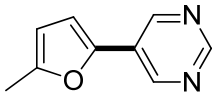
14h: 2-fluoro-5-(5-methylfuran-2-yl)pyridine



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.1 Hz, Ar-H, 1H), 8.01 – 7.88 (m, Ar-H, 1H), 6.91 (dd, *J* = 8.5, 2.9 Hz, Ar-H, 1H), 6.55 (d, *J* = 3.2 Hz, Ar-H, 1H), 6.10 – 6.04

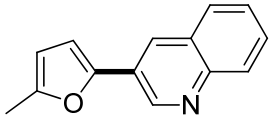
(m, Ar-H, 1H), 2.36 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 238.7 Hz), 152.9, 148.2, 142.3 (d, *J* = 14.9 Hz), 135.7 (d, *J* = 7.6 Hz), 125.4 (d, *J* = 4.7 Hz), 109.3 (d, *J* = 37.9 Hz), 107.8, 107.0, 13.5. EIS-MS: 178 $[M + H]^+$.

14j: 5-(5-methylfuran-2-yl)pyrimidine



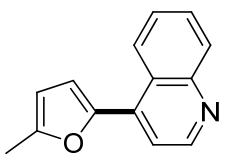
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, Ar-H, 1H), 8.94 (s, Ar-H, 2H), 6.72 (d, *J* = 2.9 Hz, Ar-H, 1H), 6.13 (d, *J* = 2.2 Hz, Ar-H, 1H), 2.40 (s, CH_3, 3H).^{13}C NMR (101 MHz, CDCl3) δ 156.4, 154.3, 151.2, 146.1, 125.2, 109.0, 108.2, 13.7. EIS-MS: 161 $[M + H]^+$.

14k: 3-(5-methylfuran-2-yl)quinoline



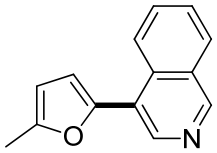
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 2.2 Hz, Ar-H, 1H), 8.25 (d, *J* = 2.1 Hz, Ar-H, 1H), 8.05 (d, *J* = 8.5 Hz, Ar-H, 1H), 7.77 (dd, *J* = 8.1, 1.2 Hz, Ar-H, 1H), 7.62 (ddd, *J* = 8.4, 6.9, 1.4 Hz, Ar-H, 1H), 7.49 (ddd, *J* = 8.1, 6.9, 1.1 Hz, Ar-H, 1H), 6.72 (d, *J* = 3.2 Hz, Ar-H, 1H), 6.18 – 6.05 (m, Ar-H, 1H), 2.39 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 149.6, 146.9, 146.7, 129.1, 128.8, 128.0, 127.9, 127.7, 127.0, 124.2, 108.0, 107.7, 13.7.

14l: 4-(5-methylfuran-2-yl)quinolone



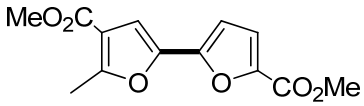
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 4.6 Hz, Ar-H, 1H), 8.48 (d, *J* = 8.5 Hz, Ar-H, 1H), 8.12 (d, *J* = 8.4 Hz, Ar-H, 1H), 7.69 (t, *J* = 7.6 Hz, Ar-H, 1H), 7.55 (dd, *J* = 12.7, 5.8 Hz, Ar-H, 2H), 6.86 (d, *J* = 3.0 Hz, Ar-H, 1H), 6.19 (d, *J* = 2.0 Hz, Ar-H, 1H), 2.43 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 149.8, 149.1, 148.9, 135.8, 129.9, 129.1, 126.7, 125.4, 124.1, 117.7, 113.5, 108.3, 13.7.

14m: 4-(5-methylfuran-2-yl)isoquinoline



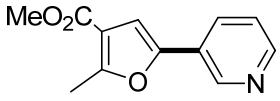
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, Ar-H, 1H), 8.74 (s, Ar-H, 1H), 8.43 (d, *J* = 8.5 Hz, Ar-H, 1H), 7.98 (d, *J* = 8.1 Hz, Ar-H, 1H), 7.73 (s, Ar-H, 1H), 7.62 (d, *J* = 7.7 Hz, Ar-H, 1H), 6.69 (d, *J* = 2.9 Hz, Ar-H, 1H), 6.19 (s, Ar-H, 1H), 2.45 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 151.6, 149.1, 141.4, 132.3, 130.8, 128.4, 128.0, 127.2, 124.7, 122.5, 111.0, 107.7, 13.8. EIS-MS: 210 $[M + H]^+$.

15d: dimethyl-5-methyl-[2,2'-bifuran]-4,5'-dicarboxylate



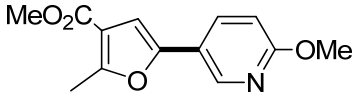
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 3.6 Hz, Ar-H, 1H), 7.01 (s, Ar-H, 1H), 6.61 (d, *J* = 3.6 Hz, Ar-H, 1H), 3.90 (s, OCH_3, 3H), 3.83 (s, OCH_3, 3H), 2.63 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 159.9, 158.9, 148.7, 143.4, 143.0, 119.7, 115.2, 108.5, 107.0, 51. 9, 51.5, 13.8.

15e: methyl 2-methyl-5-(pyridin-3-yl)furan-3-carboxylate



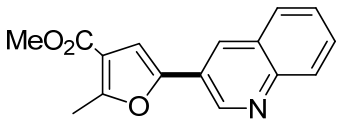
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, Ar-H, 1H), 8.49 (d, *J* = 3.7 Hz, Ar-H, 1H), 7.88 (d, *J* = 7.9 Hz, Ar-H, 1H), 7.30 (dd, *J* = 7.5, 5.1 Hz, Ar-H, 1H), 6.96 (s, Ar-H, 1H), 3.85 (s, OCH_3, 3H), 2.65 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 159.6, 148.8, 148.5, 145.2, 130.6, 126.0, 123.5, 115.3, 106.9, 51.5, 13.9.

15g: methyl-5-(6-methoxypyridin-3-yl)-2-methylfuran-3-carboxylate



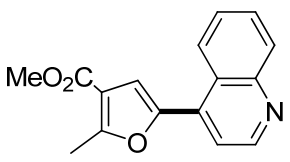
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, Ar-H, 1H), 7.99 – 7.59 (m, Ar-H, 1H), 6.76 (d, *J* = 9.3 Hz, Ar-H, 2H), 3.95 (s, OCH_3, 3H), 3.84 (s, OCH_3, 3H), 2.63 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 163.5, 158.7, 149.4, 142.5, 134.2, 120.0, 115.0, 110.9, 104.7, 53.6, 51.4, 13.8.

15k: methyl -2-methyl-5-(quinolin-3-yl)-furan-3-carboxylate



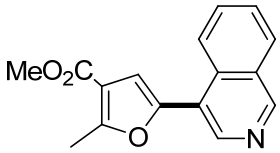
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, Ar-H, 1H), 8.34 (s, Ar-H, 1H), 8.09 (d, *J* = 8.4 Hz, Ar-H, 1H), 7.84 (d, *J* = 8.1 Hz, Ar-H, 1H), 7.69 (t, *J* = 7.6 Hz, Ar-H, 1H), 7.56 (t, *J* = 7.5 Hz, Ar-H, 1H), 7.10 (s, Ar-H, 1H), 3.88 (s, OCH_3, 3H), 2.71 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 159.8, 149.2, 147.2, 146.7, 129.5, 129.3, 129.1, 127.9, 127.7, 127.3, 123.3, 115.5, 107.2, 51.5, 13.9. EIS-MS: 268 $[M + H]^+$.

15l: methyl -2-methyl-5-(quinolin-4-yl)furan-3-carboxylate



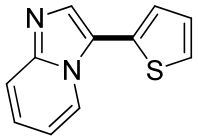
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 4.6 Hz, Ar-H, 1H), 8.42 (dd, *J* = 8.5, 0.8 Hz, Ar-H, 1H), 8.15 (dd, *J* = 8.4, 0.7 Hz, Ar-H, 1H), 7.80 – 7.68 (m, Ar-H, 1H), 7.66 – 7.58 (m, Ar-H, 2H), 7.23 (s, Ar-H, 1H), 3.89 (s, OCH_3, 3H), 2.74 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 160.5, 149.9, 148.9, 148.5, 134.8, 130.2, 129.4, 127.2, 125.0, 124.1, 118.4, 115.6, 112.9, 51.6, 14.1. EIS-MS: 268 $[M + H]^+$.

15m: methyl- 5-(isoquinolin-4-yl)-2-methylfuran-3-carboxylate



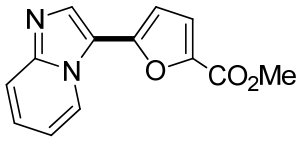
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, Ar-H, 1H), 8.75 (s, Ar-H, 1H), 8.34 (d, *J* = 8.5 Hz, Ar-H, 1H), 8.01 (d, *J* = 8.1 Hz, Ar-H, 1H), 7.77 (t, *J* = 7.6 Hz, Ar-H, 1H), 7.65 (t, *J* = 7.5 Hz, Ar-H, 1H), 7.05 (s, Ar-H, 1H), 3.88 (s, OCH_3, 3H), 2.73 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 159.9, 152.6, 148.6, 142.1, 132.3, 131.2, 128.4, 128.2, 127.4, 124.2, 121.4, 115.2, 110.7, 51.5, 14.0. EIS-MS: 268 $[M + H]^+$.

16b: 3-(thiophen-2-yl)imidazo[1,2-a]pyridine



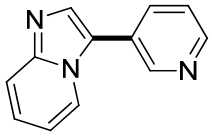
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dt, *J* = 6.9, 1.0 Hz, Ar-H, 1H), 7.65 (s, Ar-H, 1H), 7.55 (dt, *J* = 9.1, 1.0 Hz, Ar-H, 1H), 7.30 (dd, *J* = 5.2, 1.1 Hz, Ar-H, 1H), 7.15 (dd, *J* = 3.6, 1.1 Hz, Ar-H, 1H), 7.10 – 7.04 (m, Ar-H, 2H), 6.72 (td, *J* = 6.8, 1.1 Hz, Ar-H, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 133.1, 129.5, 127.5, 125.6,125.5, 124.2, 123.4, 118.8, 117.7, 112.5.

16d: methyl 5-(imidazo[1,2-a]pyridin-3-yl)furan-2-carboxylate



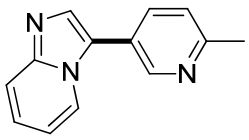
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (dt, *J* = 7.0, 1.1 Hz, Ar-H, 1H), 8.01 (s, Ar-H, 1H), 7.70 (dt, *J* = 9.1, 1.1 Hz, Ar-H, 1H), 7.33 – 7.29 (m, Ar-H, 2H), 6.99 (td, *J* = 6.9, 1.2 Hz, Ar-H, 1H), 6.71 (d, *J* = 3.7 Hz, Ar-H, 1H), 3.94 (s, OCH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 148.9, 146.7, 143.0, 134.4, 125.7, 125.6, 119.8, 118.2, 116.4, 113.8, 107.2, 52.0.

16e: 3-(pyridin-3-yl)imidazo[1,2-a]pyridine



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 2.3, 0.8 Hz, Ar-H, 1H), 8.50 (dd, *J* = 4.9, 1.6 Hz, Ar-H, 1H), 8.15 (dt, *J* = 6.9, 1.1 Hz, Ar-H, 1H), 7.74 (ddd, *J* = 7.9, 2.2, 1.8 Hz, Ar-H, 1H), 7.60 (s, Ar-H, 1H), 7.54 (dt, *J* = 9.1, 1.1 Hz, Ar-H, 1H), 7.32 (ddd, *J* = 7.9, 4.9, 0.8 Hz, Ar-H, 1H), 7.09 (ddd, *J* = 9.1, 6.7, 1.2 Hz, Ar-H, 1H), 6.72 (td, *J* = 6.8, 1.1 Hz, Ar-H, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 148.3, 146.2, 134.7, 132.9, 125.2, 124.6, 123.6, 122.6, 121.9, 118.0, 112.8.

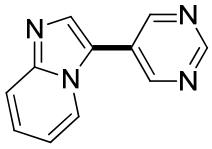
16f: 3-(6-methylpyridin-3-yl)imidazo[1,2-a]pyridine



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 1.8 Hz, Ar-H, 1H), 8.22 (dt, *J* = 7.0, 1.1 Hz, Ar-H, 1H), 7.74 (dd, *J* = 8.0, 2.3 Hz, Ar-H, 1H), 7.70 (s, Ar-H, 1H), 7.67 (dt, *J* = 9.1, 1.1 Hz, Ar-H, 1H), 7.30 (d, *J* = 8.0 Hz, Ar-H, 1H), 7.21 (ddd, *J* = 9.1, 6.7, 1.2 Hz,

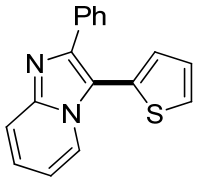
Ar-H, 1H), 6.82 (td, *J* = 6.8, 1.1 Hz, Ar-H, 1H), 2.63 (s, Ar-H, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 148.2, 146.4, 135.6, 133.0, 124.5, 123.5, 122.9, 122.5, 122.4, 118.4, 112.9, 24.3. EIS-MS: 210 $[M + H]^+$.

16j: 3-(pyrimidin-5-yl)imidazo[1,2-a]pyridine



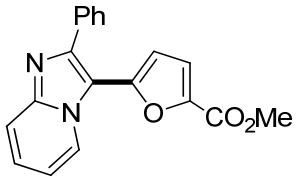
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, Ar-H, 1H), 8.98 (s, Ar-H, 2H), 8.30 – 8.26 (m, Ar-H, 1H), 7.82 (s, Ar-H, 1H), 7.74 (d, *J* = 9.1 Hz, Ar-H, 1H), 7.30 (ddd, *J* = 9.1, 6.7, 1.2 Hz, Ar-H, 1H), 6.93 (td, *J* = 6.8, 1.0 Hz, Ar-H, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 155.3, 147.2, 134.2, 125.5, 124.3, 122.6, 118.8, 118.8, 113.7.

17b: 2-phenyl-3-(thiophen-2-yl)imidazo[1,2-a]pyridine



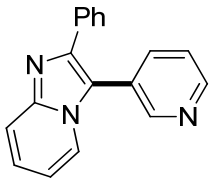
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 6.8 Hz, Ar-H, 1H), 7.76 (d, *J* = 7.4 Hz, Ar-H, 2H), 7.67 (d, *J* = 9.0 Hz, Ar-H, 1H), 7.59 (d, *J* = 4.9 Hz, Ar-H, 1H), 7.31 (dd, *J* = 13.5, 6.0 Hz, Ar-H, 3H), 7.26 – 7.19 (m, Ar-H, 3H), 6.78 (t, *J* = 6.8 Hz, Ar-H, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 144.5, 133.8, 130.3, 129.9, 128.8, 128.3, 128.1, 128.0, 127.8, 125.2, 123.9, 117.4, 113.3, 112.5.

17d: methyl 5-(2-phenylimidazo[1,2-a]pyridin-3-yl) -furan-2-carboxylate



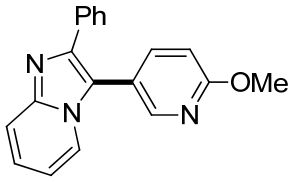
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 6.9, Ar-H, 1H), 7.74 – 7.68 (m, Ar-H, 3H), 7.43 – 7.37 (m, Ar-H, 2H), 7.31 (ddd, *J* = 9.0, 6.8, 1.2 Hz, Ar-H, 1H), 7.25 (d, *J* = 3.6 Hz, Ar-H, 1H), 6.92 (td, *J* = 6.9, 1.1 Hz, Ar-H, 1H), 6.50 (d, *J* = 3.6 Hz, Ar-H, 1H), 3.93 (s, OCH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 148.5, 146.7, 145.8, 143.8, 133.7, 128.7, 128.7, 128.6, 128.5, 126.2, 126.0, 125.5, 119.5, 117.6, 113.5, 111.5, 52.0. EIS-MS: 319 $[M + H]^+$.

17e: 2-phenyl-3-(pyridin-3-yl)imidazo[1,2-a]pyridine



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.70 (m, Ar-H, 2H), 7.97 – 7.95(m, Ar-H, 1H), 7.80 – 7.75 (m, Ar-H, 1H), 7.73 – 7.70 (m, Ar-H, 1H), 7.63 – 7.58 (m, Ar-H, 2H), 7.48 – 7.44 (m, Ar-H, 1H), 7.32 – 7.26 (m, Ar-H, 3H), 7.26 – 7.22 (m, Ar-H, 1H), 6.81 – 6.78 (m, Ar-H, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 149.8, 145.4, 143.9, 138.3, 133.6, 128.5, 128.2, 127.9, 126.3, 125.2, 124.2, 122.8, 117.8, 117.4, 112.8.

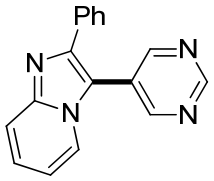
17g: 3-(6-methoxypyridin-3-yl)-2-phenylimidazo[1,2-a]pyridine



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 2.4, 0.7 Hz, Ar-H, 1H), 7.90 (dt, *J* = 6.9, 1.1 Hz, Ar-H, 1H), 7.71 – 7.64 (m, Ar-H, 3H), 7.61 (dd, *J* = 8.5, 2.4 Hz, Ar-H, 1H), 7.35 – 7.26 (m, Ar-H, 3H), 7.22 (ddd, *J* = 9.1, 6.7, 1.2 Hz, Ar-H, 1H), 6.91 (dd, *J* = 8.5, 0.7 Hz, Ar-H, 1H), 6.79 – 6.74 (m, Ar-H, 1H), 4.02 (s, OCH_3, 3H).^{13}C NMR (101

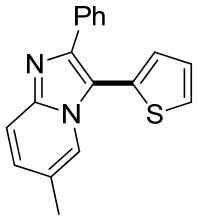
MHz, $CDCl_3$) δ 164.3, 148.9, 145.1, 141.1, 133.9, 128.7, 128.4, 128.0, 127.7, 126.0, 124.9, 123.0, 118.9, 117.7, 112.5, 111.9, 53.7. EIS-MS: 302 $[M + H]^+$.

17j: 2-phenyl-3-(pyrimidin-5-yl)imidazo[1,2-a]pyridine



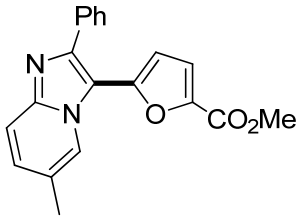
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, Ar-H, 1H), 8.83 (s, Ar-H, 2H), 7.98 (d, *J* = 6.9 Hz, Ar-H, 1H), 7.72 (d, *J* = 9.1 Hz, Ar-H, 1H), 7.54 (dd, *J* = 7.7, 1.8 Hz, Ar-H, 2H), 7.34 – 7.27 (m, Ar-H, 4H), 6.86 – 6.83 (m, Ar-H, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 158.1, 145.9, 145.1, 133.0, 128.7, 128.3, 128.2, 125.8, 125.0, 122.4, 118.0, 113.9, 113.3.

18b:6-methyl-2-phenyl-3-(thiophen-2-yl)imidazo[1,2-a] pyridine



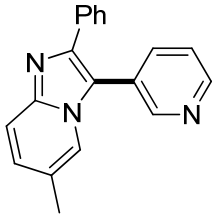
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.2, 1.4 Hz, Ar-H, 3H), 7.61 – 7.56 (m, Ar-H, 2H), 7.34 – 7.26 (m, Ar-H, 3H), 7.26 – 7.23 (m, Ar-H, 1H), 7.21 (dd, *J* = 3.5, 1.2 Hz, Ar-H, 1H), 7.09 (dd, *J* = 9.2, 1.6 Hz, Ar-H, 1H), 2.29 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 133.9, 130.2, 128.7, 128.6, 128.3, 128.2, 128.1, 127.8, 127.8, 127.6 , 125.9, 122.2, 121.4, 116.7, 18.3. EIS-MS: 291 $[M + H]^+$.

18d: methyl 5-(6-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)furan -2-carboxylate



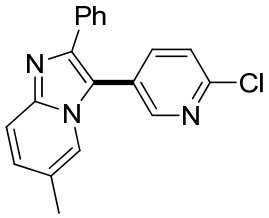
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 0.7 Hz, Ar-H, 1H), 7.71 (dd, *J* = 8.0, 1.6 Hz, Ar-H, 2H), 7.60 (d, *J* = 9.2 Hz, Ar-H, 1H), 7.39 – 7.37 (m, 6.9, 3.8, 1.6 Hz, Ar-H, 3H), 7.27 (d, *J* = 3.6 Hz, Ar-H, 1H), 7.16 (dd, *J* = 9.2, 1.6 Hz, Ar-H, 1H), 6.50 (d, *J* = 3.6 Hz, Ar-H, 1H), 3.94 (s, OCH_3, 3H), 2.37 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 148.6, 146.5, 144.9, 143.9, 133.8, 129.3, 128.6, 128.5, 128.4, 123.2, 123.1, 119.5, 116.9, 111.8, 111.0, 52.0, 18.5. EIS-MS: 333 $[M + H]^+$.

18e: 6-methyl-2-phenyl-3-(pyridin-3-yl)imidazo[1,2-a] pyridine



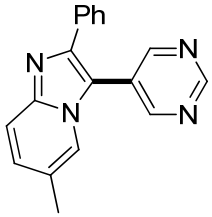
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 – 8.68 (m, Ar-H, 2H), 7.78 – 7.74 (m, Ar-H, 1H), 7.72 (s, Ar-H, 1H), 7.63 – 7.55 (m, Ar-H, 3H), 7.46 (dd, *J* = 7.8, 4.9 Hz, Ar-H, 1H), 7.32 – 7.26 (m, Ar-H, 3H), 7.10 (dd, *J* = 9.2, 1.4 Hz, Ar-H, 1H), 2.29 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 149.8, 144.5, 143.7, 138.4, 133.8, 128.5, 128.4, 128.1, 127.8, 126.6, 124.3, 122.6, 120.5, 117.2, 18.4. EIS-MS: 286 $[M + H]^+$.

18i: 3-(6-chloropyridin-3-yl)-6-methyl-2 -phenylimidazo[1,2-a]pyridine



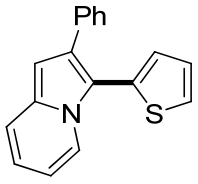
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 2.3 Hz, Ar-H, 1H), 7.70 (dd, *J* = 8.1, 2.5 Hz, Ar-H, 2H), 7.62 – 7.55 (m, Ar-H, 3H), 7.48 (d, *J* = 8.2 Hz, Ar-H, 1H), 7.34 – 7.26 (m, Ar-H, 3H), 7.11 (dd, *J* = 9.2, 1.3 Hz, Ar-H, 1H), 2.29 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 151.0, 144.6, 144.0, 140.9, 133.5, 128.6, 128.5, 128.1, 127.9, 125.4, 125.1, 122.8, 120.2, 117.2, 115.7, 18.3. EIS-MS: 320 $[M + H]^+$.

18j: 6-methyl-2-phenyl-3-(pyrimidin-5-yl)imidazo[1,2-a]pyridine



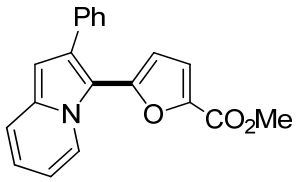
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, Ar-H, 1H), 8.85 (s, Ar-H, 2H), 7.78 – 7.73 (m, Ar-H, 1H), 7.64 (d, *J* = 9.2 Hz, Ar-H, 1H), 7.58 – 7.52 (m, Ar-H, 2H), 7.35 – 7.29 (m, Ar-H, 3H), 7.15 (dd, *J* = 9.2, 1.5 Hz, Ar-H, 1H), 2.31 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 158.1, 145.0, 144.8, 133.1, 129.0, 128.7, 128.2, 128.1, 125.3, 123.2, 120.0, 117.4, 113.6, 18.3. EIS-MS: 286 $[M + H]^+$.

19b: 2-phenyl-3-(thiophen-2-yl)indolizine



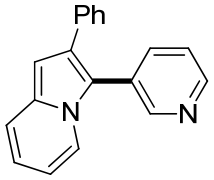
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.1 Hz, Ar-H, 1H), 7.33 – 7.27 (m, Ar-H, 3H), 7.25 (d, *J* = 9.0 Hz, Ar-H, 1H), 7.15 (dd, *J* = 8.0, 6.7 Hz, Ar-H, 2H), 7.10 – 7.05 (m, Ar-H, 1H), 7.01 – 6.97 (m, Ar-H, 2H), 6.60 – 6.54 (m, Ar-H, 2H), 6.32 (t, *J* = 6.8 Hz, Ar-H, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 133.5, 132.7, 130.1, 129.6, 128.8, 128.3, 127.8, 126.5, 123.1, 118.9, 118.2, 113.4, 110.9, 99.5. EIS-MS: 275$[M]^+$.

19d: methyl 5-(2-phenylindolizin-3-yl)furan-2 –carboxylate



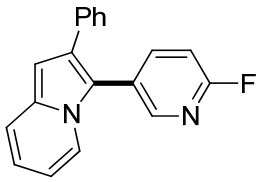
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 7.2 Hz, Ar-H, 1H), 7.45 – 7.32 (m, Ar-H, 6H), 7.18 (d, *J* = 3.6 Hz, Ar-H, 1H), 6.88 – 6.82 (m, Ar-H, 1H), 6.70 – 6.64 (m, Ar-H, 1H), 6.59 (s, Ar-H, 1H), 6.14 (d, *J* = 3.6 Hz, Ar-H, 1H), 3.92 (s, OCH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 150.9, 142.4, 135.7, 134.4, 131.9, 129.2, 128.4, 127.2, 124.8, 119.7, 119.4, 118.9, 112.0, 111.2, 110.0, 101.8, 51.8. EIS-MS: 318 $[M + H]^+$, 340 $[M + Na]^+$.

19e: 2-phenyl-3-(pyridin-3-yl)indolizine



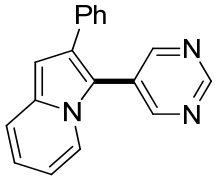
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 2.2 Hz, Ar-H, 1H), 8.61 (dd, *J* = 4.8, 1.6 Hz, Ar-H, 1H), 7.94 (dd, *J* = 7.2, 0.8 Hz, Ar-H, 1H), 7.70 – 7.66 (m, Ar-H, 1H), 7.44 (d, *J* = 9.0 Hz, Ar-H, 1H), 7.37 – 7.34 (m, Ar-H, 1H), 7.27 (dd, *J* = 8.5, 1.4 Hz, Ar-H, 4H), 7.23 – 7.19 (m, Ar-H, 1H), 6.75 (dd, *J* = 8.9, 6.5 Hz, Ar-H, 1H), 6.71 (s, Ar-H, 1H), 6.51 – 6.47 (m, Ar-H, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 148.6, 138.4, 135.4, 133.4, 129.3, 129.0, 128.8, 128.5, 126.5, 126.2, 123.9, 121.8, 119.3, 118.2, 111.2, 100.1. EIS-MS: 371 $[M + H]^+$.

19h: 3-(6-fluoropyridin-3-yl)-2-phenylindolizine



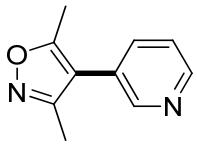
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 1.6, 0.8 Hz, Ar-H, 1H), 7.85 (dd, *J* = 7.2, 0.9 Hz, Ar-H, 1H), 7.72 (ddd, *J* = 8.3, 7.8, 2.5 Hz, Ar-H, 1H), 7.40 (dt, *J* = 9.0, 1.0 Hz, Ar-H, 1H), 7.24 (t, *J* = 4.0 Hz, Ar-H, 4H), 7.20 (dd, *J* = 8.1, 4.3 Hz, Ar-H, 1H), 6.97 (ddd, *J* = 8.4, 3.0, 0.5 Hz, Ar-H, 1H), 6.72 (ddd, *J* = 9.0, 6.5, 0.9 Hz, Ar-H, 1H), 6.68 (s, Ar-H, 1H), 6.49 – 6.44 (m, Ar-H, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, *J* = 240.8 Hz), 149.56 (d, *J* = 14.7 Hz), 143.73 (d, *J* = 8.1 Hz), 135.3, 133.5, 129.4, 129.0, 128.6, 126.7, 126.0 (d, *J* = 4.7 Hz), 121.7, 119.3, 118.3, 116.4, 111.3, 110.2 (d, *J* = 37.6 Hz), 100.1. EIS-MS: 288 $[M]^+$.

19j: 2-phenyl-3-(pyrimidin-5-yl)indolizine



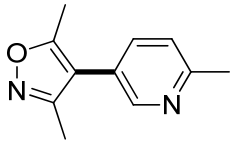
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, Ar-H, 1H), 8.75 (s, Ar-H, 2H), 7.98 (dd, *J* = 7.2, 0.9 Hz, Ar-H, 1H), 7.46 (dt, *J* = 9.0, 1.0 Hz, Ar-H, 1H), 7.30 – 7.23 (m, Ar-H, 5H), 6.80 (ddd, *J* = 9.0, 6.5, 0.9 Hz, Ar-H, 1H), 6.71 (s, Ar-H, 1H), 6.55 (td, *J* = 7.2, 1.3 Hz, Ar-H, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 157.0, 134.8, 134.1, 130.4, 129.0, 128.7, 126.9, 126.6, 121.3, 119.5, 118.9, 114.0, 111.7, 100.9. EIS-MS: 271 $[M]^+$.

20e: 3, 5-dimethyl-4-(pyridin-3-yl)isoxazole



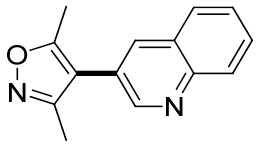
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 4.9, 1.6 Hz, Ar-H, 1H), 8.49 (d, *J* = 1.6 Hz, Ar-H, 1H), 7.58 – 7.53 (m, Ar-H, 1H), 7.36 – 7.33 (m, Ar-H, 1H), 2.37 (s, CH_3, 3H), 2.22 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 158.3, 149.6, 148.6, 136.2, 126.5, 123.5, 113.3, 11.4, 10.5.

20f: 3, 5-dimethyl-4-(6-methylpyridin-3-yl)isoxazole



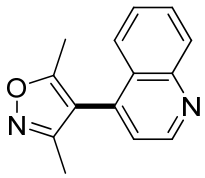
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 1.8 Hz, Ar-H, 1H), 7.42 (dd, *J* = 8.0, 2.3 Hz, Ar-H, 1H), 7.17 (d, *J* = 8.0 Hz, Ar-H, 1H), 2.52 (s, CH_3, 3H), 2.32 (s, CH_3, 3H), 2.18 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 158.4, 157.4, 148.8, 136.5, 123.3, 123.1, 113.2, 23.9, 11.3, 10.5. EIS-MS: 189 $[M + H]^+$.

20k: 3, 5-dimethyl-4-(quinolin-3-yl)isoxazole



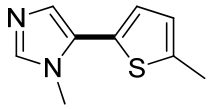
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, Ar-H, 1H), 8.17 (d, *J* = 8.5 Hz, Ar-H, 1H), 8.05 (s, Ar-H, 1H), 7.87 (d, *J* = 8.2 Hz, Ar-H, 1H), 7.77 (t, *J* = 7.7 Hz, Ar-H, 1H), 7.62 (t, *J* = 7.5 Hz, Ar-H, 1H), 2.48 (s, CH_3, 3H), 2.33 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 158.6, 150.4, 146.9, 135.8, 130.0, 129.1, 127.7, 127.7, 127.4, 123.7, 113.5, 11.6, 10.8.

20l: 3, 5-dimethyl-4-(quinolin-4-yl)isoxazole



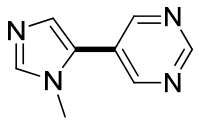
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, *J* = 4.3 Hz, Ar-H, 1H), 8.18 (d, *J* = 8.5 Hz, Ar-H, 1H), 7.77 – 7.73 (m, Ar-H, 1H), 7.62 – 7.57 (m, Ar-H, 1H), 7.57 – 7.52 (m, Ar-H, 1H), 7.24 (d, *J* = 4.3 Hz, Ar-H, 1H), 2.24 (s, CH_3, 3H), 2.07 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 159.1, 149.9, 148.5, 136.8, 130.1, 129.8, 127.1, 127.1, 124.9, 122.6, 112.9, 11.6, 10.5. EIS-MS: 225 $[M + H]^+$.

21c: 1-methyl-5-(5-methylthiophen-2-yl)-1H-imidazole



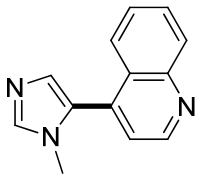
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, Ar-H, 1H), 7.08 (d, *J* = 1.0 Hz, Ar-H, 1H), 6.83 (d, *J* = 3.5 Hz, Ar-H, 1H), 6.75 – 6.68 (m, Ar-H, 1H), 3.65 (s, CH_3, 3H), 2.48 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 138.9, 128.7, 128.0, 127.0, 126.2, 125.7, 32.5, 15.2. EIS-MS: 178 $[M]^+$.

21j: 5-(1-methyl-1H-imidazol-5-yl)pyrimidine



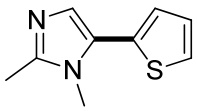
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (s, Ar-H, 1H), 8.80 (s, Ar-H, 2H), 8.80 (s, Ar-H, 2H), 7.24 (s, Ar-H, 1H), 3.71 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ 157.6, 155.4, 140.7, 130.0, 126.5, 124.5, 32.6.

21l: 4-(1-methyl-1H-imidazol-5-yl)quinoline



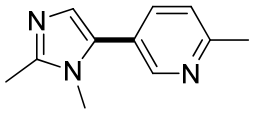
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 4.4 Hz, Ar-H, 1H), 8.15 (d, *J* = 8.4 Hz, Ar-H, 1H), 7.73 (dt, *J* = 8.3, 4.8 Hz, Ar-H, 2H), 7.66 (s, Ar-H, 1H), 7.55 – 7.50 (m, Ar-H, 1H), 7.30 (d, *J* = 4.4 Hz, Ar-H, 1H), 7.22 (s, Ar-H, 1H), 3.49 (s, N-CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 148.5, 139.6, 135.8, 130.4, 129.8, 129.8, 128.5, 127.3, 127.2, 125.3, 122.4, 32.3. EIS-MS: 209 $[M]^+$.

22b: 1, 2-dimethyl-5-(thiophen-2-yl)-1H-imidazole



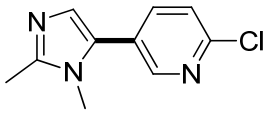
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 5.2, 1.2 Hz, Ar-H, 1H), 7.10 (dd, *J* = 5.2, 3.6 Hz, Ar-H, 1H), 7.04 (dd, *J* = 3.6, 1.1 Hz, Ar-H, 2H), 3.57 (s, N-CH_3, 3H), 2.44 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 131.4, 127.5, 127.2, 126.4, 126.3, 125.8, 31.2, 13.7.

22f: 5-(1, 2-dimethyl-1H-imidazol-5-yl)-2-methylpyridine



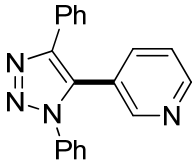
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 1.9 Hz, Ar-H, 1H), 7.53 (dd, *J* = 8.0, 2.3 Hz, Ar-H, 1H), 7.19 (d, *J* = 8.0 Hz, Ar-H, 1H), 6.94 (s, Ar-H, 1H), 3.48 (s, N-CH_3, 3H), 2.57 (s, CH_3, 3H), 2.42(s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 148.4, 146.5, 136.1, 130.1, 126.5, 123.6, 123.0, 31.2, 24.1, 13.6. EIS-MS: 187 $[M]^+$.

22i: 2-chloro-5-(1, 2-dimethyl-1H-imidazol-5-yl)pyridine



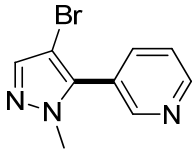
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.34 (m, Ar-H, 1H), 7.61 (dd, *J* = 8.2, 2.5 Hz, Ar-H, 1H), 7.37 (dd, *J* = 8.2, 0.5 Hz, Ar-H, 1H), 6.98 (s, Ar-H, 1H), 3.51 (s, CH_3, 3H), 2.43 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 148.6, 147.2, 138.2, 128.6, 127.2, 125.5, 124.2, 31.3, 13.6. EIS-MS: 207 $[M]^+$.

23e: 3-(1, 4-diphenyl-1H-1,2,3-triazol-5-yl)pyridine



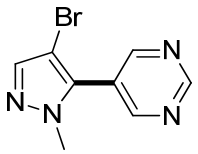
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 3.7 Hz, Ar-H, 1H), 8.46 (d, *J* = 1.0 Hz, Ar-H, 1H), 7.61 – 7.49 (m, Ar-H, 3H), 7.47 – 7.39 (m, Ar-H, 3H), 7.38 – 7.27 (m, Ar-H, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 150.4, 145.7, 137.5, 136.0, 130.5, 130.1, 129.5, 129.5, 128.7, 128.3, 127.5, 125.4, 124.2, 123.6.

24e: 3-(4-bromo-1-methyl-1H-pyrazol-5-yl)pyridine



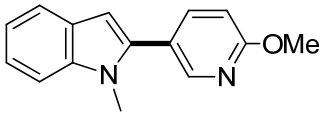
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 – 8.65 (m, Ar-H, 2H), 7.76 (dt, *J* = 7.9, 1.9 Hz, Ar-H, 1H), 7.56 (s, Ar-H, 1H), 7.45 (dd, *J* = 7.9, 4.9 Hz, Ar-H, 1H), 3.84 (s, N-CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 139.5, 138.0, 137.2, 124.8, 123.5, 94.4, 38.5.

24j: 5-(4-bromo-1-methyl-1H-pyrazol-5-yl)pyrimidine



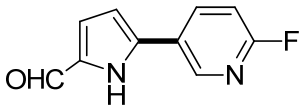
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (s, Ar-H, 1H), 8.87 (s, Ar-H, 2H), 7.62 (s, Ar-H, 1H), 3.90 (s, N-CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.8, 157.2, 139.8, 134.8, 123.5, 95.2, 38.6.

25g: 2-(6-methoxypyridin-3-yl)-1-methyl-1H-indole



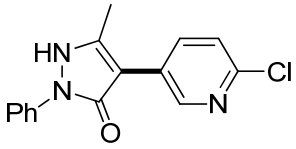
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, Ar-H, 1H), 7.56 (s, Ar-H, 1H), 7.35 – 7.21 (m, Ar-H, 5H), 6.58 (d, *J* = 3.6 Hz, Ar-H, 1H), 3.90 (s, OCH_3, 3H), 3.78 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 155.0, 141.3, 137.1, 127.7, 124.7, 122.5, 120.8, 120.4, 120.1, 109.7, 106.2, 104.7, 51.6, 33.0. EIS-MS: 278 $[M + K]^+$.

26h: 5-(6-fluoropyridin-3-yl)-1H-pyrrole-2-carbaldehyde



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, CHO-H, 1H), 8.56 (d, *J* = 2.4 Hz, Ar-H, 1H), 7.93 (dd, *J* = 8.6, 2.4 Hz, Ar-H, 1H), 7.47 (d, *J* = 1.8 Hz, Ar-H, 1H), 7.39 (d, *J* = 8.6 Hz, Ar-H, 1H), 7.21 (dd, *J* = 3.9, 1.7 Hz, Ar-H, 1H), 6.45 (dd, *J* = 3.7, 2.9 Hz, NH, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1, 149.6, 140.7, 131.9, 130.7, 126.3, 120.6, 119.1, 111.7. EIS-MS: 226 $[M + Na]^+$.

27i: 4-(6-chloropyridin-3-yl)-5-methyl-2-phenyl-1H-pyrazol -3(2H) –one



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.1 Hz, Ar-H, 1H), 7.75 (dd, *J* = 8.7, 2.5 Hz, Ar-H, 1H), 7.61 – 7.56 (m, Ar-H, 2H), 7.38 – 7.33 (m, Ar-H, 2H), 7.26 – 7.21 (m, Ar-H, 1H), 6.85 (dd, *J* = 8.7, 0.4 Hz, Ar-H, 1H), 5.97 (s, Ar-H, 1H), 2.34 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 148.9, 148.3, 147.0, 142.3, 138.1, 128.8, 126.7, 122.6, 115.0, 112.6, 94.8, 14.6. EIS-MS: 285 $[M + H]^+$.

