Supporting Information

Rigid hindered N-heterocyclic carbene palladium precatalysts: synthesis, characterization and catalytic amination

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Contents

1. Physical Measurements and Materials

The NMR spectra were recorded on a Bruker DMX 400 MHz instrument at room temperature with the decoupled nucleus, employing TMS as an internal standard and $CDCl_3$ as solvent. Elemental analysis was carried out using a Flash EA1112 microanalyzer. The X-ray diffraction data of single crystals were obtained with the ω-2θ scan mode on a Bruker SMART 1000 CCD diffractionmeter with graphite-monochromated Mo Kα radiation (λ=0.71073Å) at 173K for **C1** and **C3**. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

2. Experimental Procedure

General Procedures for the Synthesis of α-Diimine Compounds (2a-b). α-Ketoimine (5 mmol) and 2, 6-dibenzhydryl-4-methylaniline (5 mmol) were mixed in toluene (20 mL) with the presence of a catalytic amount of para-toluenesulfonic acid under nitrogen atmosphere, and then the reaction was heated to 110 °C for 16 h. When having reached the determined time, the solution was cooled to room temperature, and the solvent was evaporated. The rude material was crystallized from ethanol or purified by column chromatography as yellow crystals.

[2, 6-$(CHPh_2)_2$-4-(CH_3)-C_6H_2-N =C-(An)-(An)-C=N-2, 6-$(CHPh_2)_2$-4-(CH_3)-C_6H_2] (2a). **2a** was received as yellow powder (4.153 g) in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, Ar-H, 2H), 7.17 – 7.03 (m, Ar-H, 20H), 6.91 (s, Ar-H, 4H), 6.86 (s, Ar-H, 10H), 6.65 (s, Ar-H, 12H), 6.12 (d, *J* = 7.0 Hz, Ar-H, 2H), 5.69 (s, *CH*$(Ph)_2$, 4H), 2.29 (s, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 146.6, 143.8, 142.6, 139.8, 132.6, 131.5, 129.7, 129.5, 128.0, 127.7, 126.5, 125.9, 125.7, 124.2, 51.4, 21.5. HRMS calcd for $C_{78}H_{60}N_2$ $[M+ H]^+$ 1025.4835, found 1025.4838.

[2,6-$(CHPh_2)_2$-4-(OCH_3)-C_6H_2-N=C-(An)-(An)-C=N-2,6-$(CHPh_2)_2$-4-(OCH_3)-C_6H_2] (2b). 2b was received as orange powder (4.124 g) in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, Ar-H, 2H), 7.18 – 7.06 (m, Ar-H, 20H), 6.88 (m, Ar-H, 10H), 6.69 (s, Ar-H, 4H), 6.65 (d, *J* = 3.1 Hz, Ar-H, 12H), 6.16 (d, *J* = 7.1 Hz, Ar-H, 2H), 5.70 (s, *CH*$(Ph)_2$, 4H), 3.67 (s, Ar-OCH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 155.6, 143.5, 142.8, 142.3, 133.0, 129.7, 129.4, 128.0, 127.8, 126.6, 126.1, 125.8, 124.2, 114.5, 55.2, 51.5. HRMS calcd for $C_{78}H_{60}N_2O_2$ $[M+ H]^+$ 1057.4733, found 1057.4731.

General Procedures for the Synthesis of Imidazolium Salts. α-Diimine compounds (1 mmol) and chloromethyl ethyl (3 mL) ether were combined under a nitrogen atmosphere, and then the reaction was heated to 100 °C for 24 h. When having reached the determined time, the solution was cooled to room temperature, and the reaction mixture was treated with anhydrous Et_2O and stirred to form a large portion of precipitate. The solid was isolated by filtration and washed with anhydrous Et_2O

three times. The imidazolium salts was finally obtained after filtration.

$[(IPr^*)^{An}]^+Cl^-$ (L1). L1 was obtained as yellowish powder (0.923 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.40 (s, NC*H*N, 1H), 7.63 (d, *J* = 8.2 Hz, Ar-H, 2H), 7.16 (s, Ar-H, 16H), 7.00 (d, *J* = 11.2 Hz, Ar-H, 10H), 6.73 (m, Ar-H, 12H), 6.61 (d, *J* = 7.1 Hz, Ar-H, 8H), 6.24 (d, *J* = 6.9 Hz, Ar-H, 2H), 5.26 (s, *CH*$(Ph)_2$, 4H), 2.30 (s, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 141.6, 141.0, 140.7, 137.7, 131.3, 130.8, 129.7, 129.5, 128.8, 128.6, 128.1, 126.8, 126.7, 126.6, 123.1, 51.6, 22.0. HRMS calcd for $C_{79}H_{61}N_2$ $[M-Cl]^+$ 1037.4829, found 1037.4813.

$[(IPr^{OMe*})^{An}]^+Cl^-$ (L2). **L2** was obtained as yellowish powder (0.907 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.09 (s, NC*H*N, 1H), 7.65 (d, *J* = 8.0 Hz, Ar-H, 2H), 7.16 (d, *J* = 16.8 Hz, Ar-H, 16H), 7.02 (d, *J* = 7.5 Hz, Ar-H, 6H), 6.79 – 6.67 (m, Ar-H, 16H), 6.63 (d, *J* = 7.1 Hz, Ar-H, 8H), 6.29 (d, *J* = 6.9 Hz, Ar-H, 2H), 5.24 (s, *CH*$(Ph)_2$, 4H), 3.62 (s, Ar-OCH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 143.0, 141.3, 140.5, 137.9, 129.6, 129.4, 129.2, 128.6, 128.3, 128.1, 127.0, 126.7, 124.6, 123.1, 115.7, 55.4, 51.8. HRMS calcd for $C_{79}H_{61}N_2O_2$ $[M-Cl]^+$ 1069.4728, found 1069.4751.

General Procedures for the Synthesis of Pd-PEPPSI Compounds. $PdCl_2$ (177 mg, 1.0 mmol), imidazolium salt (1.0 mmol), K_2CO_3 (1382 mg, 10 mmol), and pyridine or 3-chloropyridine (5.0 mL) was stirred at 80 °C for 24 h under a nitrogen atmosphere. When cooling to room temperature, the reaction mixture was diluted in CH_2Cl_2 and passed through a pad of silica covered with Celite eluted with CH_2Cl_2. The solvents were removed under reduced pressure to furnish the desired product, which was recrystallized in a DCM/ n-hexane. The pure palladium complex was finally obtained after filtration to give yellowish products.

[Pd(IPr*)^{An}PdCl$_2$(pyridinyl)] (**C1**). **C1** was obtained as yellow powder (0.856 g, 66%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.26 (d, *J* = 5.0 Hz, Ar-H, 2H), 7.80 (m, Ar-H, 1H), 7.38 (m, Ar-H, 2H), 7.23 (d, *J* = 4.3 Hz, Ar-H, 8H), 7.19 (s, Ar-H, 4H), 7.10 (m, Ar-H, 12H), 6.60 – 6.49 (m, Ar-H, 10H), 6.45 (d, *J* = 7.3 Hz, Ar-H, 8H), 6.36 (m, Ar-H, 8H), 5.30 (s, *CH*(Ph)$_2$, 4H), 2.36 (s, CH$_3$, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 152.2, 145.8, 142.1, 141.5, 140.8, 138.4, 135.7, 131.9, 130.6, 129.6, 128.0, 127.5, 127.0, 126.2, 125.9, 125.6, 125.4, 124.2, 121.3, 50.9, 21.8. Anal. calcd for $C_{84}H_{65}Cl_2N_3Pd$: C, 77.98; H, 5.06; N, 3.25. Found: C, 77.43; H, 4.92; N, 3.14.

[Pd(IPr*)^{An}PdCl$_2$**(3-Cl-pyridinyl)]** (**C2**)**. C2** was obtained as yellow powder (0.811 g, 61%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.26 (dd, *J* = 8.9, 7.7 Hz, Ar-H,4H), 7.94 (dd, *J* = 8.4, 6.4 Hz, Ar-H,4H), 7.50 (d, *J* = 2.4 Hz, Ar-H,2H), 7.49 – 7.46 (m, Ar-H,6H), 7.44 – 7.39 (m, Ar-H,4H), 7.29 (dd, *J* = 10.9, 3.9 Hz, Ar-H,10H), 7.11 (d, *J* = 7.2 Hz, Ar-H,8H), 7.04 (s, Ar-H,4H), 6.84 (t, *J* = 7.7 Hz, Ar-H,8H), 6.67 (t, *J* = 7.4 Hz, Ar-H,4H), 6.38 (d, *J* = 7.0 Hz, Ar-H, 2H), 5.68 (s, CH, 4H), 2.50 (s, CH$_3$, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 162.3, 145.8, 142.9, 142.4, 141.7, 133.1, 131.8, 131.7, 129.9, 129.8, 129.6, 129.4, 128.6, 128.3, 128.1, 127.7, 127.5, 127.1, 126.9, 126.1, 125.4, 123.8, 121.4, 52.1, 21.5. HRMS calcd for $C_{79}H_{61}N_2$, $[M-C_5H_4NCl_3Pd]^+$ 1037.4829, found 1037.4830.