4. NMR spectrums for the products

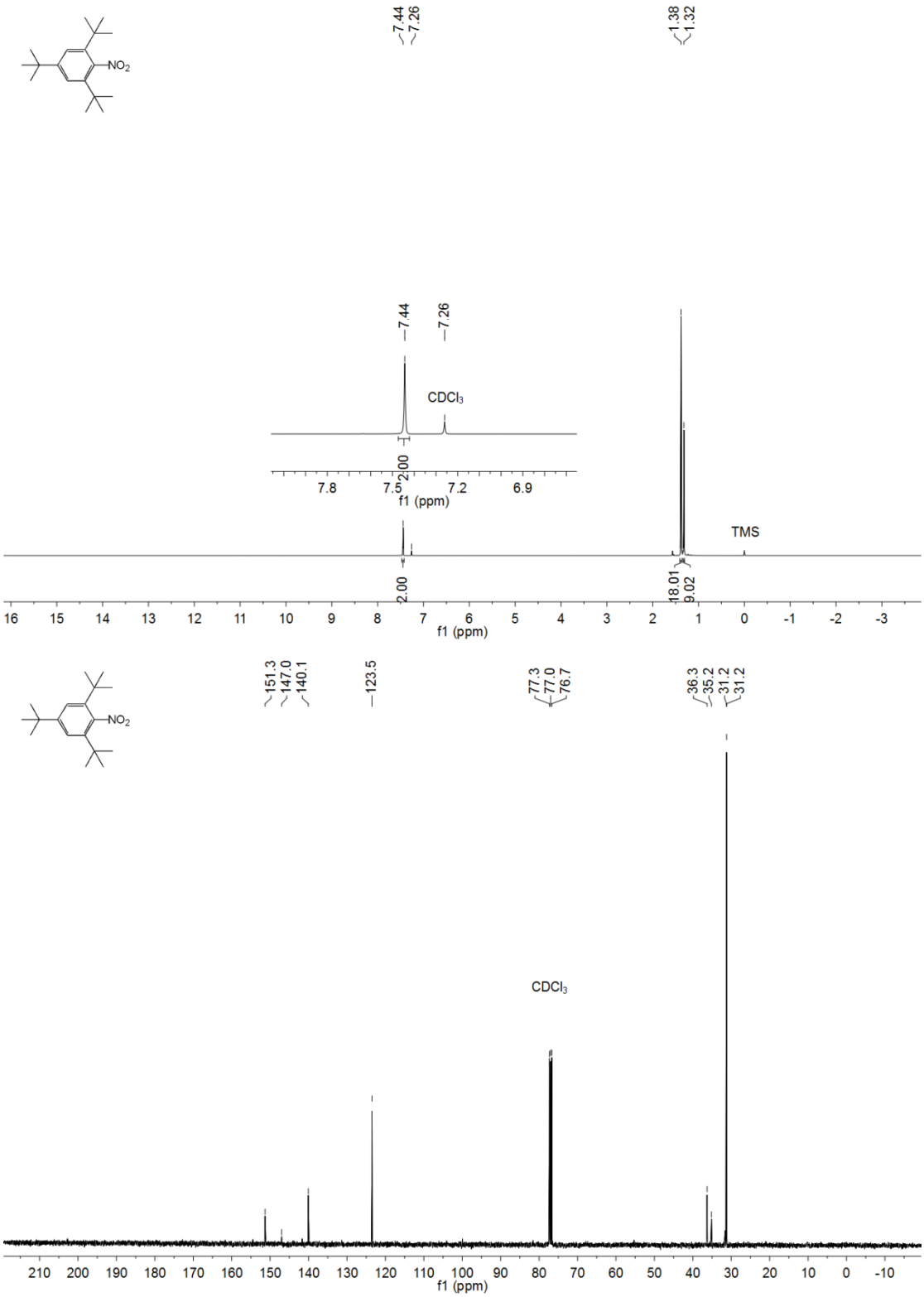


Figure **S1**.The NMR spectrums of **n1**

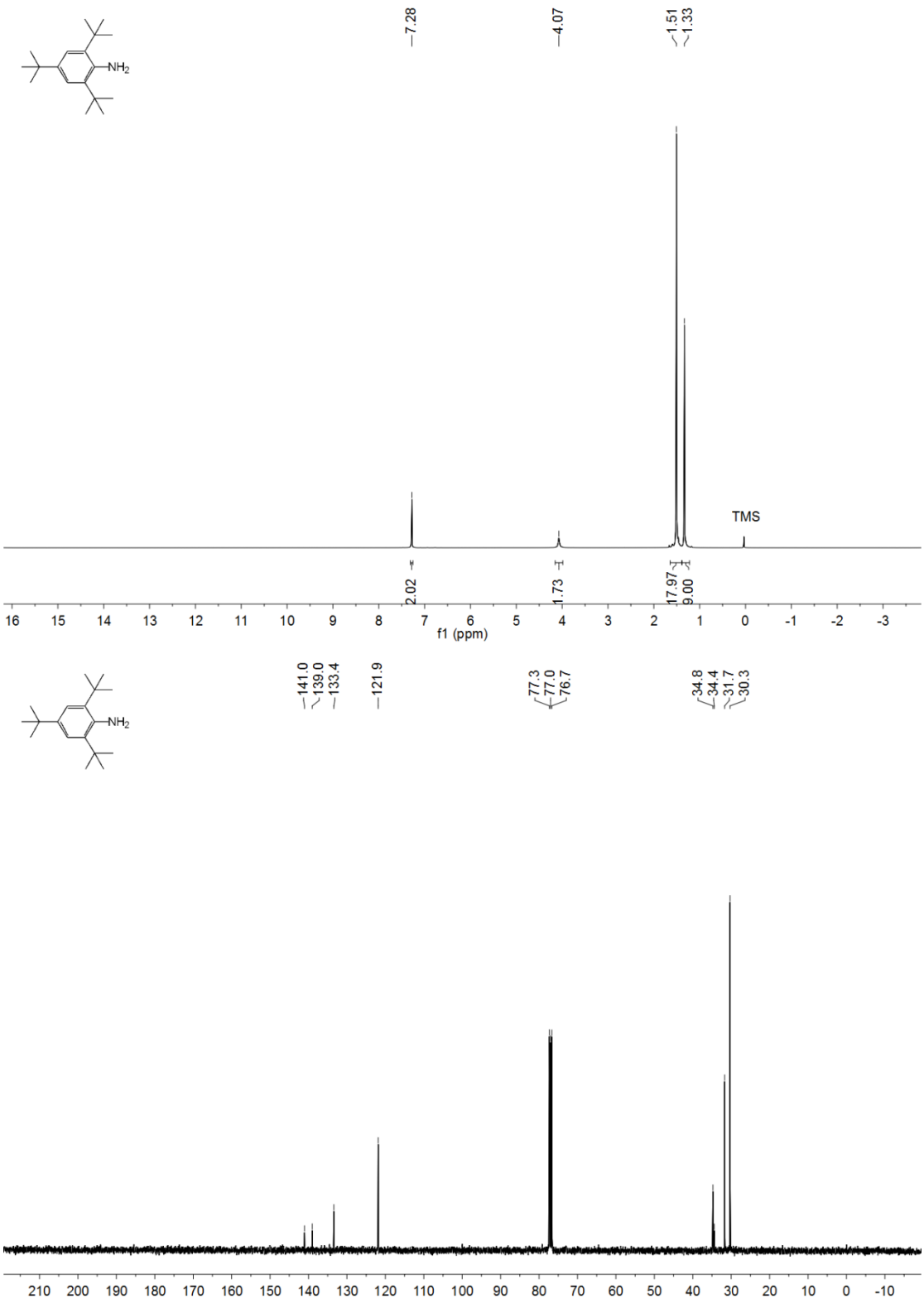


Figure **S2**.The NMR spectrums of **a1**

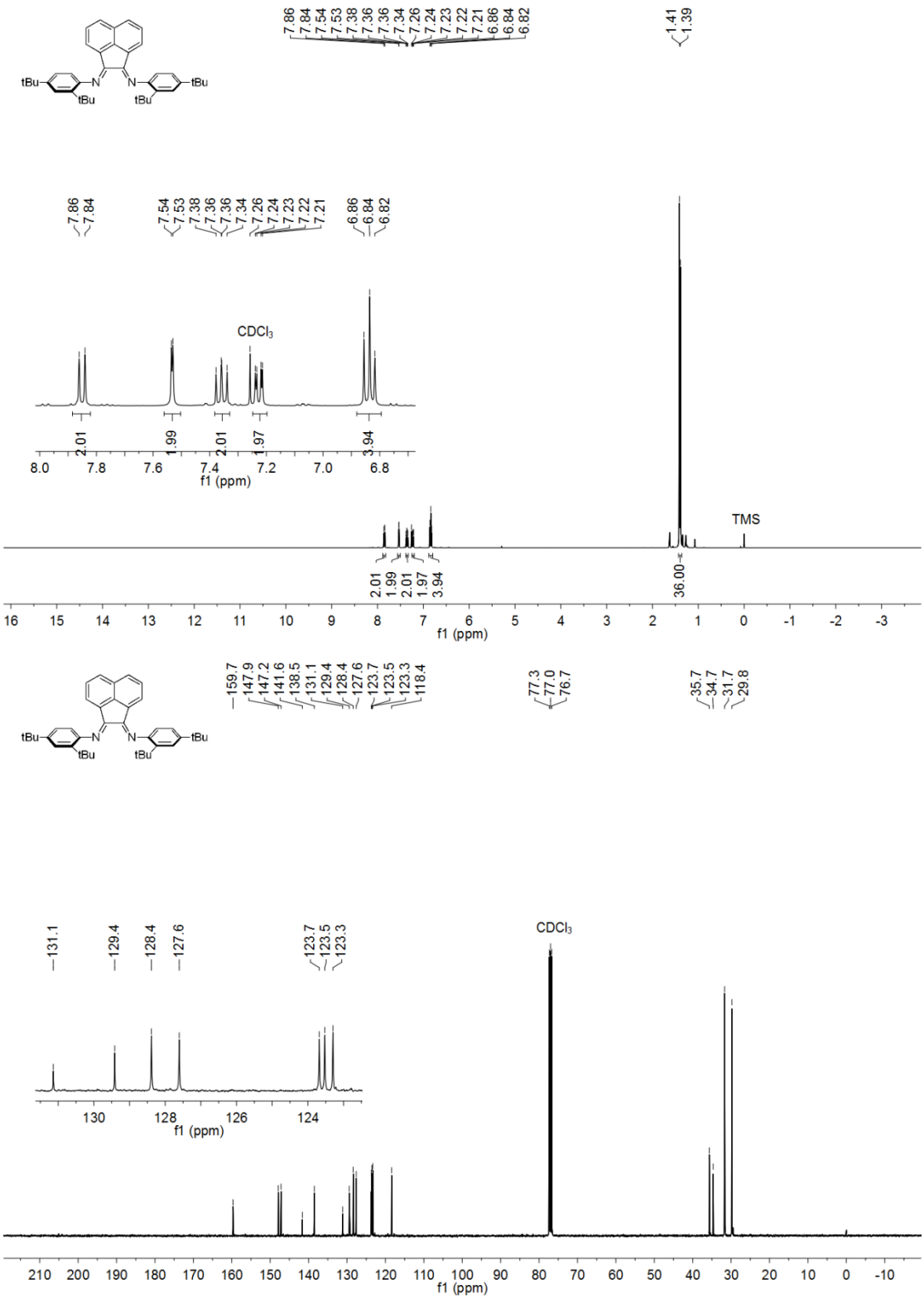


Figure **S3**.The NMR spectrums of **L1**

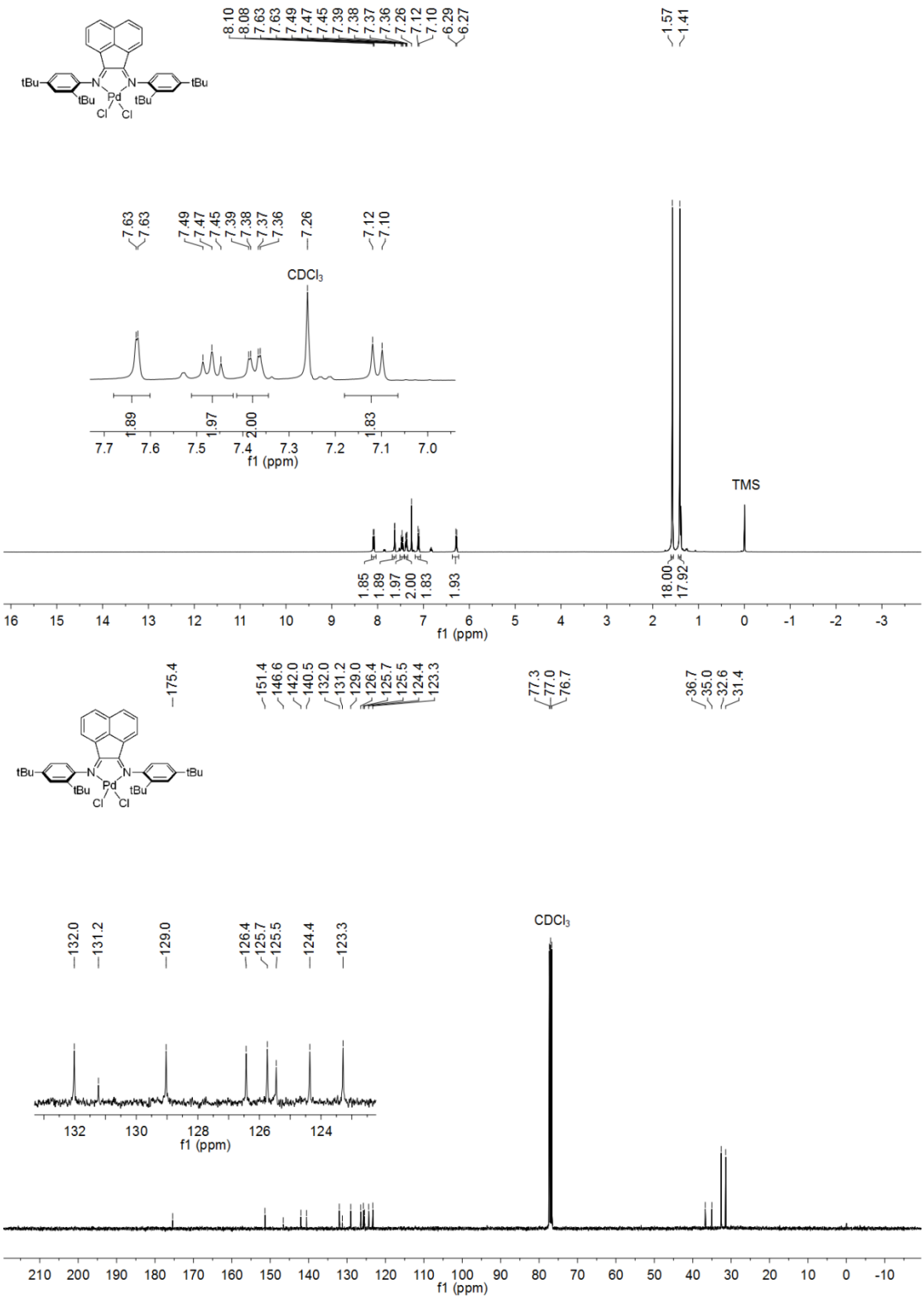


Figure **S4**.The NMR spectrums of **C1**

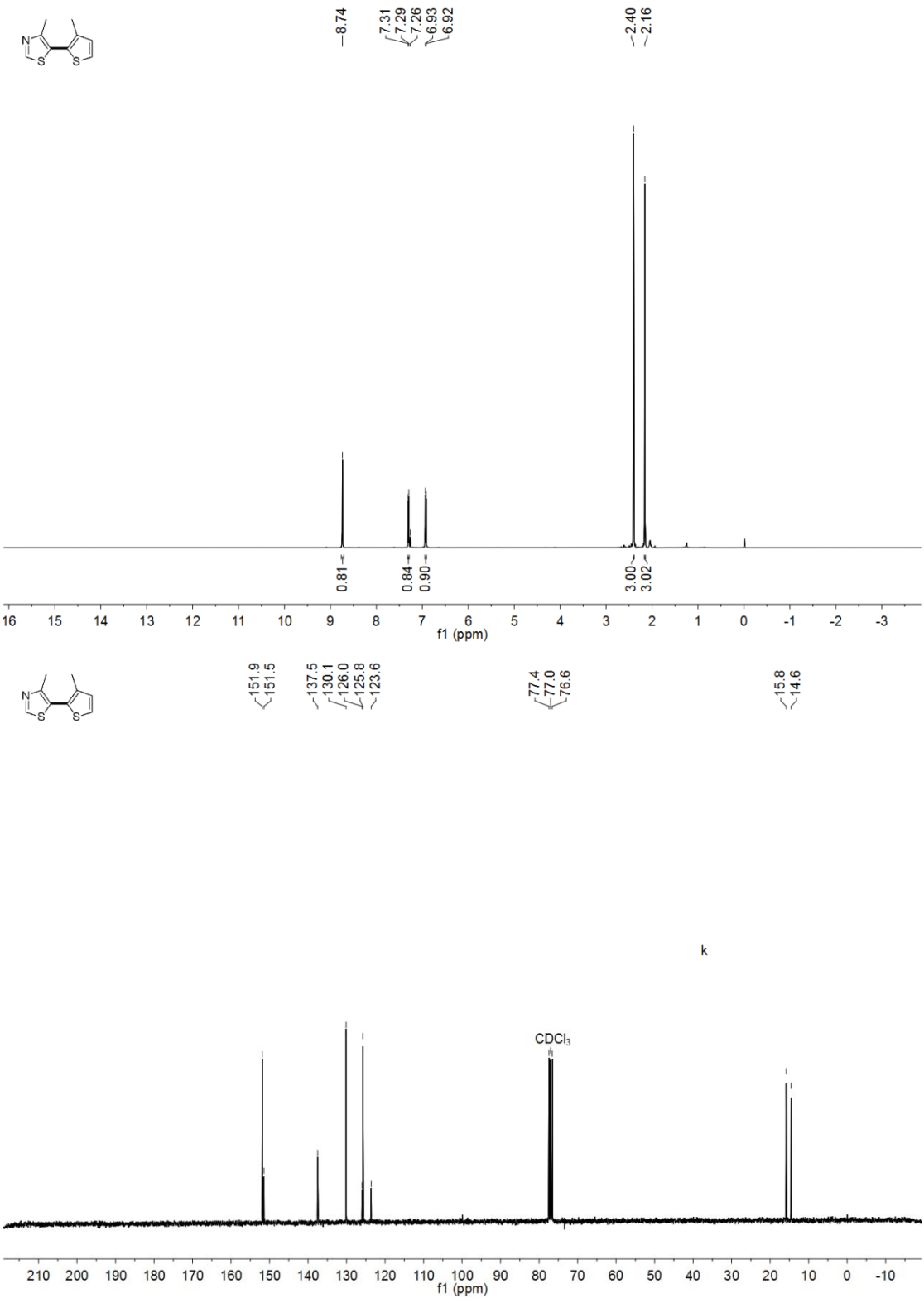


Figure **S5**.The NMR spectrums of **3a**

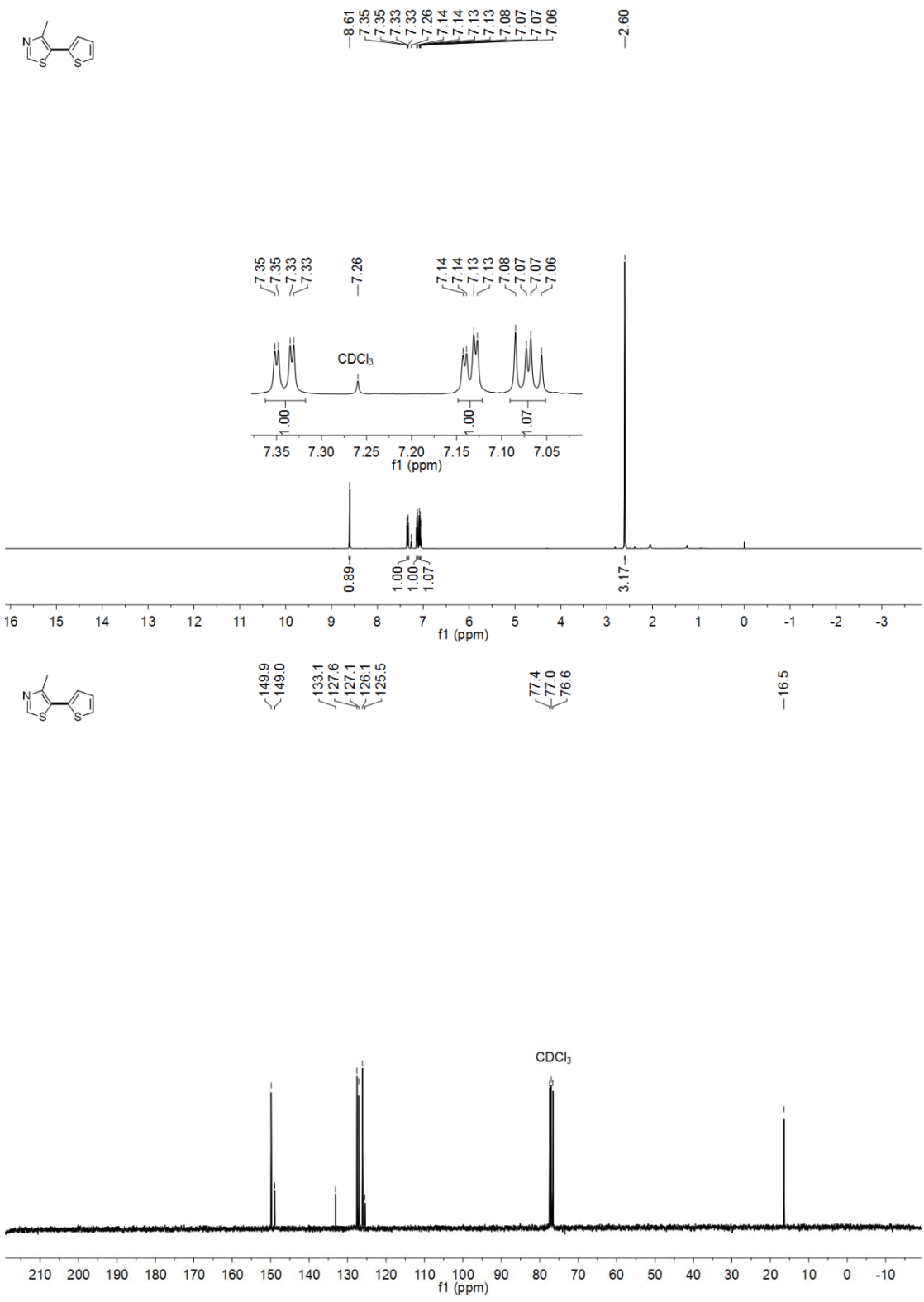


Figure **S6**.The NMR spectrums of **3b**

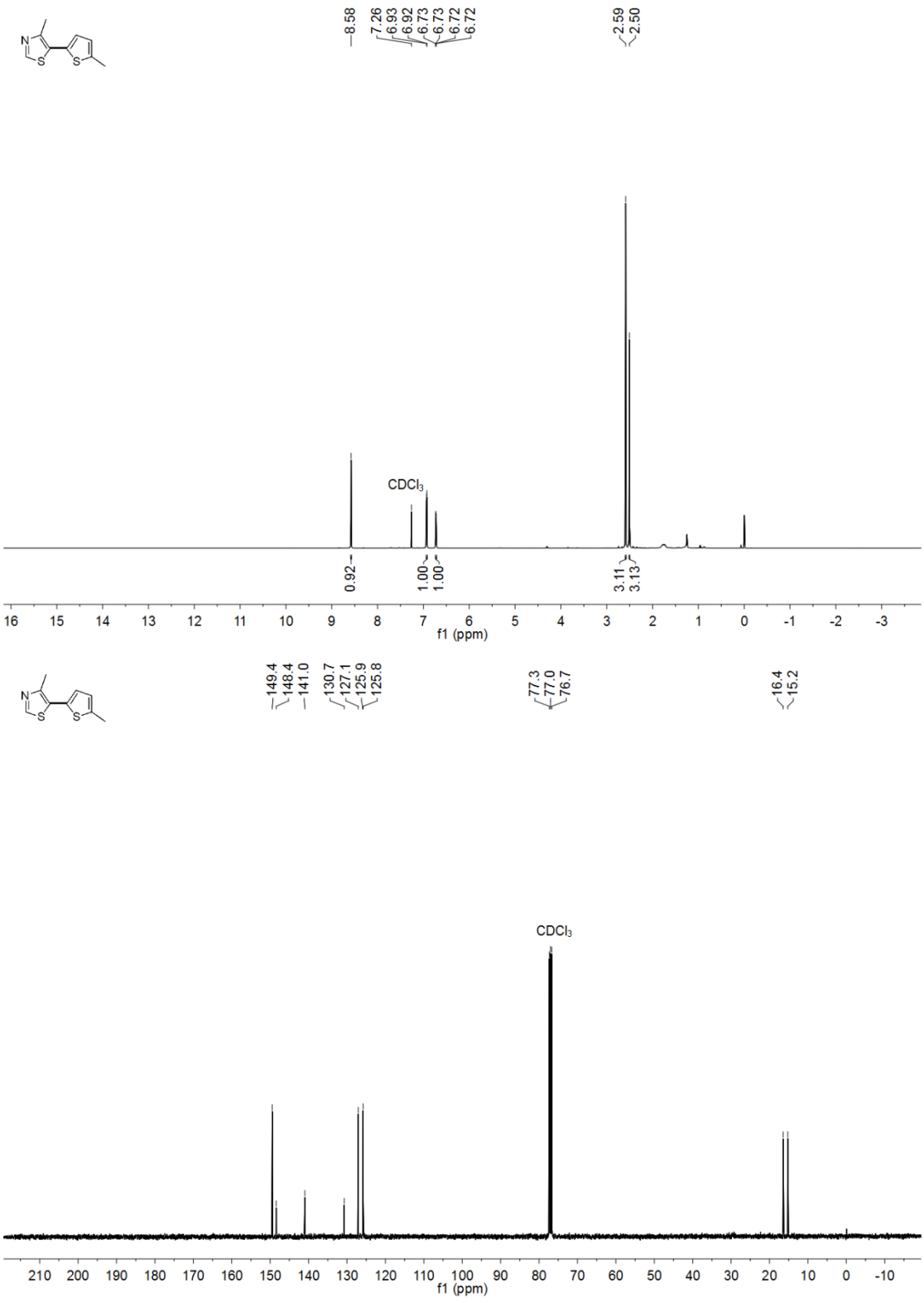


Figure **S7**.The NMR spectrums of 3**c**

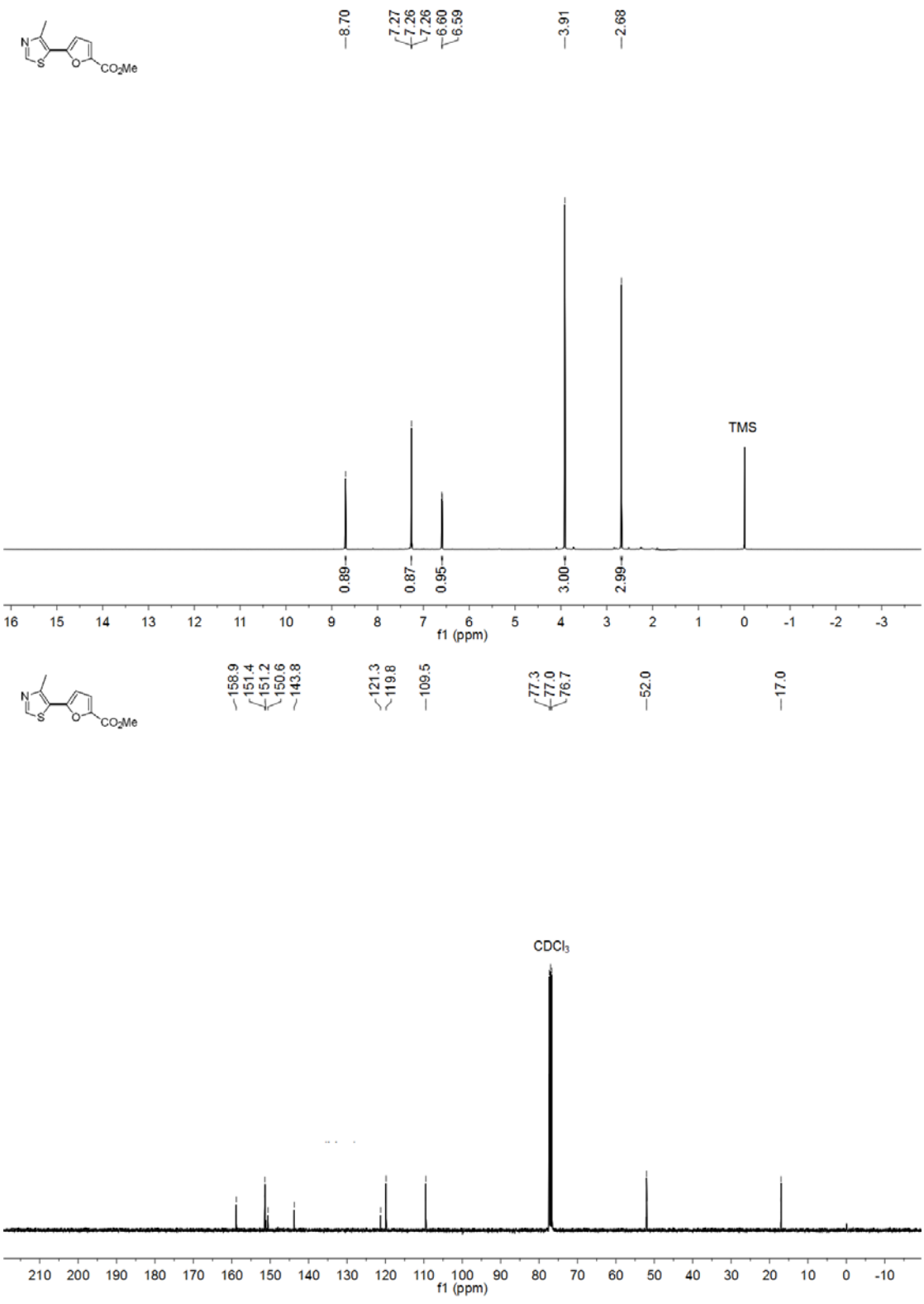


Figure **S8**.The NMR spectrums of **3d**

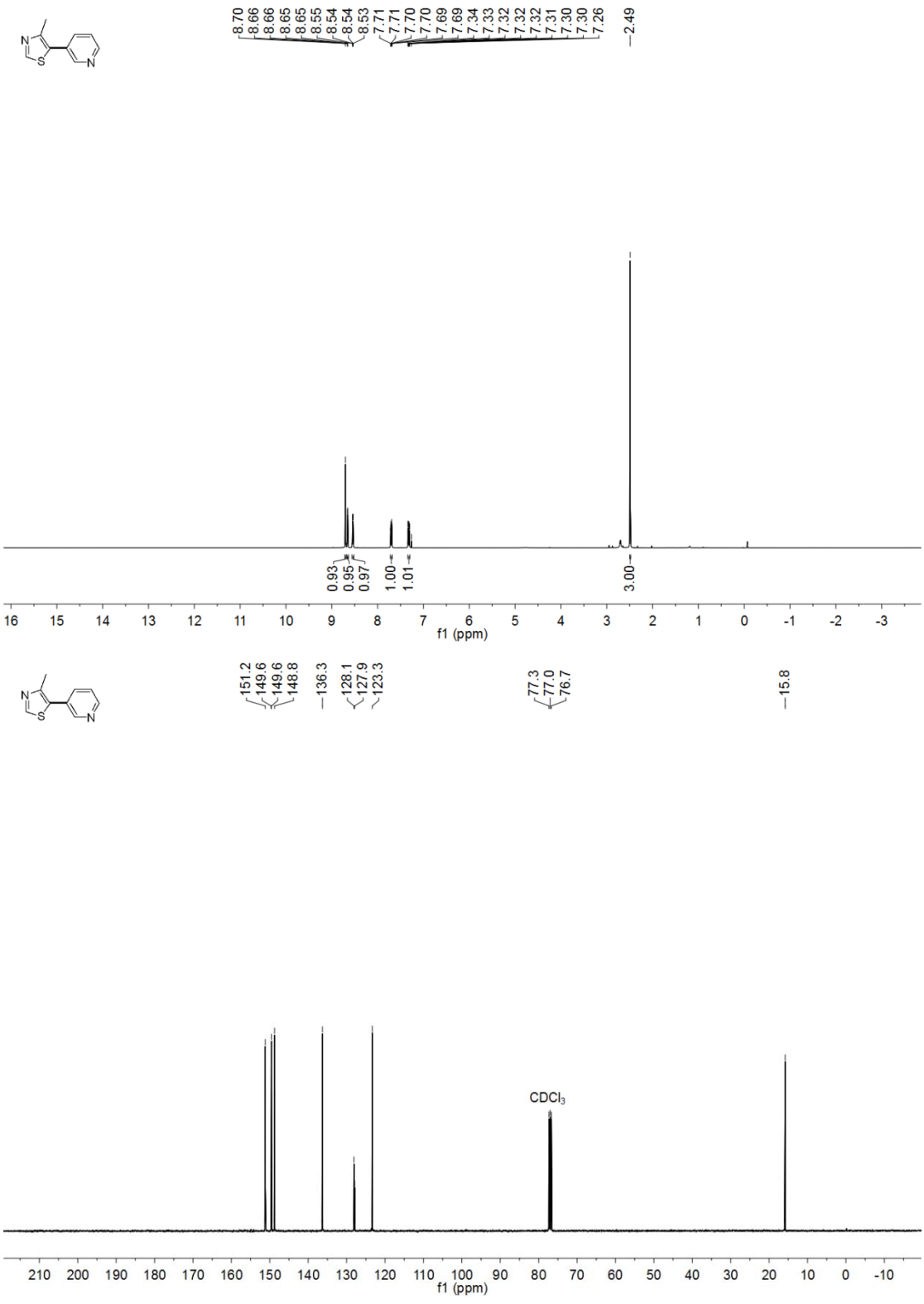


Figure S**9**.The NMR spectrums of 3**e**

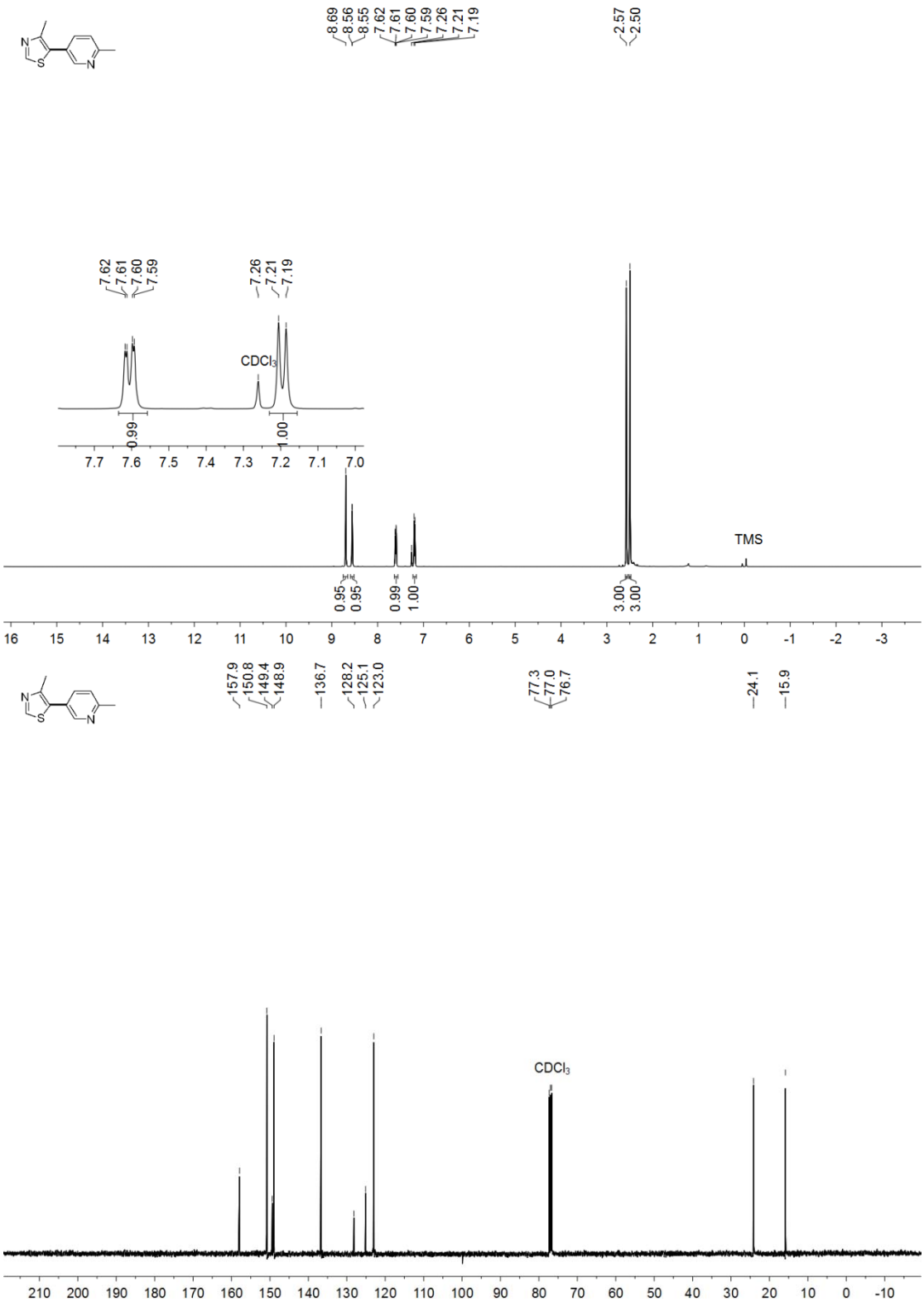


Figure **S10**.The NMR spectrums of **3f**

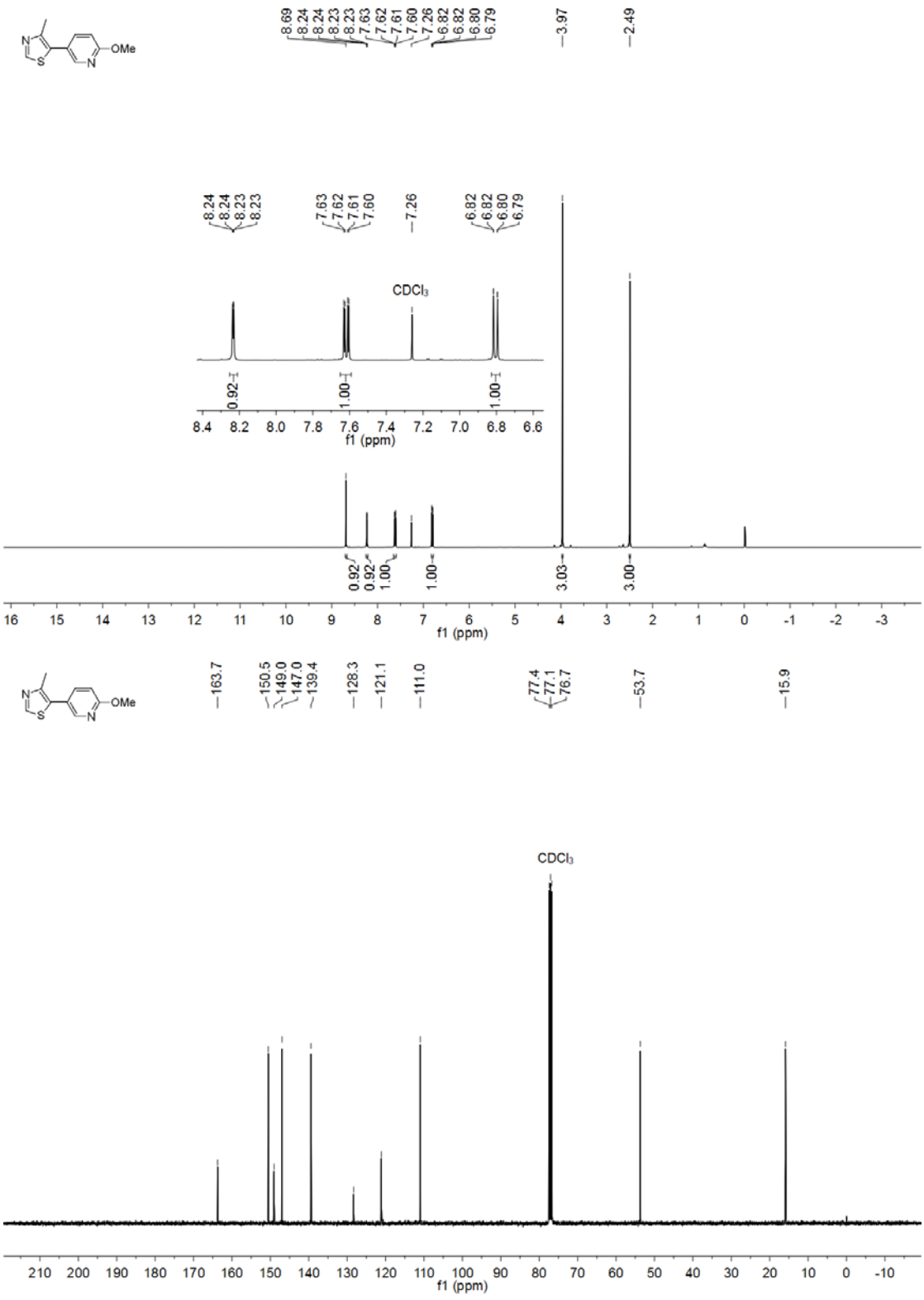


Figure **S11**.The NMR spectrums of **3g**

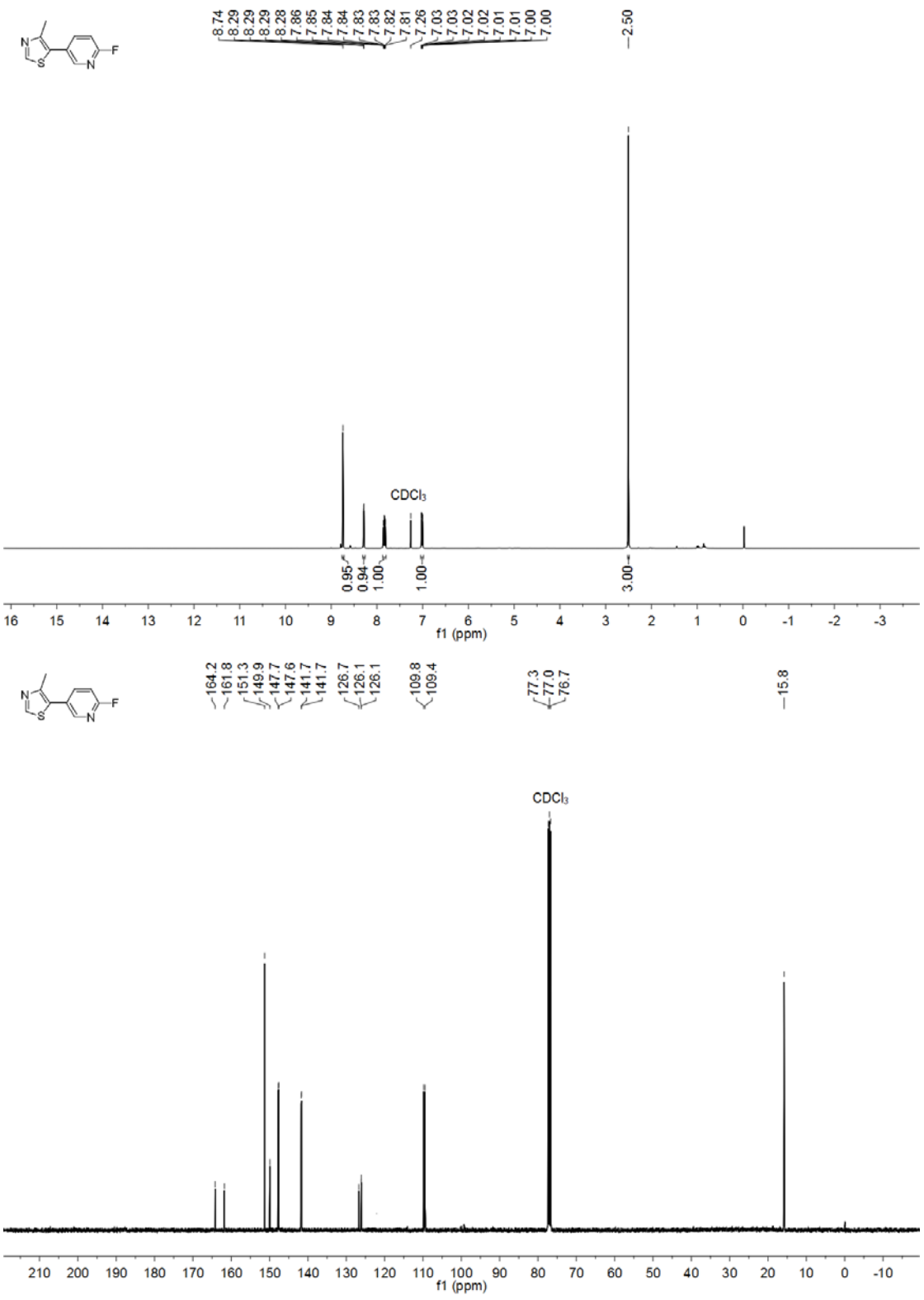


Figure **S12**.The NMR spectrums of **3h**

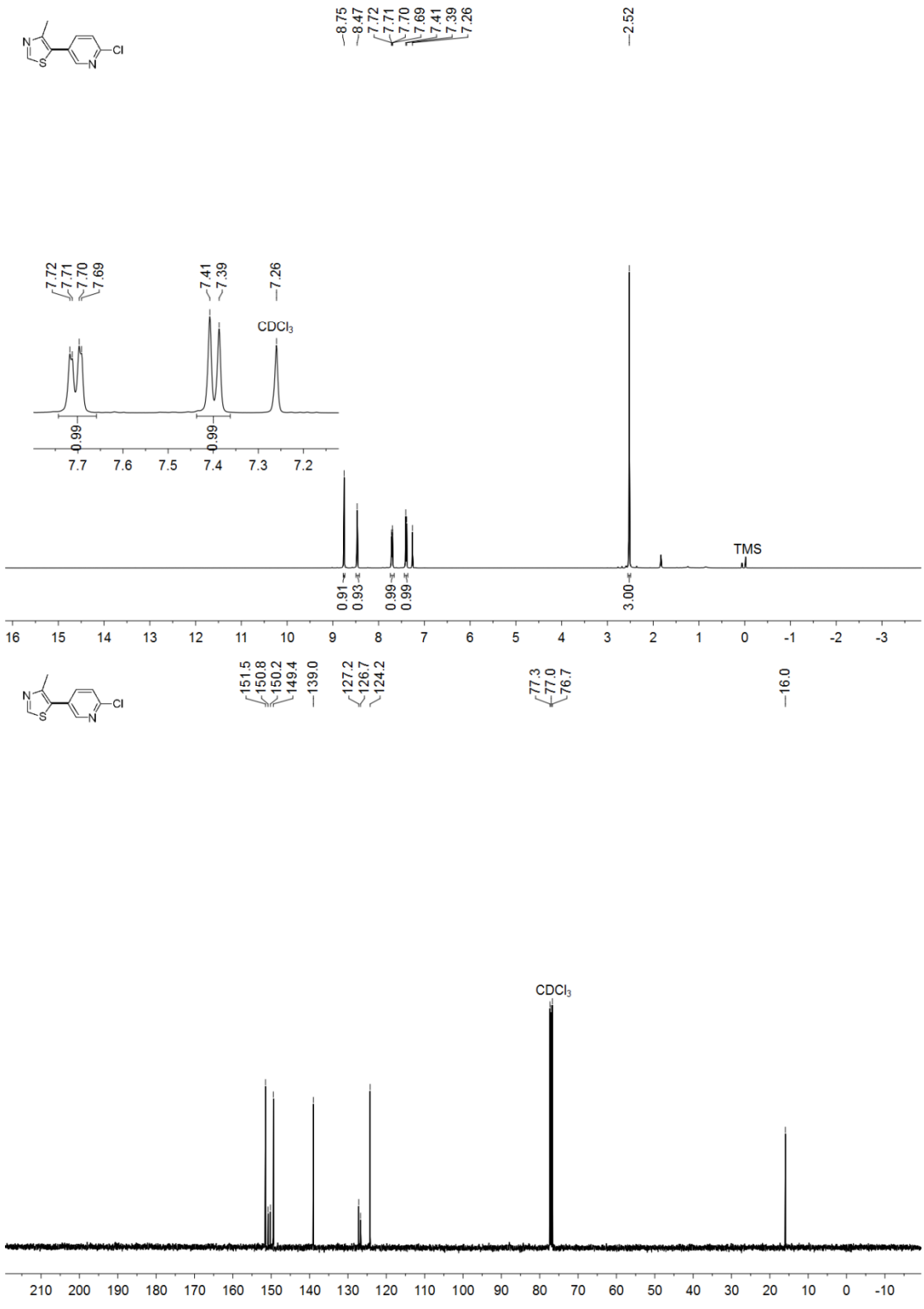


Figure **S13**.The NMR spectrums of **3i**

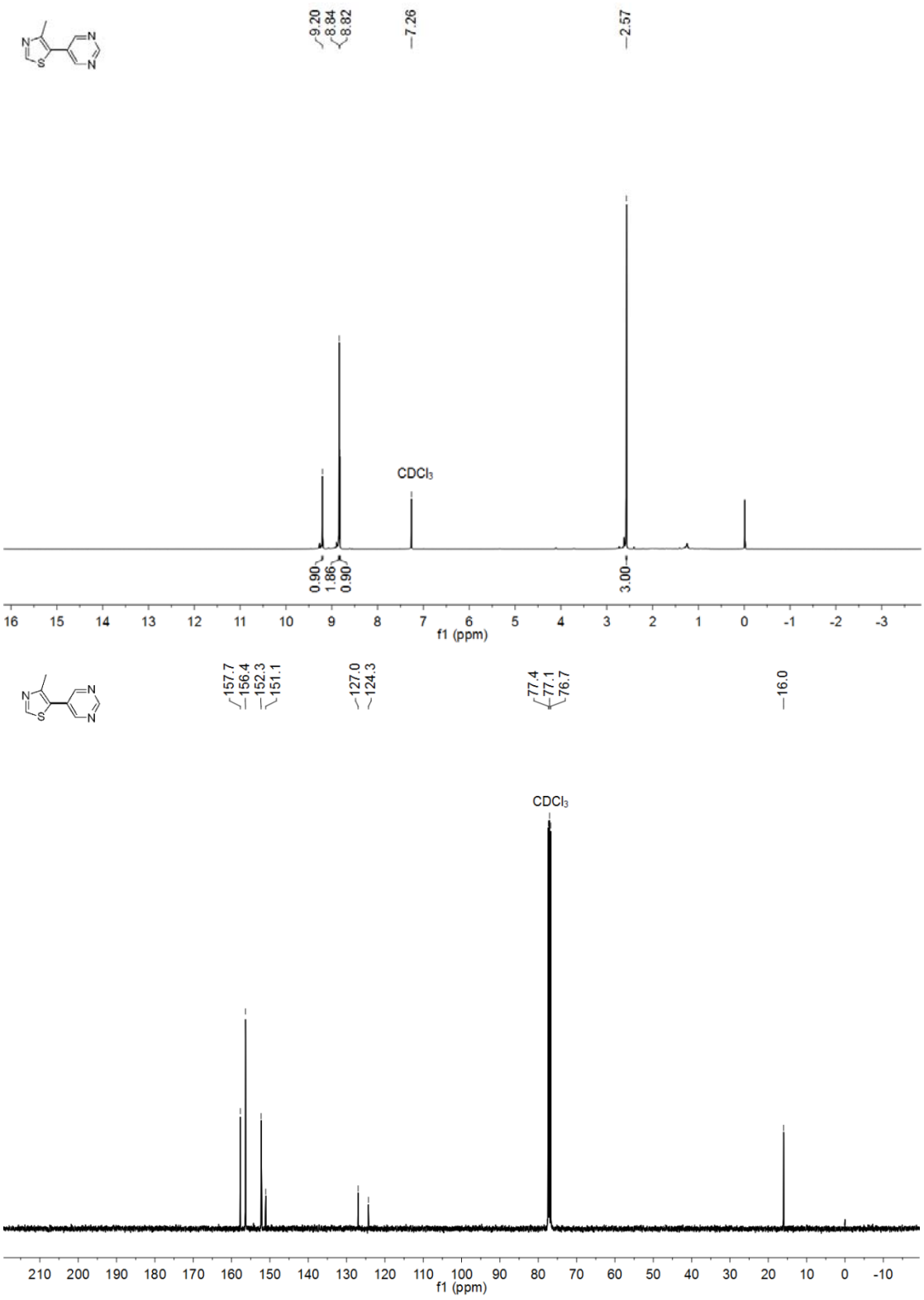