[Pd(IPr^{OMe}*)^{An}PdCl$_2$(pyridinyl)] (**C3**). **C3** was obtained as yellow powder (0.783 g, 59%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.27 (d, *J* = 5.0 Hz, Ar-H, 2H), 7.82 (m, Ar-H, 1H), 7.46 – 7.34 (m, Ar-H, 2H), 7.23 (s, Ar-H, 4H), 7.16 – 7.03 (m, Ar-H, 15H), 6.90

(s, Ar-H, 4H), 6.55 (m, Ar-H, 11H), 6.46 (d, *J* = 7.3 Hz, Ar-H, 8H), 6.36 (m, Ar-H, 8H), 5.68 (s, *CH*(Ph)$_2$, 4H), 3.69 (s, Ar-OCH$_3$, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.8, 152.1, 145.5, 144.0, 141.2, 131.2, 130.6, 129.6, 129.4, 128.0, 127.8, 127.6, 127.0, 126.2, 126.0, 125.7, 124.3, 121.3, 116.6, 55.2, 51.1. HRMS calcd for $C_{79}H_{61}N_2O_2$, [M-$C_5H_5NCl_2Pd$]$^+$ 1069.4728, found 1069.4718.

[Pd(IPr^{OMe}*)^{An}PdCl$_2$(3-Cl-pyridinyl)] (**C4**). **C4** was obtained as yellow powder (0.775 g, 57%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 (d, *J* = 8.2 Hz, Ar-H, 2H), 7.20 – 7.06 (m, Ar-H, 20H), 6.93 – 6.83 (m, Ar-H, 10H), 6.74 – 6.59 (m, Ar-H, 16H), 6.17 (d, *J* = 7.1 Hz, Ar-H, 2H), 5.70 (s, CH, 4H), 5.29 (s, Ar-H, 2H), 3.67 (s, OCH$_3$, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 164.2, 155.6, 143.4, 142.7, 142.2, 139.8, 133.0, 129.7, 129.4, 129.3, 128.4, 128.0, 128.0, 127.8, 126.6, 126.1, 125.8, 124.2, 114.4, 99.9, 55.2, 51.5. HRMS calcd for $C_{79}H_{61}N_2O_2$, [M-$C_5H_4NCl_3Pd$]$^+$ 1069.4728, found 1069.4735.

General Procedures for the Synthesis of Ir-(NHCs)(Cl)(CO)$_2$ Compounds.

A mixture of imidazolium salt **L1** or **L2** (0.2 mmol), [Ir(COD)Cl]$_2$ (0.1 mmol), and K_2CO_3 (0.6 mmol) in acetone (8 mL) was stirred at 60 °C for 20 h. When the determined time was reached, the solution cooled to room temperature; 15 mL of dichloromethane was added, and stirred under 1 atm CO gas for 1 h. Then the reaction mixture was placed on a short silica gel column and washed with substantial dichloromethane. Evaporating solvent under reduced pressure provided **Ir-1** in 31%, and **Ir-2** in 37% yield, respectively.

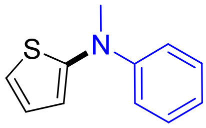
Ir-1 [**Ir(IPr^{*An})(Cl)(CO)$_2$**]. ^{1}H NMR (400 MHz, DMSO) δ 7.43 – 7.02 (m, 30H), 6.70 – 6.33 (m, 20H), 5.82 (s, 4H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 179.70, 167.67, 144.53, 143.52, 141.44, 141.03, 140.67, 140.11, 139.17, 133.94, 130.89, 129.87, 128.92, 127.49, 126.18, 123.47, 121.42, 50.89, 21.38. HRMS calcd for $C_{81}H_{60}IrN_2O_2$ [M-Cl]$^+$ 1285.4287, found 1285.4290.

Ir-2 [**Ir(IPr^{OMe*An})(Cl)(CO)$_2$**]. ^{1}H NMR (400 MHz, DMSO) δ 7.81 (d, J = 8.2 Hz, 2H), 7.19 (t, J = 5.1 Hz, 12H), 7.16 – 7.11 (m, 2H), 7.05 – 7.00 (m, 8H), 6.85 – 6.73 (m, 20H), 6.63 (s, 4H), 6.22 (d, J = 7.1 Hz, 2H), 5.48 (s, 4H), 3.61 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 163.42, 156.87, 155.18, 142.83, 141.95, 139.51, 131.83, 128.95, 128.68, 128.31, 127.87, 126.38, 126.01, 123.43, 113.80, 54.92, 51.15. HRMS calcd for $C_{79}H_{60}N_2O_2$ [M-Cl-2CO-Ir]$^+$ 1069.4683, found 1069.4690.

General Procedure for Buchwald−Hartwig Amination Reactions. Unless otherwise noted, the C–N amination reactions were carried out under aerobic conditions. All solvents were used as received and no further purification was needed. (Hetero)Aryl chlorides (1.0 mmol), (heterocyclic) aryl amine compounds (1.2 mmol), Pd-PEPPSI complexes (2−0.05 mol %), base (2 mmol)，and 4 mL of solvent were added into a parallel reactor and stirred at 100 °C for 2 h. After completion of the reaction, the reaction mixture was cooled to ambient temperature, and 20 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.

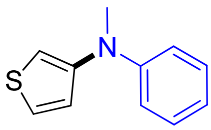
3. NMR data for the products

N-methyl-N-phenylthiophen-2-amine (5a, 167 mg, 88%**)**[1]



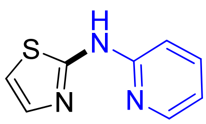
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, Ar-H, 3H), 7.10 – 7.05 (m, Ar-H, 2H), 7.00 – 6.92 (m, Ar-H, 2H), 6.63 (dd, *J* = 3.0, 1.4 Hz, Ar-H, 1H), 3.35 (s, CH_3 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 148.3, 129.0, 124.9, 123.2, 120. 7, 118.8, 107.7, 40.9.

N-methyl-N-phenylthiophen-3-amine (5b, 142 mg, 75%**)**[2]



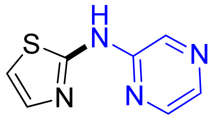
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, Ar-H, 3H), 7.08 (d, *J* = 7.8 Hz, Ar-H, 2H), 7.00 – 6.93 (m, Ar-H, 2H), 6.63 (dd, *J* = 3.1, 1.4 Hz, Ar-H, 1H), 3.35 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 148.3, 129.0, 124.8, 123.2, 120.7, 118.8, 107.7, 40.9.

N-(pyridin-2-yl)thiazol-2-amine (5c, 76 mg, 43%**)**[3]



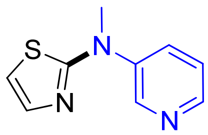
^{1}H NMR (400 MHz, DMSO) δ 11.30 (s, NH, 1H), 8.28 (ddd, *J* = 5.1, 1.9, 0.9 Hz, Ar-H, 1H), 7.68 (ddd, *J* = 8.4, 7.2, 1.9 Hz, Ar-H, 1H), 7.37 (d, *J* = 3.6 Hz, Ar-H, 1H), 7.08 (dt, *J* = 8.4, 0.9 Hz, Ar-H, 1H), 6.98 (d, *J* = 3.6 Hz, Ar-H, 1H), 6.89 (ddd, *J* = 7.2, 5.1, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 159.8, 151.9, 146.5, 137.8, 137.5, 115.8, 110.9, 110.7.

N-(pyrazin-2-yl)thiazol-2-amine (5d, 103 mg, 58%**)**



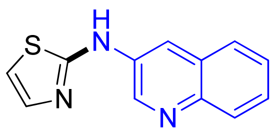
^{1}H NMR (400 MHz, DMSO) δ 8.51 (s, Ar-H, 1H), 8.36 – 8.26 (m, Ar-H, 1H), 8.12 (d, *J* = 2.7 Hz, Ar-H, 1H), 7.47 (d, *J* = 3.6 Hz, Ar-H, 1H), 7.12 (d, *J* = 3.6 Hz, Ar-H, 1H). ^{13}C NMR (101 MHz, DMSO) δ 159.1, 148.6, 140.5, 137.7, 135.2, 134.9, 111.7. **HRMS calcd for $C_7H_6N_4S$ [M-H]$^+$ 177.0235, found 177.0241.**

N-methyl-N-(pyridin-3-yl)thiazol-2-amine (5e, 119 mg, 62%**)**



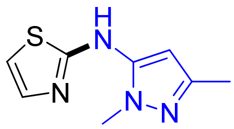
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 2.4 Hz, Ar-H, 1H), 8.47 (dd, *J* = 4.7, 1.4 Hz, Ar-H, 1H), 7.82 (ddd, *J* = 8.3, 2.7, 1.5 Hz, Ar-H, 1H), 7.35 (ddd, *J* = 8.3, 4.7, 0.7 Hz, Ar-H, 1H), 7.26 (t, *J* = 1.8 Hz, Ar-H, 2H), 6.61 (d, *J* = 3.6 Hz, Ar-H, 1H), 3.56 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 146.6, 145.9, 142.6, 139.6, 131.6, 123.9, 108.6, 40.5. **HRMS calcd for $C_9H_9N_3S$ [M+ H]$^+$ 192.0595, found 192.0591.**

N-(quinolin-3-yl)thiazol-2-amine (5f, 209 mg, 92%**)**



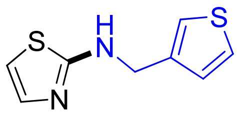
^{1}H NMR (400 MHz, DMSO) δ 10.77 (s, Ar-H, 1H), 8.86 (dd, *J* = 9.5, 2.4 Hz, Ar-H, 2H), 7.96 – 7.84 (m, Ar-H, 2H), 7.59 – 7.50 (m, Ar-H, 2H), 7.39 (d, *J* = 3.6 Hz, Ar-H, 1H), 7.04 (d, *J* = 3.6 Hz, NH, 1H).^{13}C NMR (101 MHz, DMSO) δ 163.3, 143.6, 143.0, 139.1, 135.0, 128.6, 128.4, 127.2, 127.1, 126.6, 117.2, 109.8. **HRMS calcd for $C_{12}H_9N_3S$ [M+ H]$^+$ 228.0595, found 228.0588.**

N-(1,3-dimethyl-1H-pyrazol-5-yl)thiazol-2-amine (5g, 165 mg, 85%**)**



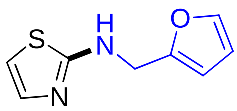
[1]H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 3.7 Hz, Ar-H, 1H), 6.59 (d, *J* = 3.7 Hz, Ar-H, 1H), 6.05 (s, Ar-H, 1H), 3.72 (s, CH_3, 3H), 2.26 (s, CH_3, 3H). [13]C NMR (101 MHz, $CDCl_3$) δ 168.4, 147.7, 140.1, 137.5, 108.3, 97.5, 34.8, 14.1. **HRMS calcd for $C_8H_{10}N_4S$ [M+ H]$^+$ 195.0704, found 195.0698.**

N-(thiophen-3-ylmethyl)thiazol-2-amine (5h, 185 mg, 94%**)**



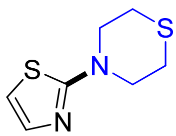
[1]H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 5.0, 3.0 Hz, Ar-H, 1H), 7.24 (ddd, *J* = 3.0, 2.1, 0.9 Hz, Ar-H, 1H), 7.09 (dd, *J* = 4.9, 1.3 Hz, Ar-H, 1H), 7.04 (d, *J* = 3.6 Hz, Ar-H, 1H), 6.49 (t, *J* = 3.9 Hz, Ar-H, 1H), 6.13 (s, NH, 1H), 4.47 (s, CH_2, 2H).[13]C NMR (101 MHz, $CDCl_3$) δ 170.1, 139.0, 138.5, 127.2, 126.4, 122.5, 106.7, 45.2. **HRMS calcd for $C_8H_8N_2S_2$ [M+ H]$^+$ 197.0207, found 197.0200.**

N-(furan-2-ylmethyl)thiazol-2-amine (5i, 168 mg, 93%**)**[4]



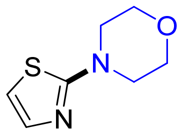
[1]H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 1.8, 0.8 Hz, Ar-H, 1H), 7.09 (d, *J* = 3.6 Hz, Ar-H, 1H), 6.50 (d, *J* = 3.6 Hz, Ar-H, 1H), 6.36 – 6.27 (m, Ar-H, 2H), 6.18 (s, NH, 1H), 4.47 (s, CH_2, 2H). [13]C NMR (101 MHz, $CDCl_3$) δ 169.7, 150.9, 142.3, 139.0, 110.7, 107.8, 106.9, 42.7.

4-(thiazol-2-yl)thiomorpholine (5j, 179 mg, 96%**)**



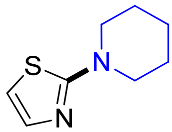
[1]H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 3.6 Hz, Ar-H, 1H), 6.55 (d, *J* = 3.6 Hz, Ar-H, 1H), 3.87 – 3.80 (m, CH_2, 4H), 2.73 – 2.67 (m, CH_2, 4H). [13]C NMR (101 MHz, $CDCl_3$) δ 171.4, 139.4, 107.3, 51.2, 26.2. **HRMS calcd for $C_7H_{10}N_2S_2$ [M+ H] $^+$ 187.0364, found 187.0360.**

4-(thiazol-2-yl)morpholine (5k, 109 mg, 64%**)**[5]



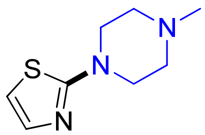
[1]H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 3.6 Hz, Ar-H, 1H), 6.59 (d, *J* = 3.6 Hz, Ar-H, 1H), 3.82 – 3.79 (m, CH_2, 4H), 3.45 (dd, *J* = 5.6, 4.3 Hz, CH_2, 4H). [13]C NMR (101 MHz, $CDCl_3$) δ 172.4, 139.5, 107.7, 66.1, 48.6.

2-(piperidin-1-yl)thiazole (5l, 163 mg, 97%**)**[26]



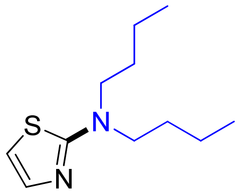
[1]H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 3.7 Hz, Ar-H, 1H), 6.49 (d, *J* = 3.7 Hz, Ar-H, 1H), 3.45 (dd, *J* = 7.0, 3.8 Hz, CH_2, 4H), 1.70 – 1.58 (m, CH_2, 6H). [13]C NMR (101 MHz, $CDCl_3$) δ 172.5, 139.4, 106.5, 49.7, 25.0, 24.1.

2-(4-methylpiperazin-1-yl)thiazole (5m, 179 mg, 98%**)**



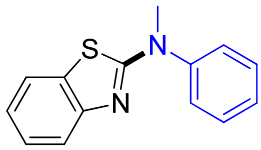
[1]H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 3.6 Hz, Ar-H, 1H), 6.56 (d, *J* = 3.6 Hz, Ar-H, 1H), 3.53 – 3.48 (m, CH_2, 4H), 2.54 – 2.49 (m, CH_2, 4H), 2.33 (s, CH_3, 3H). [13]C NMR (101 MHz, $CDCl_3$) δ 172.2, 139.5, 107.4, 54.2, 48.4, 46.1. **HRMS calcd for $C_8H_{13}N_3S$ [M+ H]$^+$ 184.0908, found 184.0902.**

N,N-dibutylthiazol-2-amine (5n, 204 mg, 96%**)**[6]



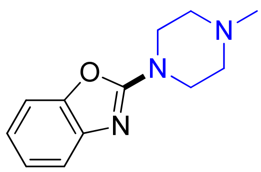
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.10 (m, Ar-H, 1H), 6.43 – 6.38 (m, Ar-H, 1H), 3.43 – 3.35 (m, CH_2, 4H), 1.66 – 1.57 (m, CH_2, 4H), 1.40 – 1.29 (m, CH_2, 4H), 0.94 (t, *J* = 7.4 Hz, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 139.5, 105.1, 51.4, 29.4, 20.1, 13.9.

N-methyl-N-phenylbenzo[d]thiazol-2-amine (5o, 197 mg, 82%**)**



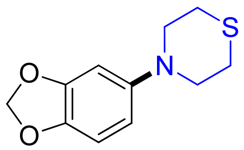
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (ddd, *J* = 8.1, 1.0, 0.5 Hz, Ar-H, 1H), 7.51 – 7.46 (m, Ar-H, 2H), 7.46 – 7.41 (m, Ar-H, 3H), 7.37 – 7.28 (m, Ar-H, 2H), 7.10 – 7.05 (m, Ar-H, 1H), 3.65 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 152.6, 145.8, 131.2, 129.9, 127.4, 126.0, 125.8, 121.7, 120.4, 119.2, 40.4. **HRMS calcd for $C_{14}H_{13}N_2S$ $[M+H]^+$ 241.0799, found 241.0793.**

2-(4-methylpiperazin-1-yl)benzo[d]oxazole (5p, 213 mg, 98%**)**[7]



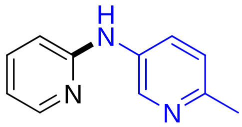
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.8, 0.6 Hz, Ar-H, 1H), 7.27 – 7.23 (m, Ar-H, 1H), 7.16 (td, *J* = 7.7, 1.1 Hz, Ar-H, 1H), 7.02 (td, *J* = 7.8, 1.2 Hz, Ar-H, 1H), 3.75 – 3.70 (m, CH_2, 4H), 2.55 – 2.50 (m, CH_2, 4H), 2.35 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 148.7, 143.0, 124.0, 120.7, 116.3, 108.7, 54.2, 46.2, 45.5.