Figure **S14**.The NMR spectrums of **3j**

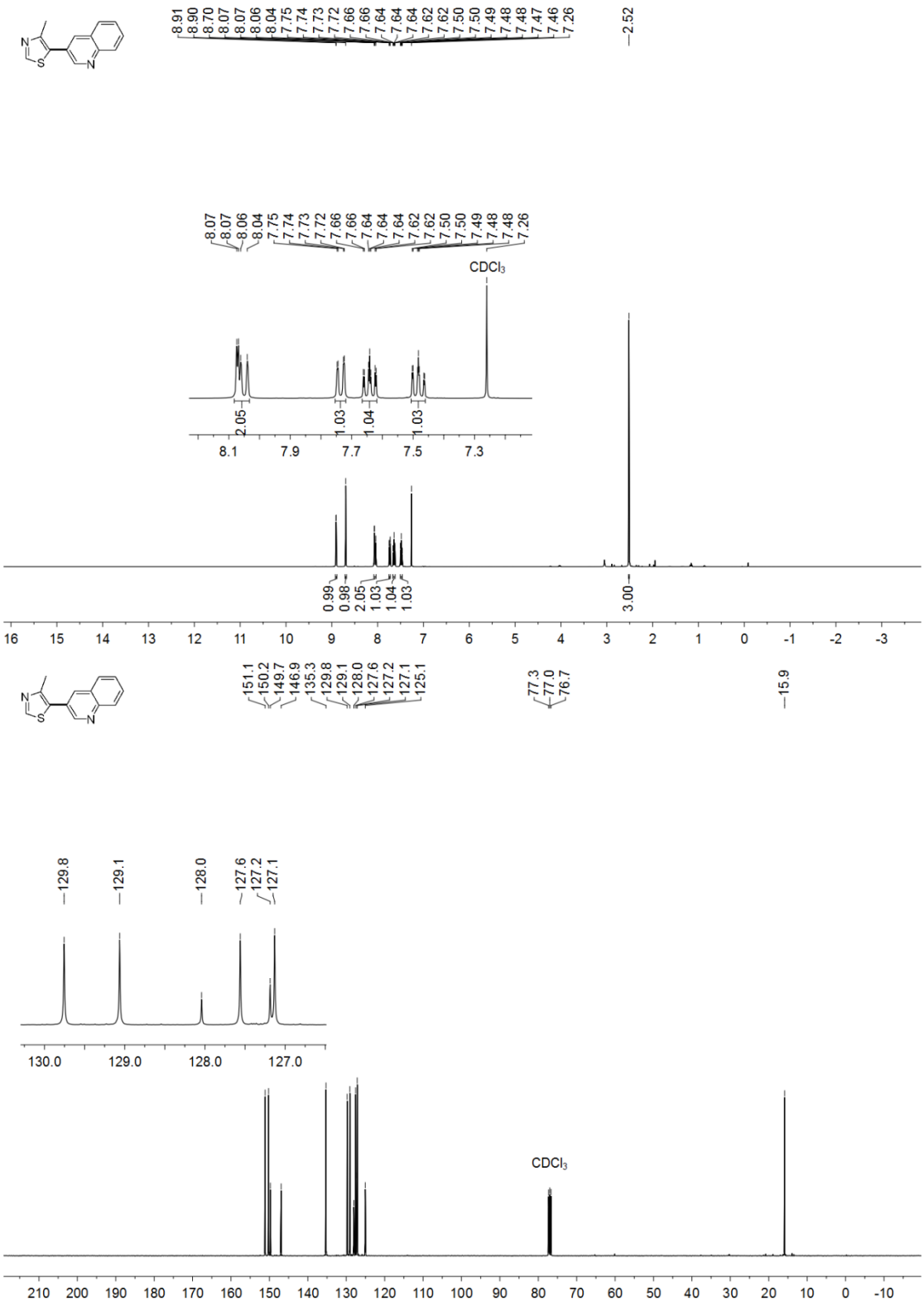


Figure **S15**.The NMR spectrums of **3k**

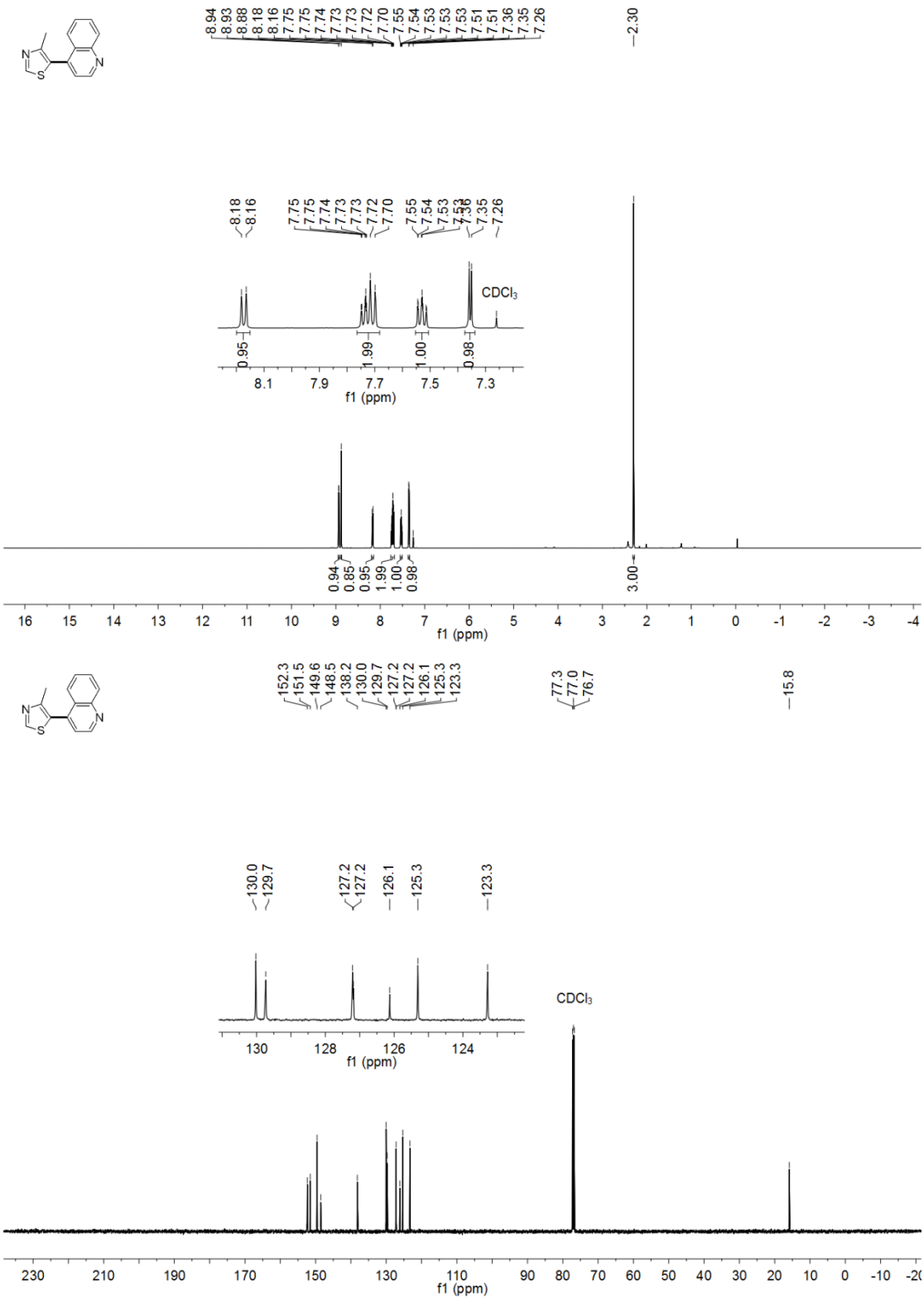


Figure **S16**.The NMR spectrums of **3l**

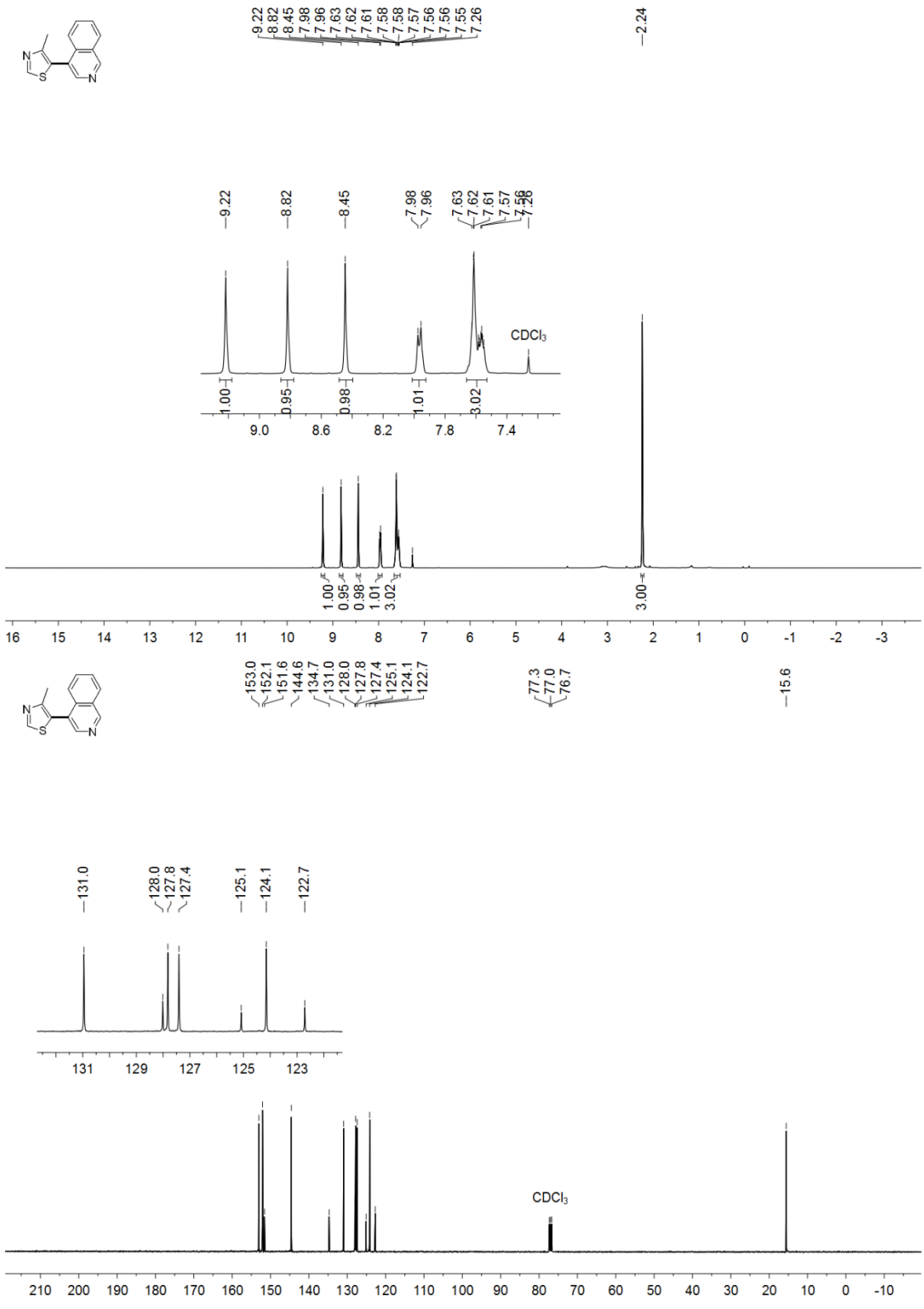


Figure **S17**.The NMR spectrums of **3m**

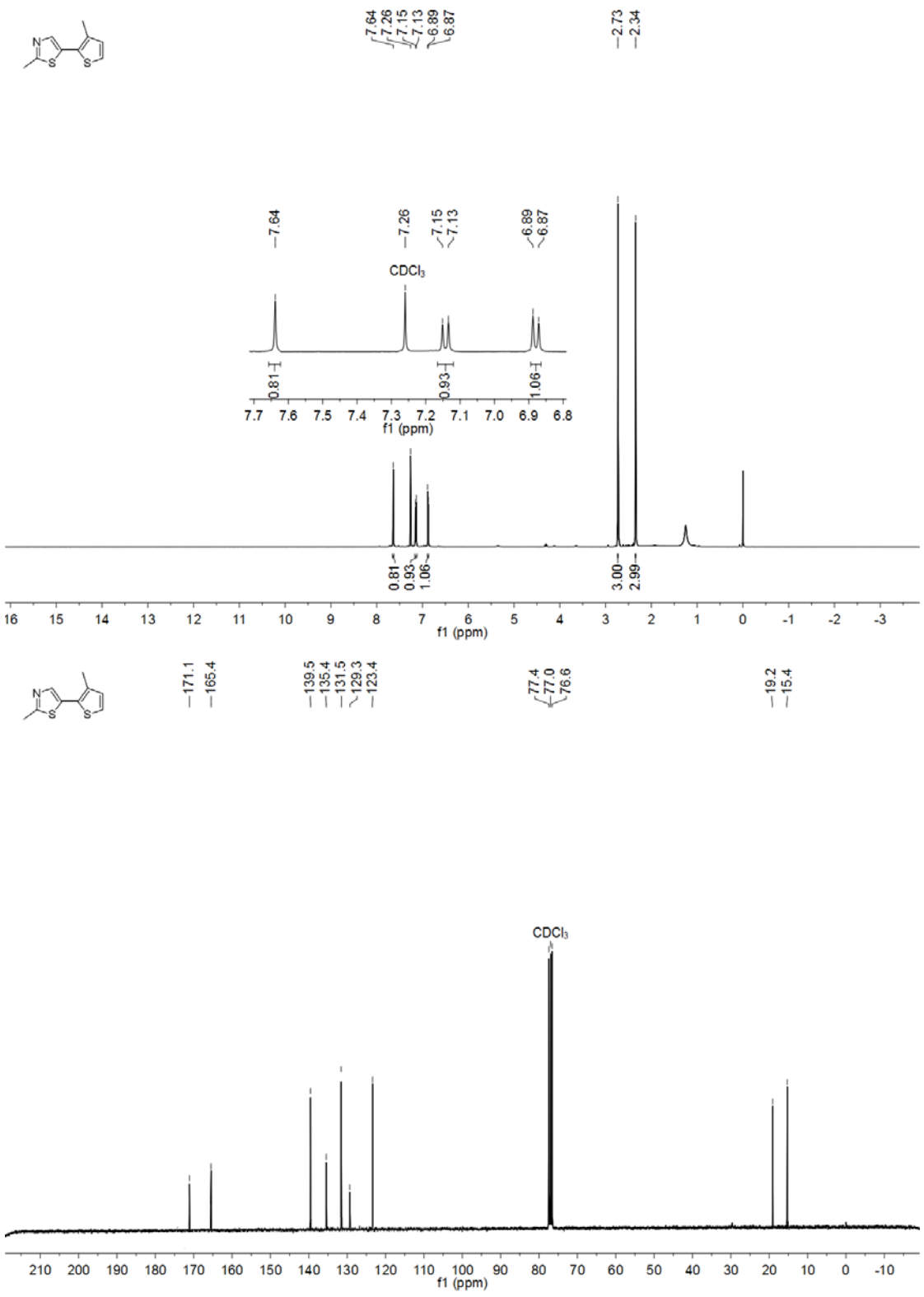


Figure **S18**.The NMR spectrums of **4a**

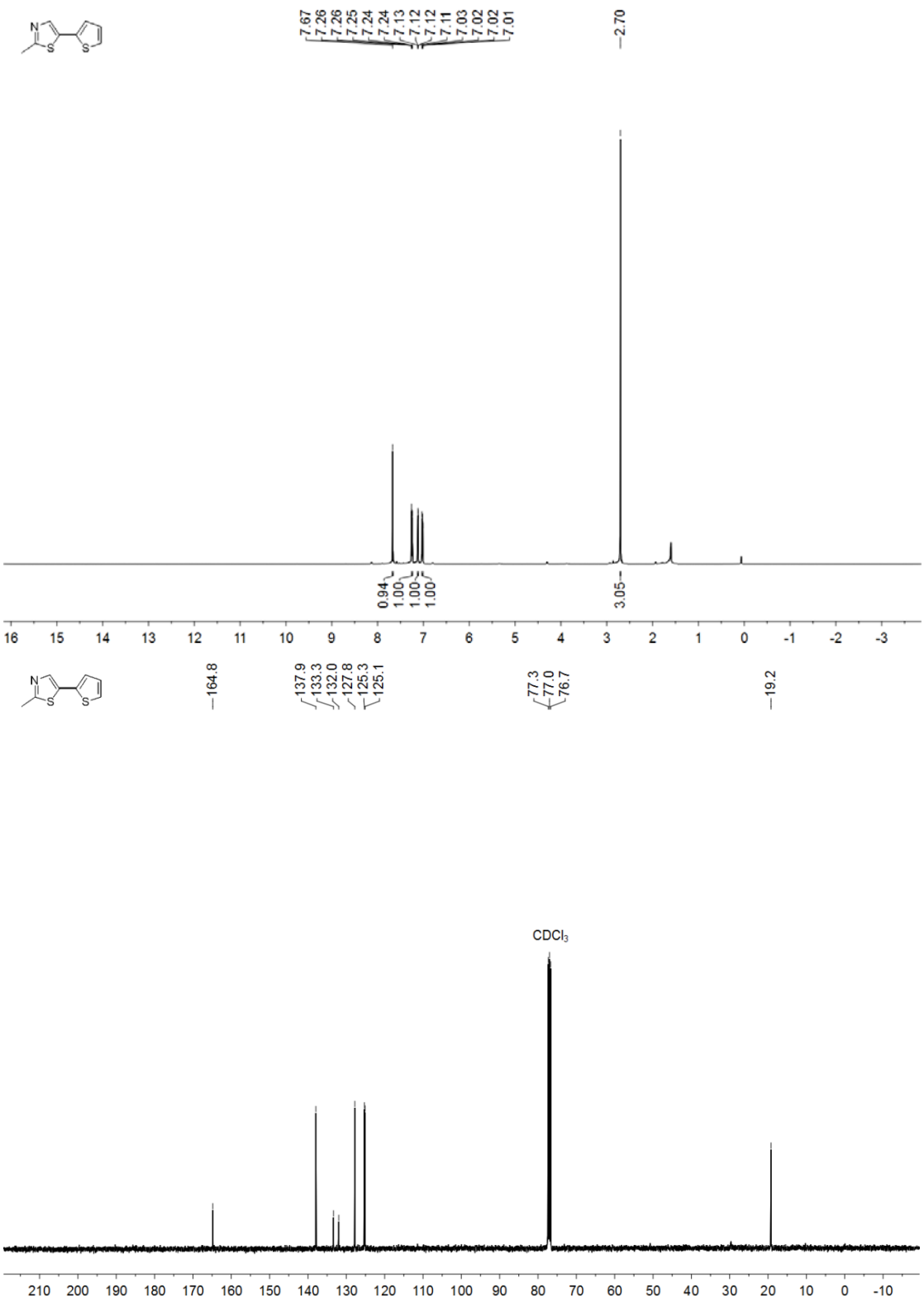


Figure **S19**.The NMR spectrums of **4b**

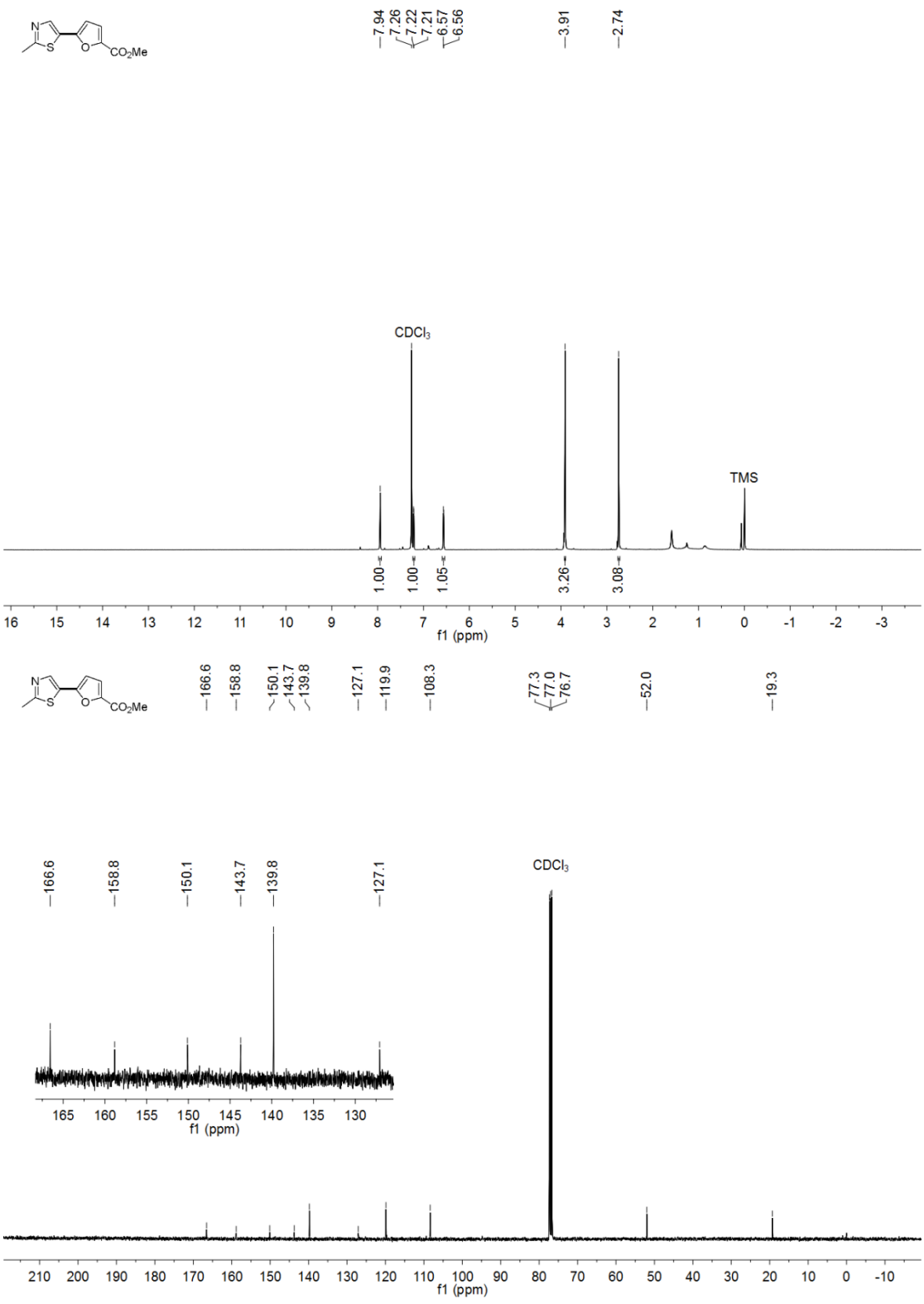


Figure **S20**.The NMR spectrums of **4d**

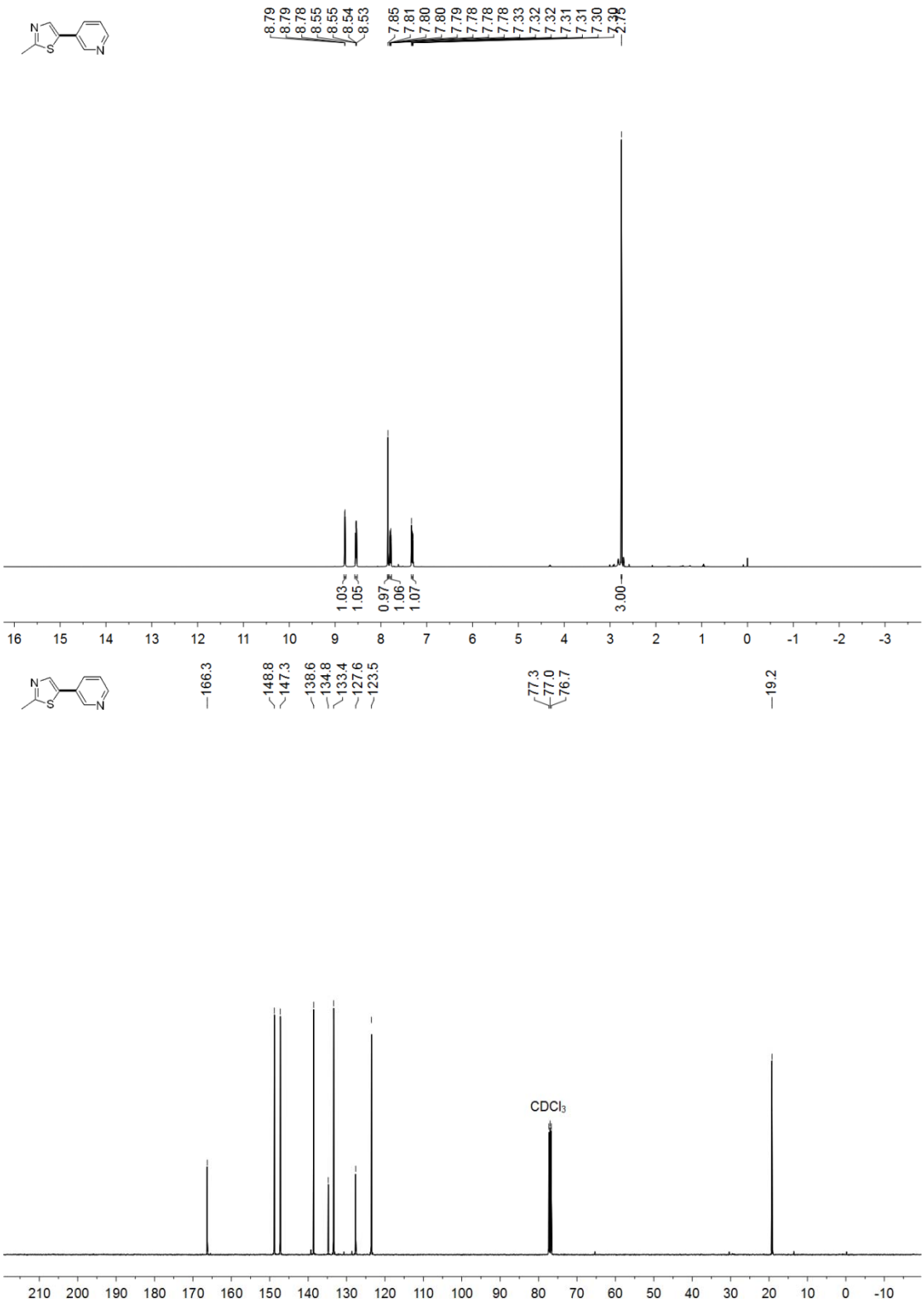


Figure **S21**.The NMR spectrums of **4e**

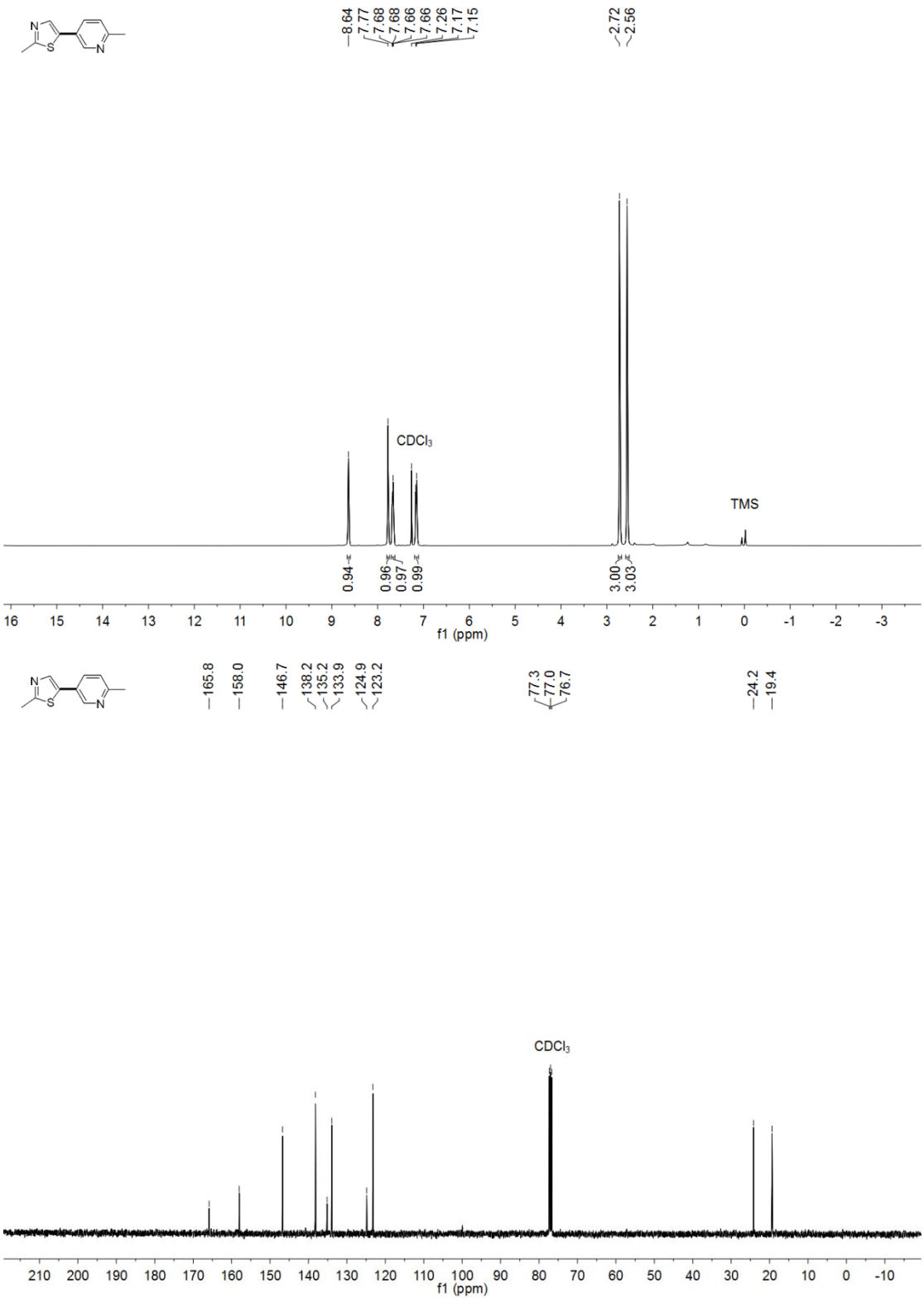


Figure **S22**.The NMR spectrums of **4f**

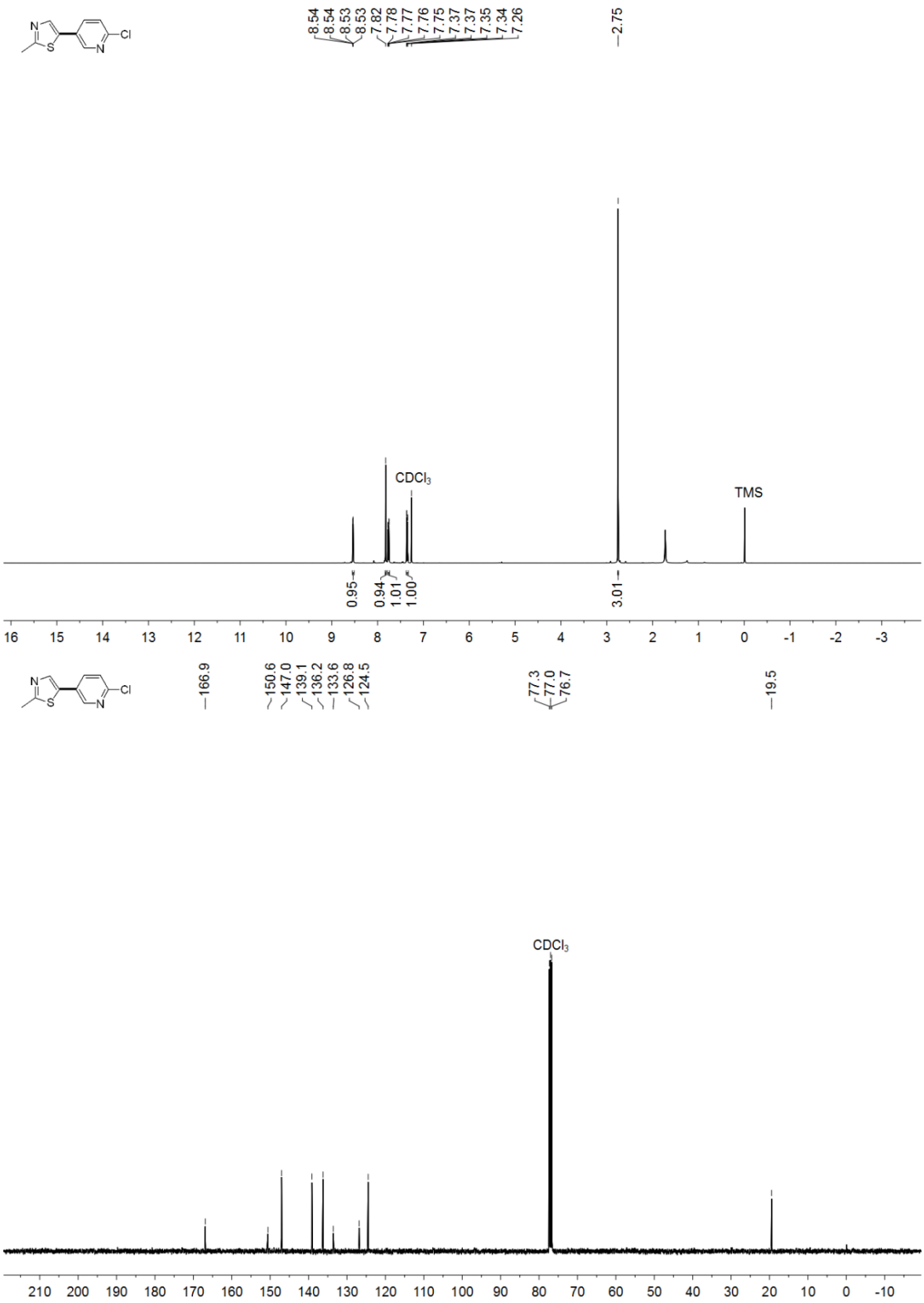


Figure **S23**.The NMR spectrums of **4i**

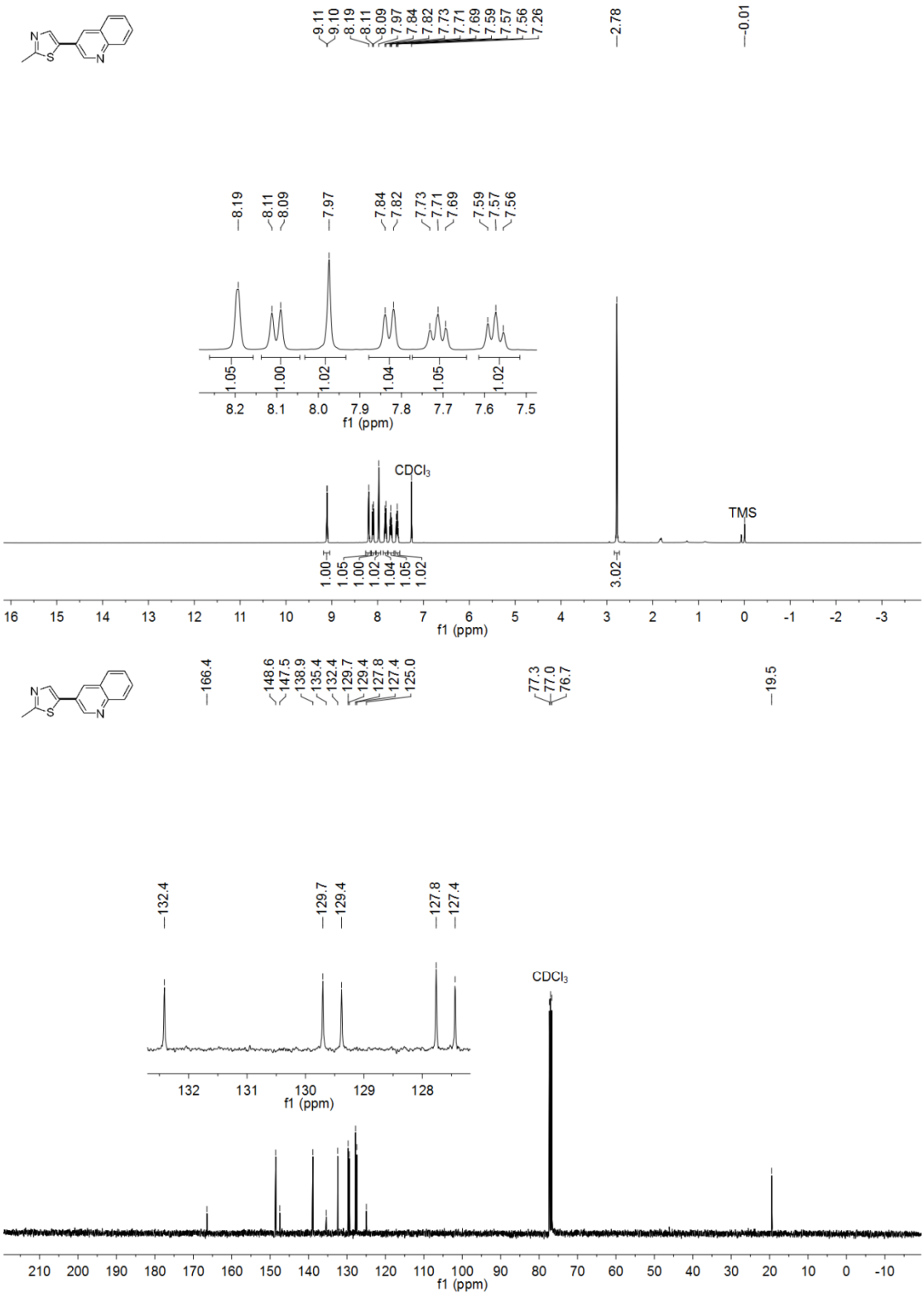


Figure **S24**.The NMR spectrums of **4k**

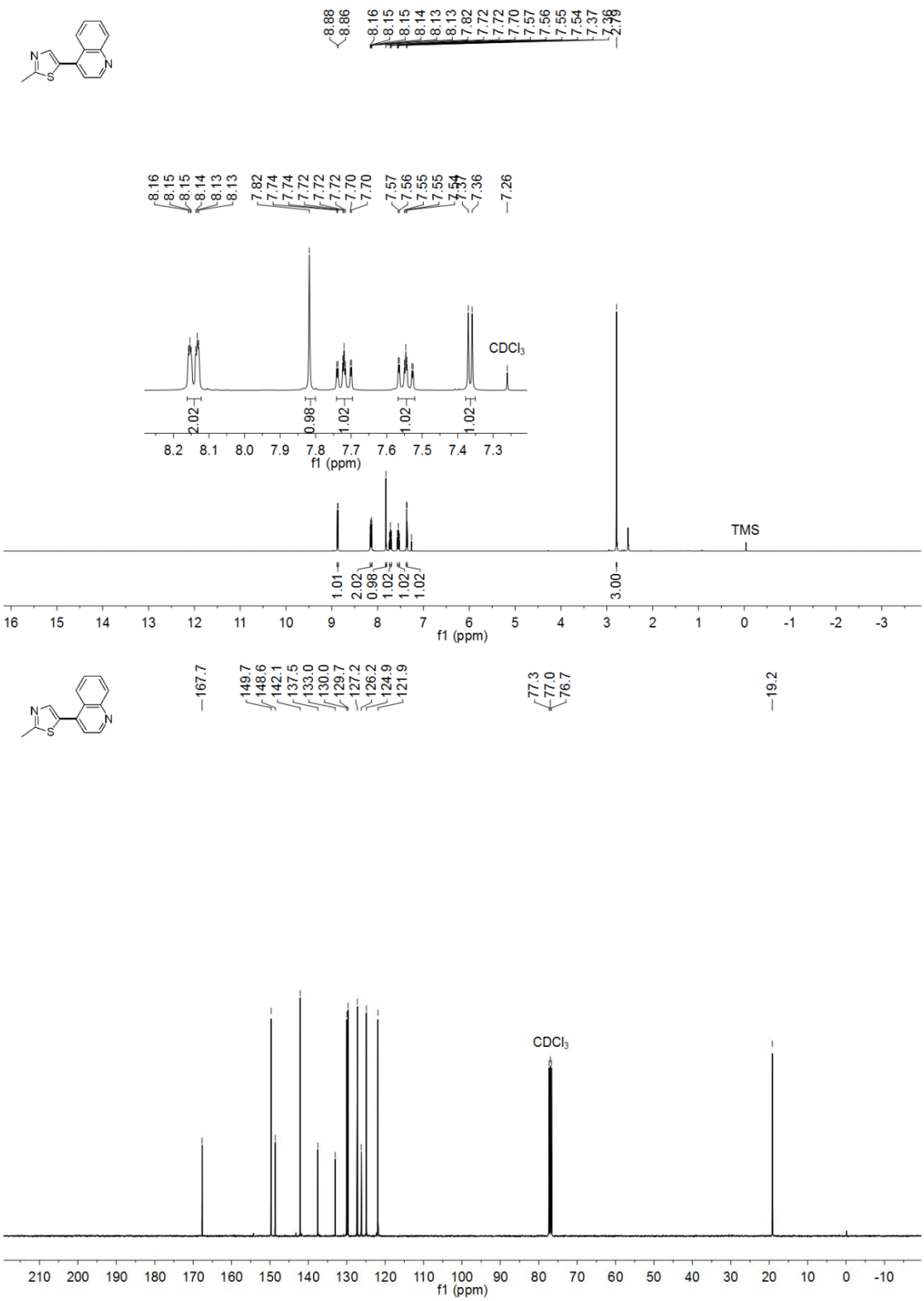


Figure **S25**.The NMR spectrums of **4l**

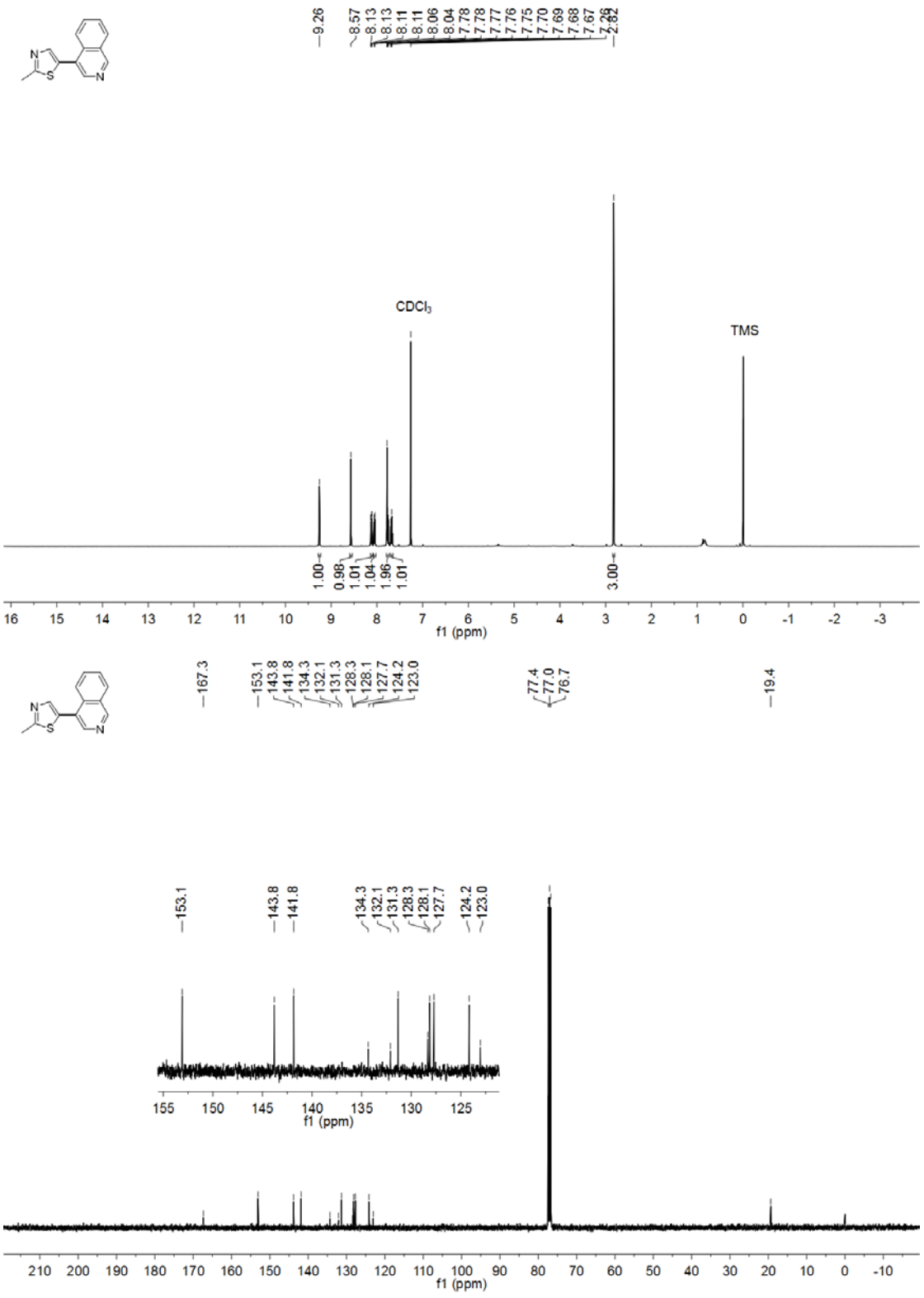


Figure **S26**.The NMR spectrums of **4m**

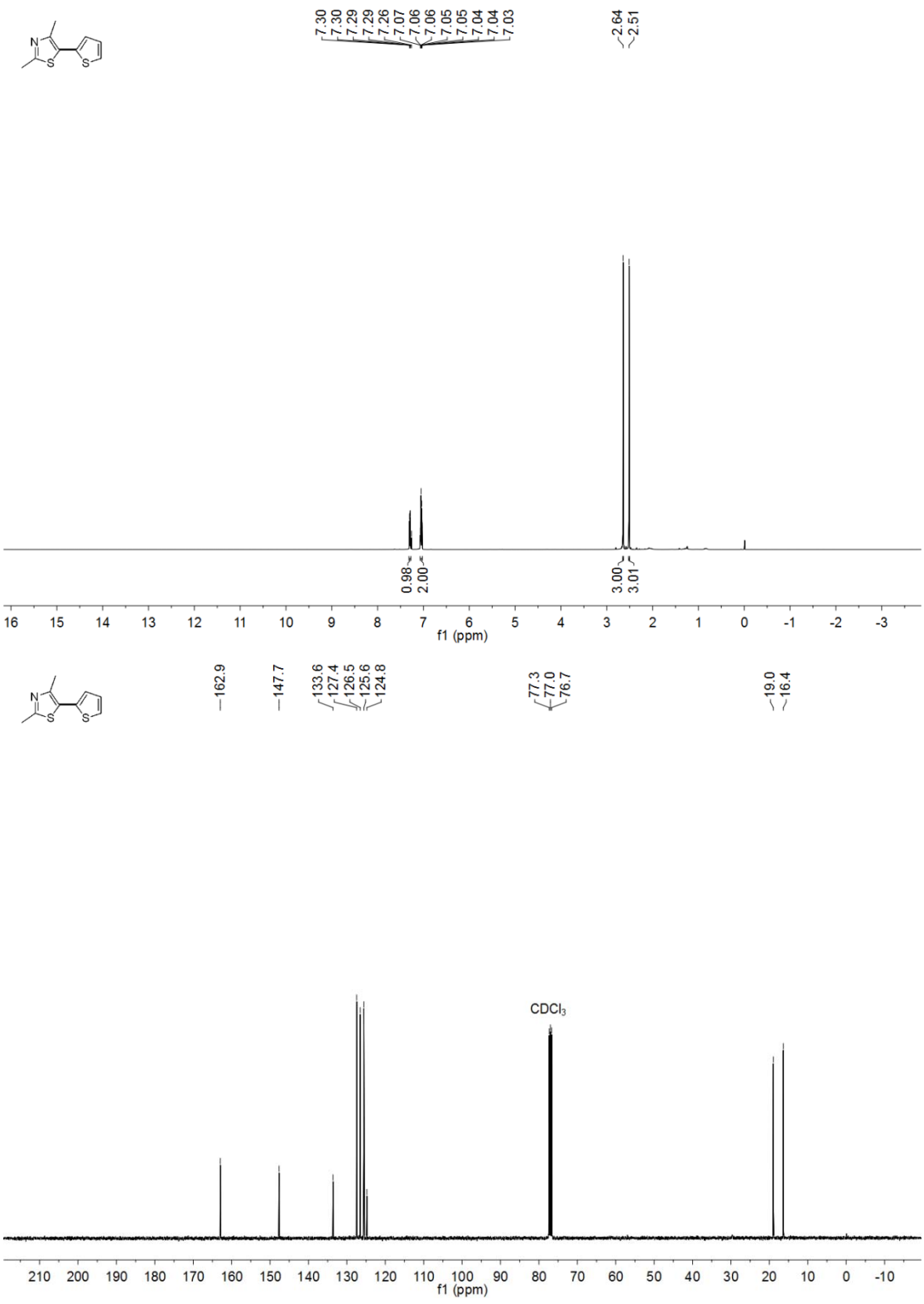


Figure **S27**.The NMR spectrums of **5b**

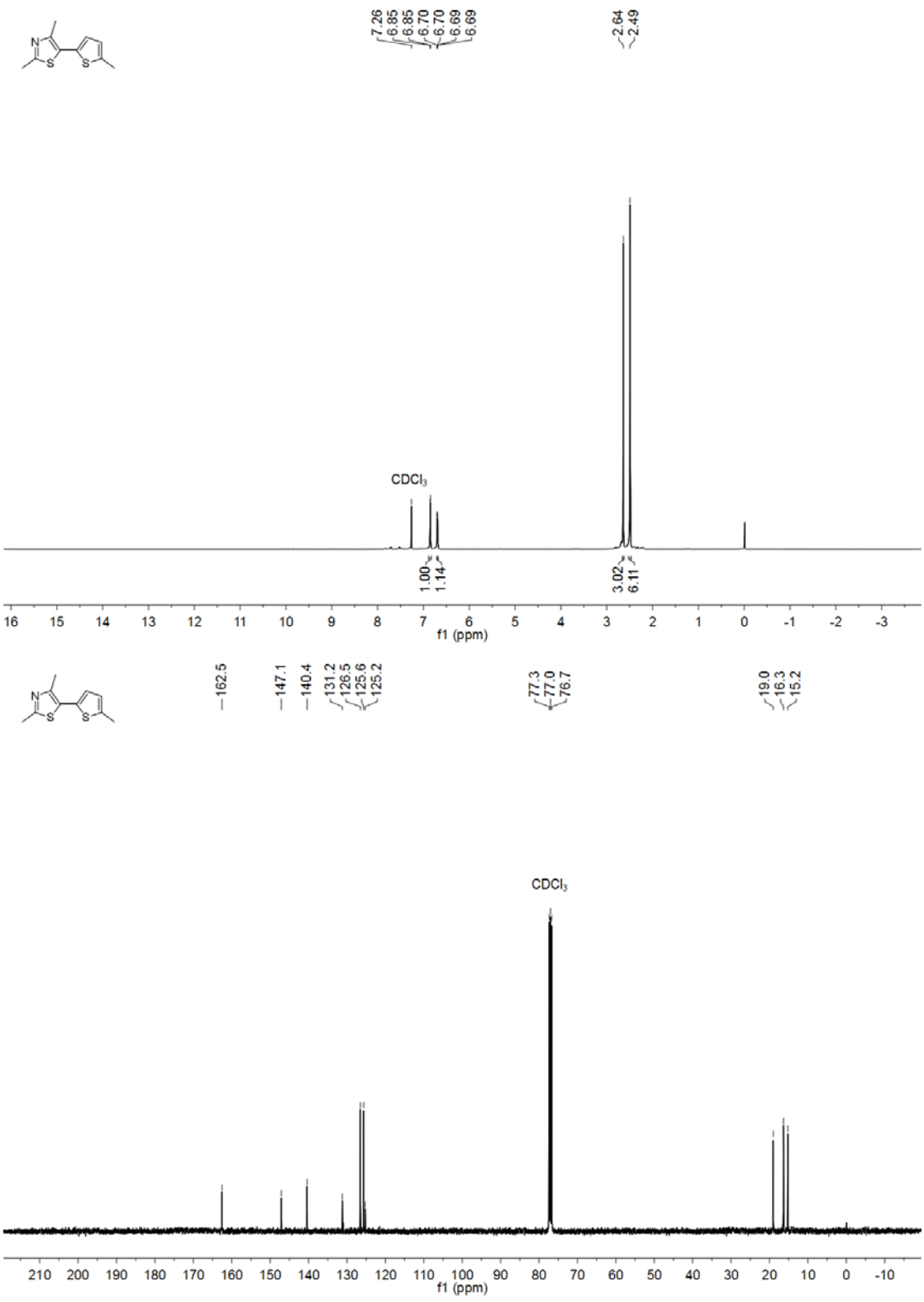