4-(benzo[d][1,3]dioxol-5-yl)thiomorpholine (5q, 156 mg, 70%**)**



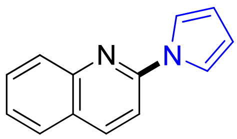
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, *J* = 8.4 Hz, Ar-H, 1H), 6.53 (d, *J* = 2.4 Hz, Ar-H, 1H), 6.36 (dd, *J* = 8.4, 2.4 Hz, Ar-H, 1H), 5.89 (s, CH_2, 2H), 3.36 – 3.31 (m, CH_2, 4H), 2.78 – 2.73 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 148.0, 141.9, 110.7, 108.2, 101.4, 100.9, 53.9, 27.6. **HRMS calcd for $C_{11}H_{13}NO_2S$ [M+ H]$^+$ 224.0745, found 224.0737.**

N-(6-methylpyridin-3-yl)pyridin-2-amine(5r, 91 mg, 49%**)**



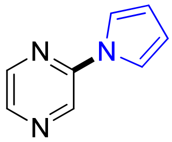
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.6 Hz, Ar-H, 1H), 8.23 – 8.15 (m, Ar-H, 1H), 7.80 (dd, *J* = 8.4, 2.7 Hz, Ar-H, 1H), 7.55 – 7.44 (m, Ar-H, 1H), 7.12 (d, *J* = 8.4 Hz, Ar-H, 1H), 6.82 – 6.65 (m, Ar-H, 3H), 2.52 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 152.4, 148.2, 141.6, 137.8, 134.6, 128.2, 123.2, 115.4, 108.6, 23.6. **HRMS calcd for $C_{11}H_{11}N_3$ [M+ H] $^+$ 186.1031, found 186.1026.**

2-(1H-pyrrol-1-yl)quinoline (5s, 188 mg, 97%**)**



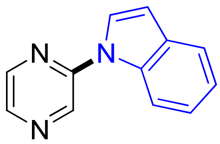
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, Ar-H, 1H), 8.01 (d, *J* = 8.5 Hz, Ar-H, 1H), 7.79 (dd, *J* = 8.1, 1.2 Hz, Ar-H, 1H), 7.75 – 7.68 (m, Ar-H, 3H), 7.54 – 7.44 (m, Ar-H, 2H), 6.48 – 6.37 (m, Ar-H, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 147.1, 138.9, 130.3, 128.5, 127.4, 126.2, 125.5, 118.4, 111.6, 111.6,. **HRMS calcd for $C_{13}H_{10}N_2$ [M+ H]$^+$ 195.0922, found 195.0917.**

2-(1H-pyrrol-1-yl)pyrazine (5t, 113 mg, 78%**)**



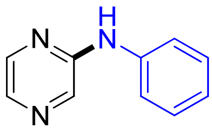
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 0.9 Hz, Ar-H, 1H), 8.40 – 8.35 (m, Ar-H, 2H), 7.55 – 7.51 (m, Ar-H, 2H), 6.44 – 6.39 (m, Ar-H, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 142.6, 140.5, 134.1, 117.9, 112.5. **HRMS calcd for $C_8H_7N_3$ [M+ H]$^+$ 146.0718, found 146.0713.**

1-(pyrazin-2-yl)-1H-indole (5u, 189 mg, 97%**)**[8]



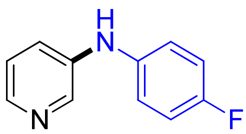
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 1.4 Hz, Ar-H, 1H), 8.51 (dd, *J* = 2.5, 1.5 Hz, Ar-H, 1H), 8.42 (d, *J* = 2.5 Hz, Ar-H, 1H), 8.29 (dd, *J* = 8.4, 0.8 Hz, Ar-H, 1H), 7.74 (d, *J* = 3.6 Hz, Ar-H, 1H), 7.70 – 7.65 (m, Ar-H, 1H), 7.34 (ddd, *J* = 8.4, 7.2, 1.2 Hz, Ar-H, 1H), 7.28 – 7.23 (m, Ar-H, 1H), 6.79 (dd, *J* = 3.6, 0.7 Hz, Ar-H, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 142.7, 140.0, 136.3, 135.0, 130.5, 124.9, 123.8, 122.1, 121.3, 113.3, 107.2.

N-phenylpyrazin-2-amine (5v, 130 mg, 76%**)**[9]



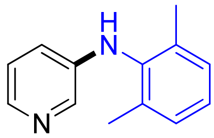
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 1.3 Hz, Ar-H, 1H), 8.10 (dd, *J* = 2.6, 1.5 Hz, Ar-H, 1H), 7.97 (d, *J* = 2.7 Hz, Ar-H, 1H), 7.45 – 7.33 (m, Ar-H, 4H), 7.10 (t, *J* = 7.3 Hz, Ar-H, 1H), 6.96 (s, NH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 141.9, 139.2, 134.7, 132.9, 129.3, 123.5, 120.3.

N-(4-fluorophenyl)pyridin-3-amine(5w, 184 mg, 98%**)**[27]



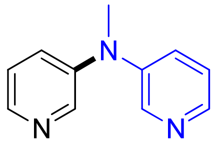
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, Ar-H, 1H), 8.09 (s, Ar-H, 1H), 7.26 (s, Ar-H, 1H), 7.02 (dd, J = 36.5, 20.9 Hz, Ar-H, 5H), 6.14 (s, NH, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4 (d, J = 241.3 Hz), 141.2, 140.7, 139.0, 137.7, 123.7, 122.2, 121.1 (d, J = 7.9 Hz), 116.1 (d, J = 22.6 Hz).

N-(2,6-dimethylphenyl)pyridin-3-amine(5x, 180 mg, 91%)[27]



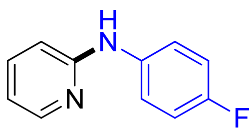
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, Ar-H, 2H), 7.16 – 7.08 (m, Ar-H, 3H), 7.04 (dd, J = 8.3, 4.7 Hz, 1H), 6.65 (ddd, J = 8.3, 2.9, 1.4 Hz, Ar-H, 1H), 5.24 (s, NH, 1H), 2.20 (s, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 139.5, 136.8, 136.6, 136.0, 128.7, 126.4, 123.7, 119.1, 18.3.

N-methyl-N-(pyridin-3-yl)pyridin-3-amine(5y, 182 mg, 98%)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 2.5 Hz, Ar-H, 2H), 8.21 (dd, J = 4.7, 1.4 Hz, Ar-H, 2H), 7.30 (ddd, J = 8.3, 2.8, 1.4 Hz, Ar-H, 2H), 7.18 (ddd, J = 8.3, 4.7, 0.7 Hz, Ar-H, 2H), 3.33 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 143.0, 142.3, 127.0, 123.7, 39.9. **HRMS calcd for $C_{11}H_{11}N_3$ $[M+H]^+$ 186.1031, found 186.1027.**

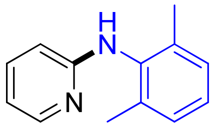
N-(4-fluorophenyl)pyridin-2-amine(5z, 173 mg, 92%)[27]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (ddd, J = 5.0, 1.8, 0.8 Hz, Ar-H, 1H), 7.47 (ddd, J = 8.5, 7.2, 1.9 Hz, Ar-H, 1H), 7.33 – 7.25 (m, Ar-H, 2H), 7.06 – 6.99 (m, Ar-H, 2H), 6.87 (s, NH, 1H), 6.72

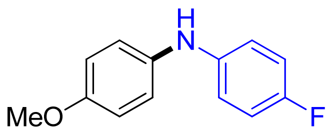
(ddt, J = 7.2, 5.0, 0.9 Hz, Ar-H, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9 (d, J = 242.1 Hz), 156.5 (s), 148.3 (s), 137.8 (s), 136.4 (d, J = 2.7 Hz), 122.9 (d, J = 7.9 Hz), 115.9 (d, J = 22.5 Hz), 114.8 (s), 107.8 (s).

N-(2,6-dimethylphenyl)pyridin-2-amine(5aa, 190 mg, 96%**)**[27]



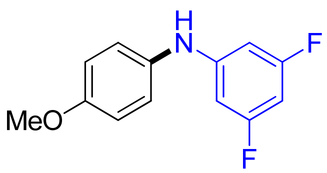
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (ddd, J = 5.0, 1.8, 0.7 Hz, Ar-H, 1H), 7.36 (ddd, J = 8.8, 7.2, 1.9 Hz, Ar-H, 1H), 7.13 (s, Ar-H, 3H), 6.63 (ddd, J = 7.1, 5.0, 0.9 Hz, Ar-H, 1H), 6.10 (s, Ar-H, 1H), 6.00 (d, J = 8.4 Hz, NH, 1H), 2.23 (s, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 148.4, 137.8, 136.7, 136.3, 128.5, 126.8, 113.7, 105.7, 18.4.

4-fluoro-N-(4-methoxyphenyl)aniline (6a, 213 mg, 98%**)**[10]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 6.75 (m, Ar-H, 8H), 5.45 (s, NH, 1H), 3.82 (s, OCH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0 (d, J = 237.9 Hz), 154.8 (s), 141.0 (s), 136.4, 121.0, 117.6 (d, J = 7.6 Hz), 115.7 (d, J = 22.4 Hz), 114.6.

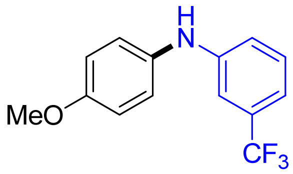
3,5-difluoro-N-(4-methoxyphenyl)aniline (6b, 219 mg, 93%**)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 8.5 Hz, Ar-H, 2H), 6.90 (d, J = 8.4 Hz, Ar-H, 2H), 6.31 (d, J = 8.9 Hz, Ar-H, 2H), 6.22 (t, J = 9.0 Hz, Ar-H, 1H), 5.66 (s, NH, 1H), 3.82 (s, OCH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (dd, J = 244.5, 15.7

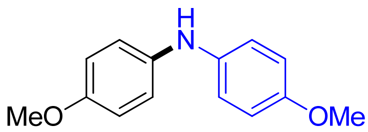
Hz), 156.6, 148.4 (t, J = 13.1 Hz), 133.5, 124.5, 114.8, 97.44 – 96.84 (m), 93.9 (t, J = 26.2 Hz).