Figure **S28**.The NMR spectrums of **5c**

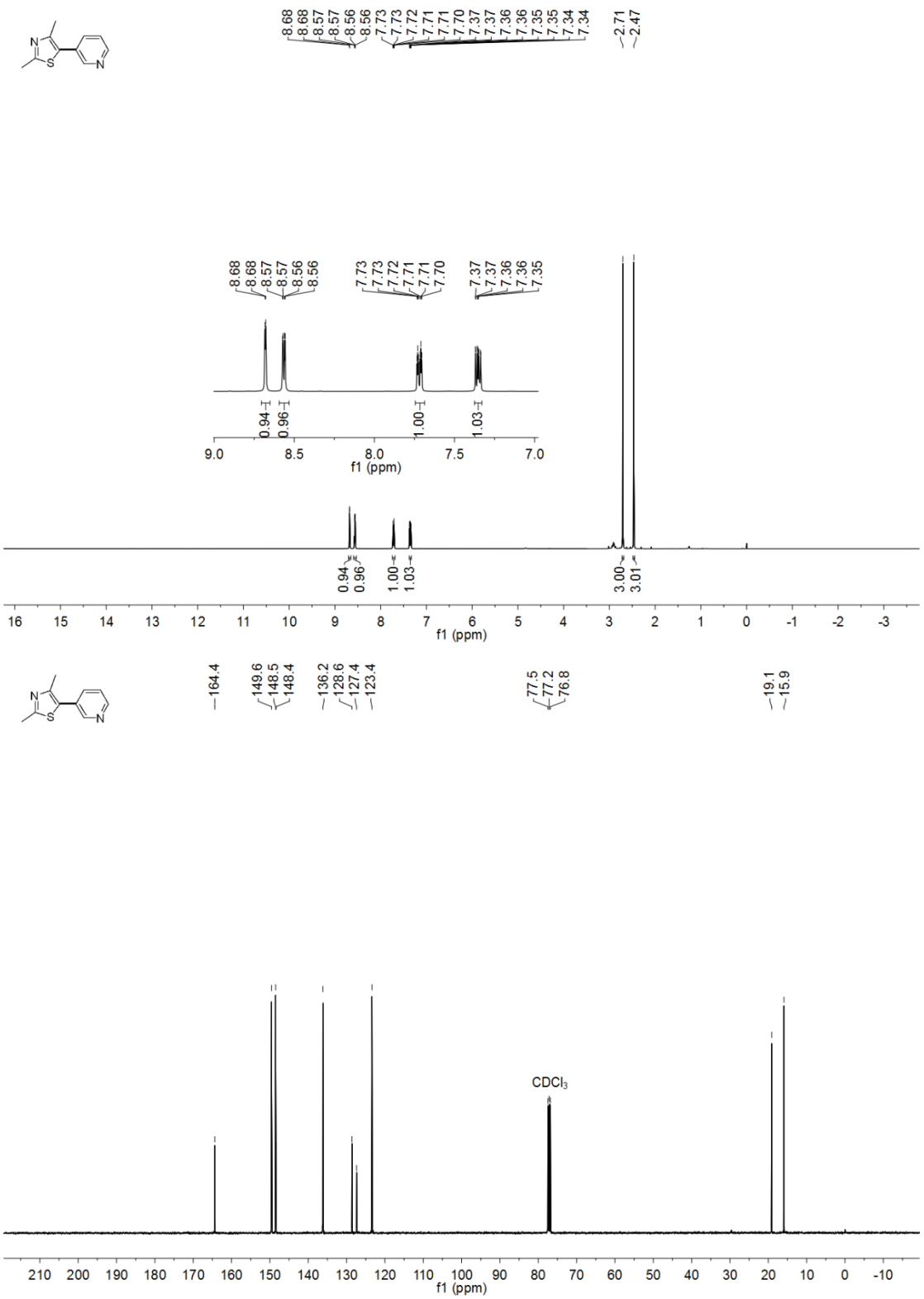


Figure **S29**.The NMR spectrums of **5e**

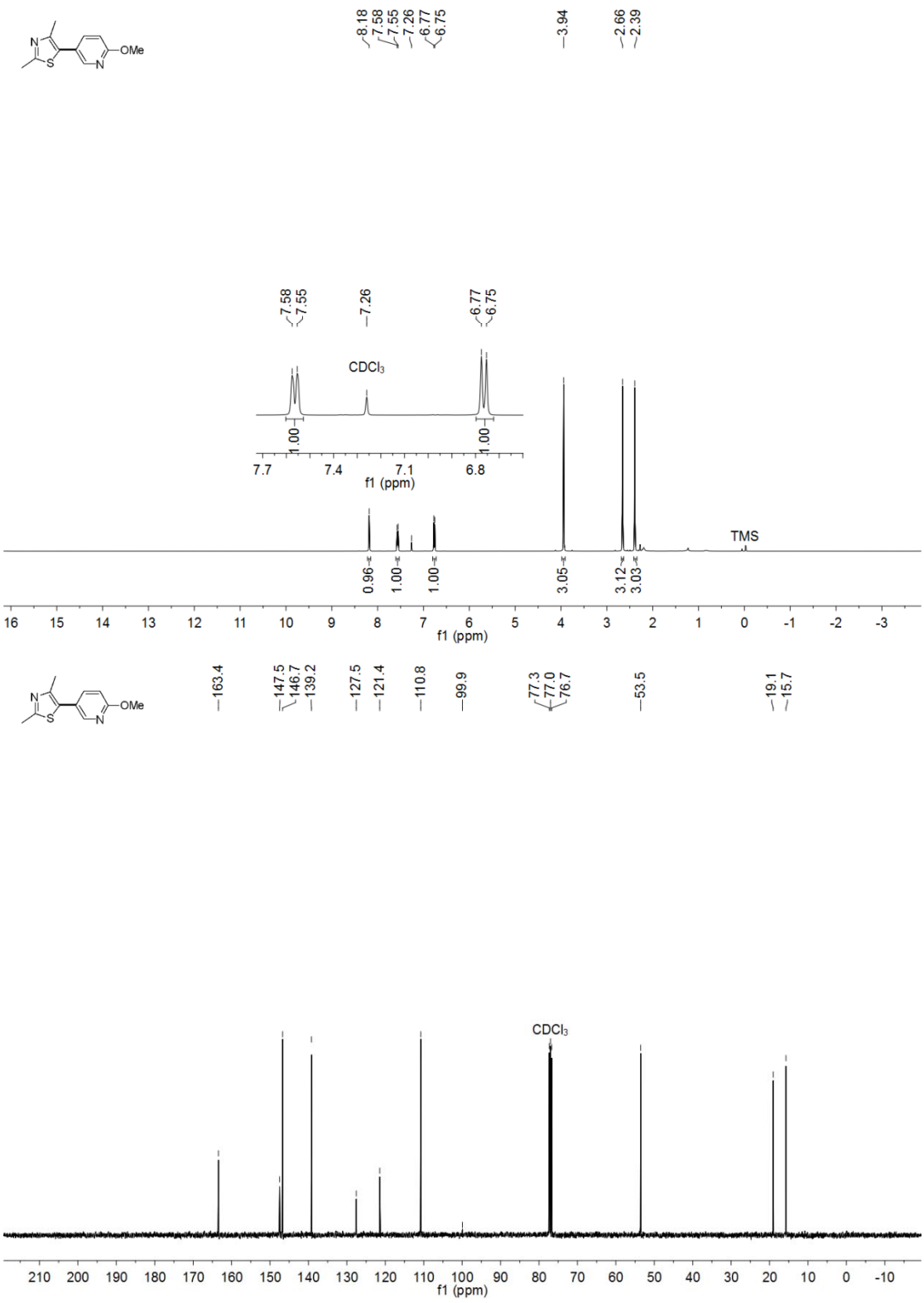


Figure **S30**.The NMR spectrums of **5g**

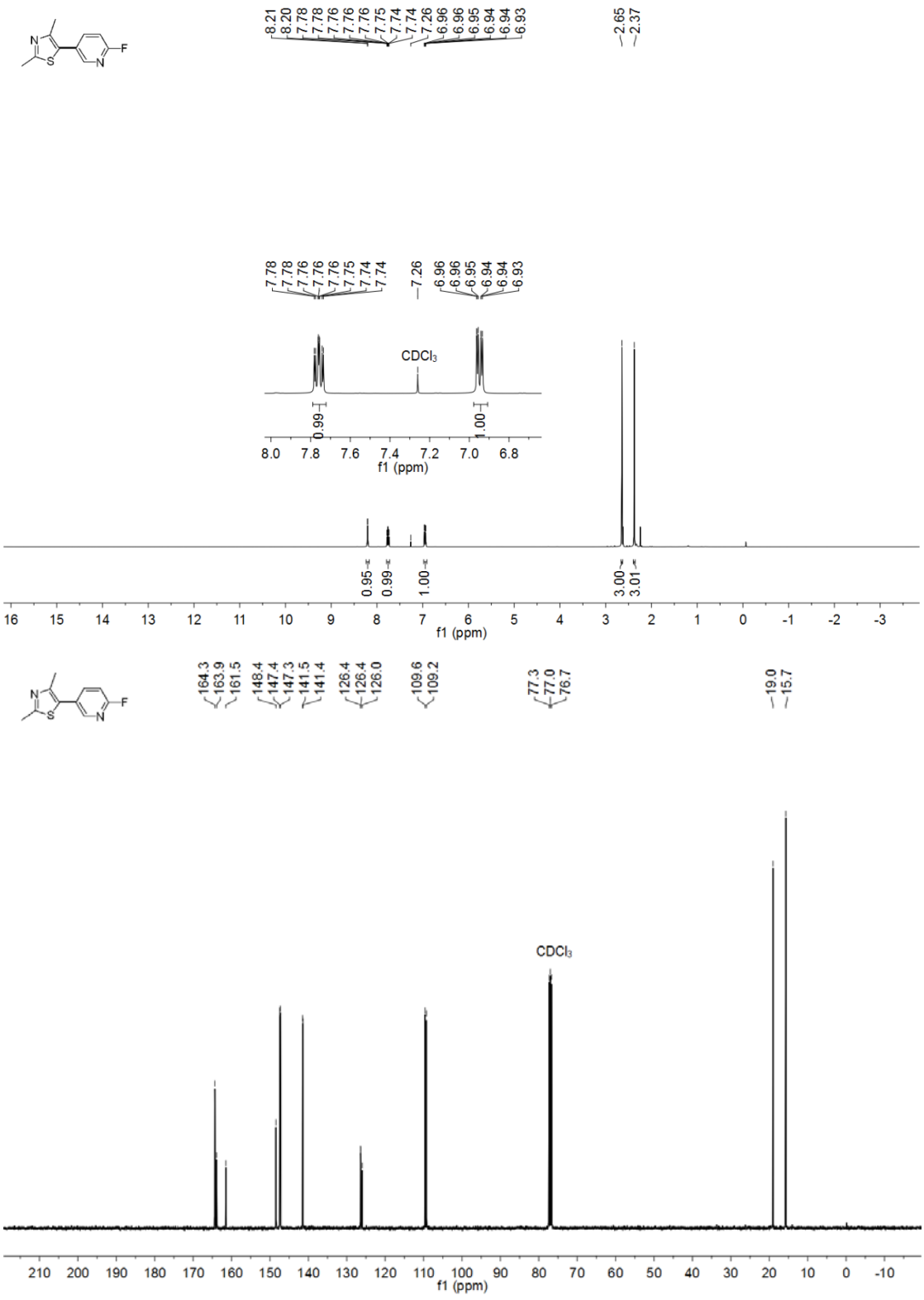


Figure **S31**.The NMR spectrums of **5h**

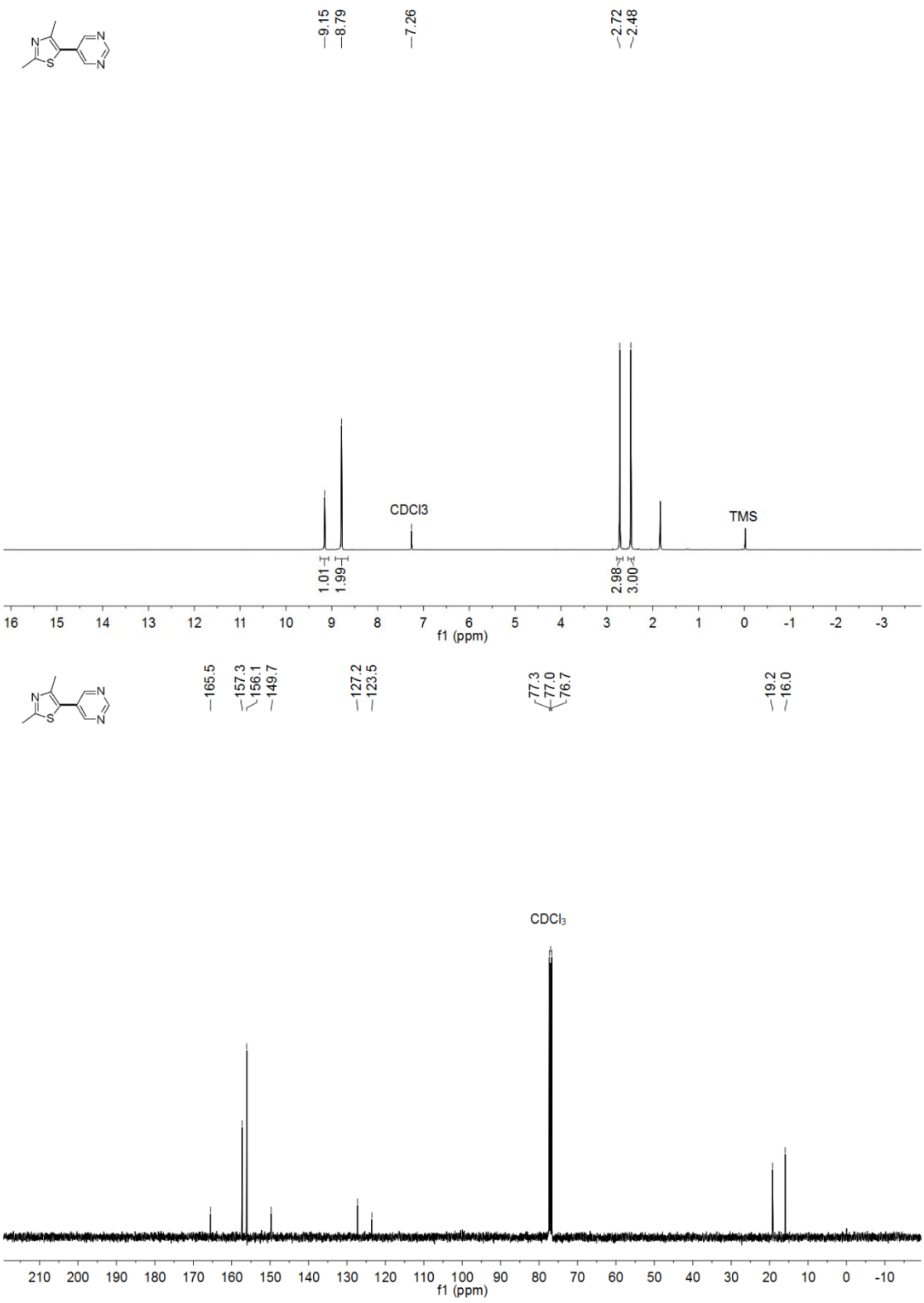


Figure **S32**.The NMR spectrums of **5j**

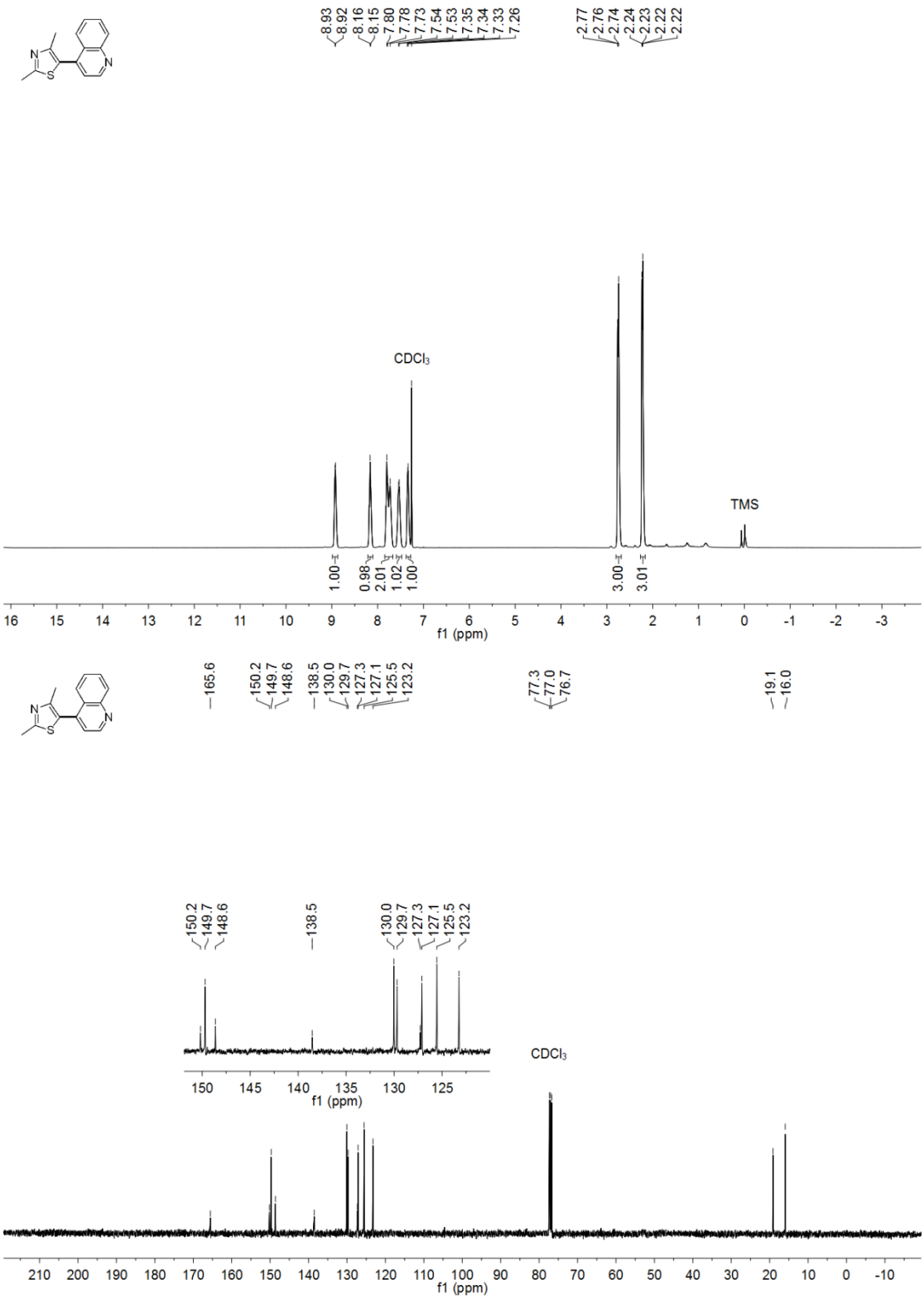


Figure **S33**.The NMR spectrums of **5l**

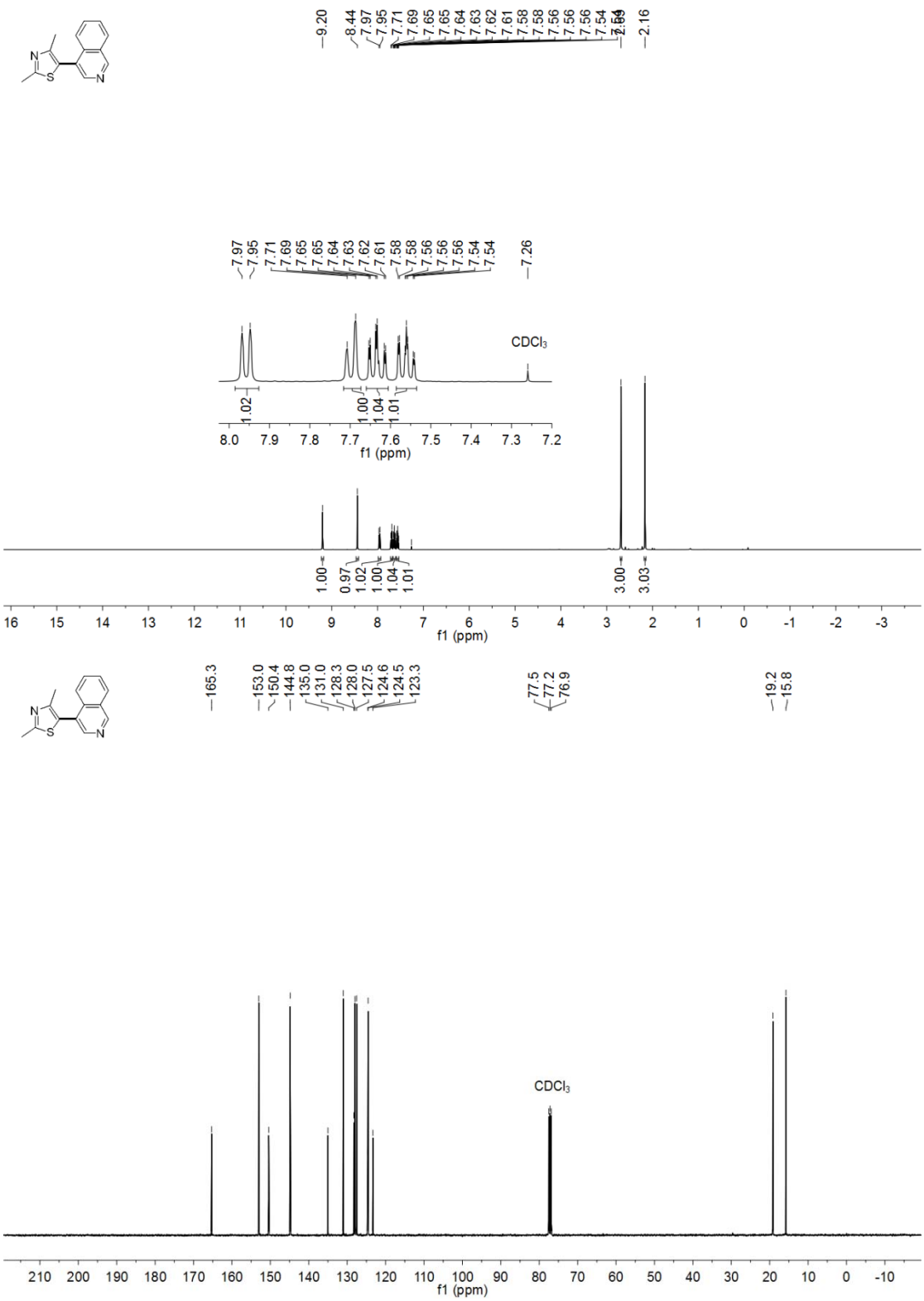


Figure **S34**.The NMR spectrums of **5m**

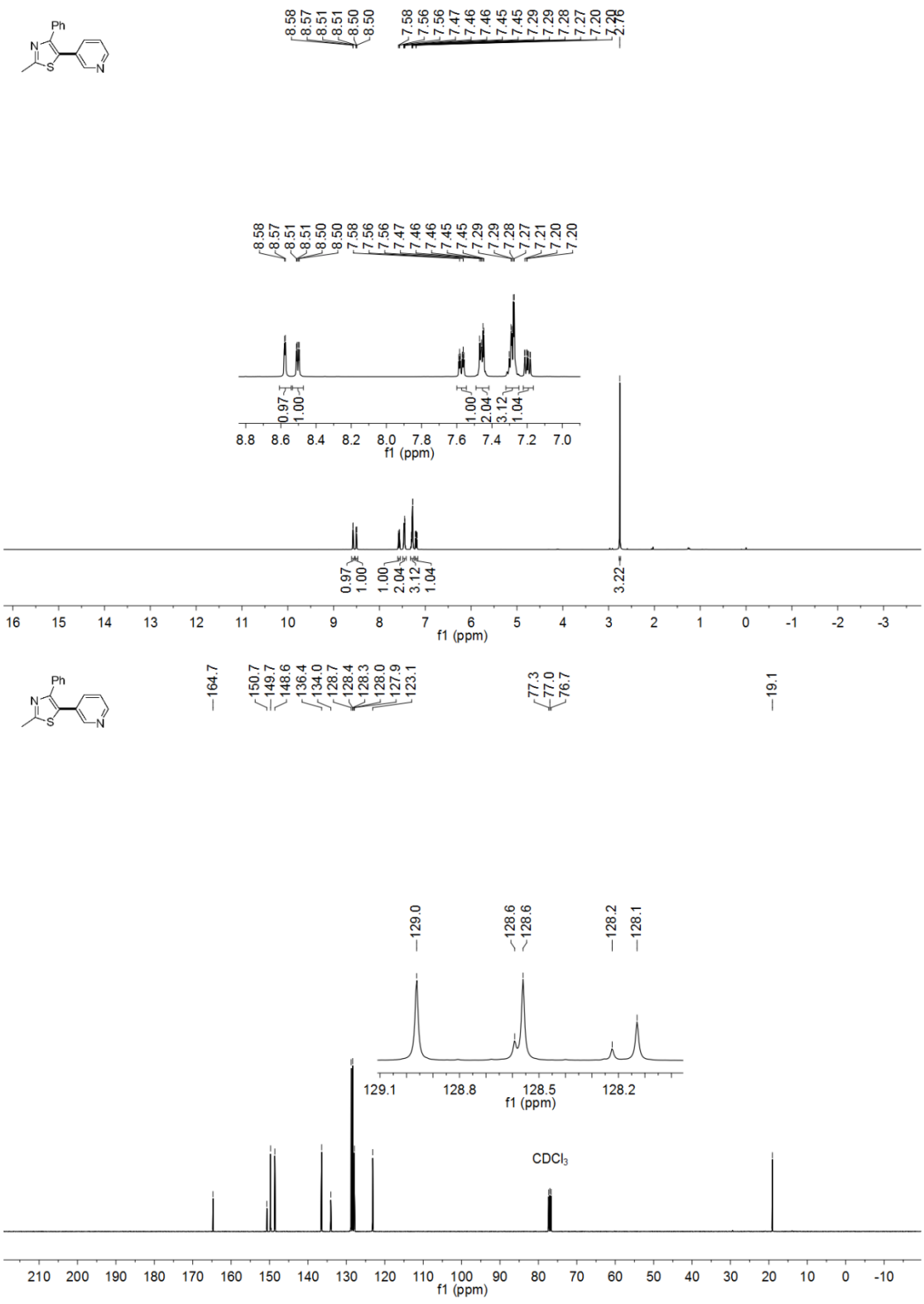


Figure **S35**. The NMR spectrums of **6e**

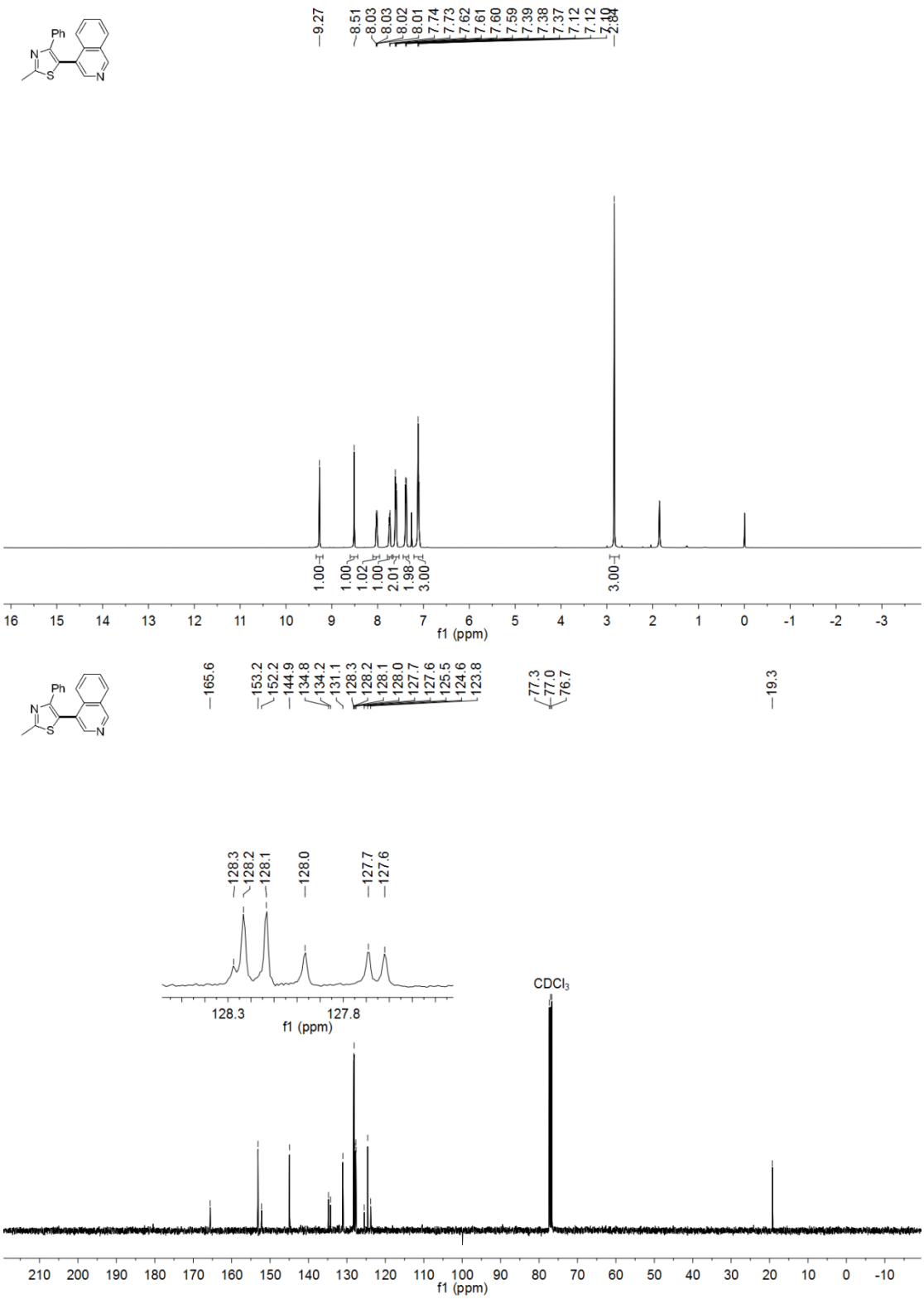


Figure **S36**.The NMR spectrums of **6m**

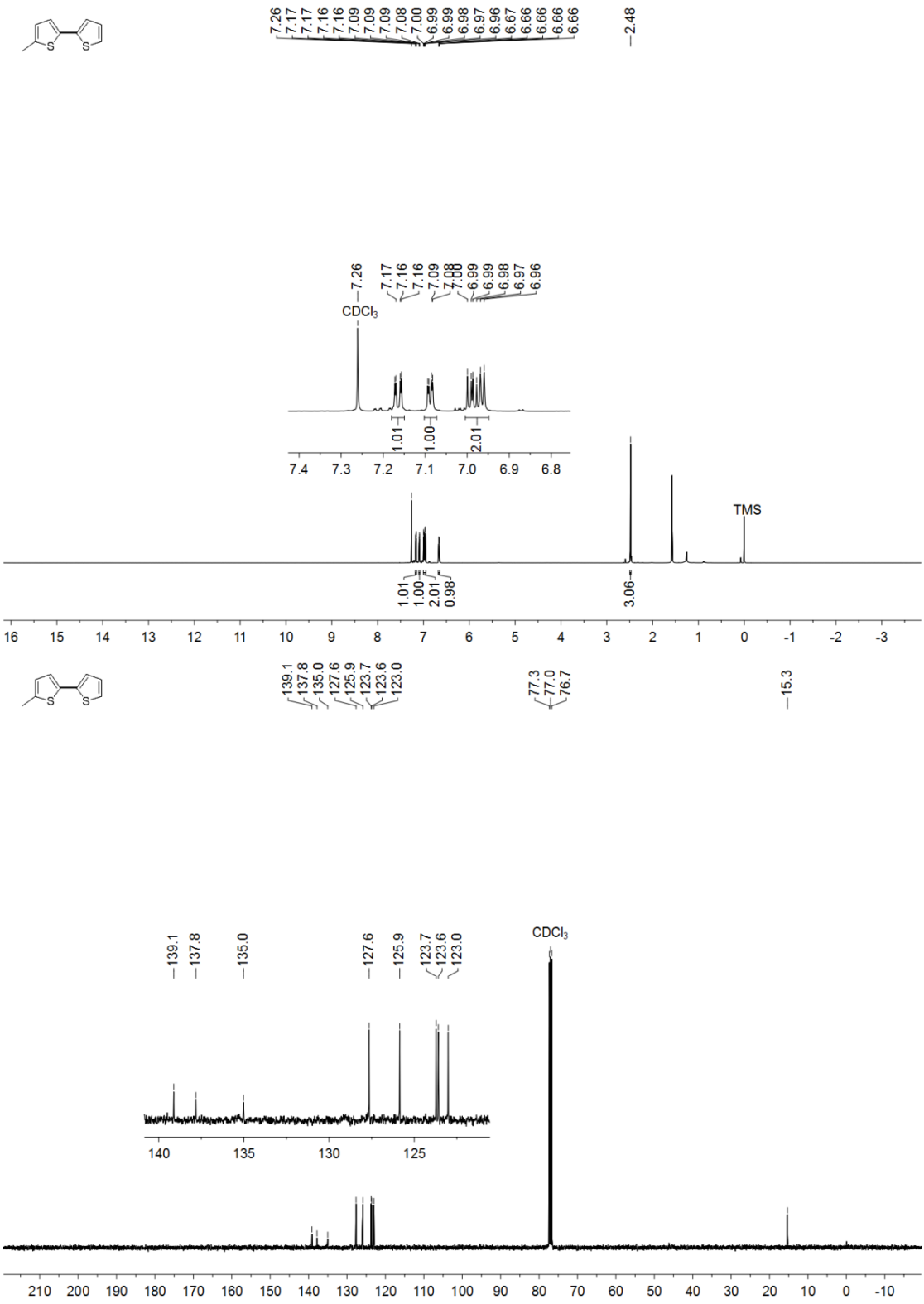


Figure S**37**.The NMR spectrums of 7**b**

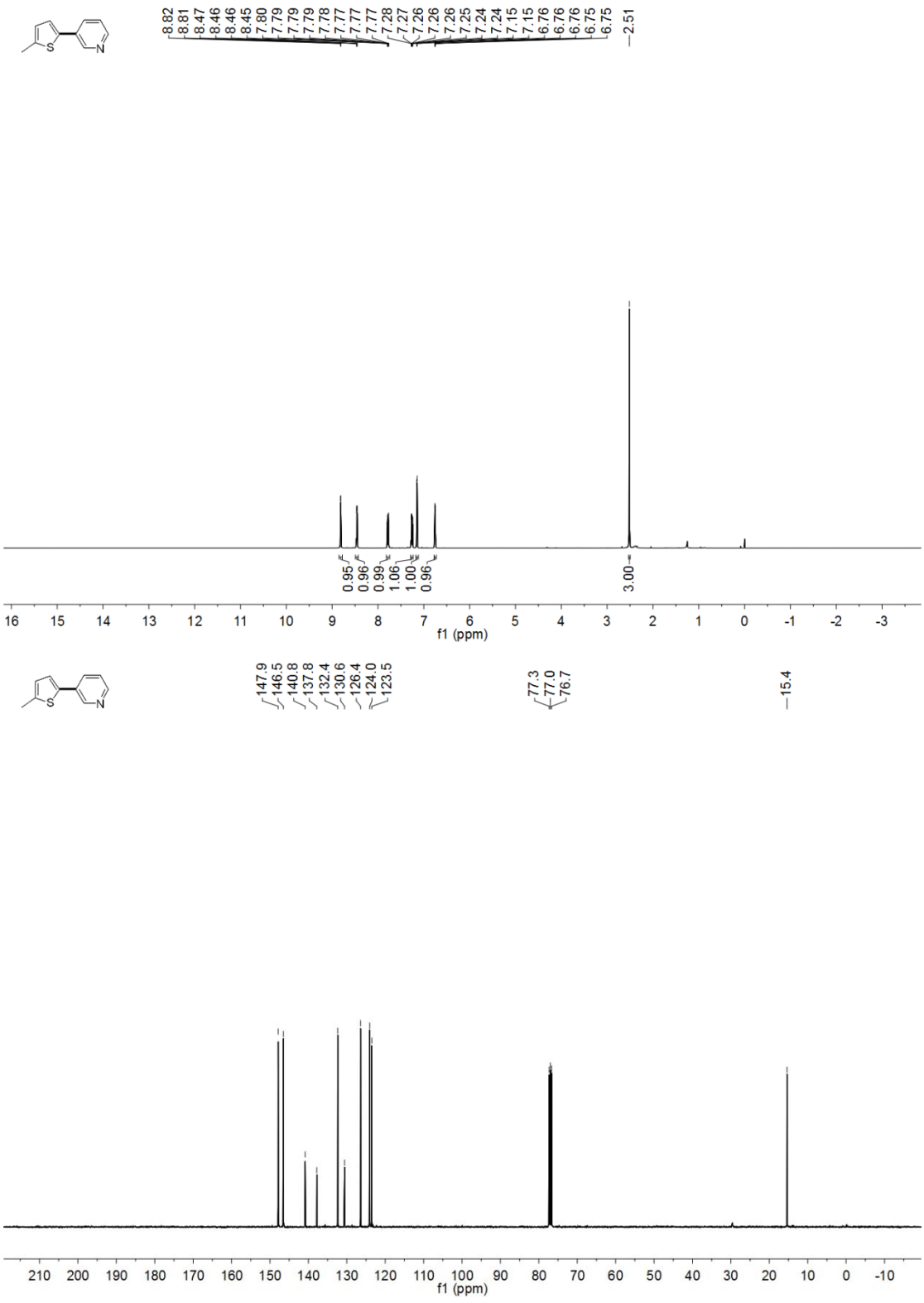


Figure **S38**.The NMR spectrums of **7e**

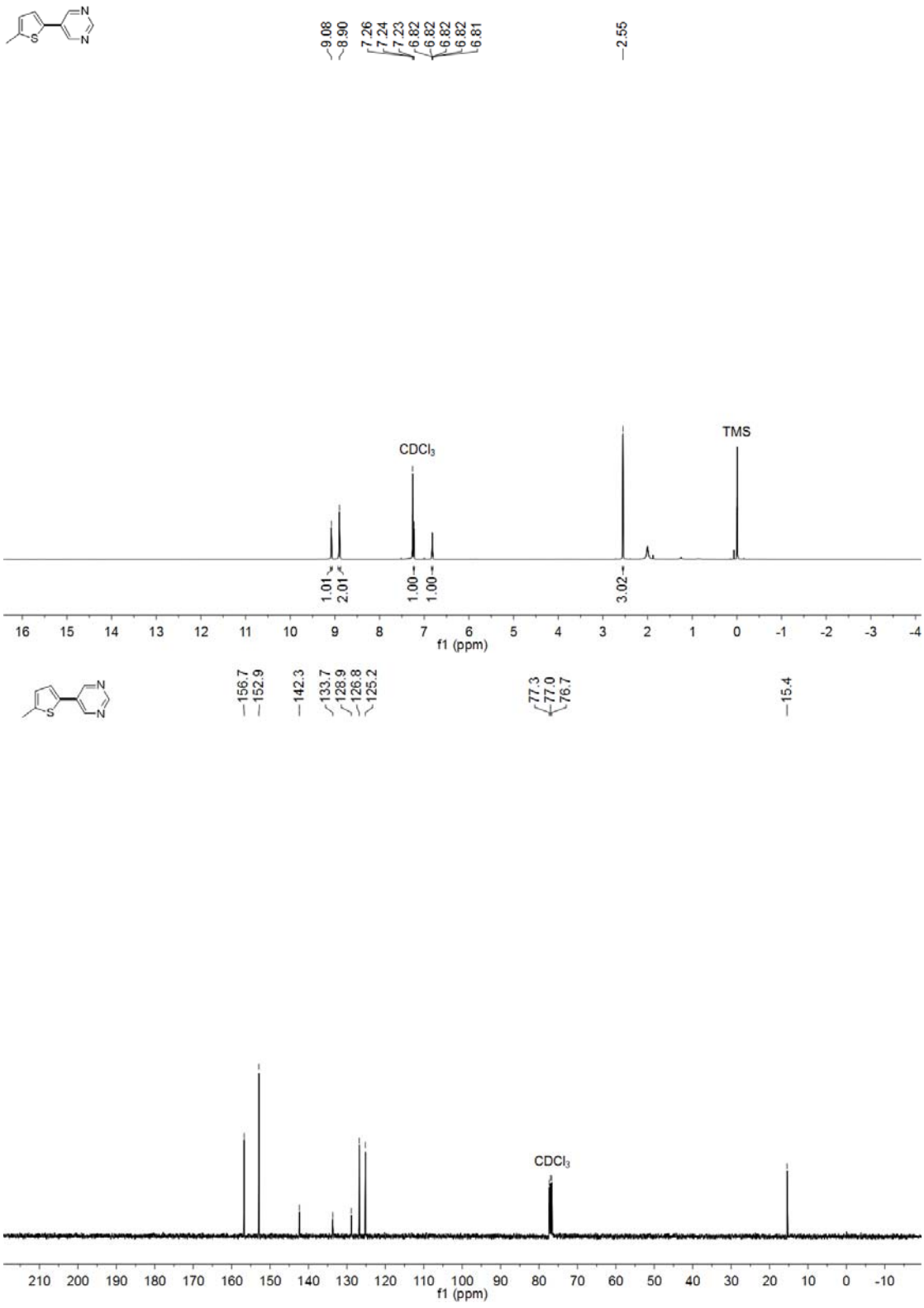


Figure **S39**.The NMR spectrums of **7j**

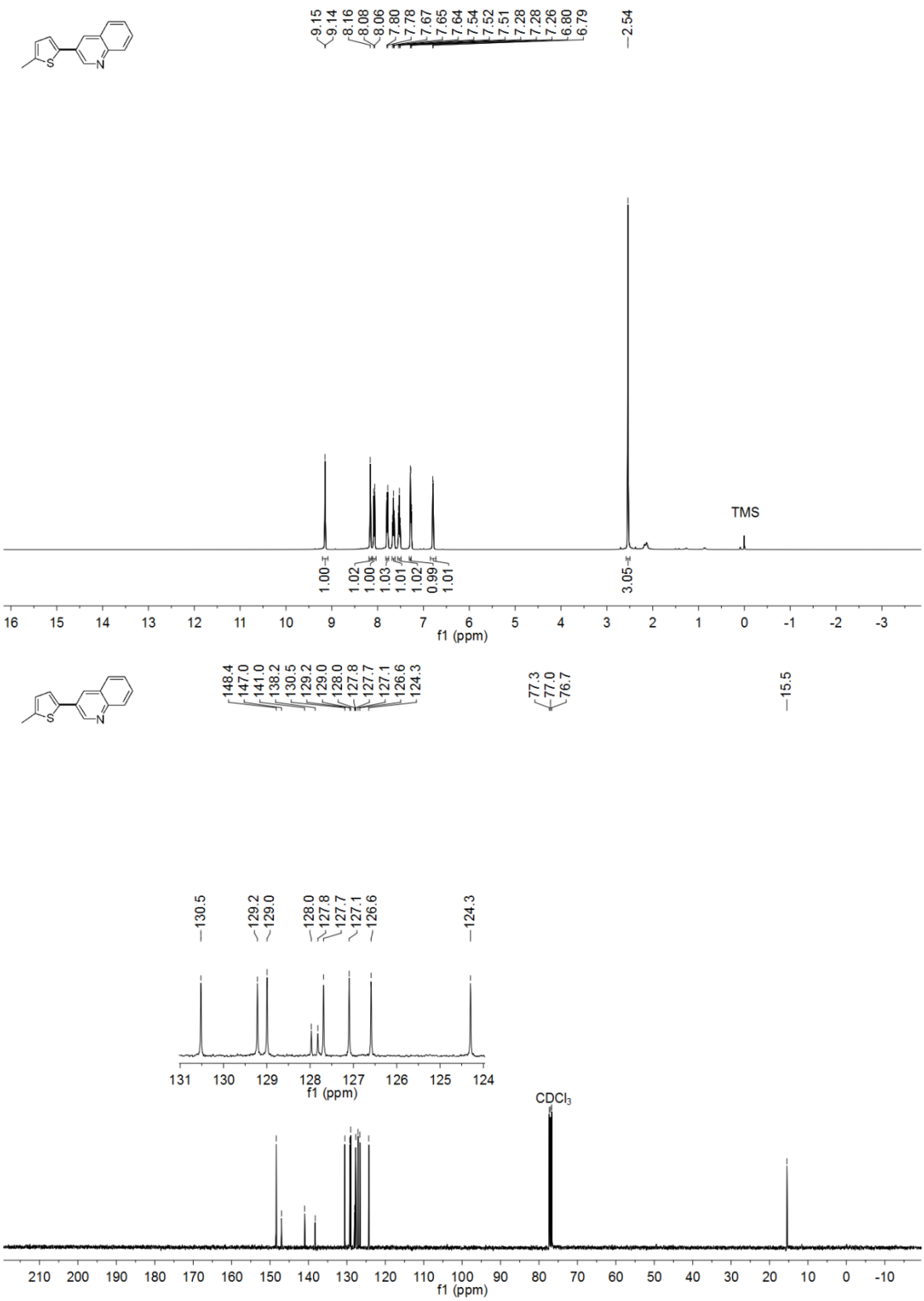


Figure **S40**.The NMR spectrums of **7k**

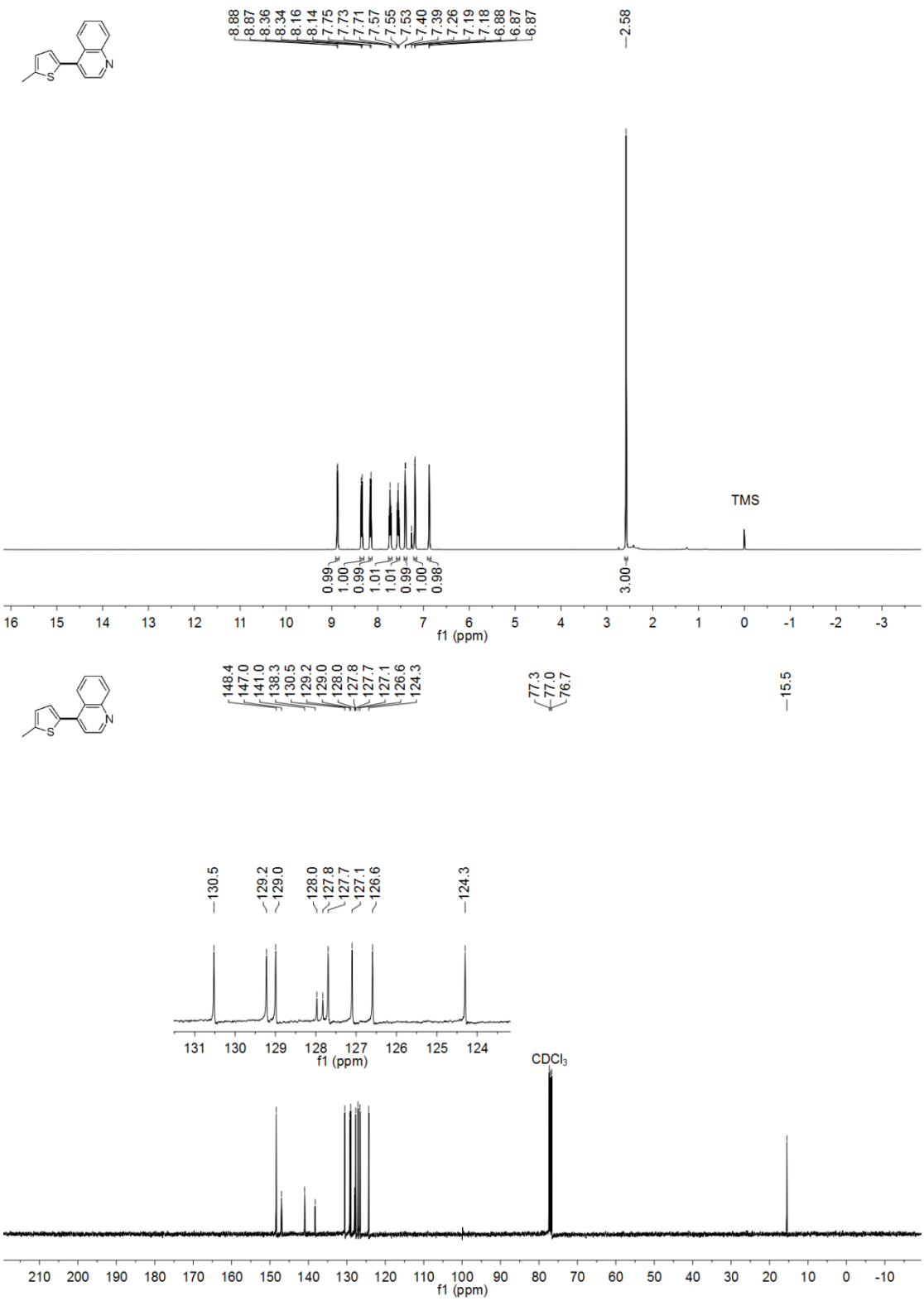


Figure **S41**.The NMR spectrums of **7l**

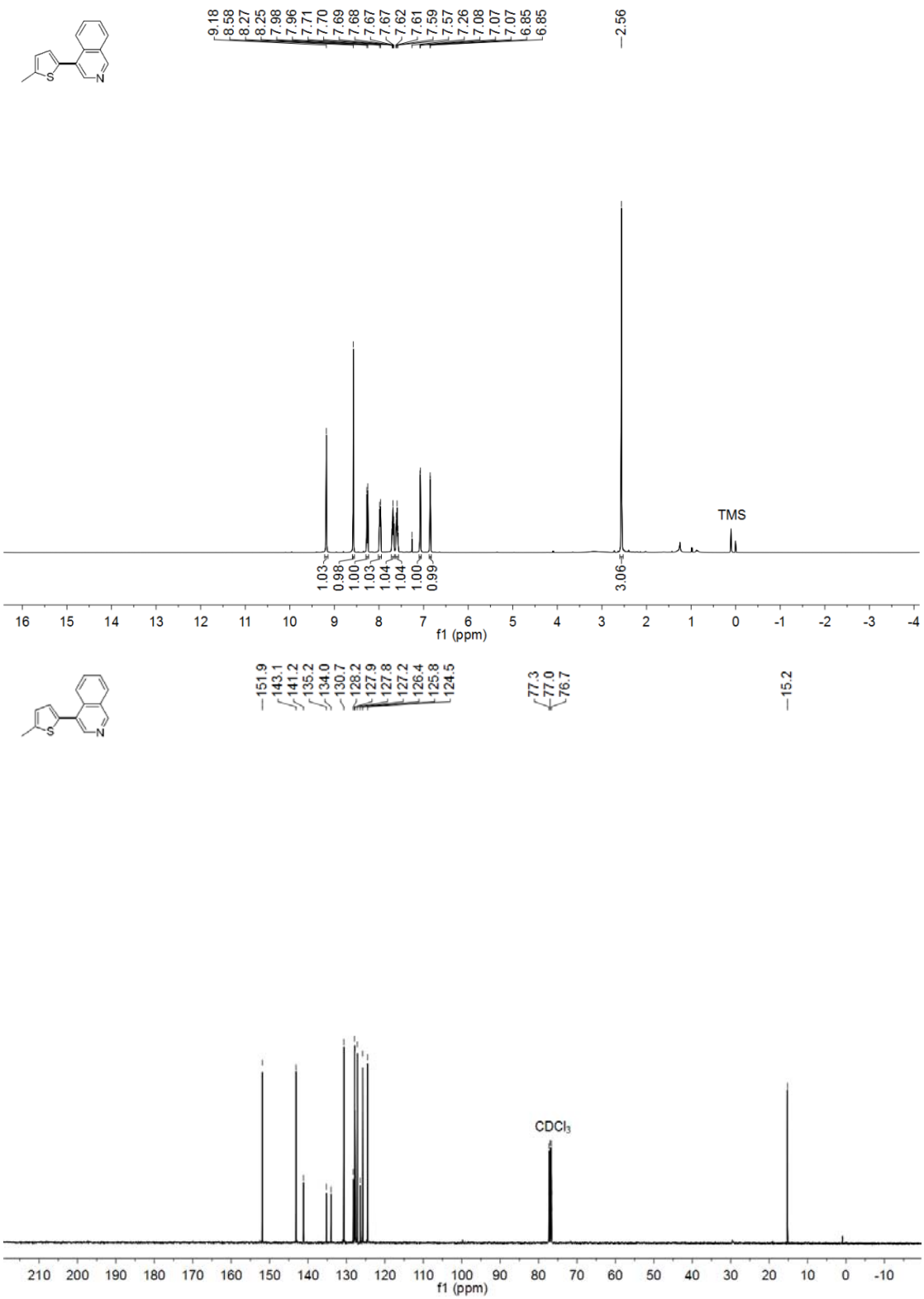


Figure **S42**.The NMR spectrums of **7m**

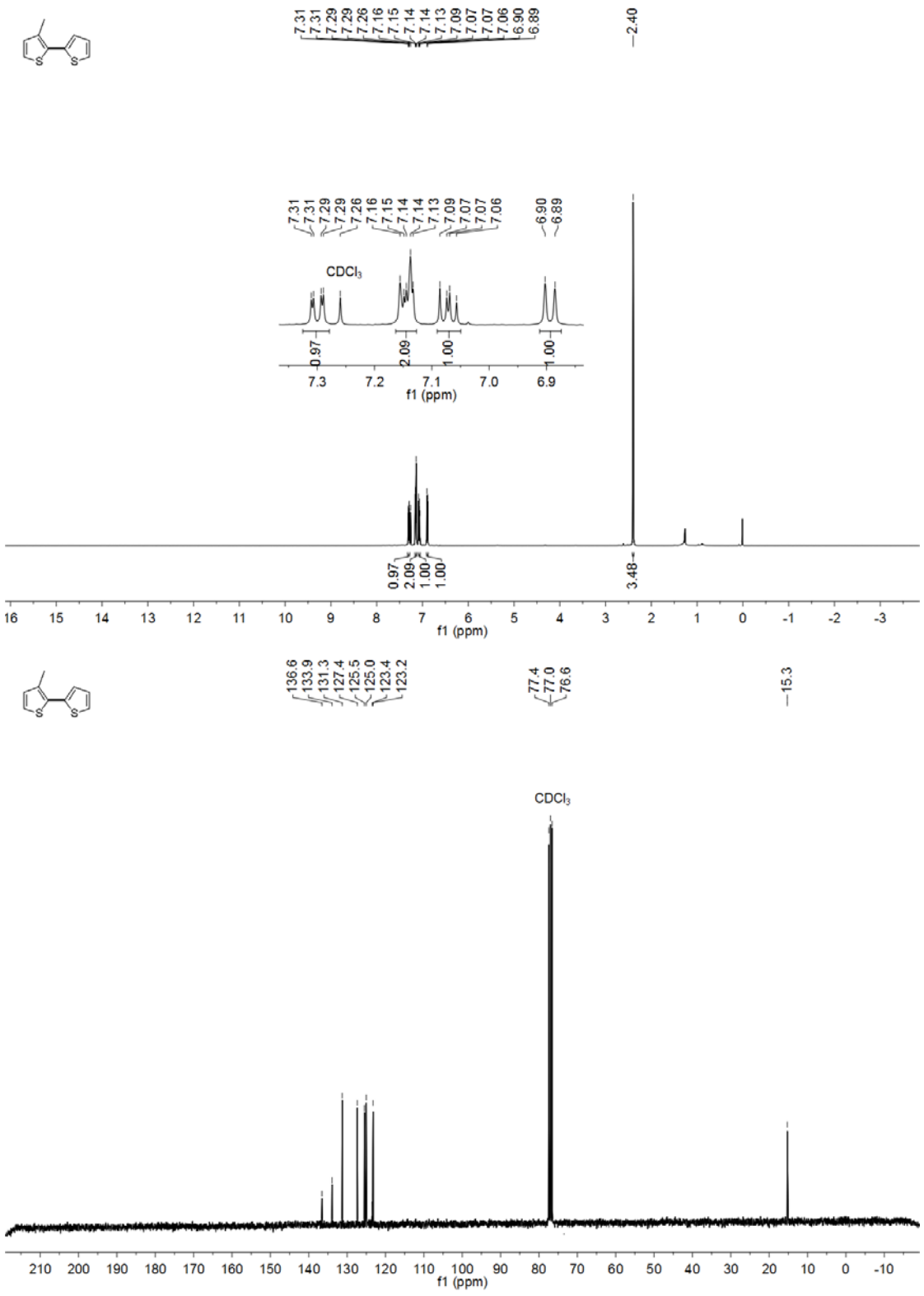


Figure **S43**.The NMR spectrums of **8b**

Figure **S44**.The NMR spectrums of **9b**

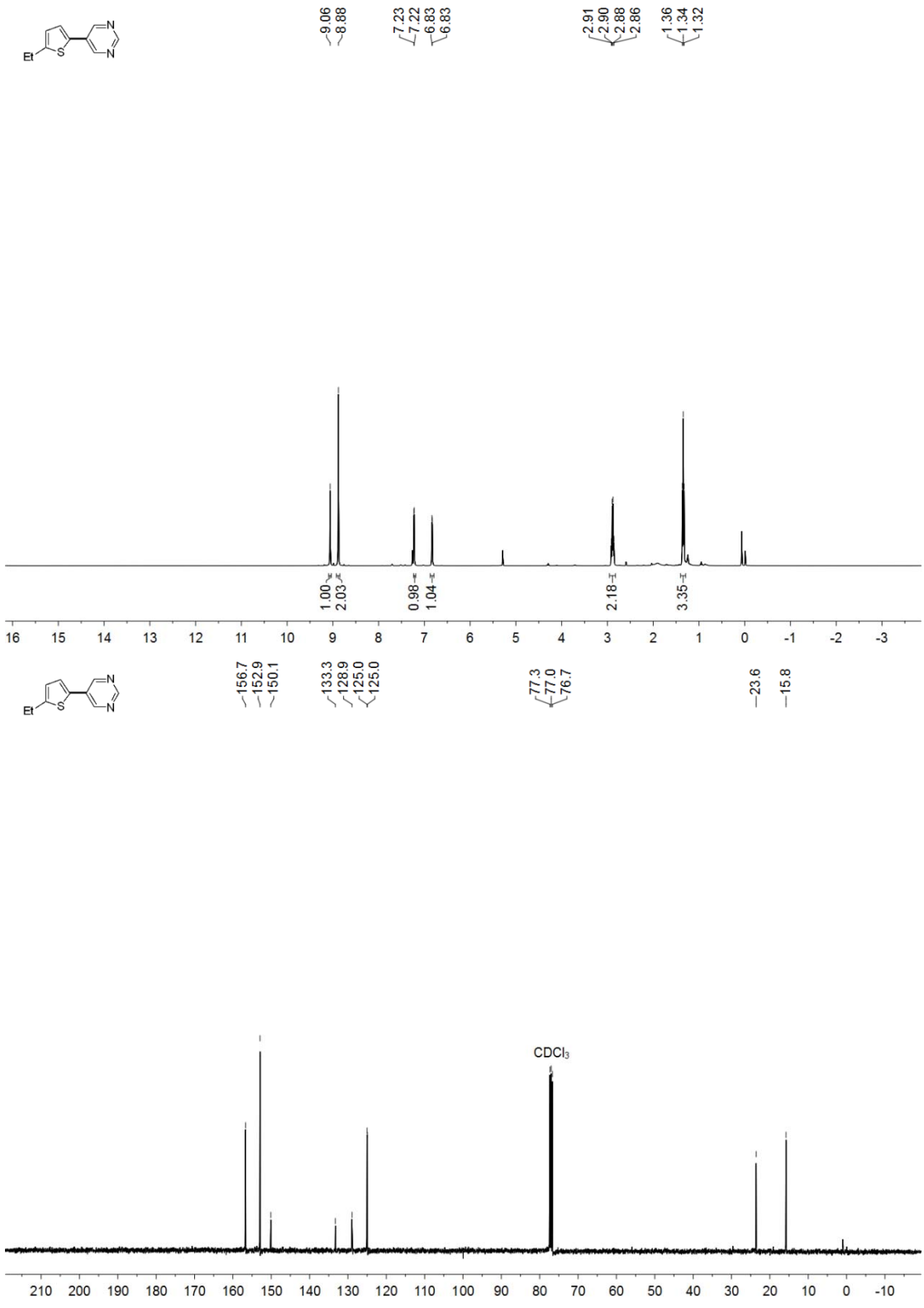


Figure **S45**.The NMR spectrums of **10j**

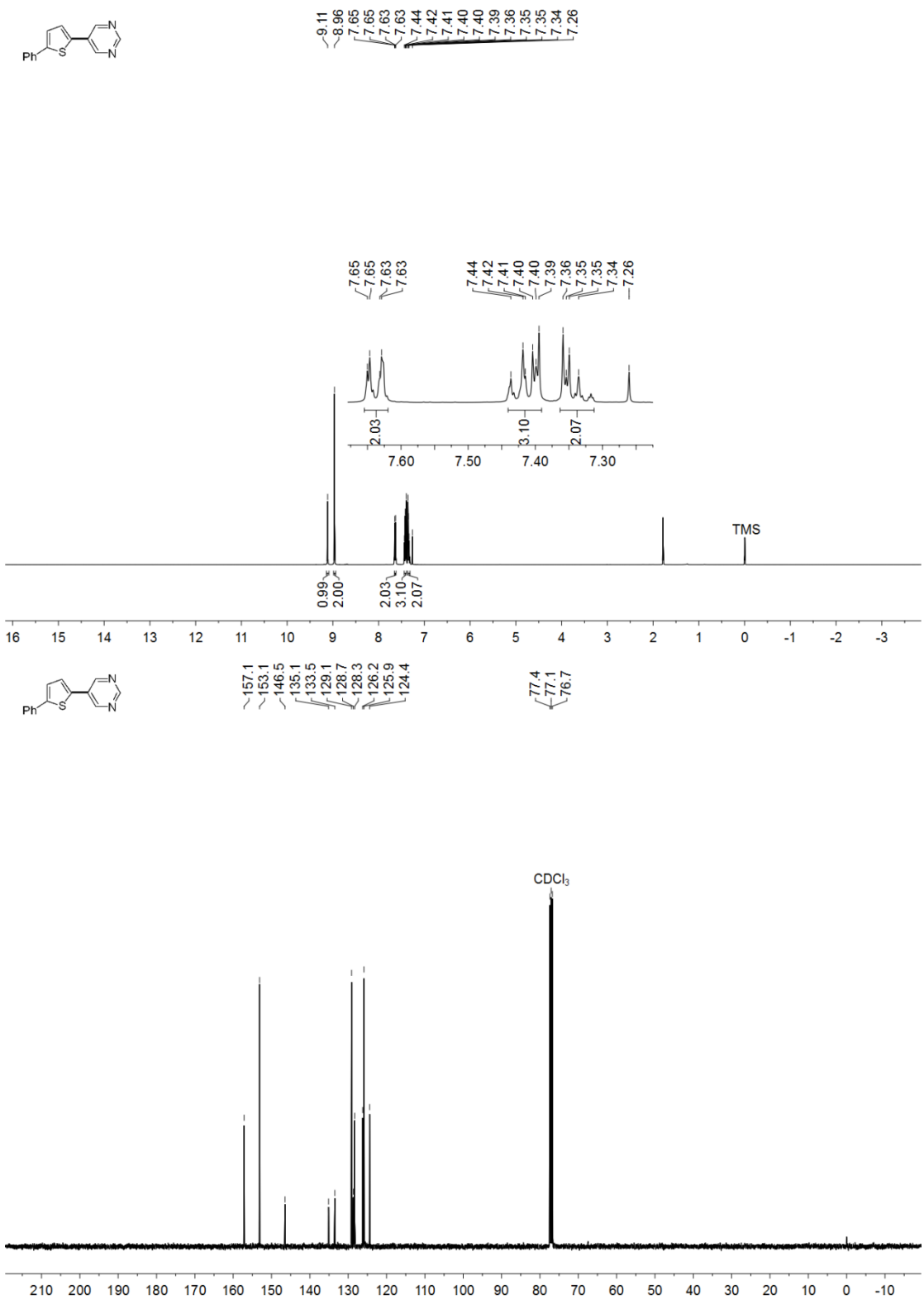


Figure **S46**. The NMR spectrums of **11j**

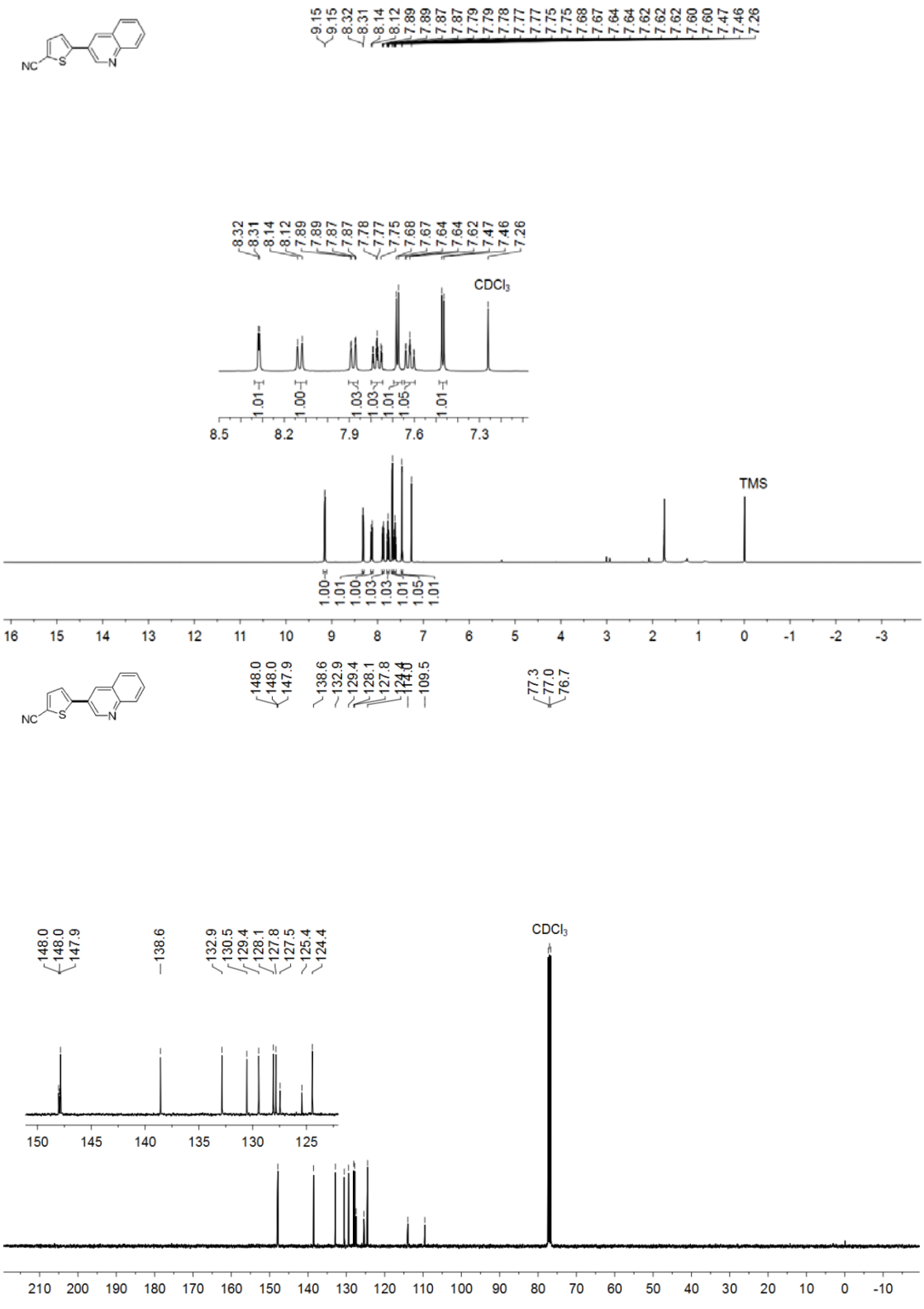


Figure **S47**.The NMR spectrums of **12k**

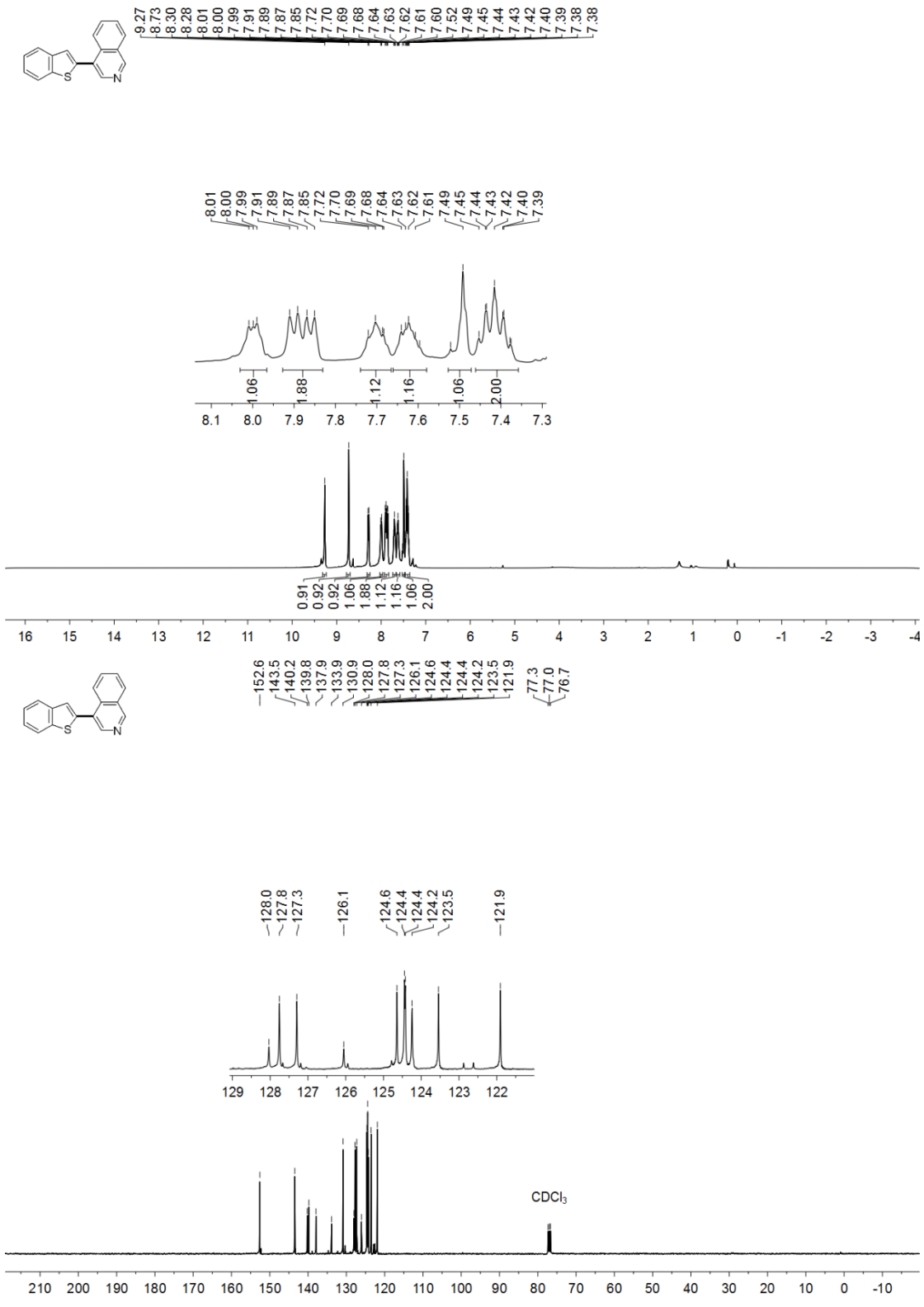


Figure **S48**. The NMR spectrums of **13m**

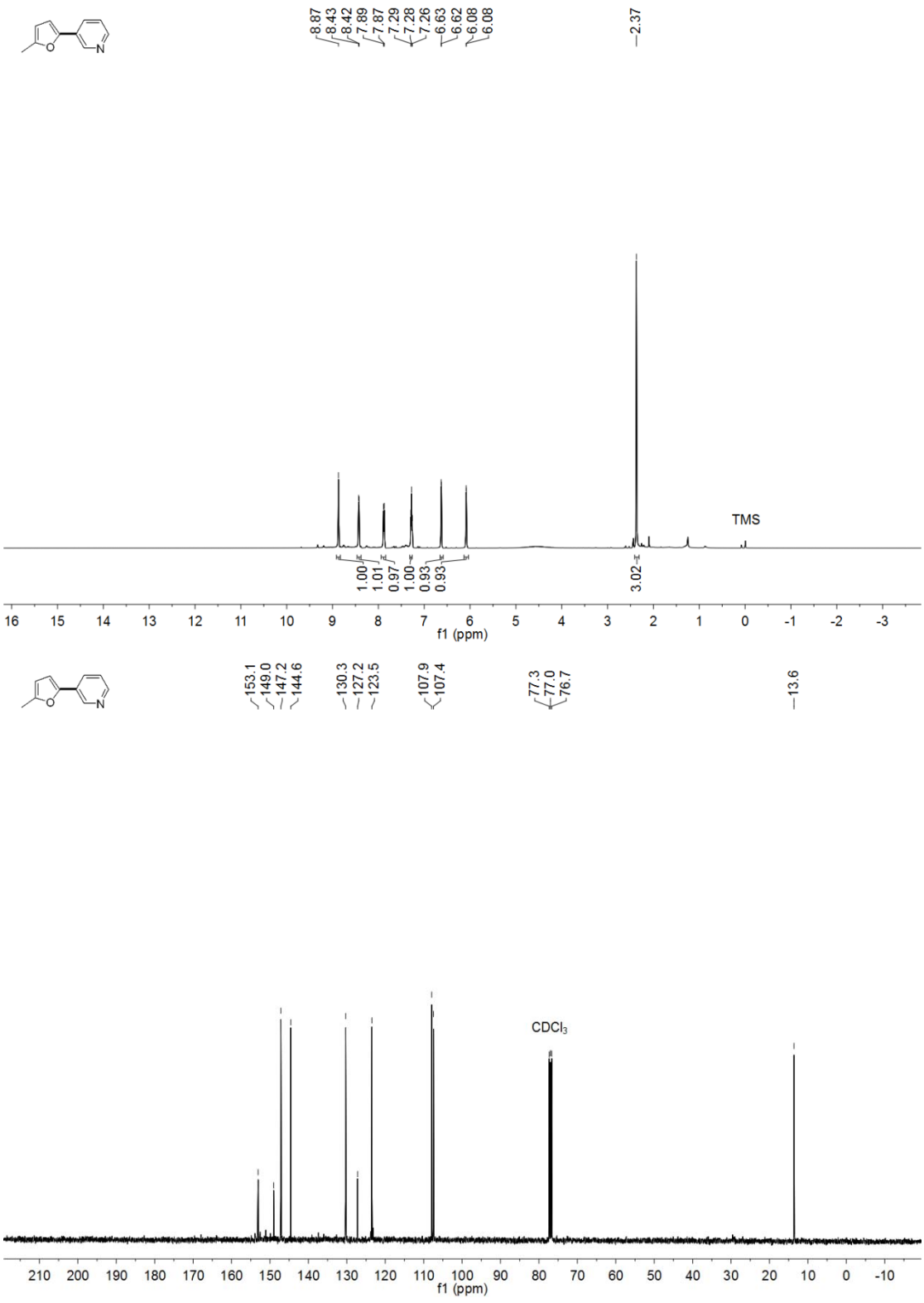


Figure **S49**. The NMR spectrums of **14e**

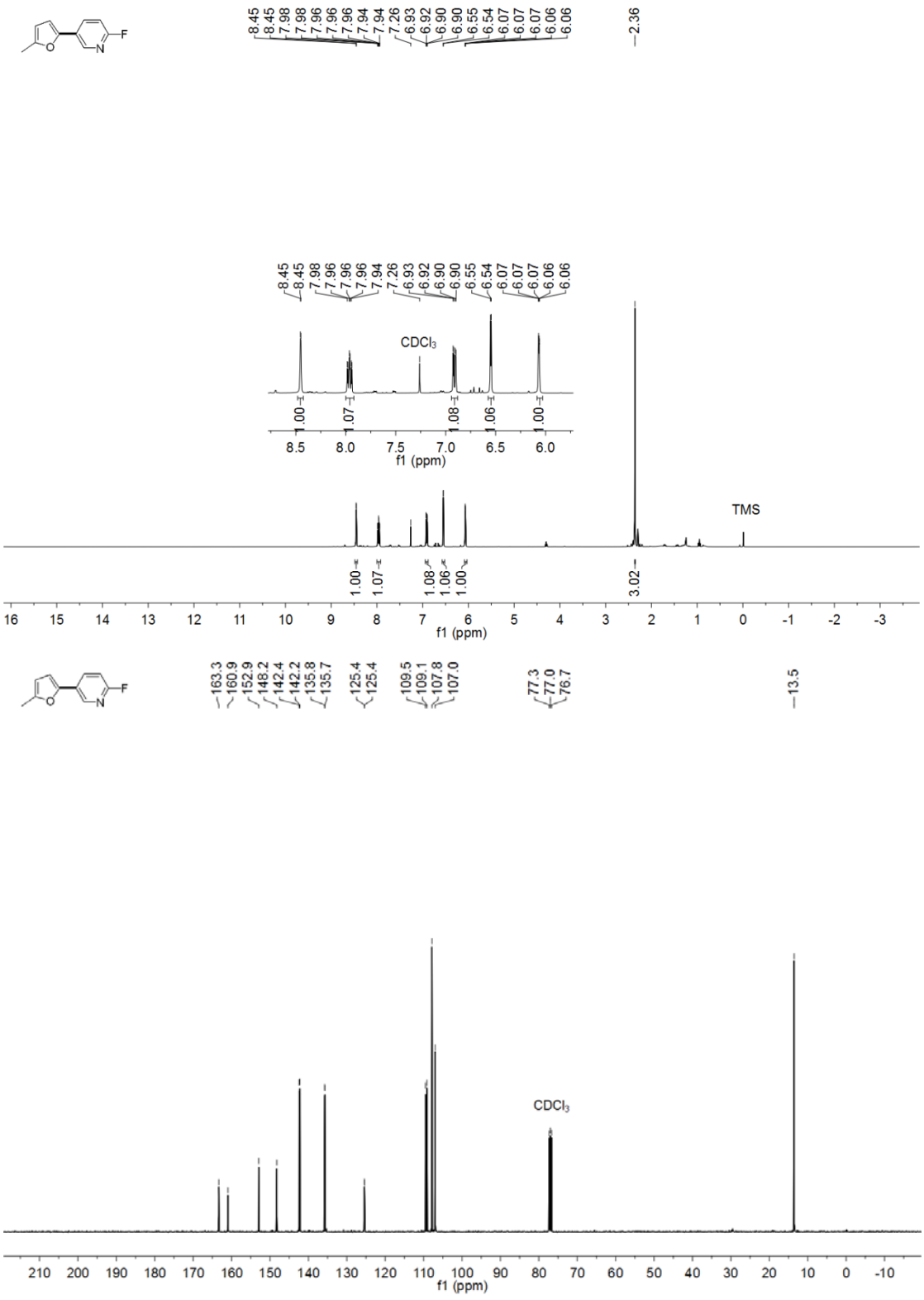


Figure **S50**. The NMR spectrums of **14h**

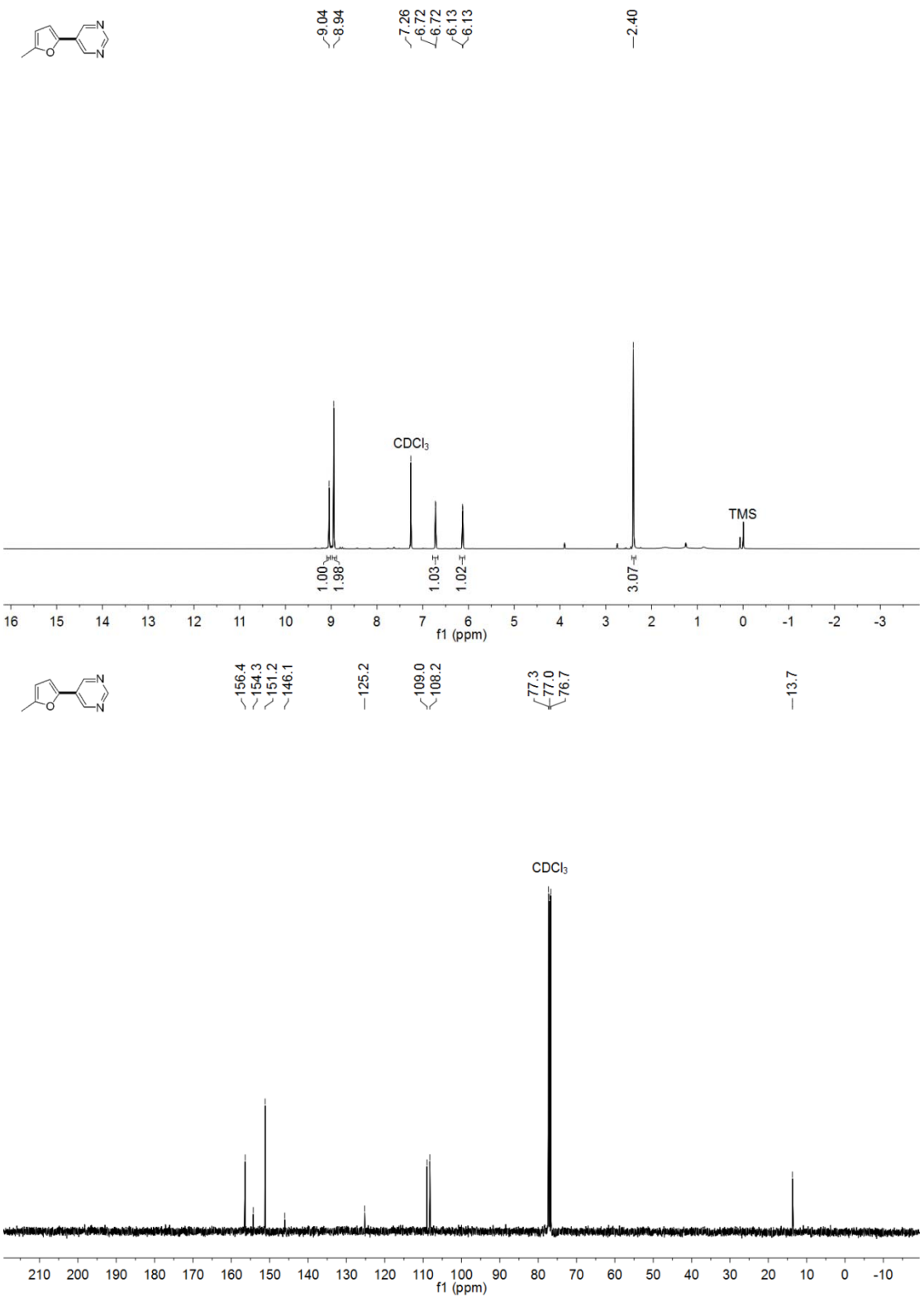


Figure **S51**. The NMR spectrums of **14j**

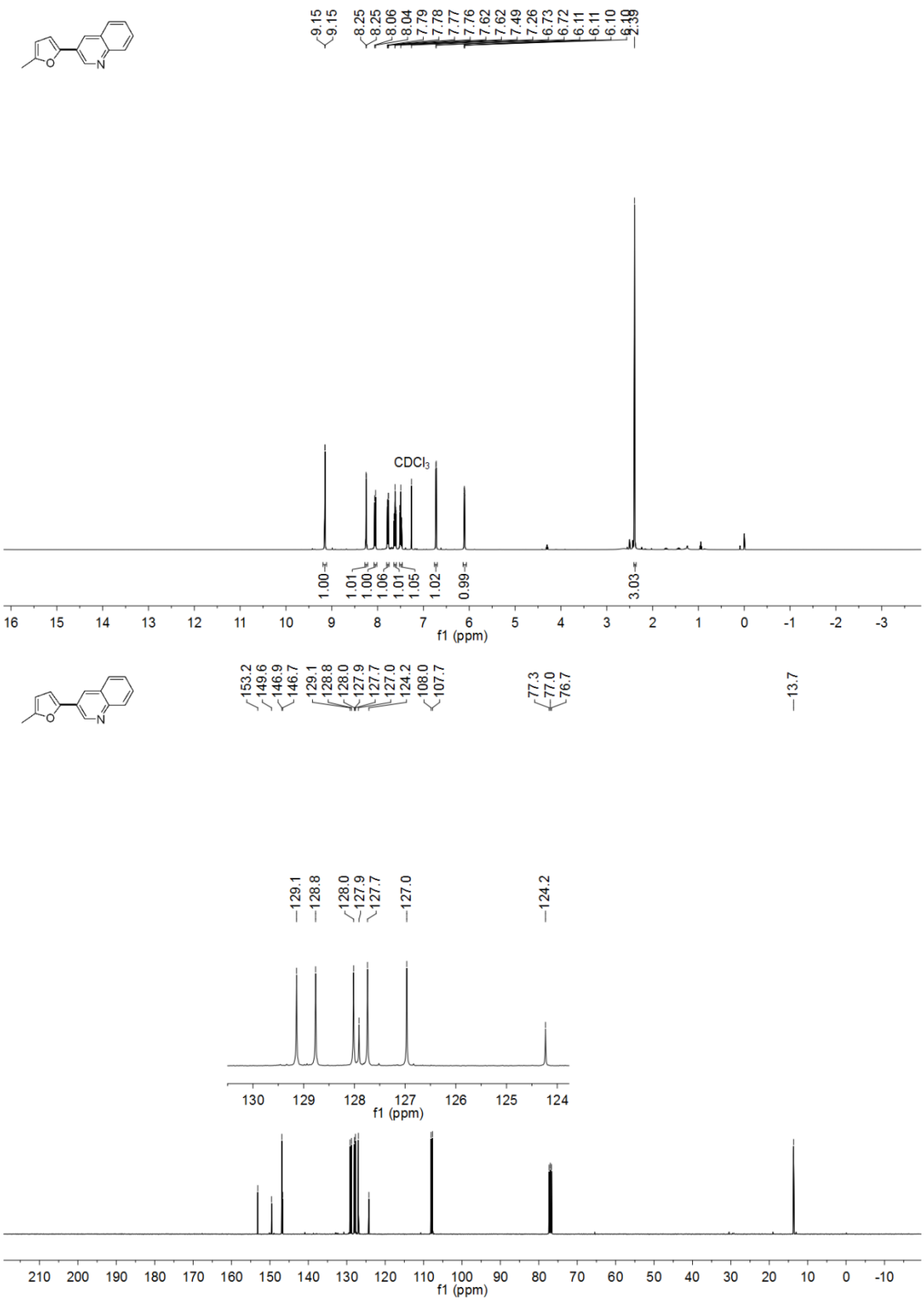


Figure **S52**. The NMR spectrums of **14k**

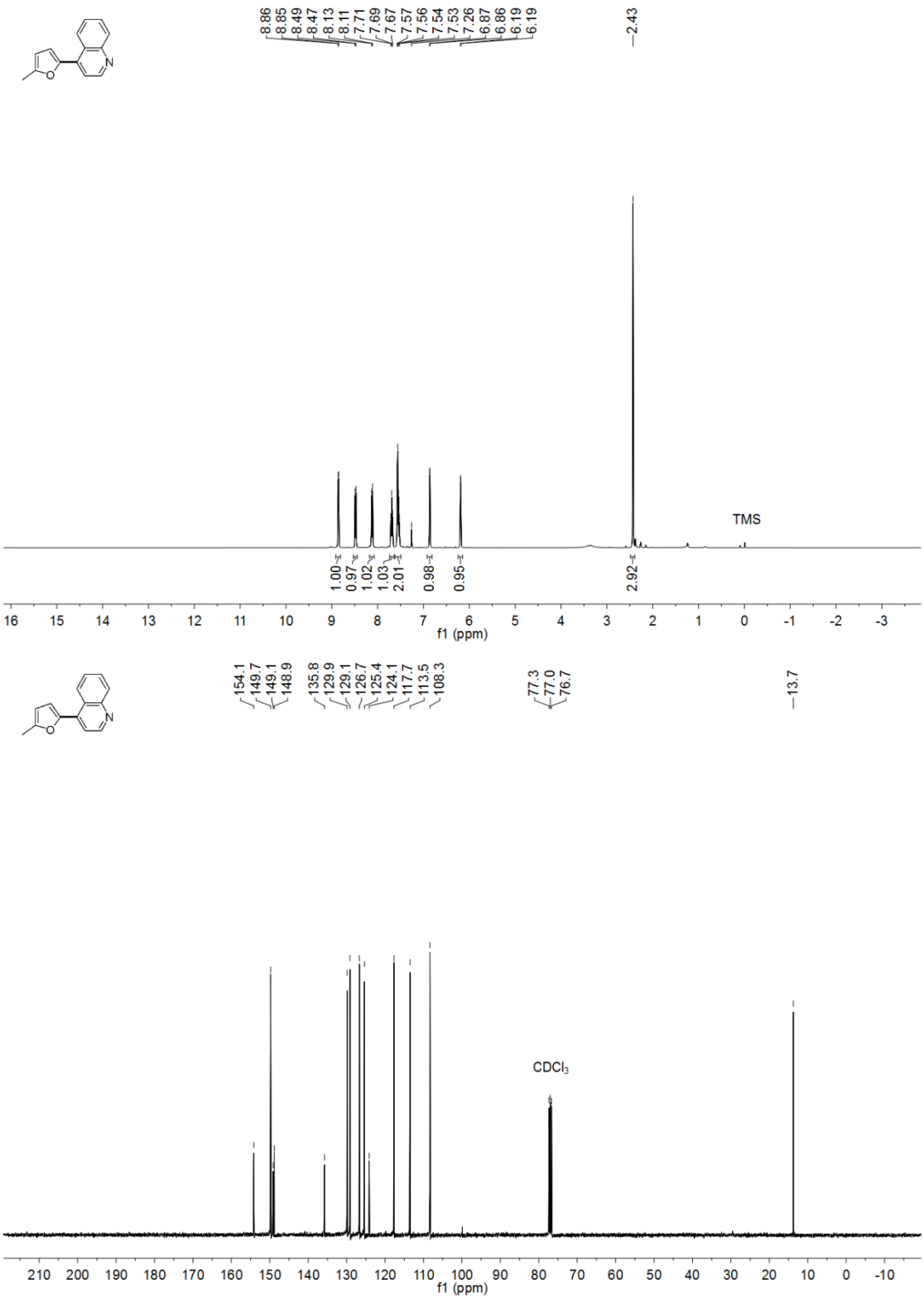


Figure **S53**. The NMR spectrums of **14l**

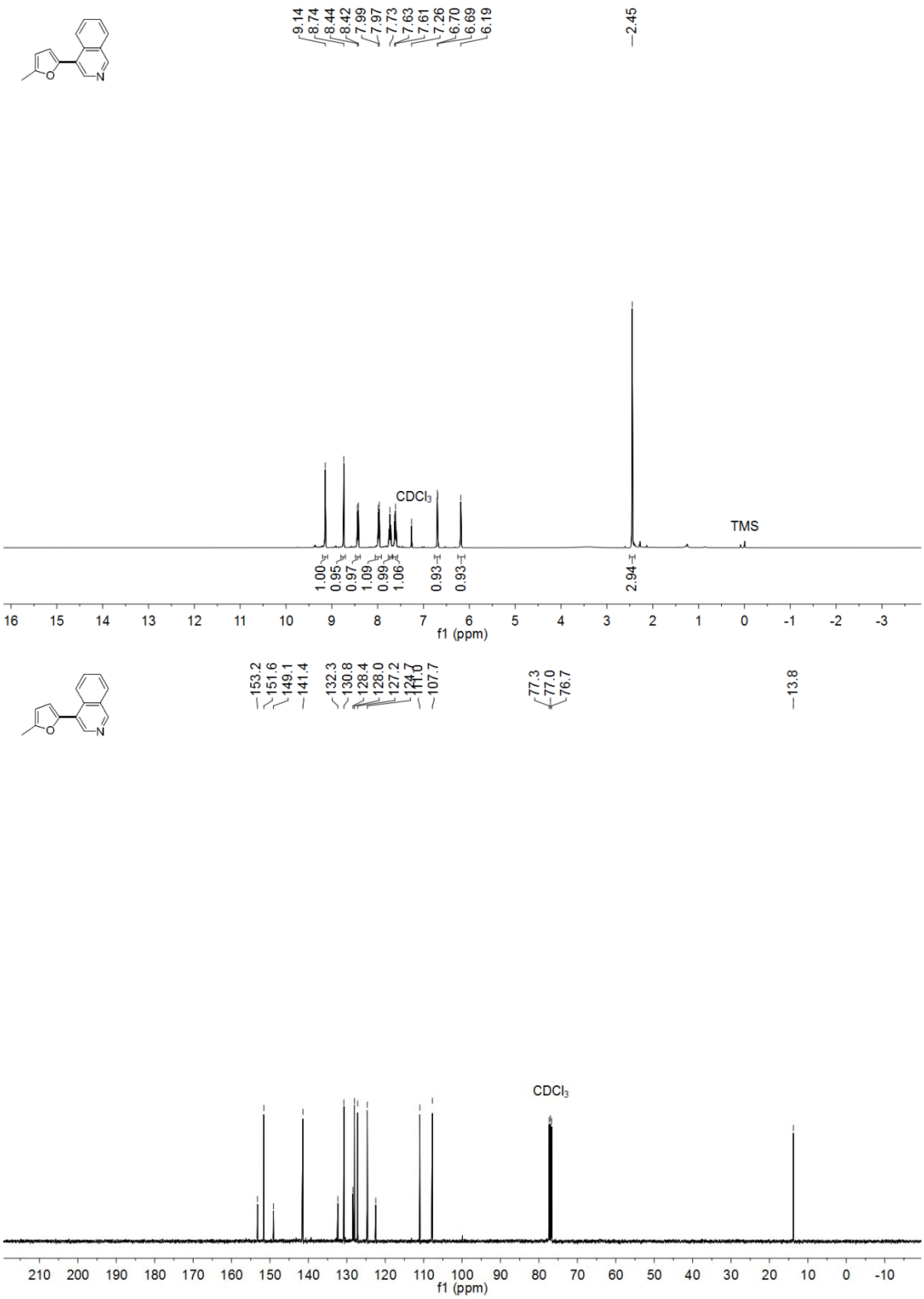


Figure **S54**. The NMR spectrums of **14m**

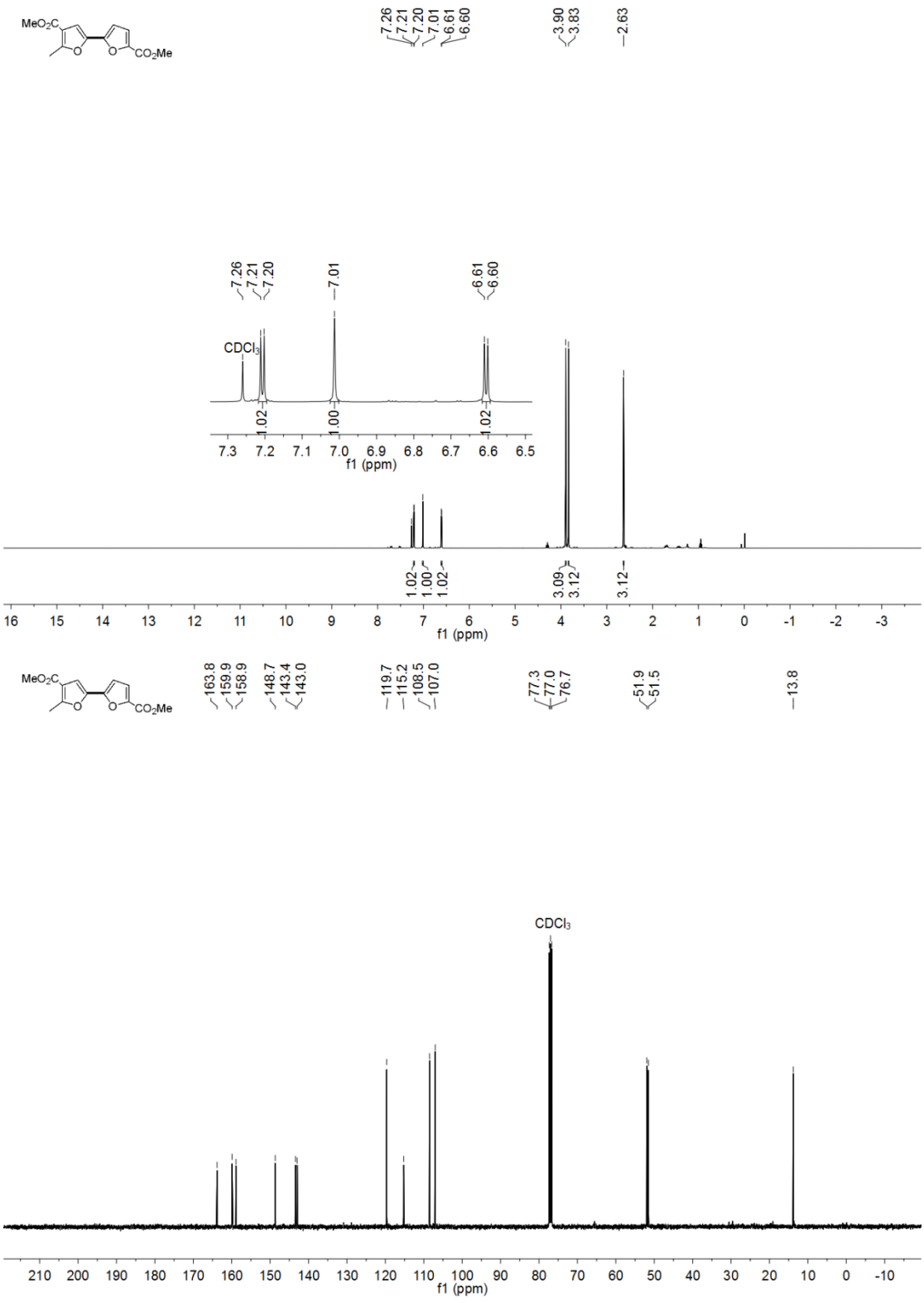


Figure **S55**.The NMR spectrums of **15d**