N-(4-methoxyphenyl)-3-(trifluoromethyl)aniline (6c, 128 mg, 48%**)**[11]



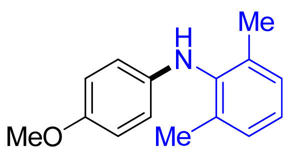
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.9 Hz, Ar-H, 1H), 7.15 – 7.10 (m, Ar-H, 3H), 7.08 (d, *J* = 7.6 Hz, Ar-H, 1H), 7.03 (dd, *J* = 8.2, 1.7 Hz, Ar-H, 1H), 6.96 – 6.92 (m, Ar-H, 2H), 5.68 (s, NH, 1H), 3.84 (s, OCH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 146.0, 134.2, 131.6 (q, J = 31.8 Hz), 129.7, 124.2 (d, J = 272.4 Hz), 123.3, 117.8, 114.8, 113.3 (dq, J = 431.6, 3.9 Hz).

bis(4-methoxyphenyl)amine (6d, 220 mg, 96%**)**[12]



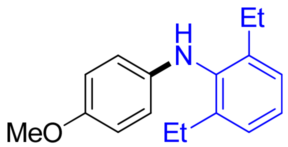
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.9 Hz, Ar-H, 4H), 6.83 (d, *J* = 8.8 Hz, Ar-H, 4H), 5.29 (s, NH, 1H), 3.78 (s, OCH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 137.9, 119.5, 114.7, 55.6.

N-(4-methoxyphenyl)-2,6-dimethylaniline (6e, 218 mg, 96%**)**[27]



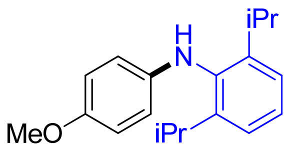
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.5 Hz, Ar-H, 2H), 7.08 (dd, *J* = 8.5, 6.3 Hz, Ar-H, 1H), 6.84 – 6.75 (m, Ar-H, 2H), 6.57 – 6.49 (m, Ar-H, 2H), 5.07 (s, NH, 1H), 3.78 (s, OCH_3, 3H), 2.24 (s, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 140.1, 139.2, 134.8, 128.5, 125.0, 115.2, 114.6, 55.6, 18.3.

2,6-diethyl-N-(4-methoxyphenyl)aniline (6f, 230 mg, 90%**)**[13]



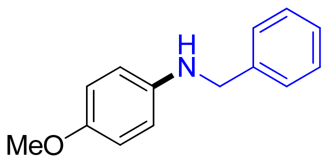
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, Ar-H, 3H), 6.74 (d, J = 8.3 Hz, Ar-H, 2H), 6.47 (d, J = 8.3 Hz, Ar-H, 2H), 5.01 (s, NH, 1H), 3.74 (s, OCH_3, 3H), 2.57 (q, J = 7.5 Hz, CH_2, 4H), 1.15 (t, J = 7.5 Hz, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 141.5, 141.3, 137.9, 126.7, 125.8, 114.8, 114.7, 55.7, 24.7, 14.6.

2,6-diisopropyl-N-(4-methoxyphenyl)aniline (6g, 269 mg, 95%**)**[14]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, Ar-H, 1H), 7.26 (d, J = 7.1 Hz, Ar-H, 2H), 6.79 (d, J = 8.2 Hz, Ar-H, 2H), 6.50 (d, J = 8.2 Hz, Ar-H, 2H), 5.02 (s, NH, 1H), 3.79 (s, OCH_3, 3H), 3.26 (dt, J = 13.6, 6.8 Hz, CH, 2H), 1.20 (d, J = 6.9 Hz, CH_3, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 147.1, 142.3, 136.1, 126.7, 123.8, 114.7, 114.2, 55.7, 28.1, 23.8.

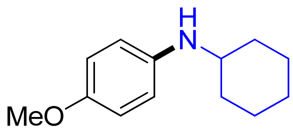
N-benzyl-4-methoxyaniline (6h, 177 mg, 83%**)**[15]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (q, J = 7.8 Hz, Ar-H, 4H), 7.30 (t, J = 6.8 Hz, Ar-H, 1H), 6.81 (d, J = 8.9 Hz, Ar-H, 2H), 6.63 (d, J = 8.9 Hz, Ar-H, 2H), 4.31 (s,

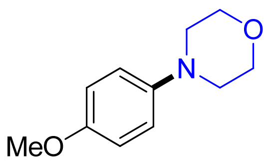
CH_2, 2H), 3.76 (s, OCH_3, 3H).[13]C NMR (101 MHz, $CDCl_3$) δ 152.1, 142.4, 139.6, 128.5, 127.5, 127.1, 114.8, 114.0, 55.7, 49.2.

N-cyclohexyl-4-methoxyaniline (6i, 181 mg, 88%**)**[16]



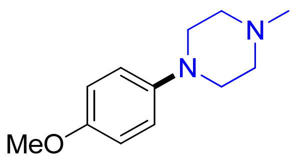
[1]H NMR (400 MHz, $CDCl_3$) δ 6.78 (d, *J* = 8.9 Hz, Ar-H, 2H), 6.59 (d, *J* = 8.9 Hz, Ar-H, 2H), 3.75 (s, OCH_3, 3H), 3.22 – 3.13 (m, CH_2, 1H), 3.07 (s, NH, 1H), 2.06 (d, *J* = 10.3 Hz, CH_2, 2H), 1.77 (dd, *J* = 9.7, 3.6 Hz, CH_2, 2H), 1.66 (dd, *J* = 8.9, 3.7 Hz, CH_2, 1H), 1.43 – 1.30 (m, CH_2, 2H), 1.29 – 1.18 (m, CH, CH_2, 1H), 1.12 (td, *J* = 12.7, 2.8 Hz, 2H).[13]C NMR (101 MHz, $CDCl_3$) δ 151.7, 141.5, 114.8, 55.7, 52.7, 33.5, 25.9, 25.0.

4-(4-methoxyphenyl)morpholine (6j, 182 mg, 94%**)**[17]



[1]H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, *J* = 6.8 Hz, Ar-H, 4H), 3.89 – 3.83 (m, CH_2, 4H), 3.77 (s, OCH_3, 3H), 3.09 – 3.02 (m, CH_2, 4H).[13]C NMR (101 MHz, $CDCl_3$) δ 153.9, 145.6, 117.8, 114.5, 67.0, 55.5, 50.8.

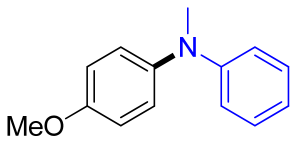
1-(4-methoxyphenyl)-4-methylpiperazine (6k, 161 mg, 78%**)**[18]



[1]H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, *J* = 9.1 Hz, Ar-H, 2H), 6.86 – 6.81 (m, Ar-H, 2H), 3.75 (s, OCH_3, 3H), 3.13 – 3.07 (m, CH_2, 4H), 2.61 – 2.55 (m, CH_2, 4H), 2.34 (s,

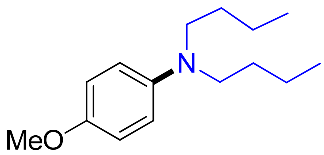
CH_3, 3H).[13]C NMR (101 MHz, $CDCl_3$) δ 153.7, 145.6, 129.2, 118.1, 115.1, 114.3, 55.5, 55.2, 50.5, 46.1.

4-methoxy-N-methyl-N-phenylaniline (6l, 192 mg, 90%**)**[19]



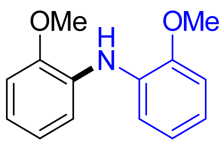
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.5 Hz, Ar-H, 2H), 7.07 (d, *J* = 8.2 Hz, Ar-H, 2H), 6.87 (d, *J* = 8.1 Hz, Ar-H, 2H), 6.76 (t, *J* = 7.7 Hz, Ar-H, 3H), 3.77 (s, OCH_3, 3H), 3.23 (s, CH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 149.7, 142.2, 128.8, 126.1, 118.3, 115.7, 114.7, 55.4, 40.4.

N,N-dibutyl-4-methoxyaniline (6m, 127 mg, 54%**)**[20]



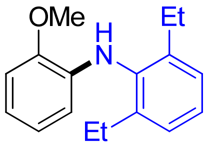
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 – 6.78 (m, Ar-H, 2H), 6.69 – 6.61 (m, Ar-H, 2H), 3.76 (s, OCH_3, 3H), 3.22 – 3.13 (m, CH_2, 4H), 1.52 (tt, *J* = 7.7, 6.5 Hz, CH_2, 4H), 1.34 (dq, *J* = 14.6, 7.3 Hz, CH_2, 4H), 0.94 (t, *J* = 7.3 Hz, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 143.3, 114.8, 114.3, 55.8, 51.7, 29.4, 20.4, 14.0.

bis(2-methoxyphenyl)amine (6n, 205 mg, 96%**)**[21]



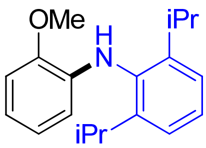
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, Ar-H, 2H), 6.98 – 6.89 (m, Ar-H, 6H), 6.56 (s, NH, 1H), 3.93 (s, OCH_3, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 132.4, 120.6, 120.0, 115.4, 110.5, 55.5.