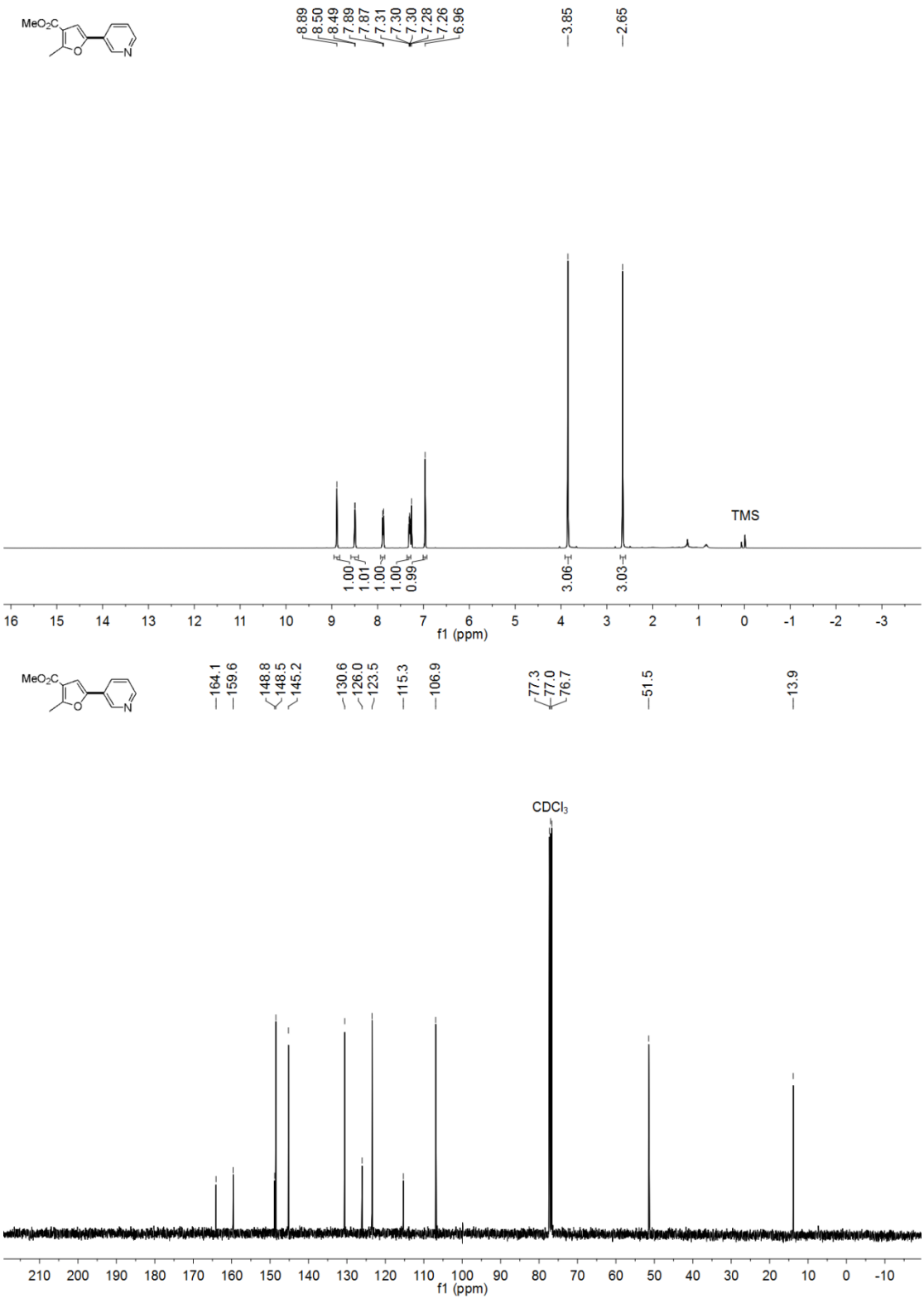


Figure **S56**. The NMR spectrums of **15e**

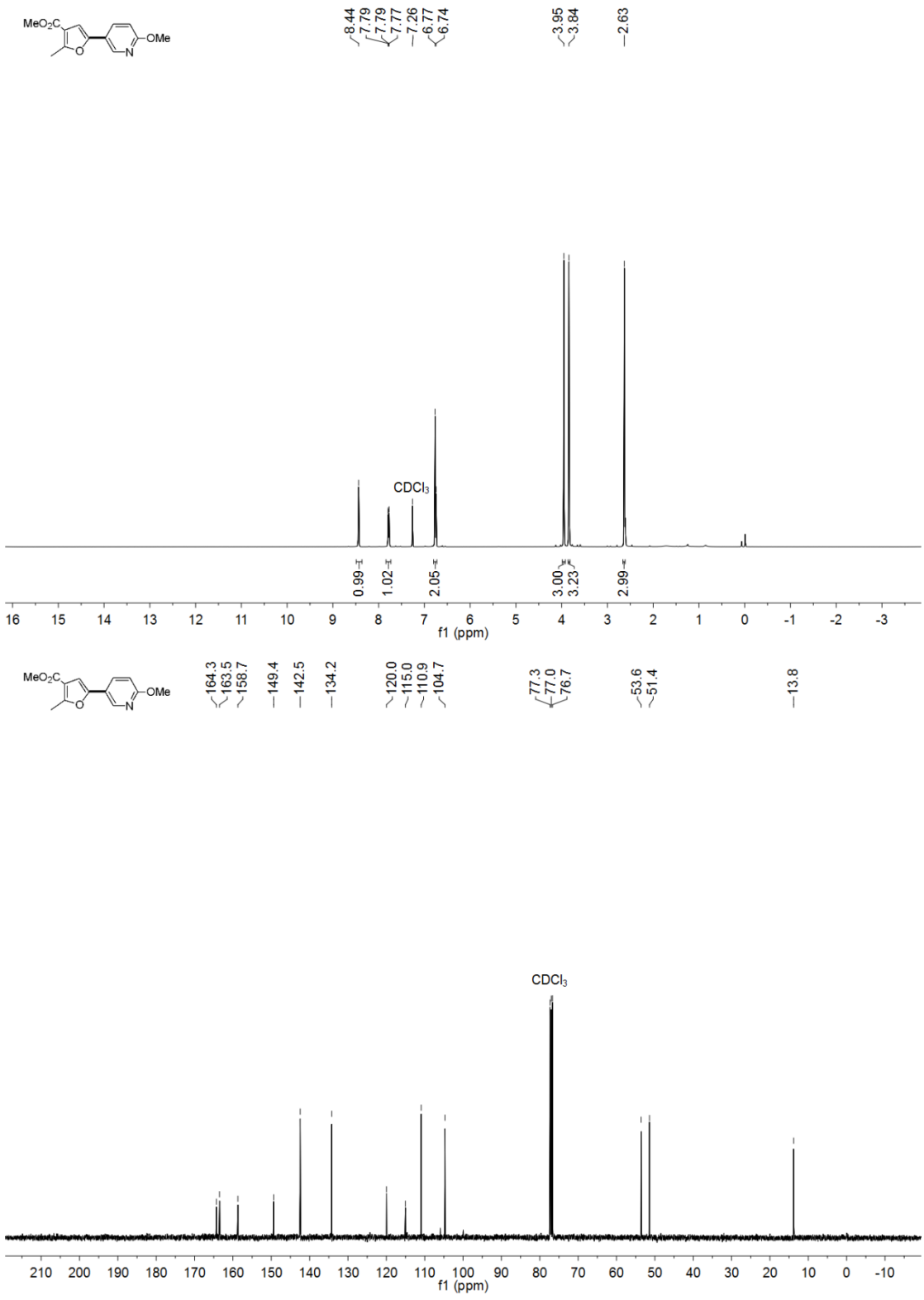


Figure **S57**.The NMR spectrums of **15g**

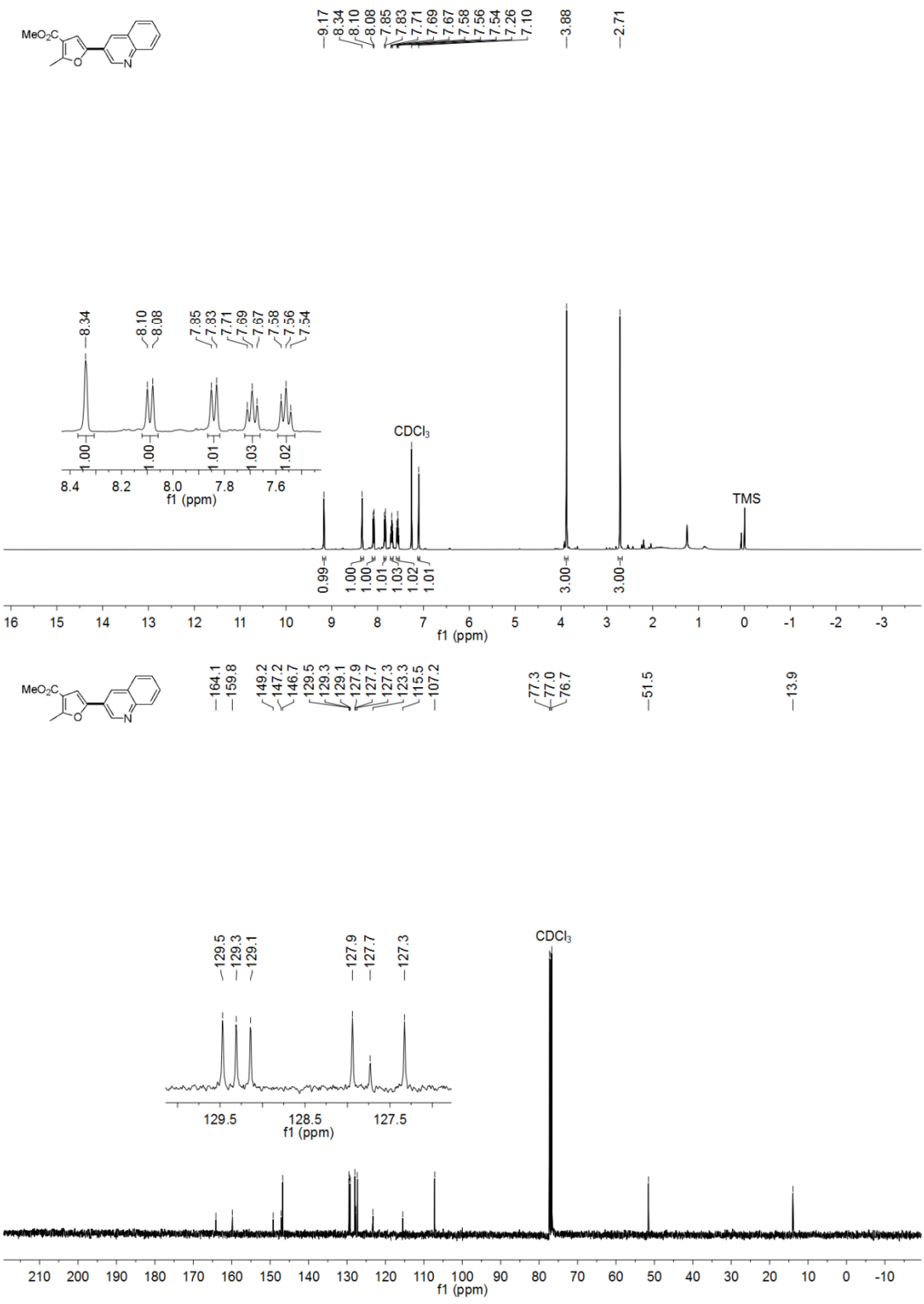


Figure **S58**.The NMR spectrums of **15k**

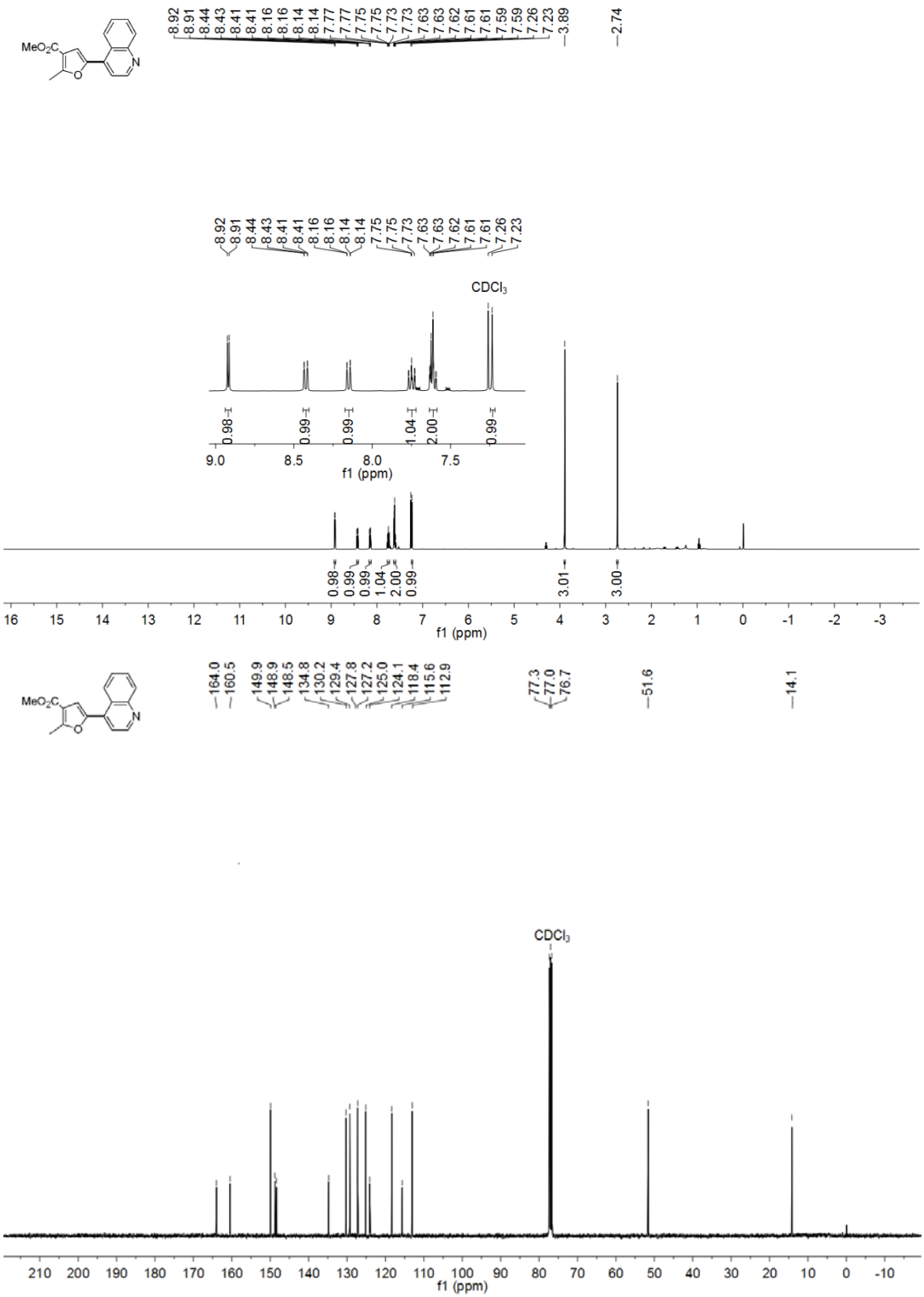


Figure **S59**.The NMR spectrums of **15l**

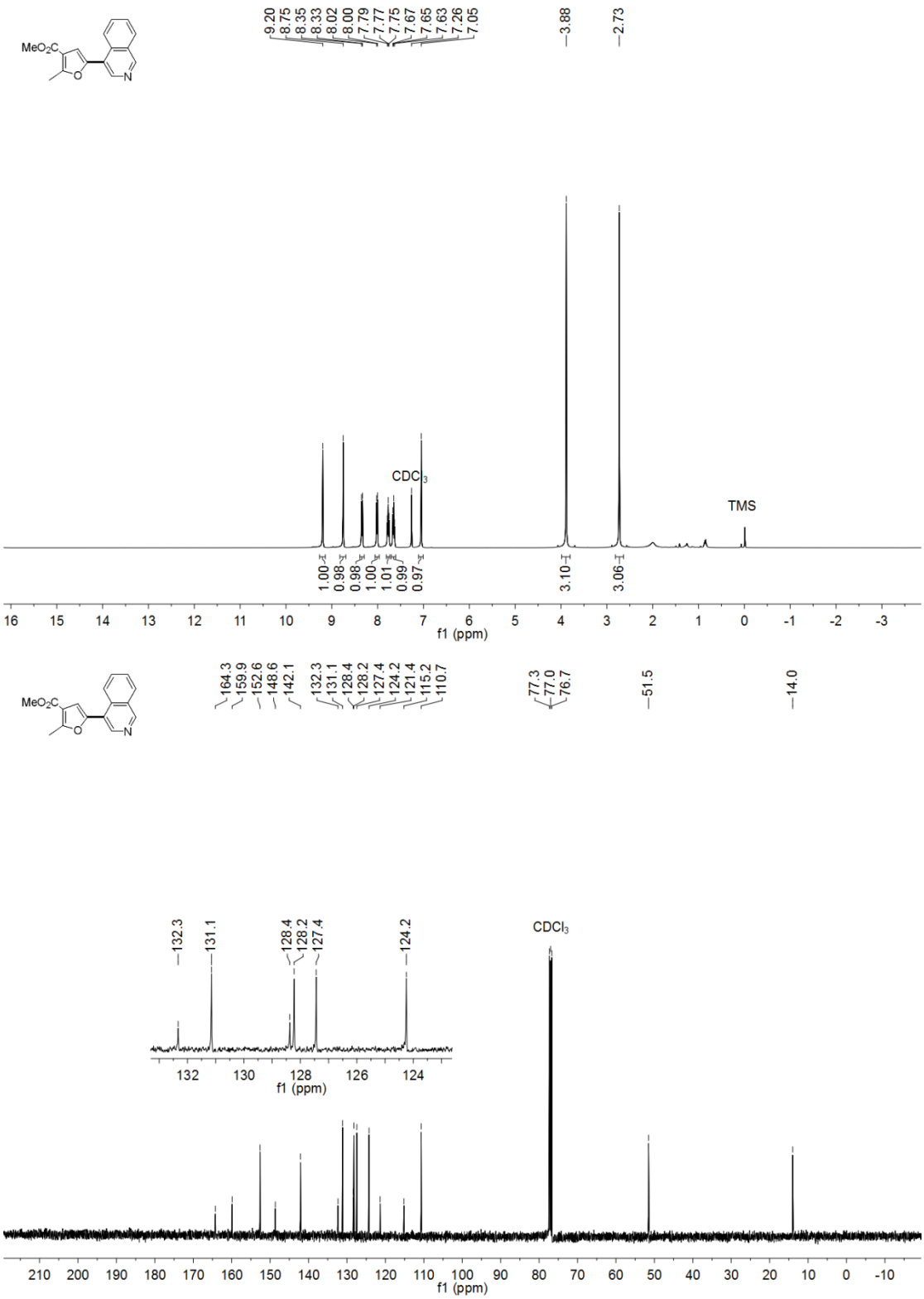


Figure **S60**.The NMR spectrums of **15m**

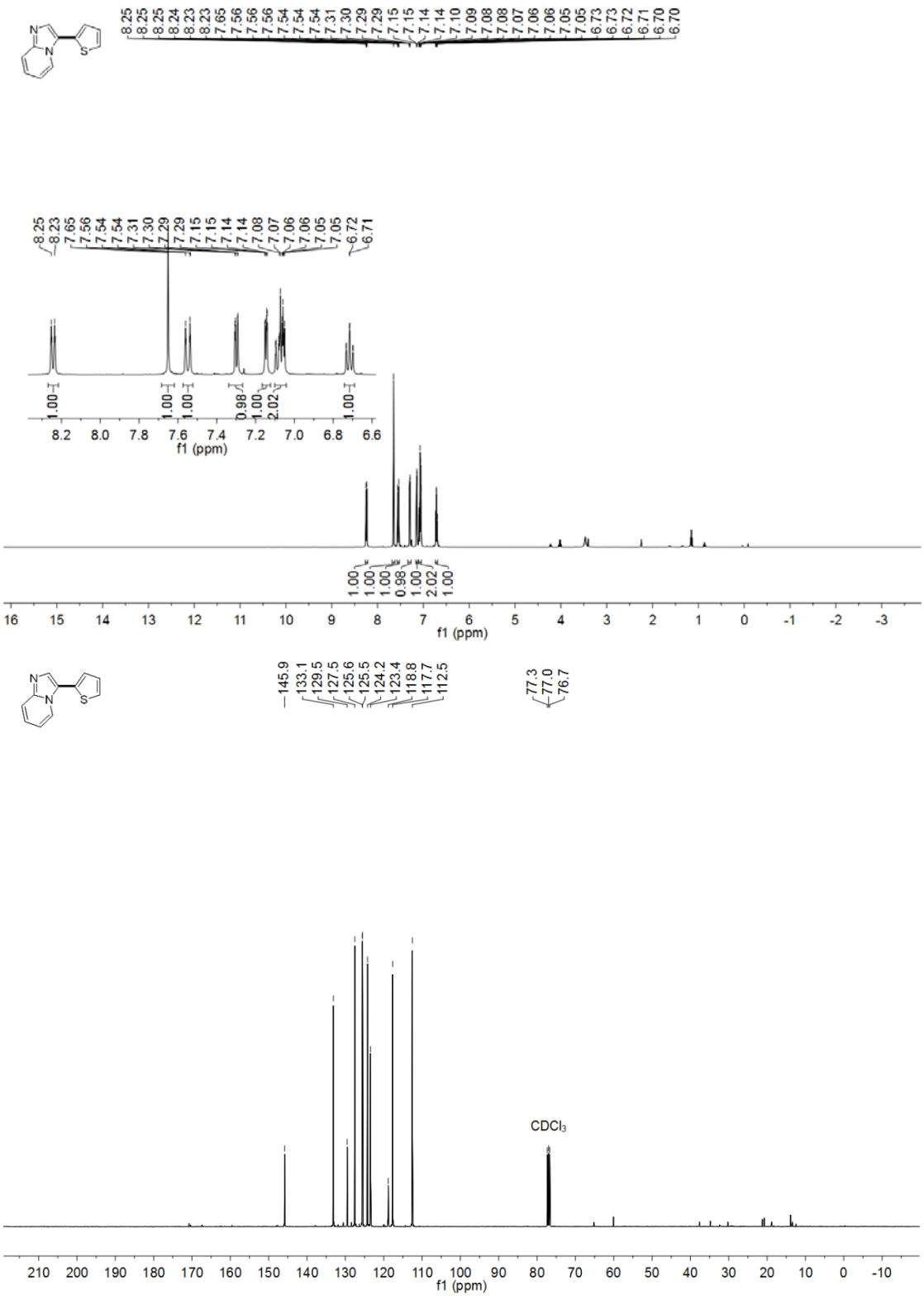


Figure **S61**.The NMR spectrums of **16b**

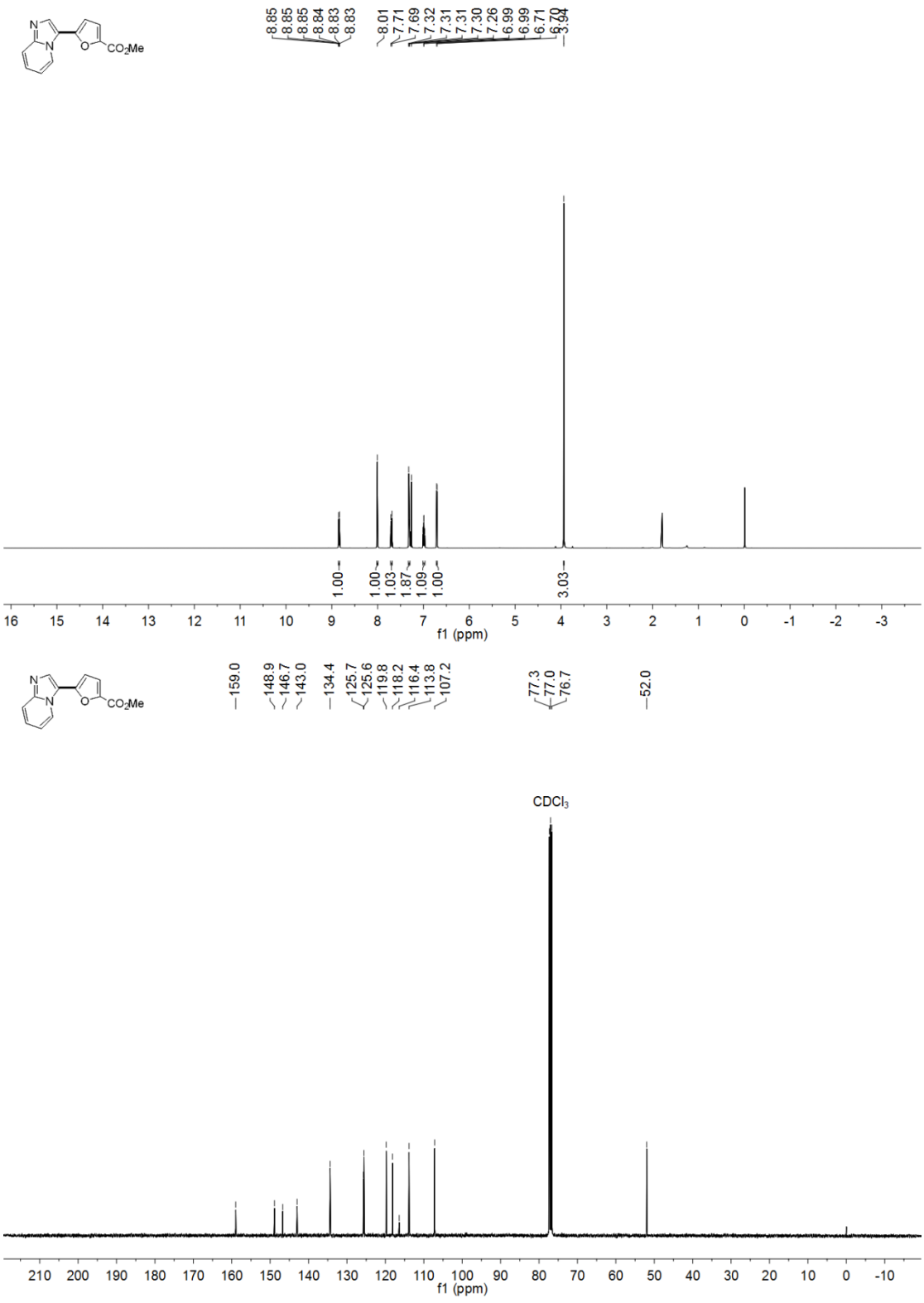


Figure **S62**.The NMR spectrums of 1**6d**

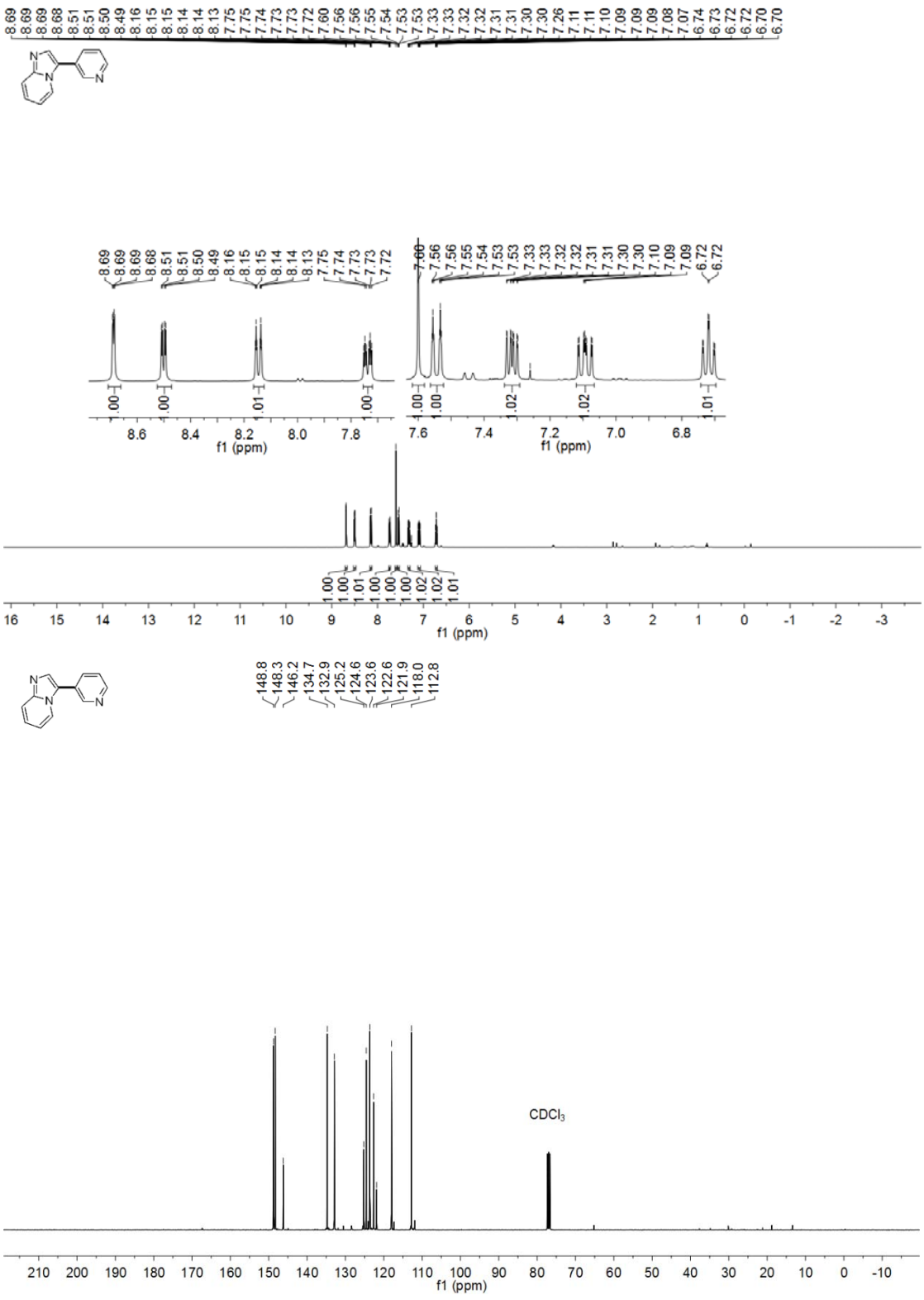


Figure **S63**.The NMR spectrums of **16e**

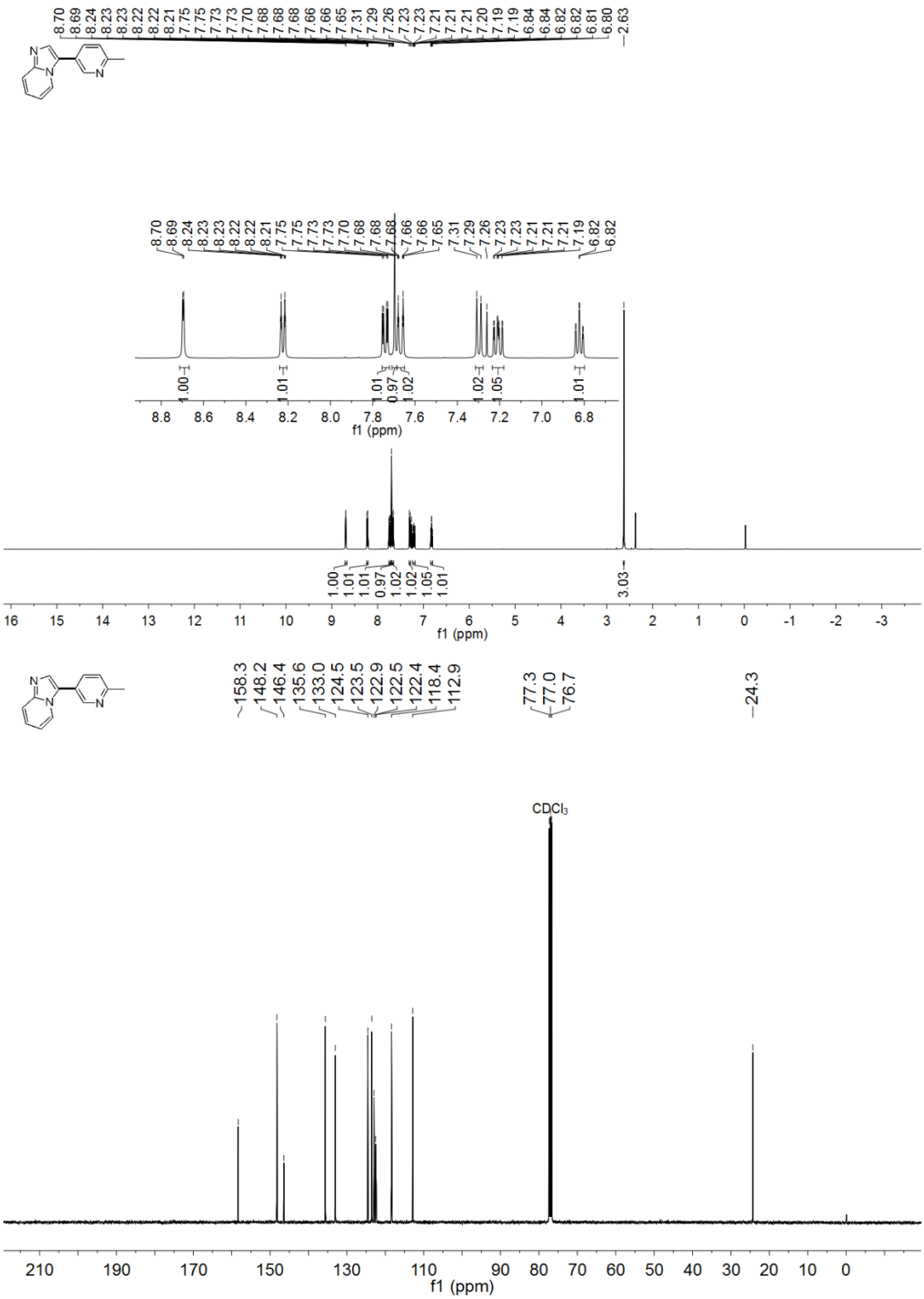


Figure **S64**.The NMR spectrums of **16f**

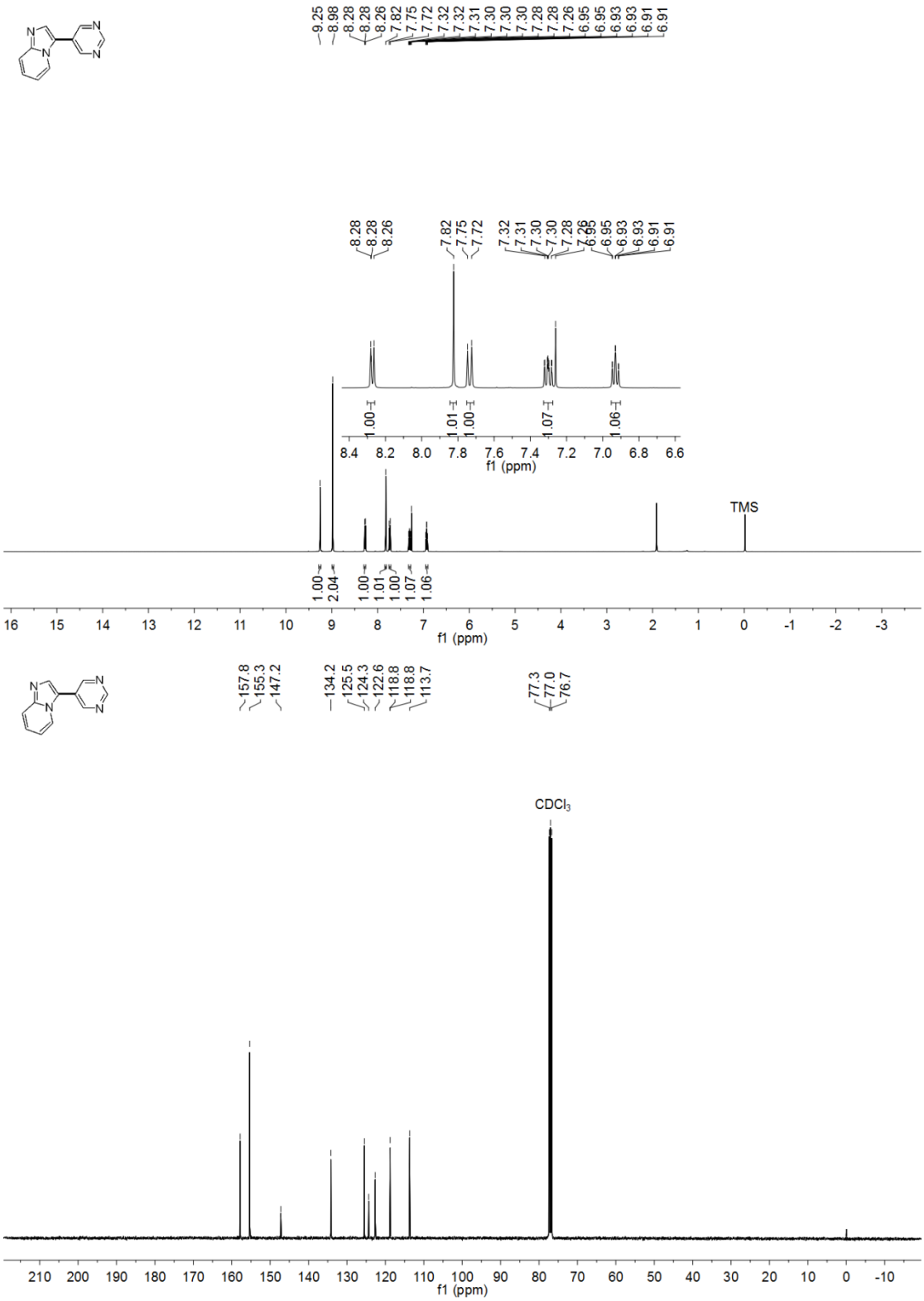


Figure **S65**.The NMR spectrums of **16j**

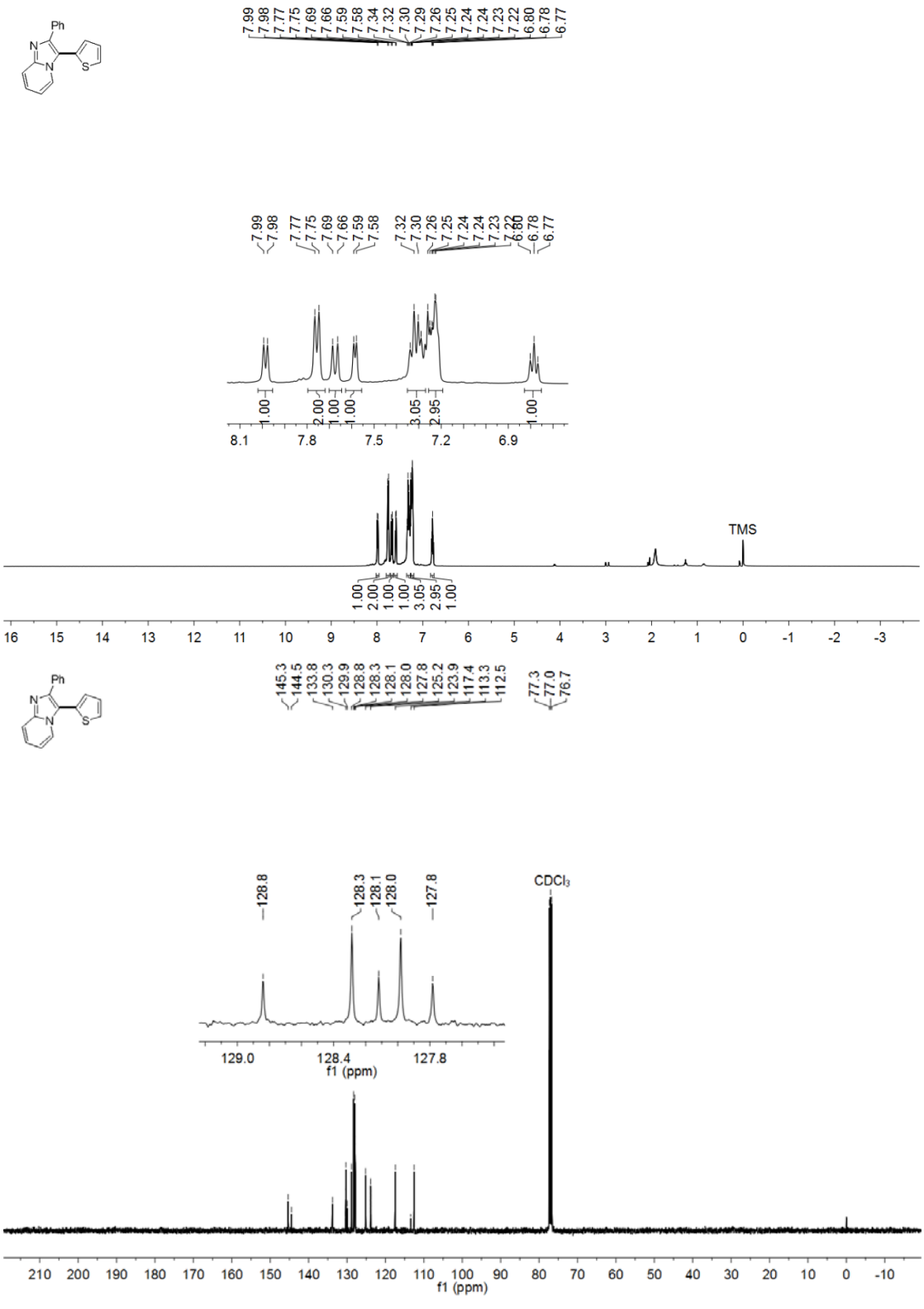


Figure **S66**.The NMR spectrums of 1**7b**

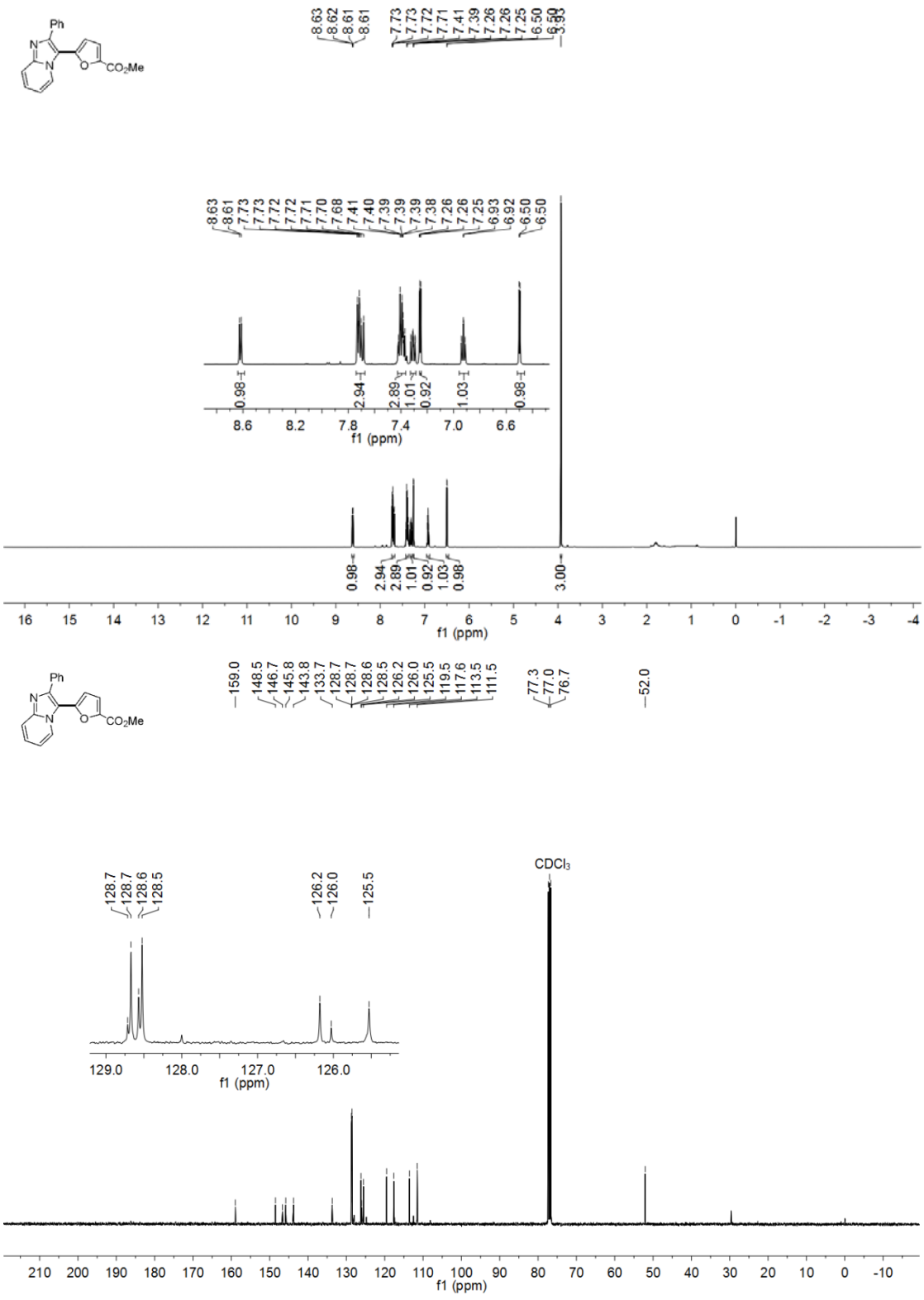


Figure **S67**.The NMR spectrums of **17d**

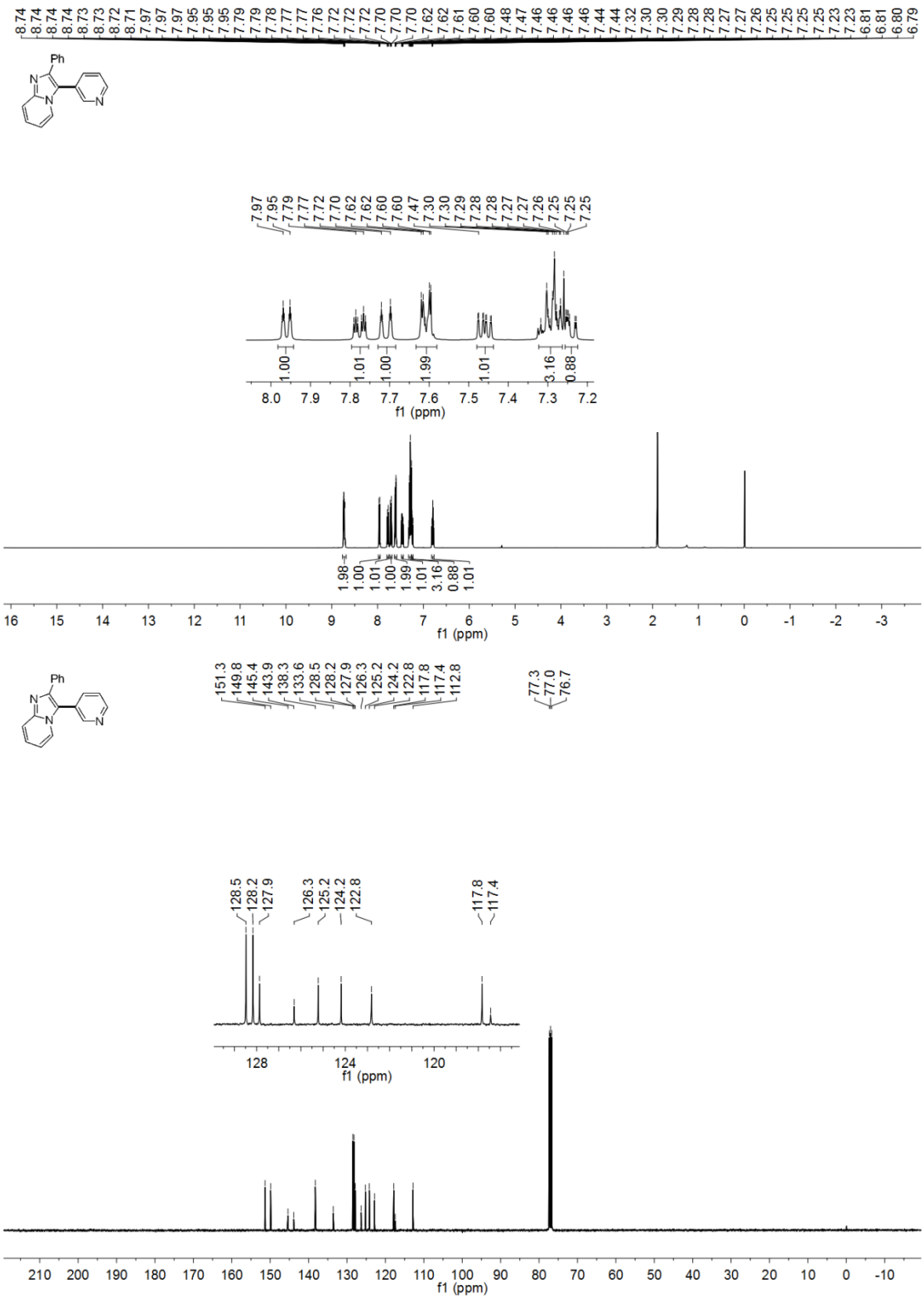


Figure **S68**.The NMR spectrums of **17e**

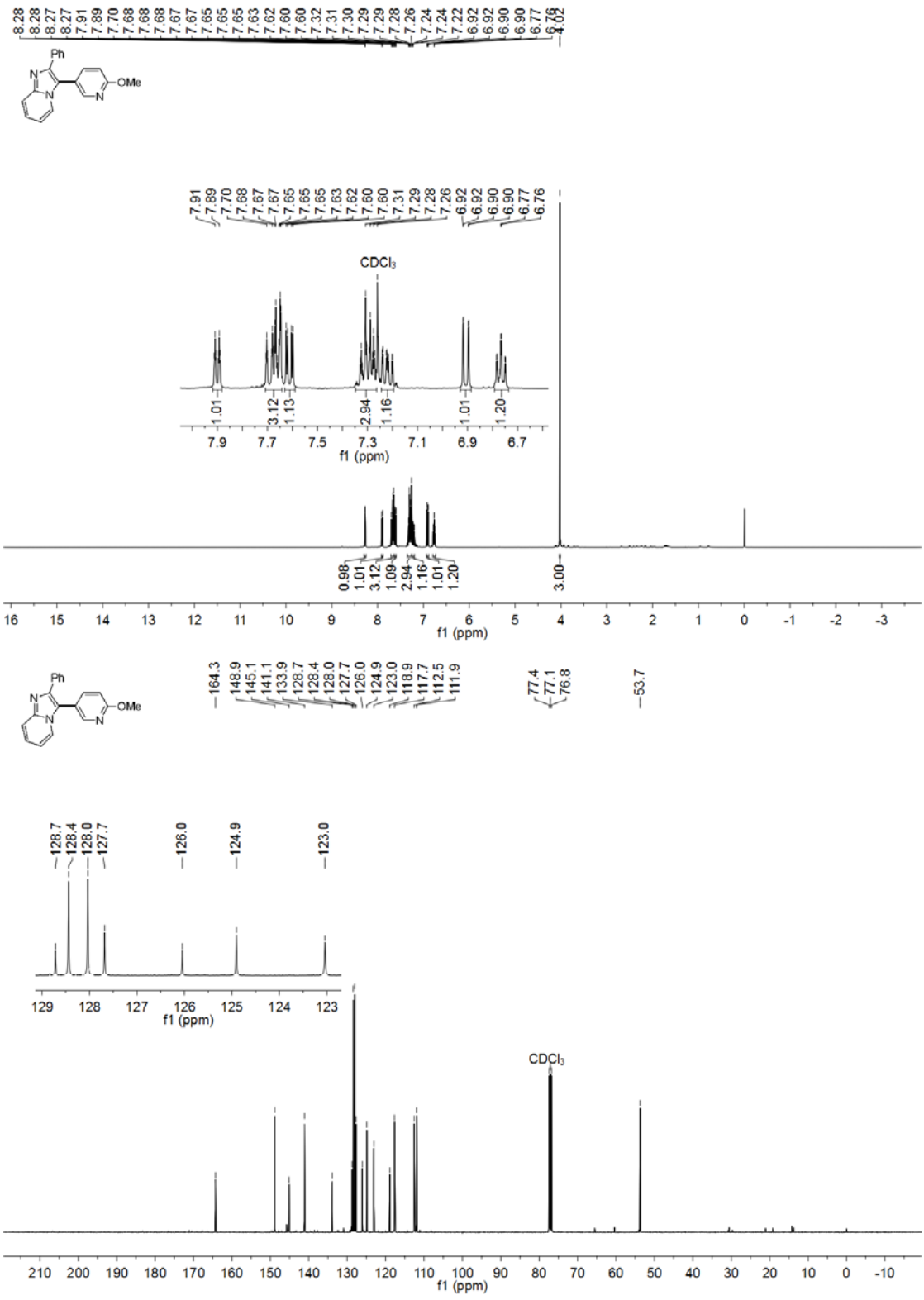


Figure **S69**.The NMR spectrums of **17g**

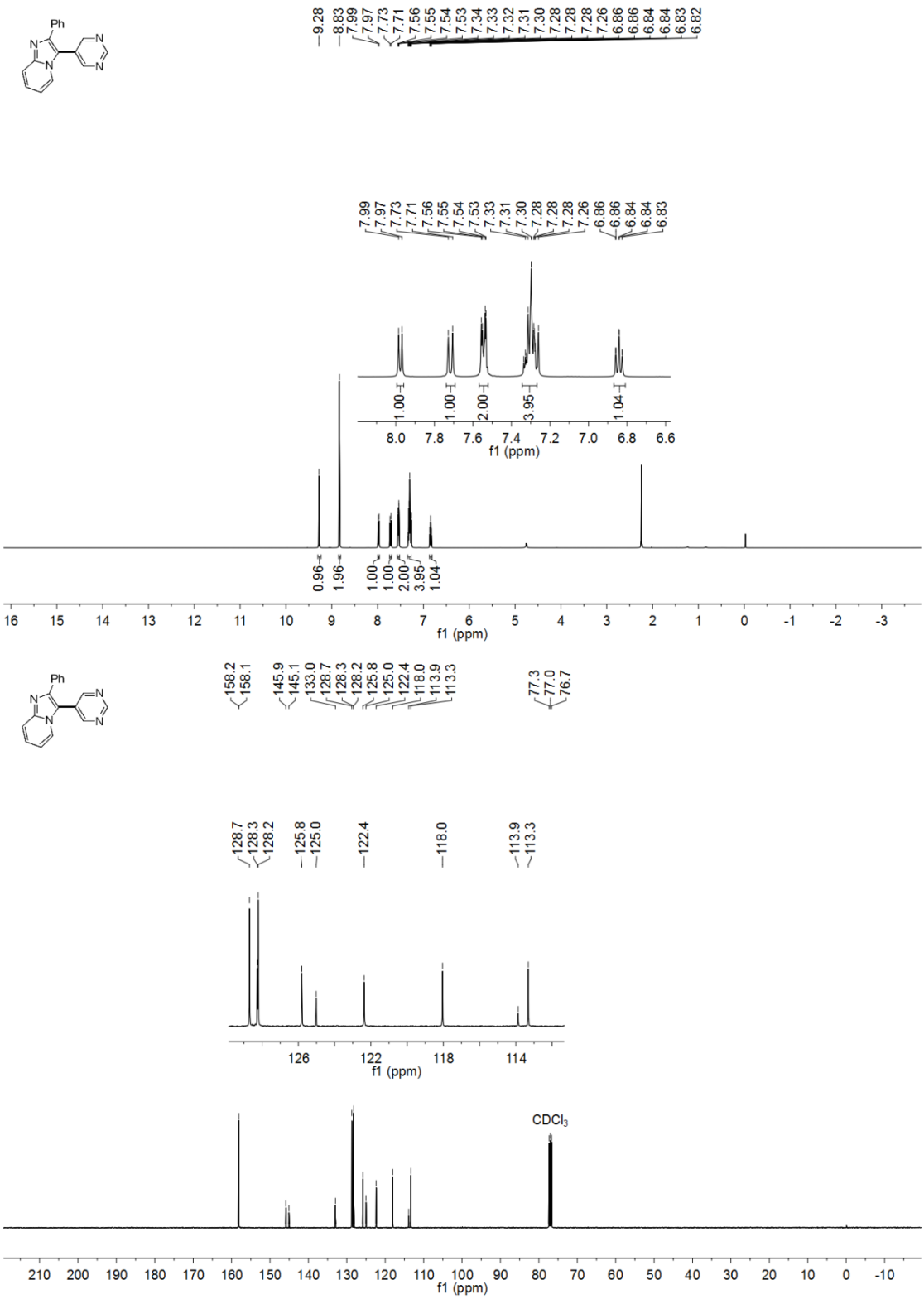


Figure **S70**.The NMR spectrums of **17j**

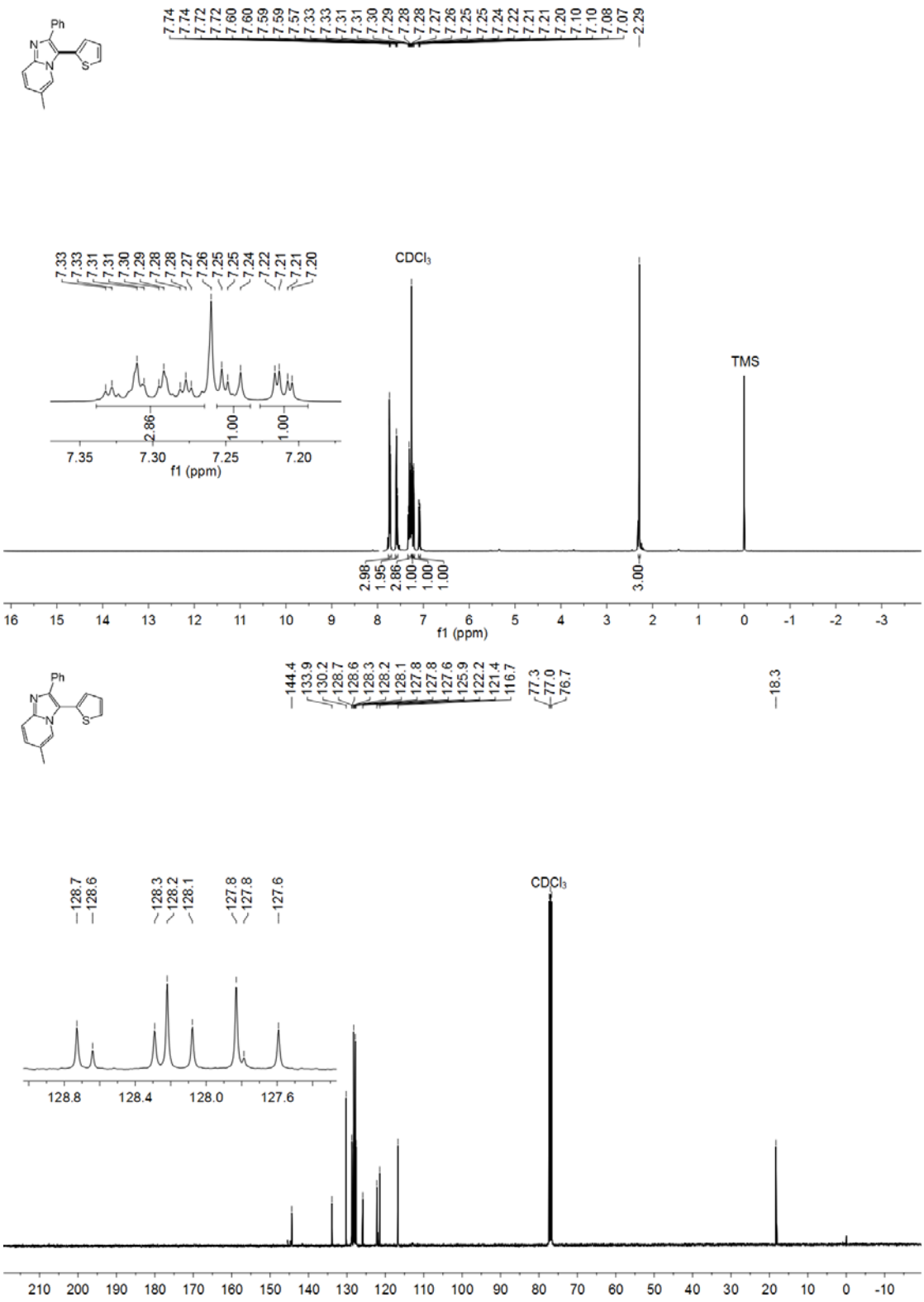


Figure **S71**.The NMR spectrums of **18b**

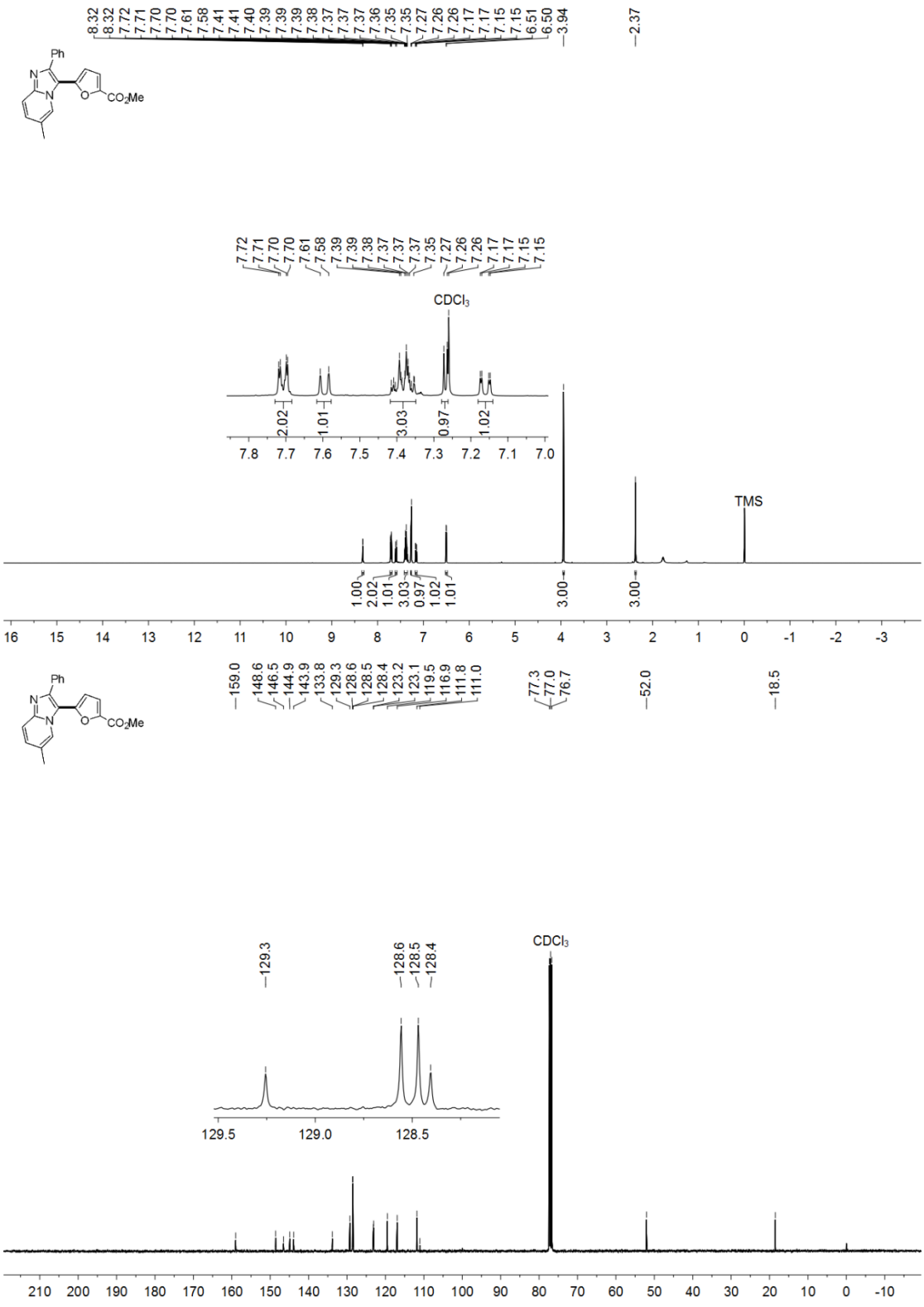


Figure **S72**.The NMR spectrums of **18d**

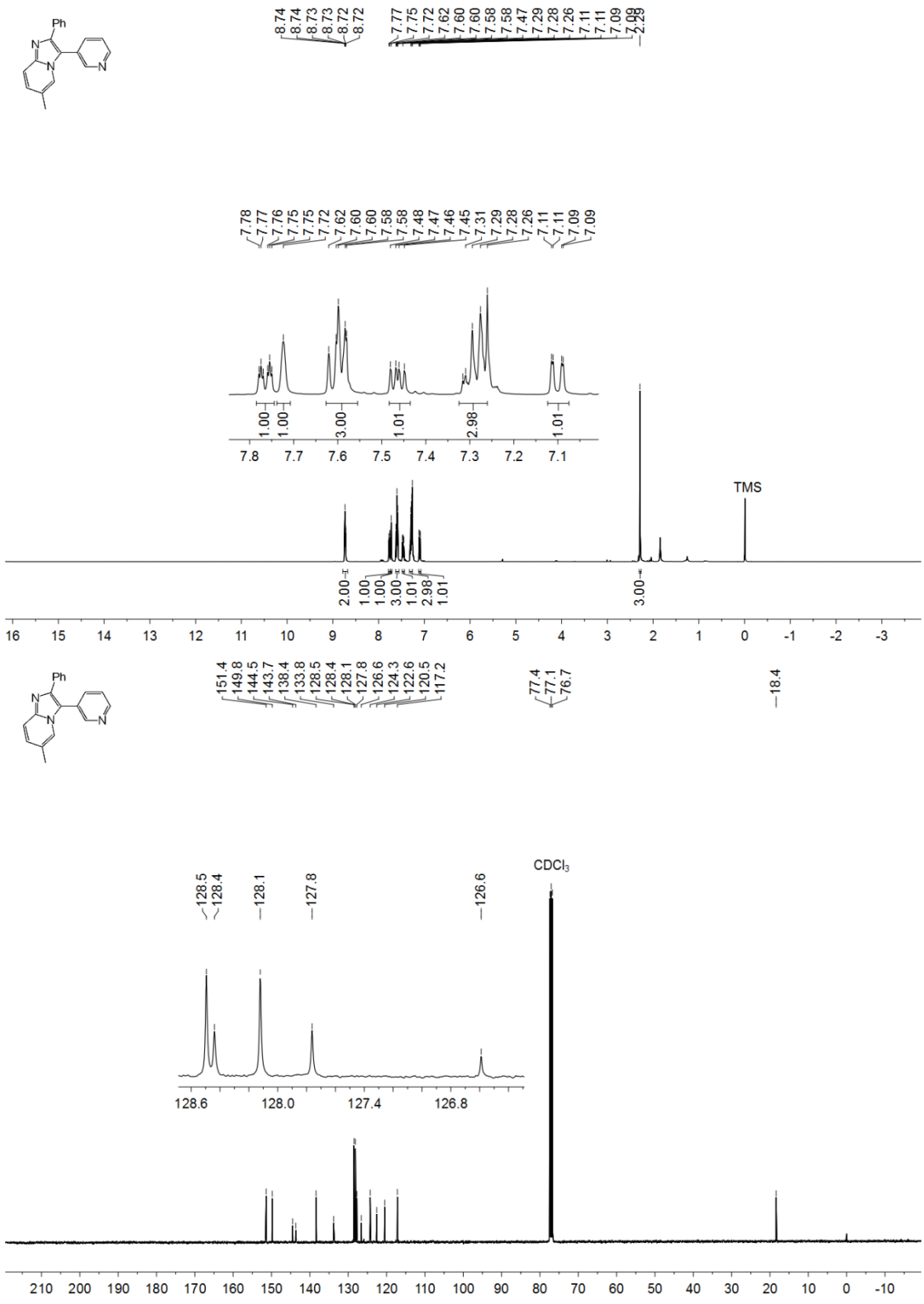


Figure **S73**.The NMR spectrums of **18e**

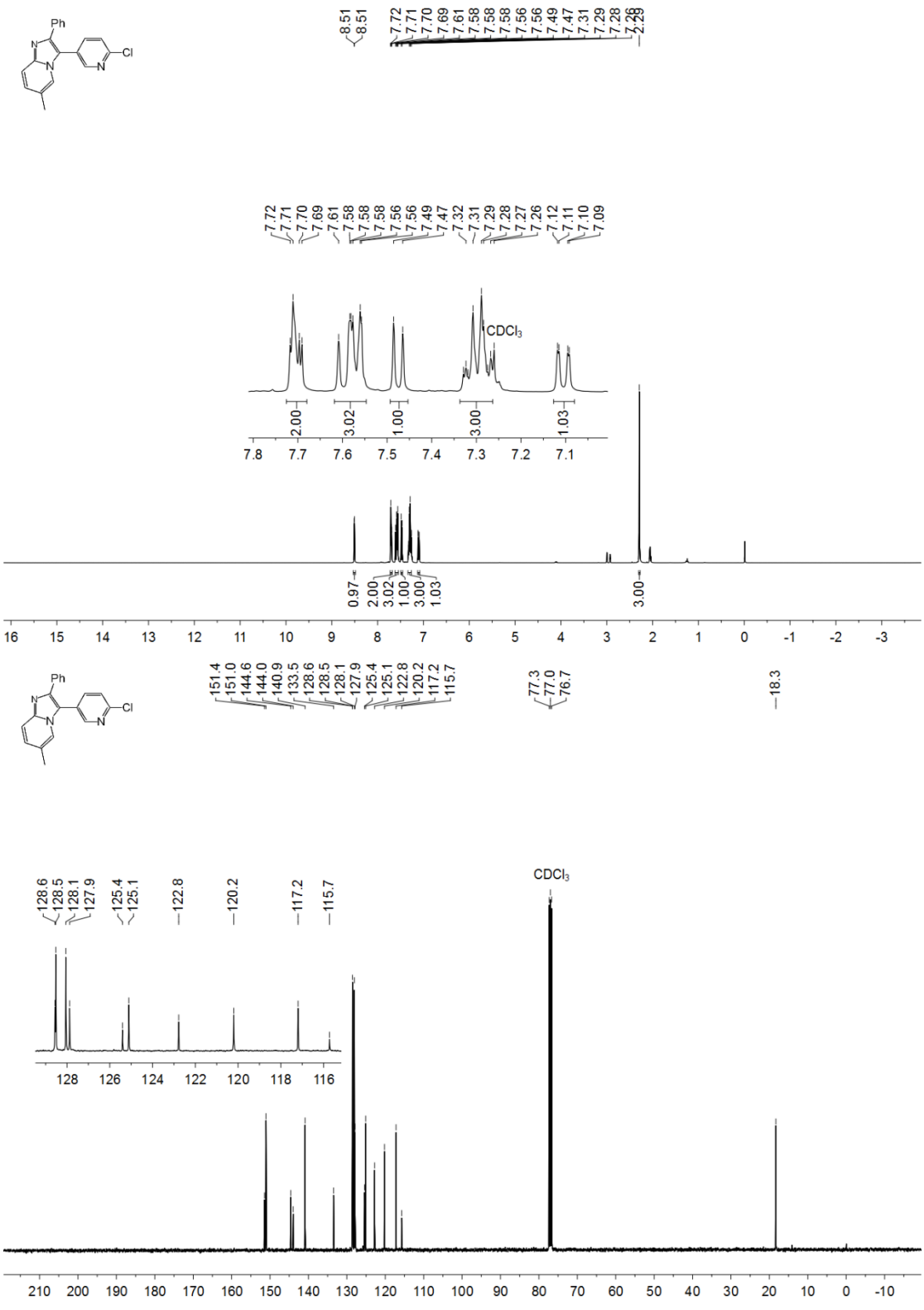


Figure **S74**.The NMR spectrums of **18i**

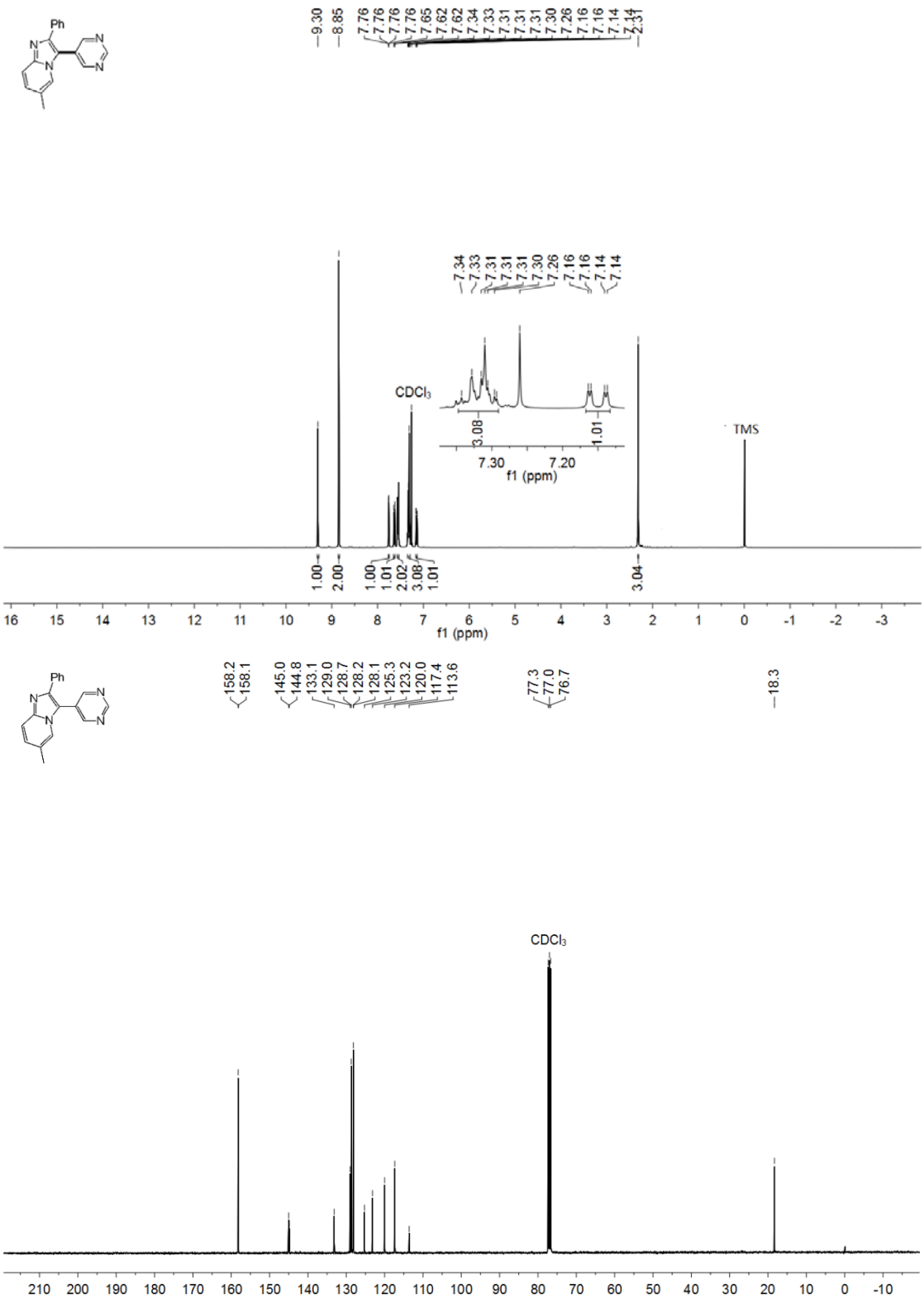


Figure **S75**.The NMR spectrums of **18j**

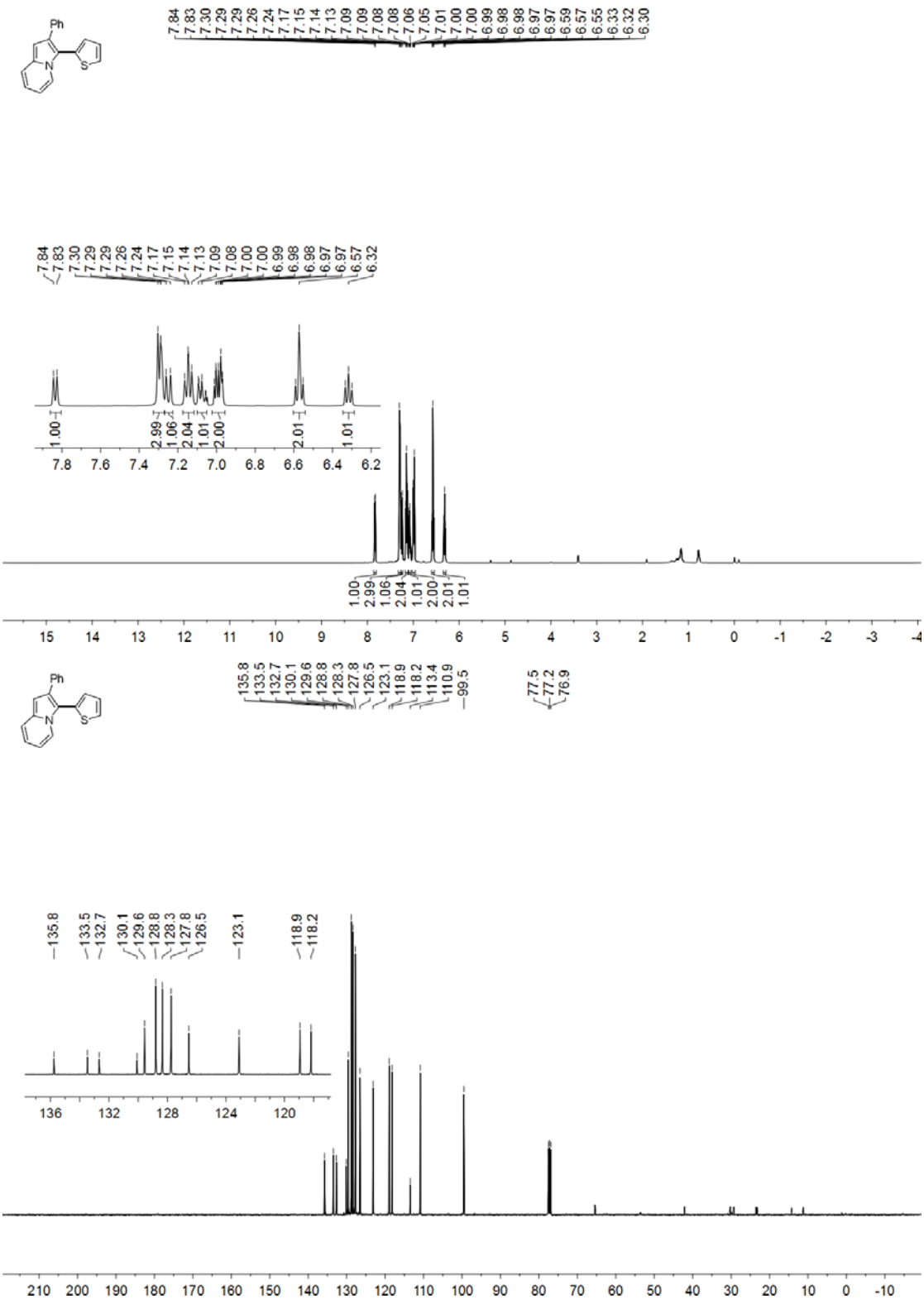


Figure **S76**.The NMR spectrums of **19b**

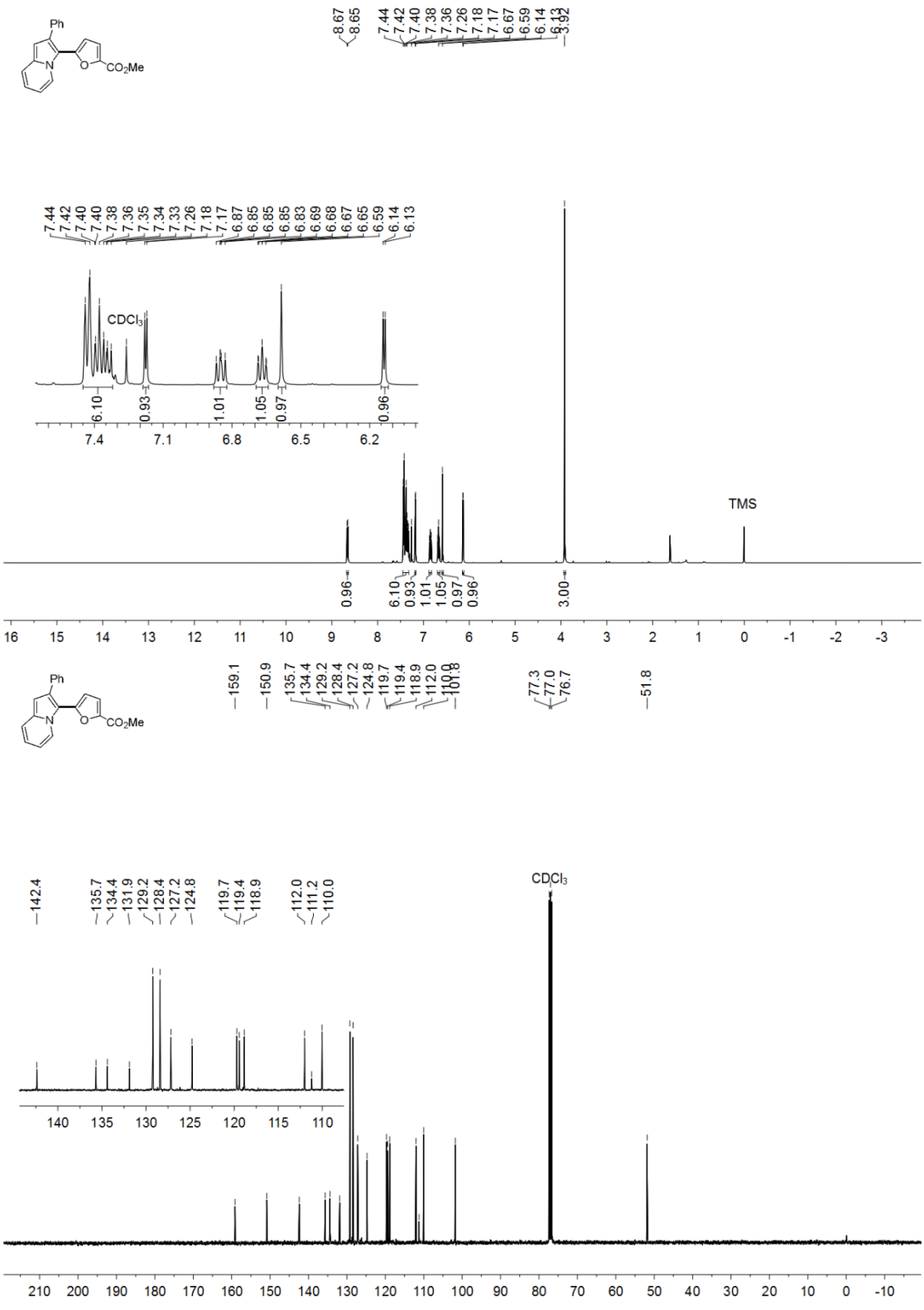


Figure **S77**.The NMR spectrums of **19d**

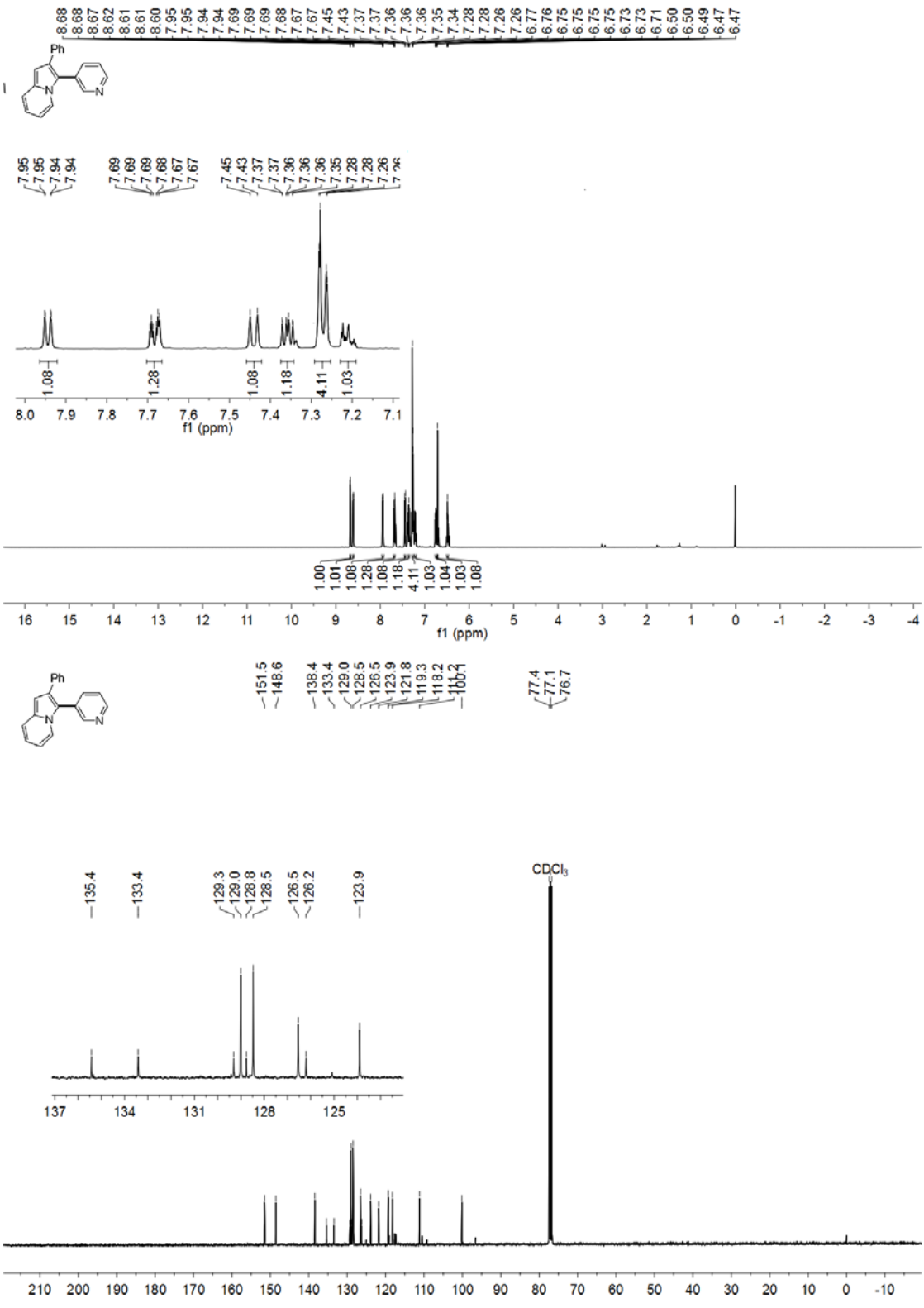


Figure **S78**.The NMR spectrums of **19e**

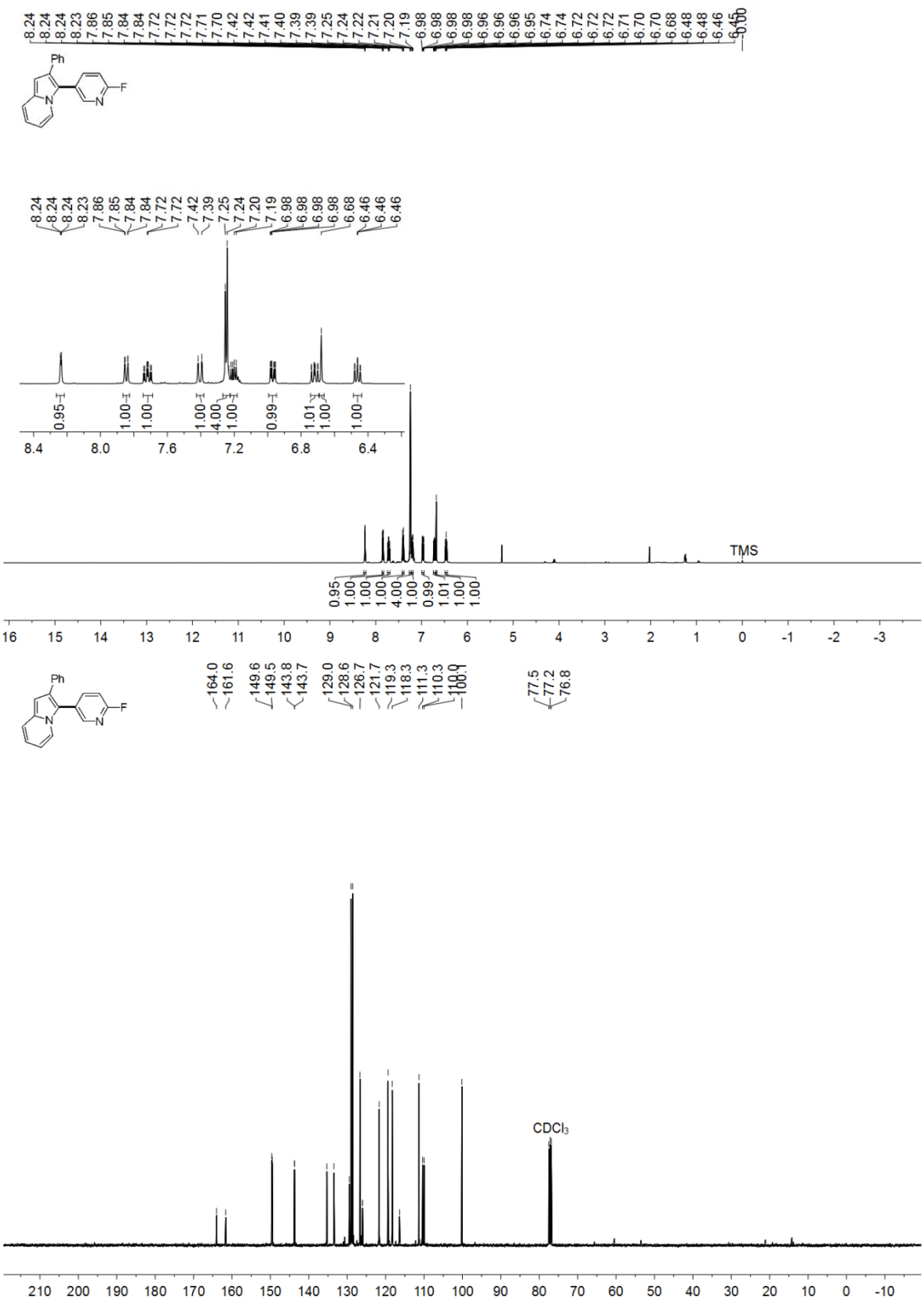


Figure **S79**.The NMR spectrums of **19h**

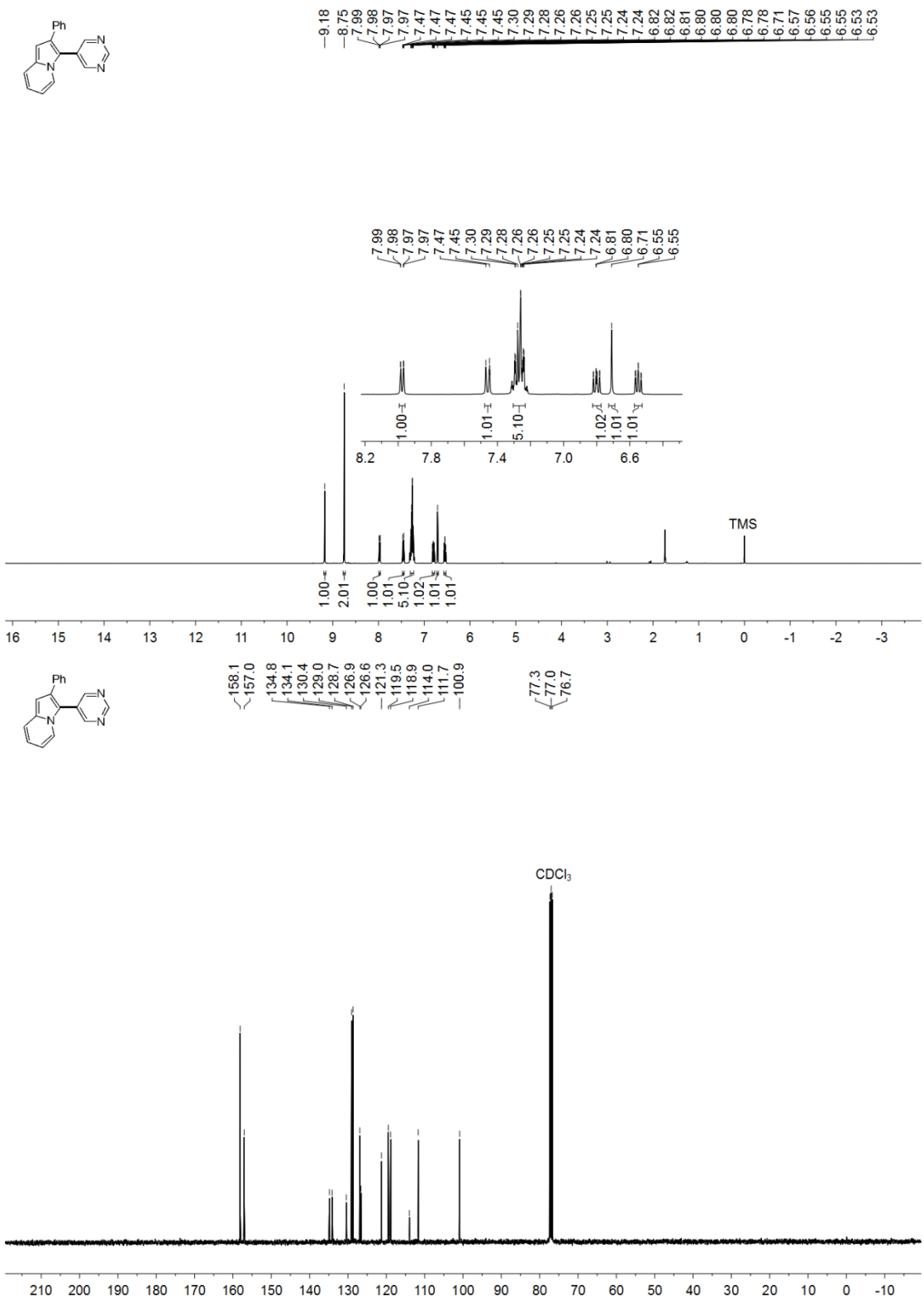


Figure **S80**.The NMR spectrums of **19j**

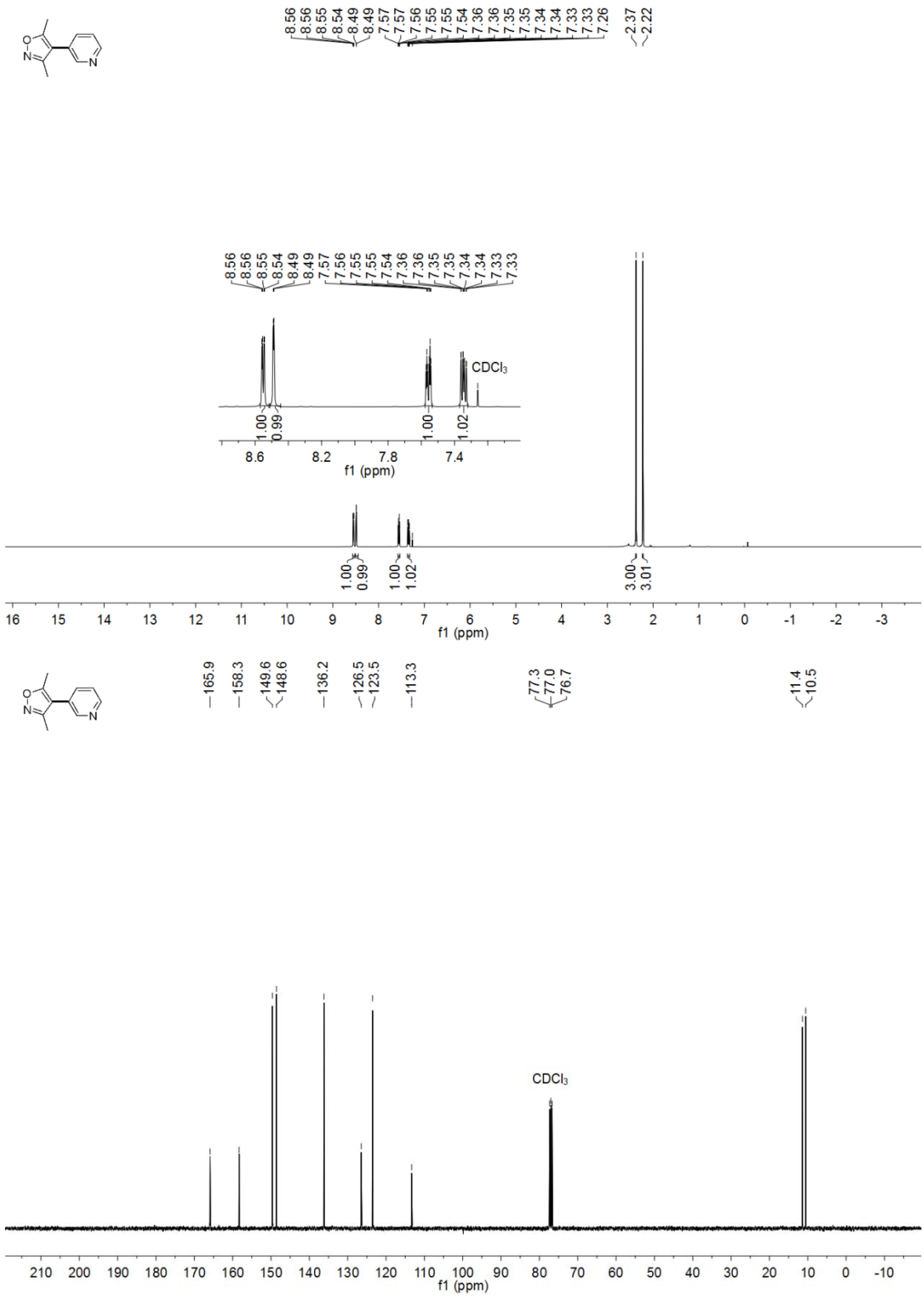


Figure **S81**.The NMR spectrums of **20e**

Figure **S82**.The NMR spectrums of **20f**

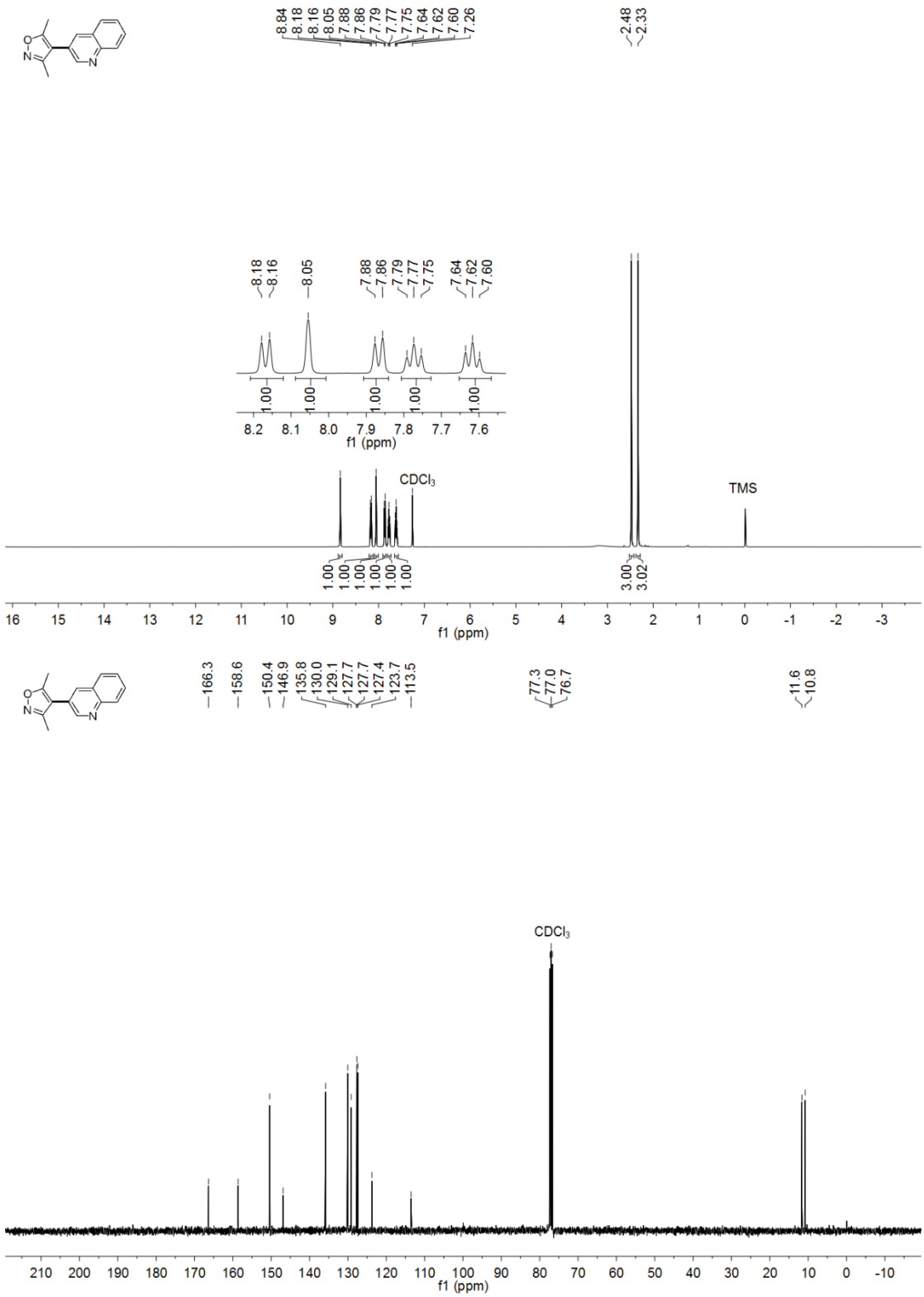


Figure **S83**.The NMR spectrums of **20k**