2,6-diethyl-N-(2-methoxyphenyl)aniline (6o, 248 mg, 97%**)**[27]



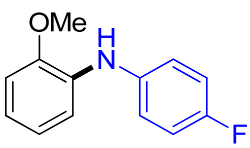
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, Ar-H, 3H), 7.02 (dd, *J* = 7.4, 1.9 Hz, Ar-H, 1H), 6.87 (pd, *J* = 7.4, 1.8 Hz, Ar-H, 2H), 6.33 (dd, *J* = 7.3, 2.1 Hz, Ar-H, 1H), 5.87 (s, NH, 1H), 4.08 (s, OCH_3, 3H), 2.77 (q, *J* = 7.5 Hz, CH_2, 4H), 1.33 (t, *J* = 7.6 Hz, CH_3, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 142.4, 137.0, 136.9, 126.5, 126.4, 121.0, 116.9, 110.9, 109.7, 55.5, 24.5, 14.7.

2,6-diisopropyl-N-(2-methoxyphenyl)aniline (6p, 272 mg, 96%**)**[27]



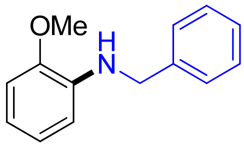
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.6, 6.5 Hz, Ar-H, 1H), 7.25 (dd, *J* = 8.9, 2.0 Hz, Ar-H, 2H), 6.89 (dd, *J* = 7.5, 1.7 Hz, Ar-H, 1H), 6.77 – 6.67 (m, Ar-H, 2H), 6.15 (dd, *J* = 7.5, 1.9 Hz, Ar-H, 1H), 5.67 (s, NH, 1H), 3.99 (s, OCH_3, 3H), 3.20 (dq, *J* = 13.8, 6.9 Hz, CH, 2H), 1.17 (d, *J* = 6.9 Hz, CH_3, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 146.2, 137.9, 135.4, 127.0, 123.7, 121.1, 116.7, 110.9, 109.7, 55.7, 28.1.

N-(4-fluorophenyl)-2-methoxyaniline (6q, 206 mg, 95%**)**[27]



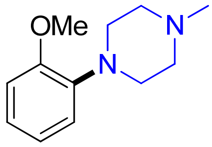
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.08 (m, Ar-H, 3H), 7.04 – 6.96 (m, Ar-H, 2H), 6.93 – 6.82 (m, Ar-H, 3H), 6.06 (s, NH, 1H), 3.91 (s, OCH_3, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 156.9, 147.8, 138.5 (d, J = 2.5 Hz), 133.7, 121.2 (d, J = 7.8 Hz), 120.8, 119.5, 115.8 (d, J = 22.4 Hz), 113.6, 110.4, 55.5.

N-benzyl-2-methoxyaniline (6r, 190 mg, 89%**)**[21]



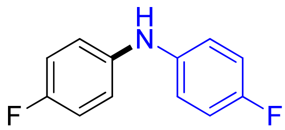
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dt, *J* = 15.0, 4.1 Hz, Ar-H, 4H), 7.30 (t, *J* = 7.1 Hz, Ar-H, 1H), 6.90 – 6.79 (m, Ar-H, 2H), 6.74 – 6.68 (m, Ar-H, 1H), 6.63 (d, *J* = 7.8 Hz, Ar-H, 1H), 4.66 (s, NH, 1H), 4.38 (s, CH_2, 2H), 3.88 (s, OCH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 139.5, 138.1, 128.5, 127.5, 127.1, 121.2, 116.6, 110.0, 109.3, 55.4, 48.0.

1-(2-methoxyphenyl)-4-methylpiperazine (6s, 194 mg, 94%**)**[27]



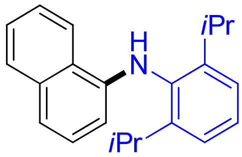
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (ddd, *J* = 8.0, 6.6, 2.5 Hz, Ar-H, 1H), 6.96 – 6.84 (m, Ar-H, 3H), 3.86 (s, OCH_3, 3H), 3.16 (s, CH_2, 4H), 2.81 (s, CH_2, 4H), 2.47 (s, CH_3, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 140.6, 123.3, 121.0, 118.4, 111.2, 55.3, 54.9, 49.7, 45.4.

bis(4-fluorophenyl)amine (6t, 183 mg, 89%**)**[22]



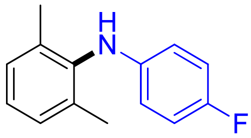
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 – 6.92 (m, Ar-H, 8H), 5.48 (s, NH, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 157.7 (d, J = 239.5 Hz), 139.7 (d, J = 2.4 Hz), 119.3 (d, J = 7.7 Hz), 115.9 (d, J = 22.5 Hz).

N-(2,6-diisopropylphenyl)naphthalen-1-amine (6u, 261 mg, 86%**)**[23]



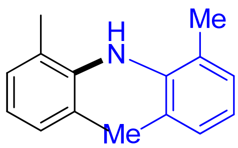
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 1H), 7.92 – 7.85 (m, Ar-H, 1H), 7.56 (dd, J = 6.5, 3.3 Hz, Ar-H, 2H), 7.39 – 7.33 (m, Ar-H, 1H), 7.30 (d, J = 7.5 Hz, Ar-H, 3H), 7.22 (t, J = 7.8 Hz, Ar-H, 1H), 6.21 (d, J = 7.4 Hz, Ar-H, 1H), 5.75 (s, NH, 1H), 3.18 (dt, J = 13.7, 6.8 Hz, CH, 2H), 1.21 (d, J = 6.8 Hz, CH_3, 6H), 1.13 (d, J = 6.8 Hz, CH_3, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 143.3, 135.5, 134.5, 128.8, 127.1, 126.5, 125.8, 124.9, 124.0, 123.2, 120.0, 118.0, 106.9, 77.3, 28.2, 23.2.

N-(4-fluorophenyl)-2,6-dimethylaniline (6v, 179 mg, 83%**)**[24]



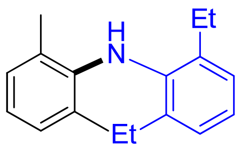
^{1}H NMR (400 MHz, CDCl3) δ 7.14 (dd, J = 14.2, 5.8 Hz, Ar-H, 3H), 6.89 (t, J = 8.4 Hz, Ar-H, 2H), 6.53 – 6.43 (m, Ar-H, 2H), 5.13 (s, NH, 1H), 2.24 (s, CH3, 6H). ^{13}C NMR (101 MHz, CDCl3) δ 156.2 (d, J = 235.8 Hz), 142.5 , 138.5 , 135.5, 128.6, 125.6, 115.6 (d, J = 22.5 Hz), 114.5 (d, J = 7.5 Hz), 18.2.

bis(2,6-dimethylphenyl)amine (6w, 216 mg, 96%**)**[27]



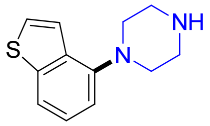
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 7.5 Hz, Ar-H, 4H), 7.00 – 6.92 (m, Ar-H, 2H), 4.91 (s, NH, 1H), 2.13 (s, CH_3, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 129.5, 128.7, 121.7, 19.1.

N-(2,6-diethylphenyl)-2,6-dimethylaniline (6x, 200 mg, 79%**)**[26]



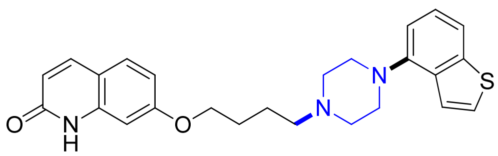
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 6.9 Hz, Ar-H, 2H), 7.06 – 7.00 (m, Ar-H, 1H), 6.98 (d, J = 7.4 Hz, Ar-H, 2H), 6.80 (t, J = 7.4 Hz, Ar-H, 1H), 4.91 (s, NH, 1H), 2.46 (q, J = 7.5 Hz, CH_2, 4H), 2.01 (s, CH_3, 6H), 1.15 (t, J = 7.5 Hz, CH_3, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 140.4, 136.9, 129.1, 127.6, 126.1, 123.0, 120.6, 24.8, 19.2, 13.8.

1-(benzo[b]thiophen-4-yl)piperazine (8a, 212 mg, 97%**)**[25]



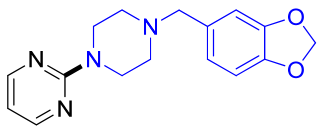
^{1}H NMR (400 MHz, DMSO) δ 9.50 (s, Ar-H, 1H), 7.75 (d, J = 5.5 Hz, Ar-H, 1H), 7.69 (d, J = 8.1 Hz, Ar-H, 1H), 7.52 (dd, J = 5.5, 0.6 Hz, Ar-H, 1H), 7.31 (t, J = 7.9 Hz, Ar-H, 1H), 6.97 – 6.93 (m, NH, 1H), 3.30 (d, J = 3.2 Hz, CH_2, 8H). ^{13}C NMR (101 MHz, DMSO) δ 147.1, 140.6, 133.4, 126.4, 125.0, 121.9, 117.6, 112.5, 48.5, 43.1.