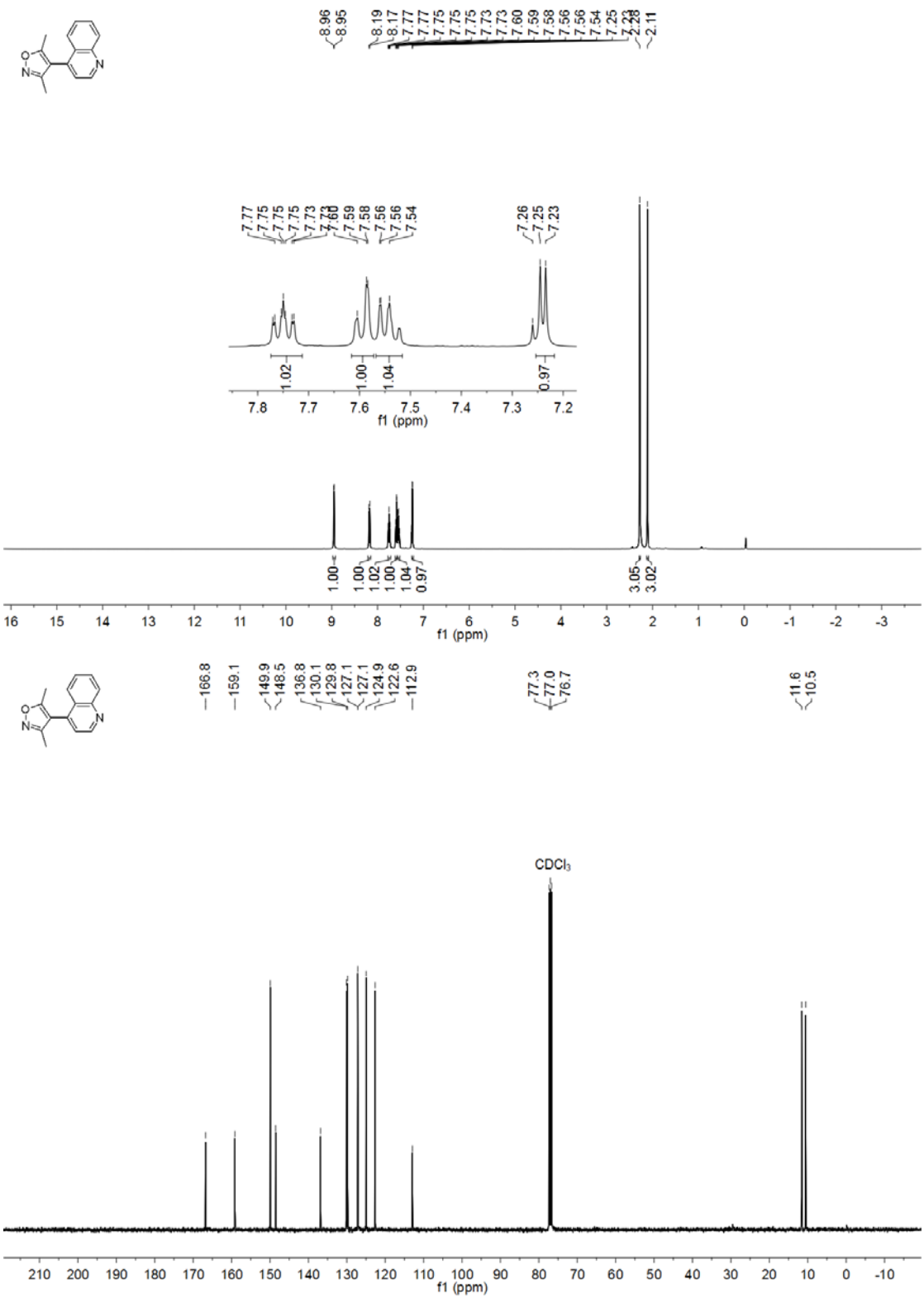


Figure **S84**.The NMR spectrums of **20l**

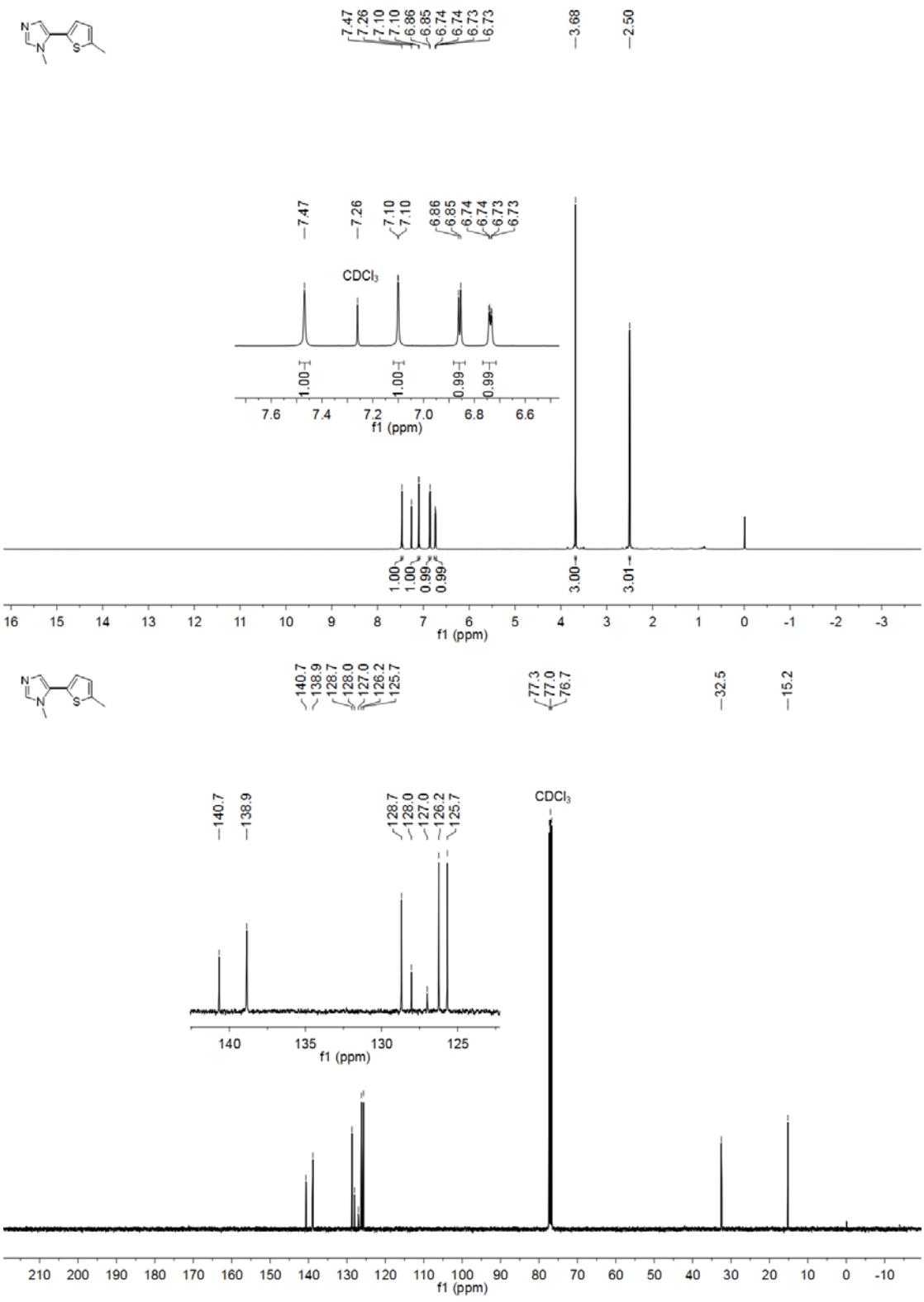


Figure **S85**.The NMR spectrums of **21c**

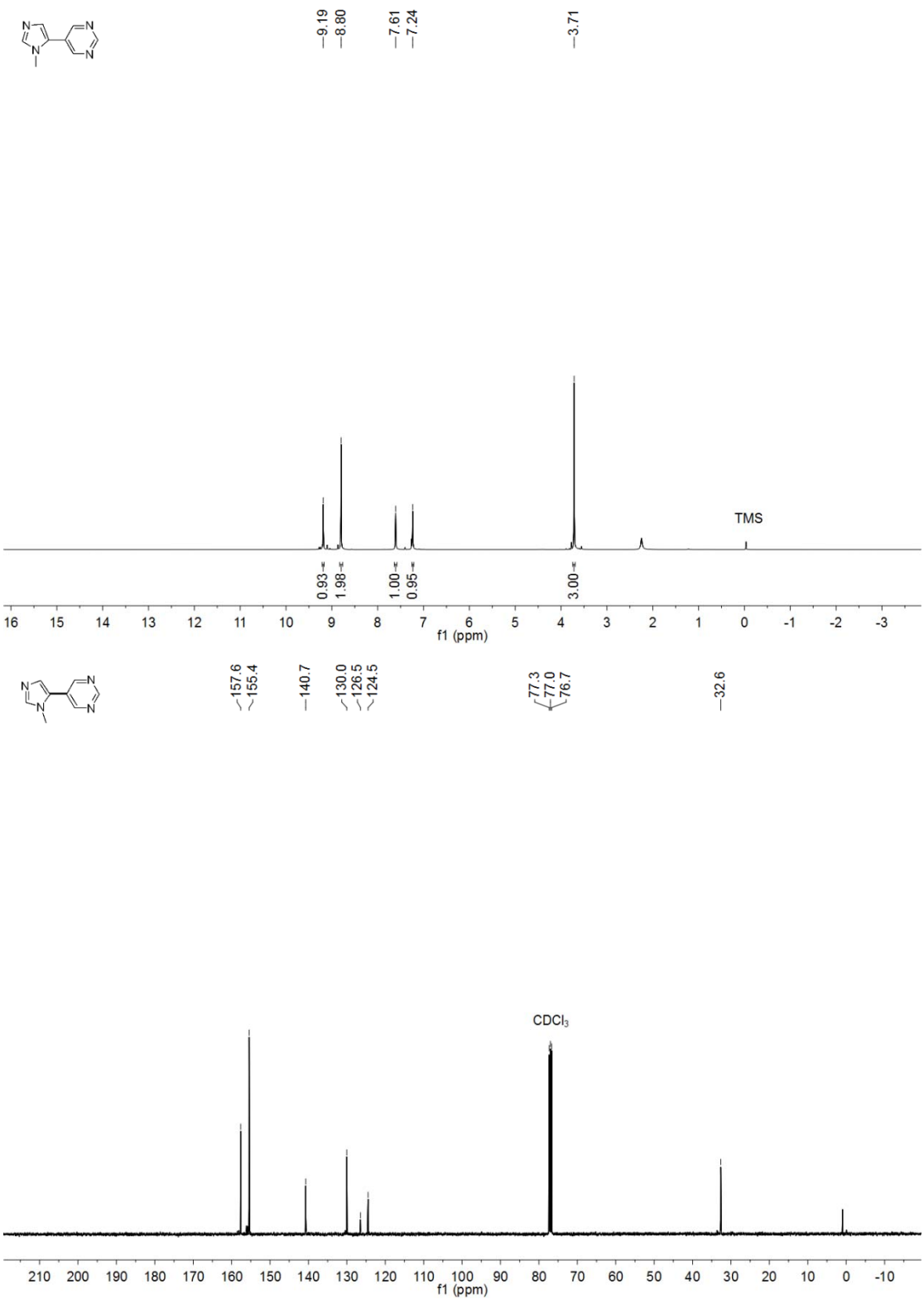


Figure **S86**.The NMR spectrums of **21j**

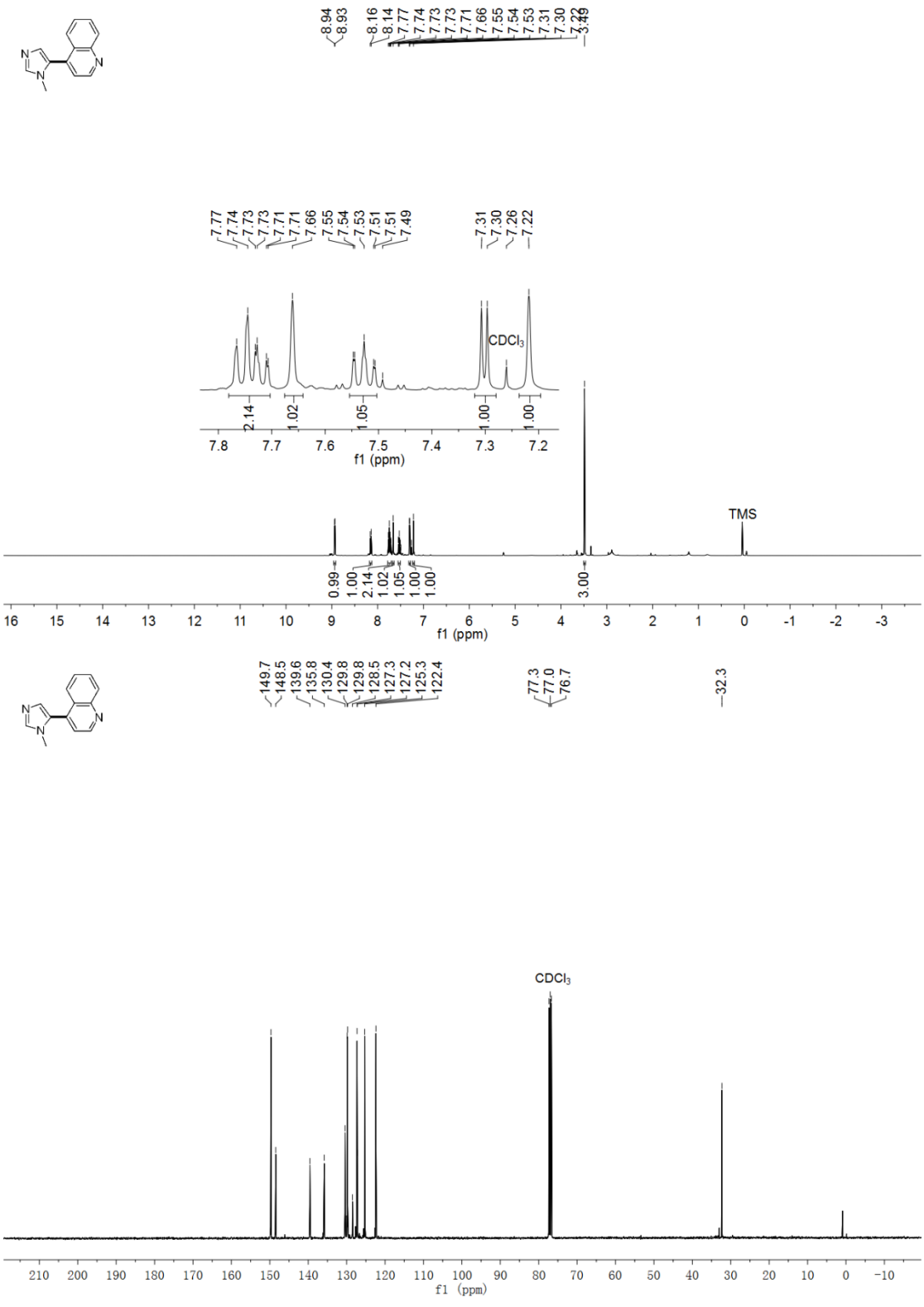


Figure **S87**.The NMR spectrums of **21l**

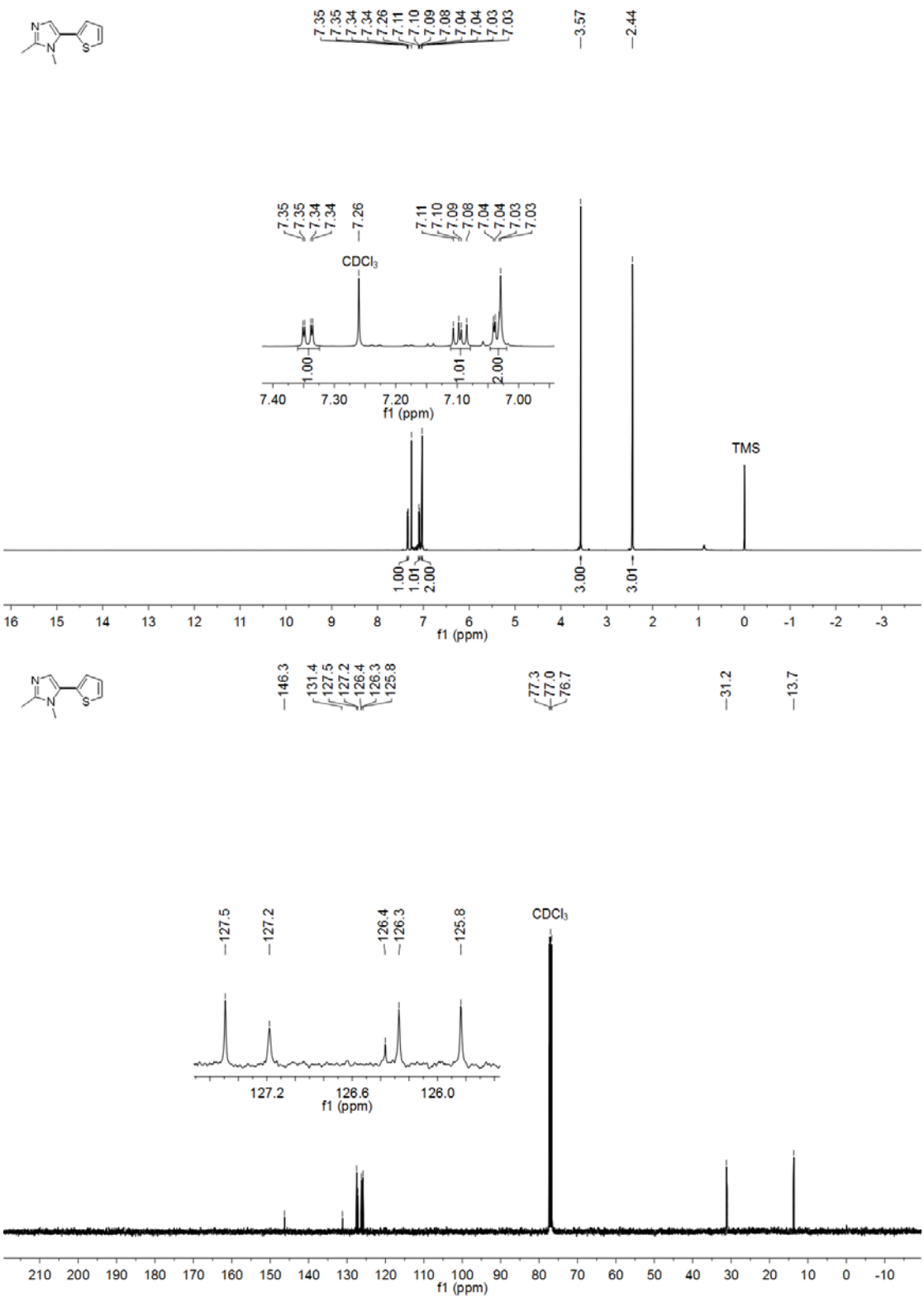


Figure **S88**.The NMR spectrums of **22b**

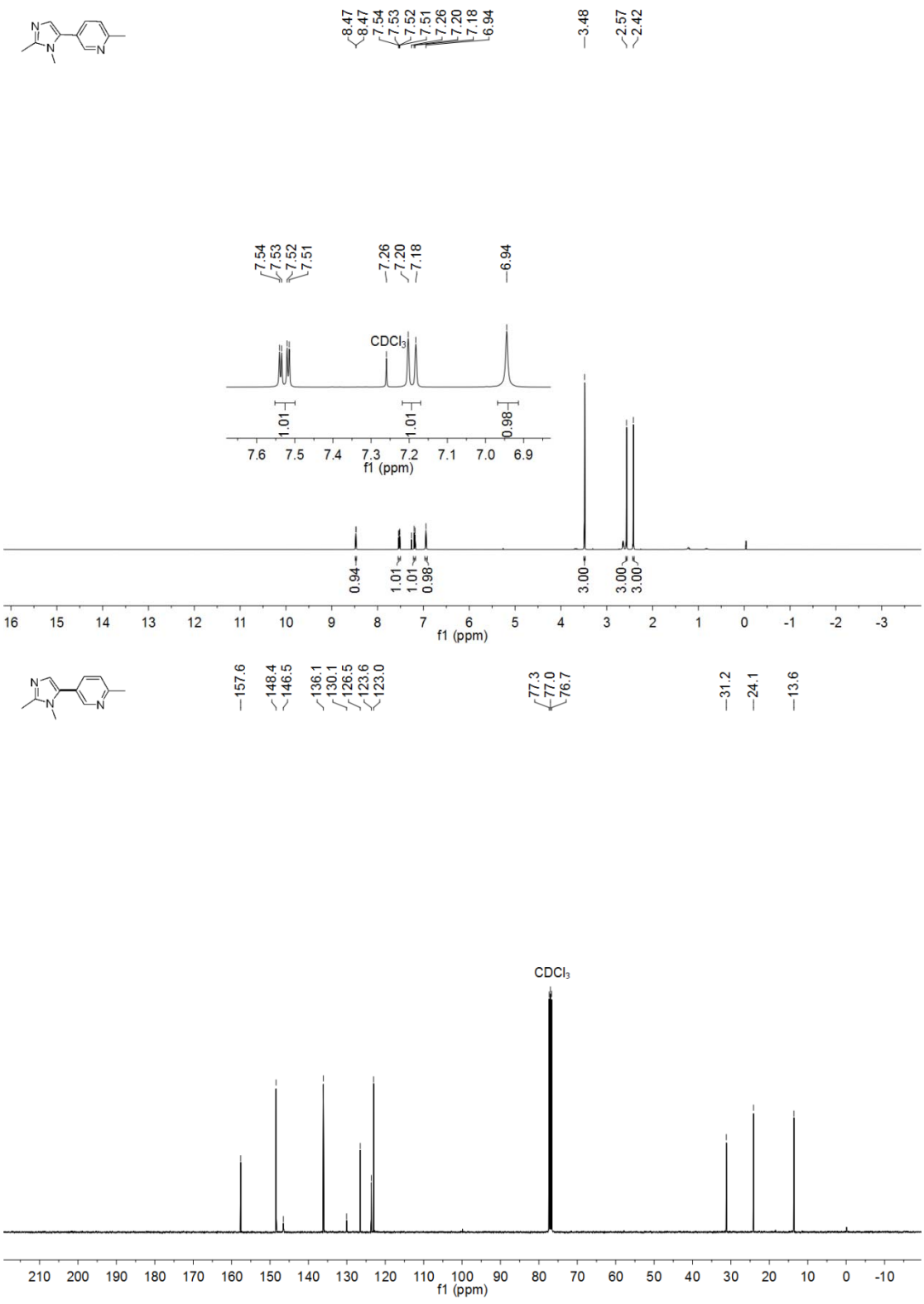


Figure **S89**.The NMR spectrums of **22f**

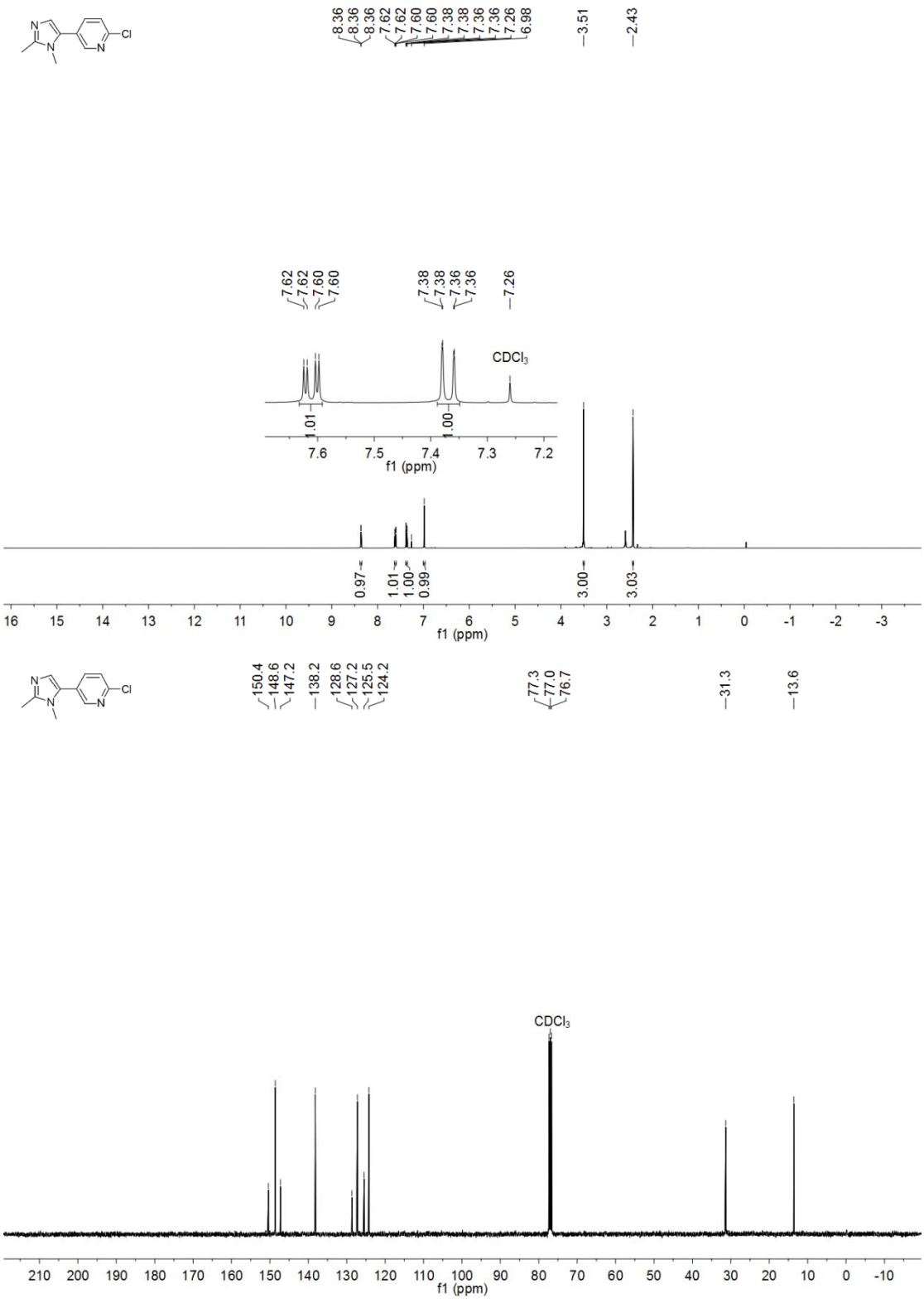


Figure **S92**.The NMR spectrums of **22i**

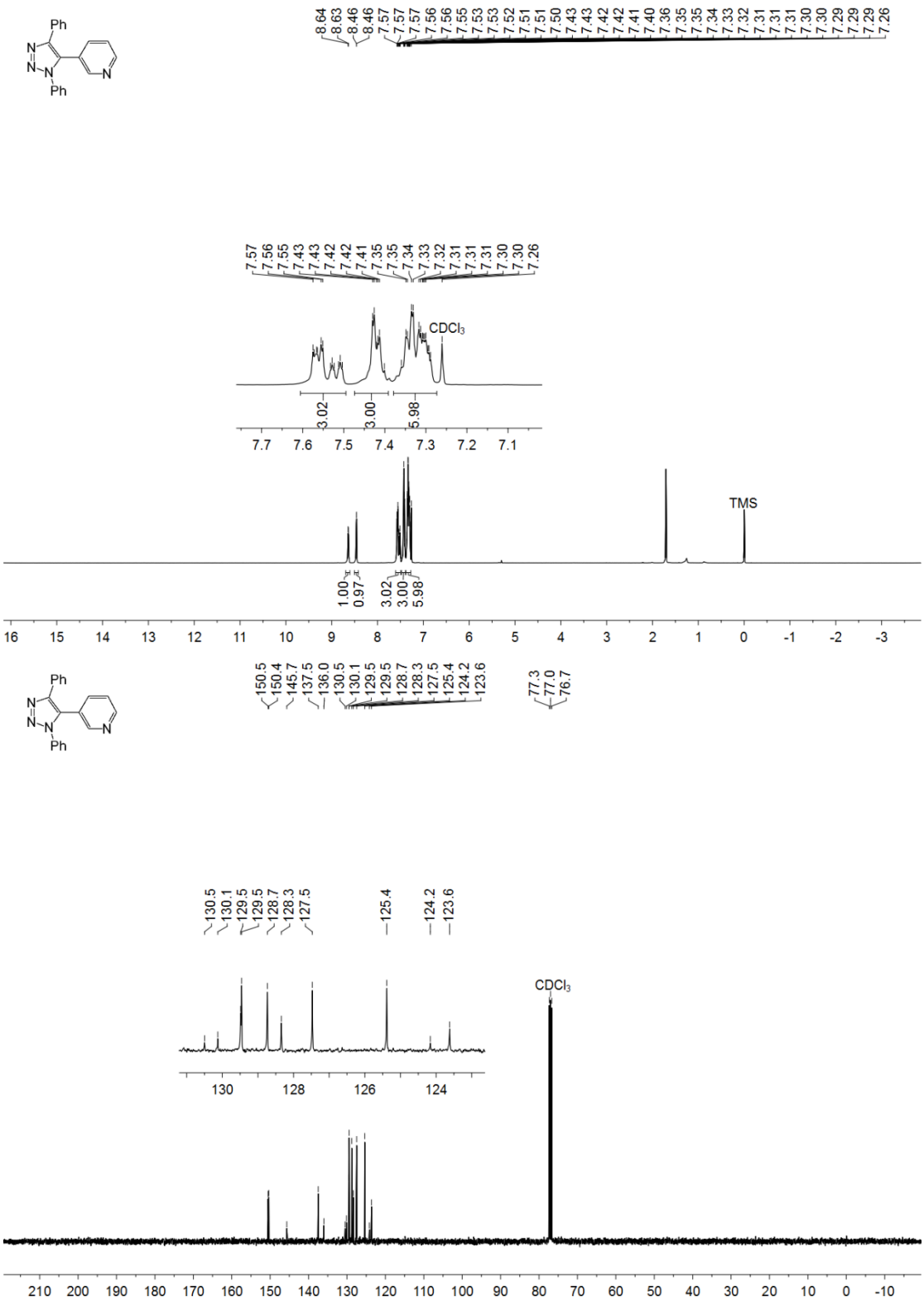


Figure **S91**.The NMR spectrums of **23e**

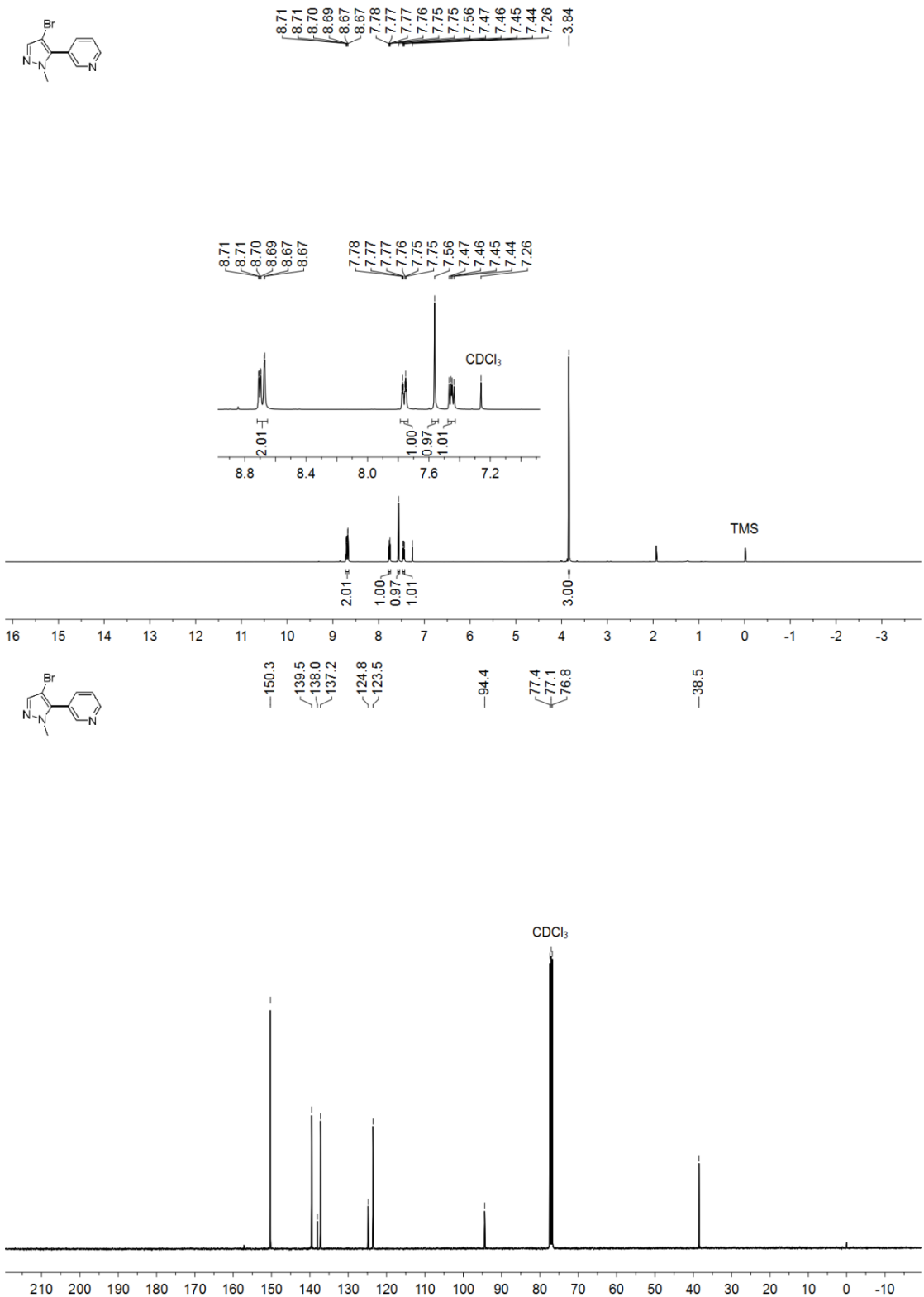
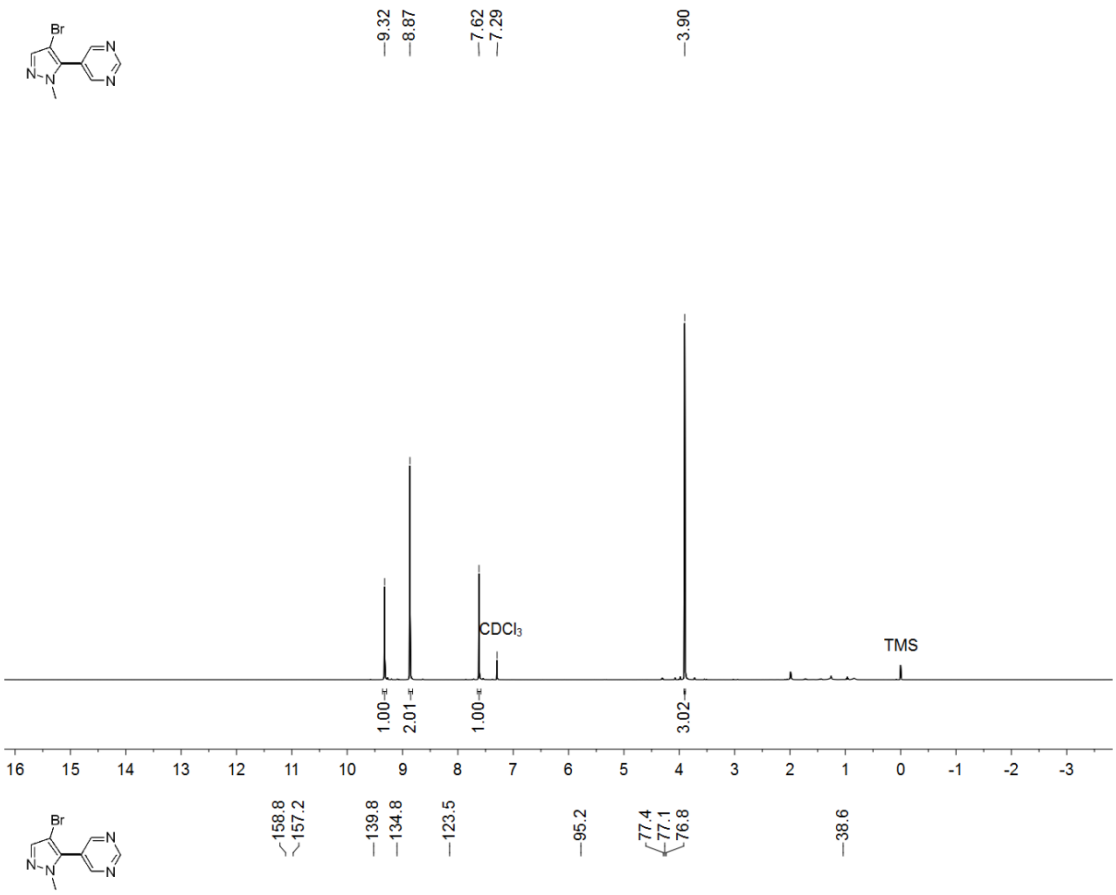


Figure **S92**.The NMR spectrums of **24e**



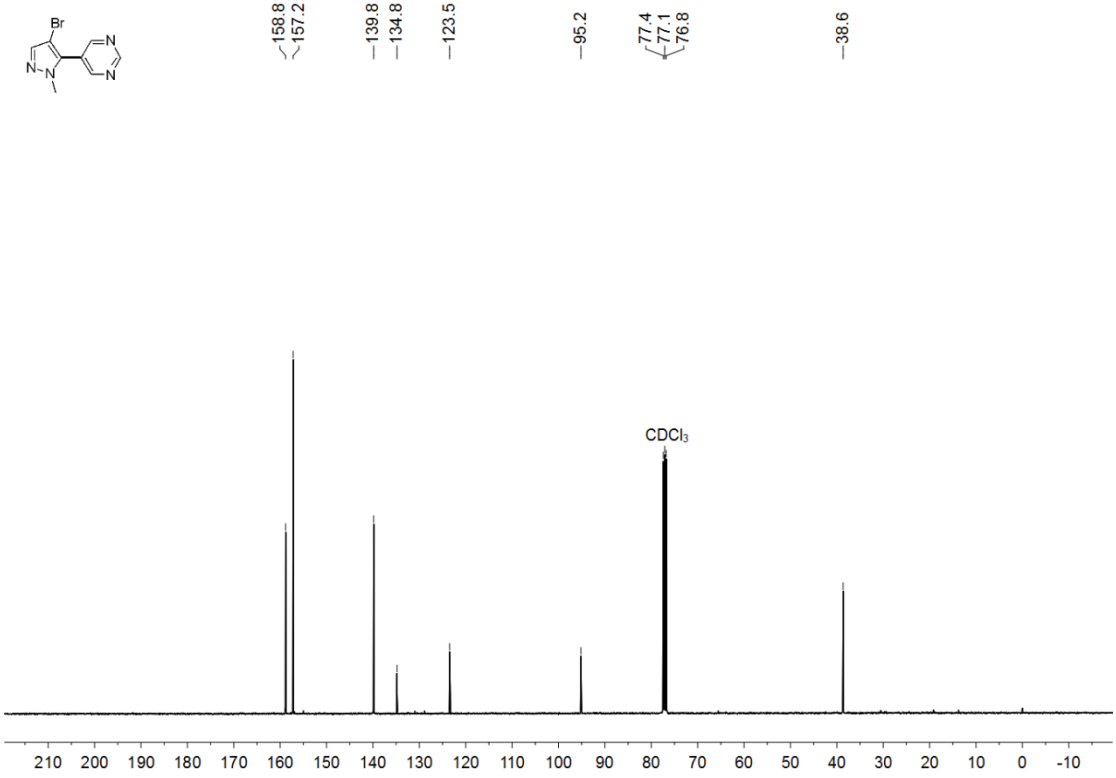


Figure **S93**.The NMR spectrums of **24j**

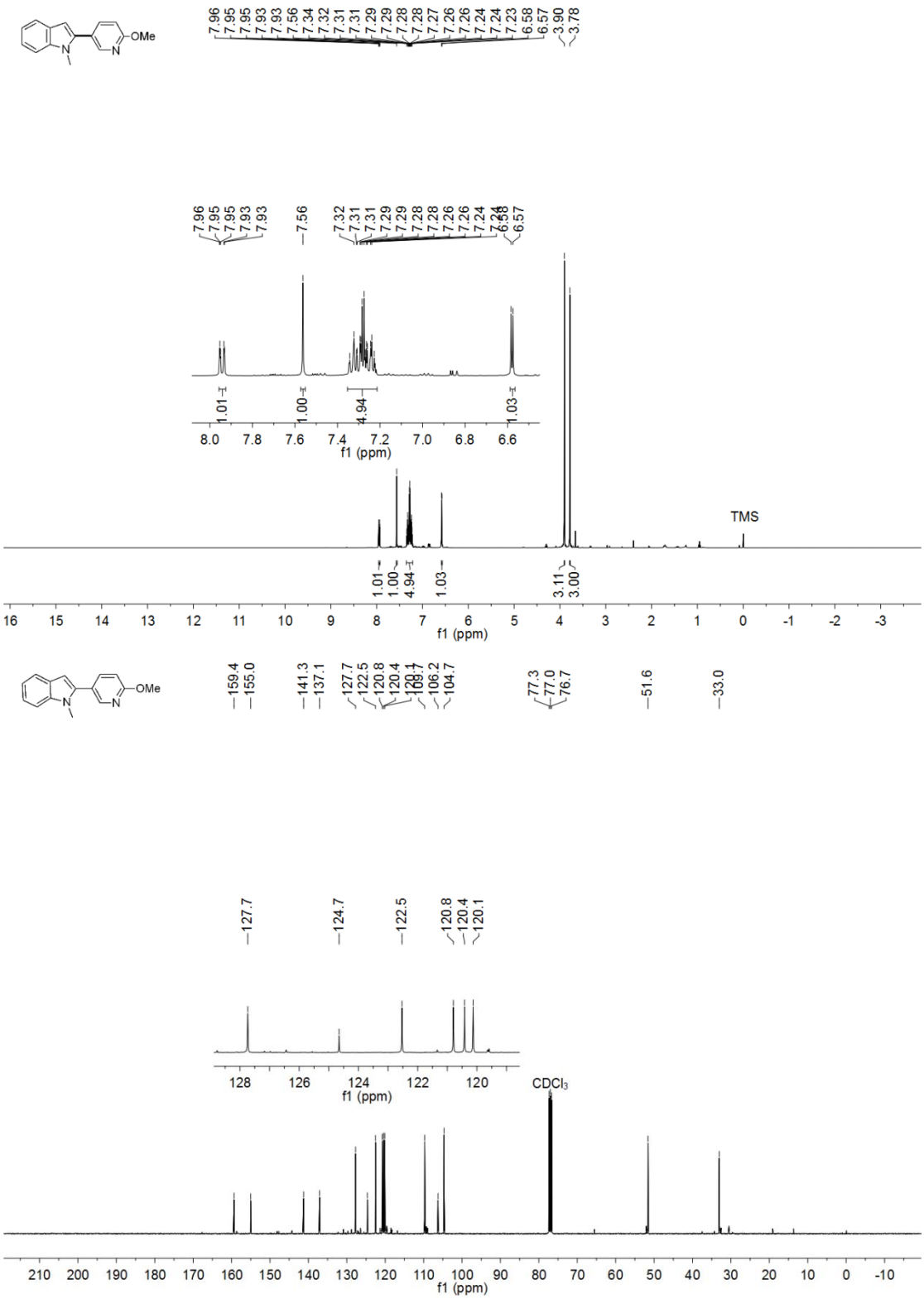


Figure **S94**.The NMR spectrums of **25g**

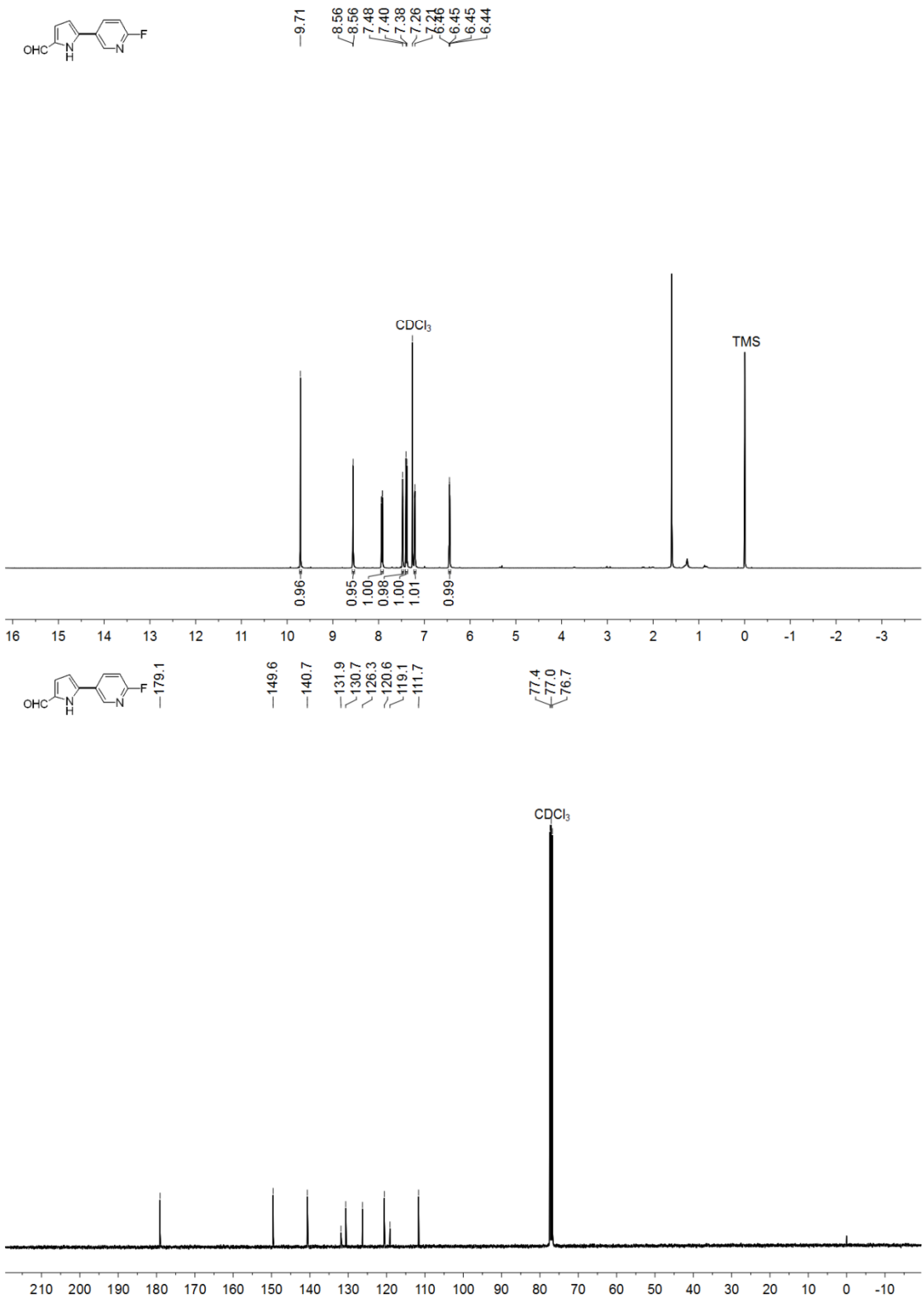


Figure **S95**.The NMR spectrums of **26h**

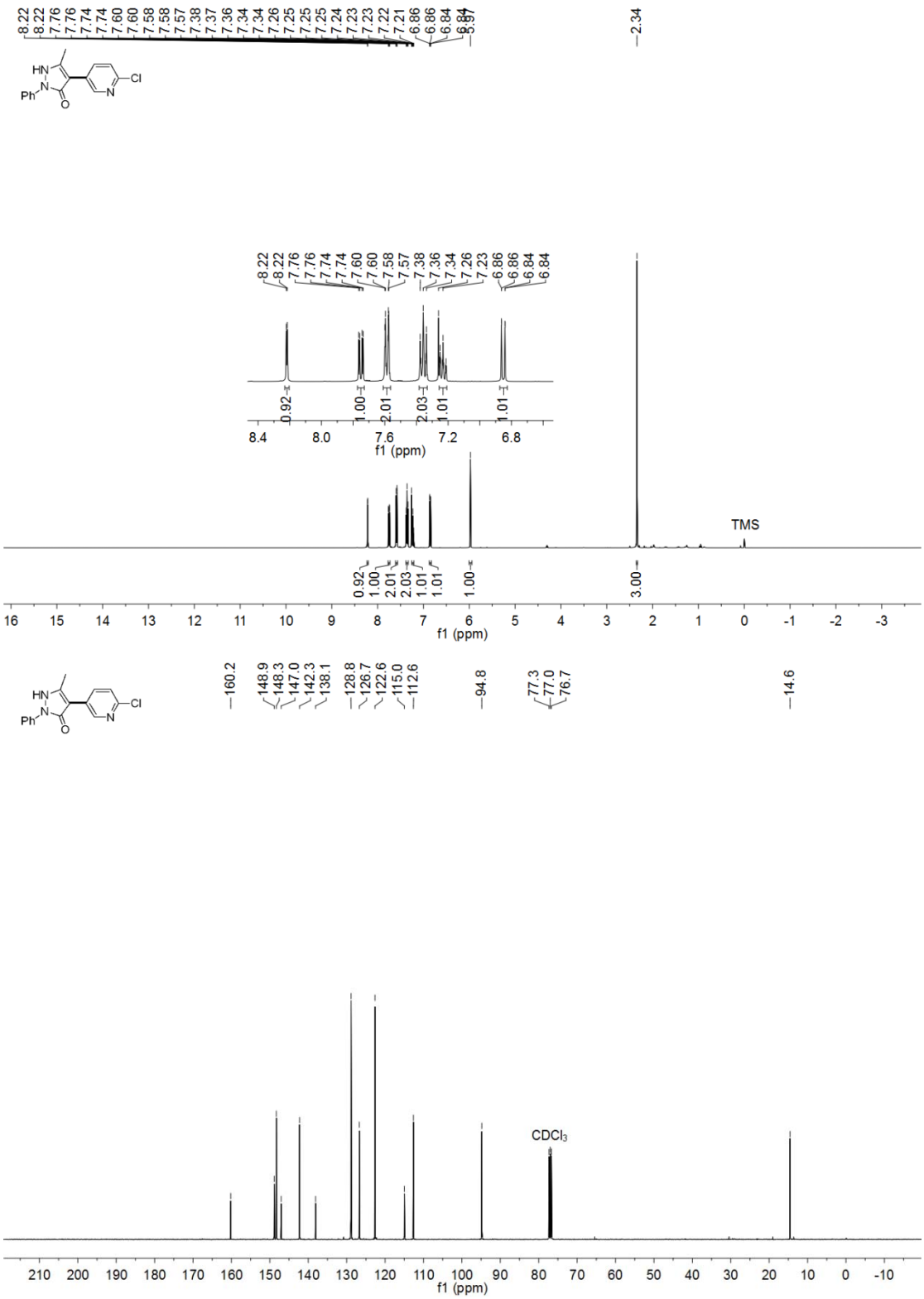


Figure **S96**.The NMR spectrums of **27i**