7-(4-(4-(benzo[b]thiophen-7-yl)piperazin-1-yl)butoxy)quinolin-2(1H)-one (9a)[25]



^{1}H NMR (400 MHz, $CDCl_3$) δ 12.65 (s, Ar-H, 1H), 7.72 (d, J = 9.4 Hz, Ar-H, 1H), 7.54 (d, J = 8.1 Hz, Ar-H, 1H), 7.41 (dt, J = 15.0, 7.2 Hz, Ar-H, 3H), 7.26 (dd, J = 8.5, 7.2 Hz, Ar-H, 1H), 6.89 (dd, J = 9.3, 1.5 Hz, Ar-H, 2H), 6.81 (dd, J = 8.7, 2.3 Hz, Ar-H, 1H), 6.56 (d, J = 9.4 Hz, NH, 1H), 4.11 (t, J = 6.2 Hz, CH_2, 2H), 3.20 (s, CH_2, 4H), 2.72 (s, CH_2, 4H), 2.57 – 2.50 (m, CH_2, 2H), 1.95 – 1.82 (m, CH_2, 2H), 1.76 (dt, J = 9.3, 7.2 Hz, CH_2, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 161.4, 148.4, 141.0, 140.8, 140.4, 134.0, 128.9, 125.0, 124.9, 121.9, 117.8, 116.9, 114.1, 112.7, 112.1, 98.9, 68.1, 58.2, 53.5, 52.1, 27.2, 23.4.

2-(4-(benzo[d][1,3]dioxol-5-ylmethyl)piperazin-1-yl)pyrimidine (10a, 292 mg, 98%**)**[26]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 4.7 Hz, Ar-H, 2H), 6.88 (s, Ar-H, 1H), 6.75 (d, *J* = 0.8 Hz, Ar-H, 2H), 6.45 (t, *J* = 4.7 Hz, Ar-H, 1H), 5.94 (s, CH_2, 2H), 3.84 – 3.78 (m, CH_2, 4H), 3.44 (s, CH_2, 2H), 2.50 – 2.45 (m, CH_2, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 157.6, 147.6, 146.6, 131.8, 122.2, 109.7, 109.5, 107.8, 100.9, 62.8, 52.8, 43.6.

4. NMR spectrums for the products

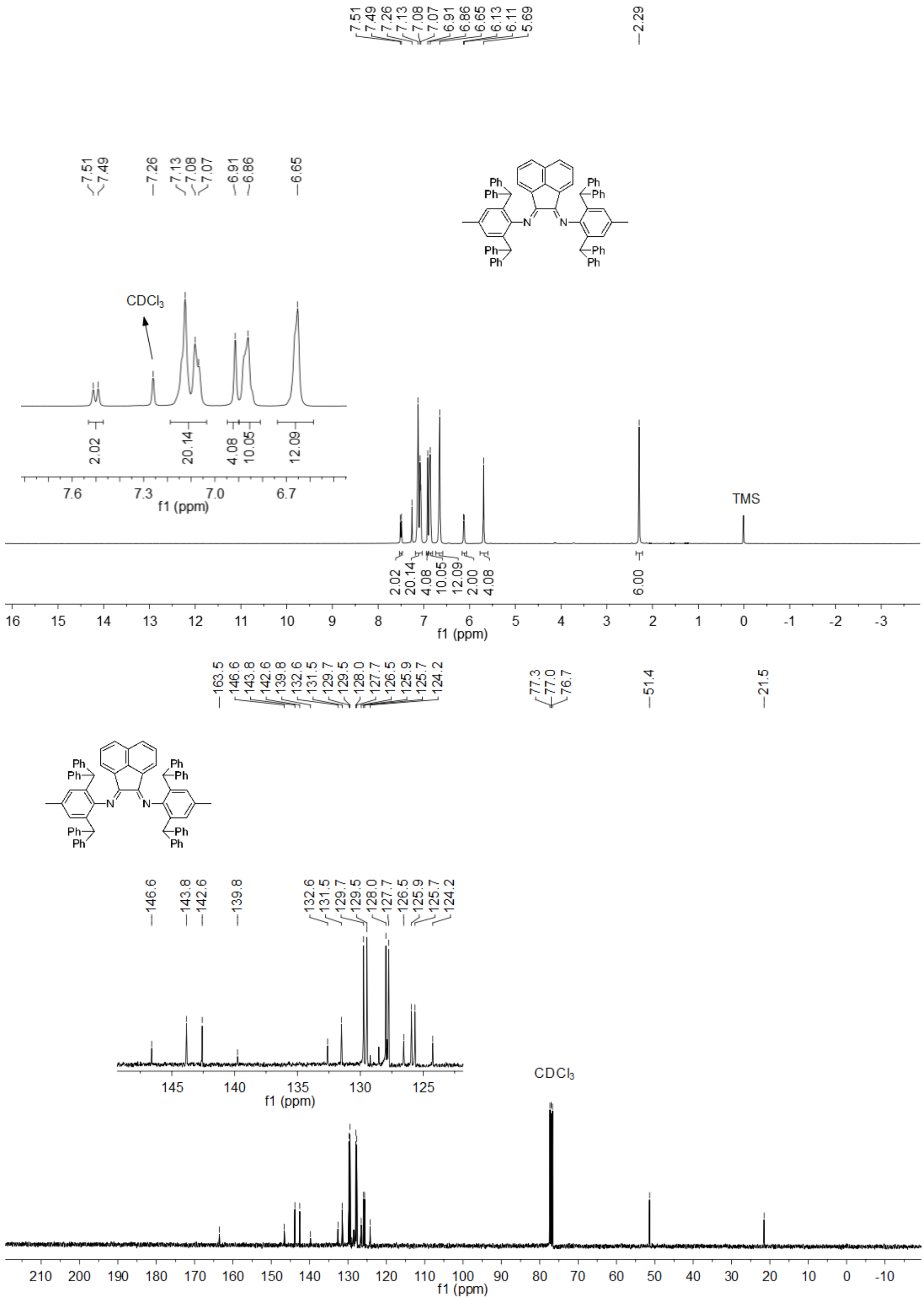


Figure S1. The NMR spectrum of **2a**

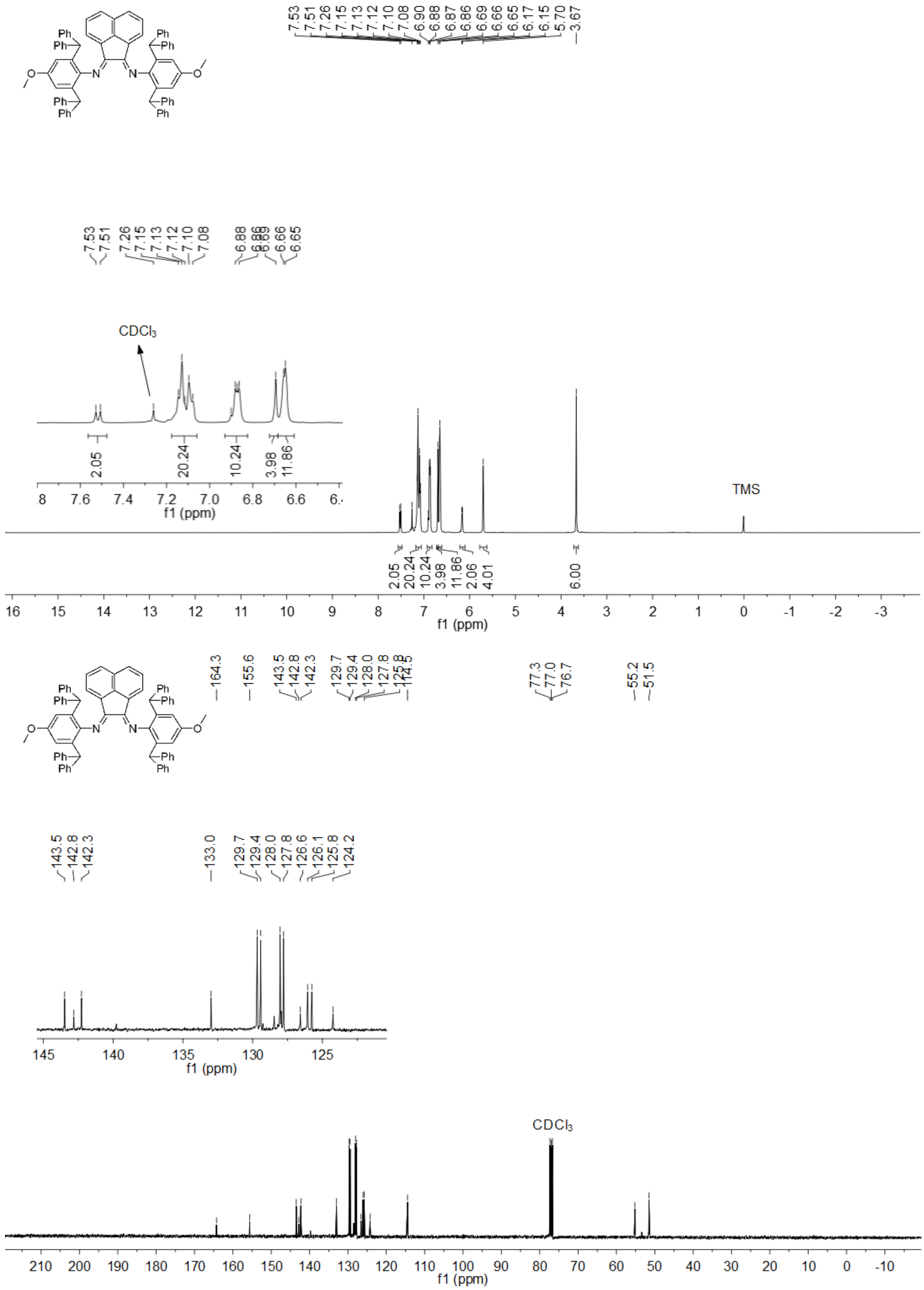
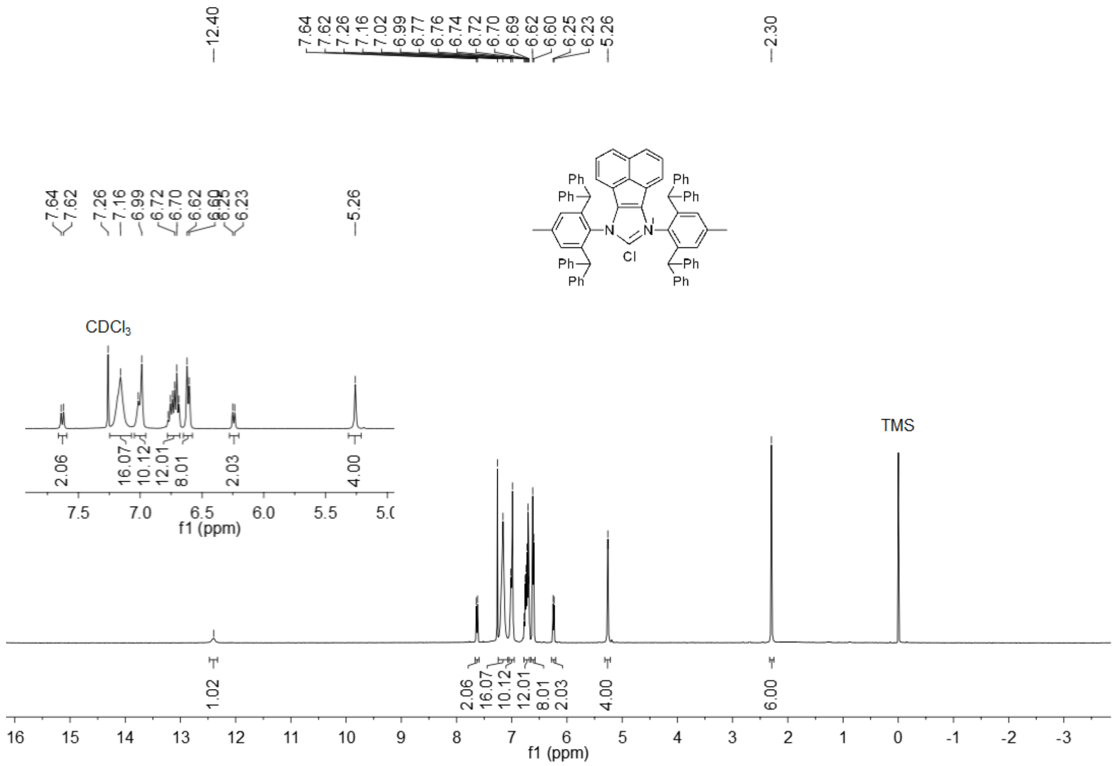


Figure S2. The NMR spectrum of **2b**



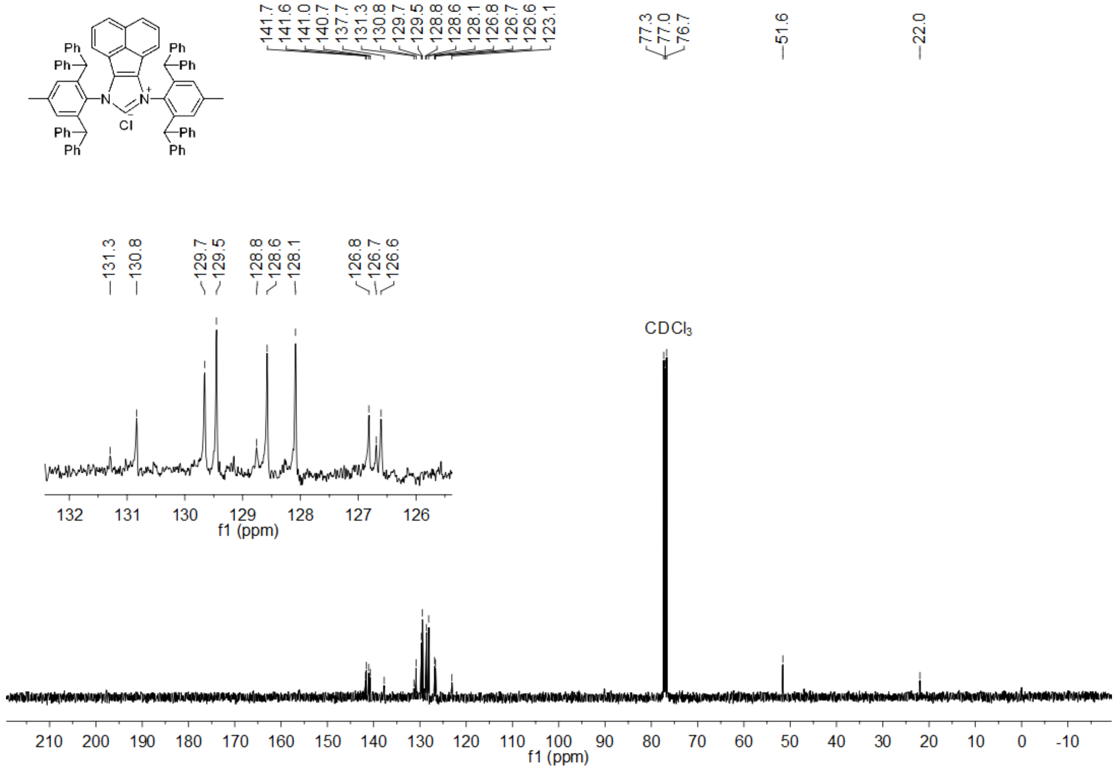


Figure S3. The NMR spectrum of **L1**

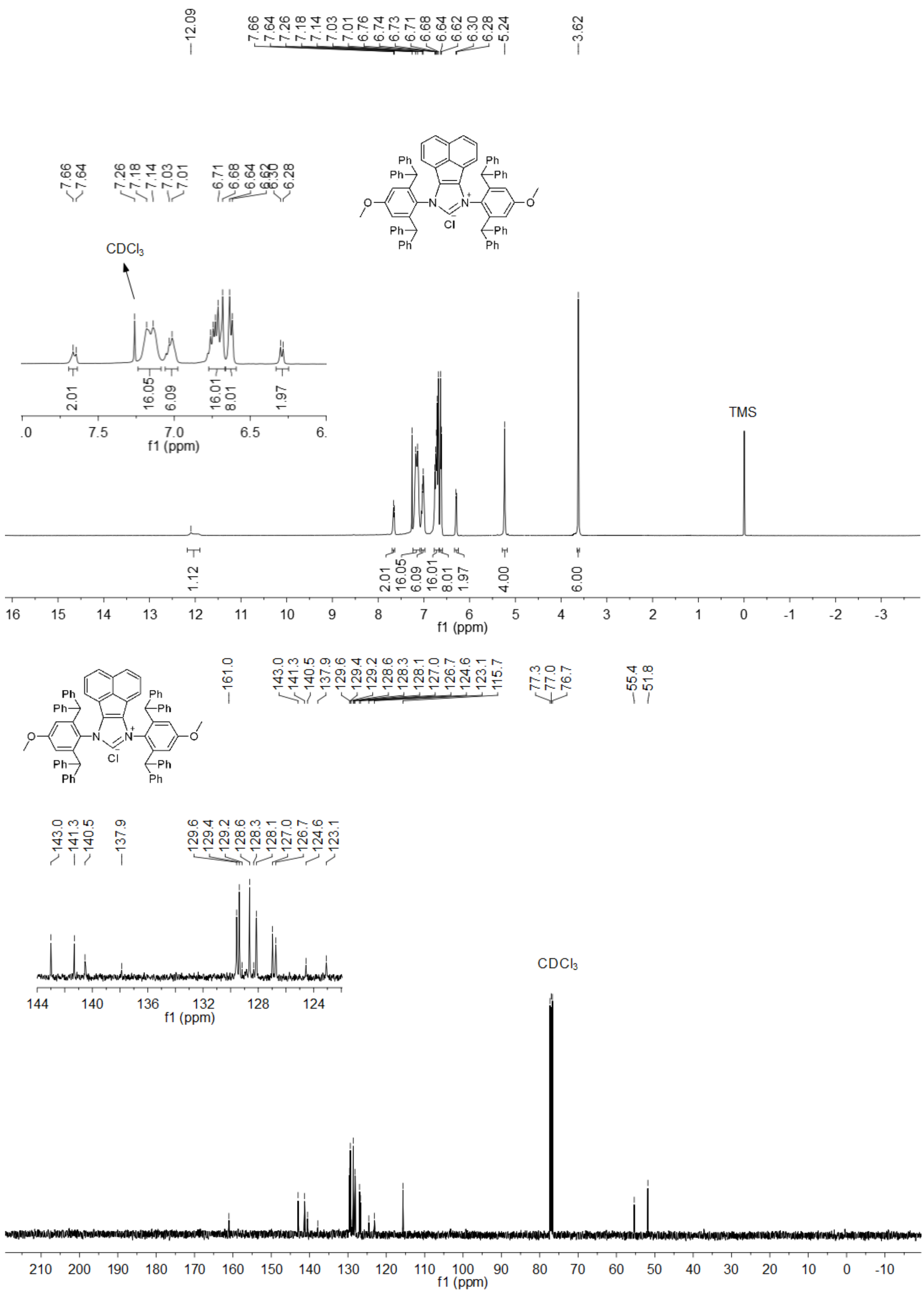
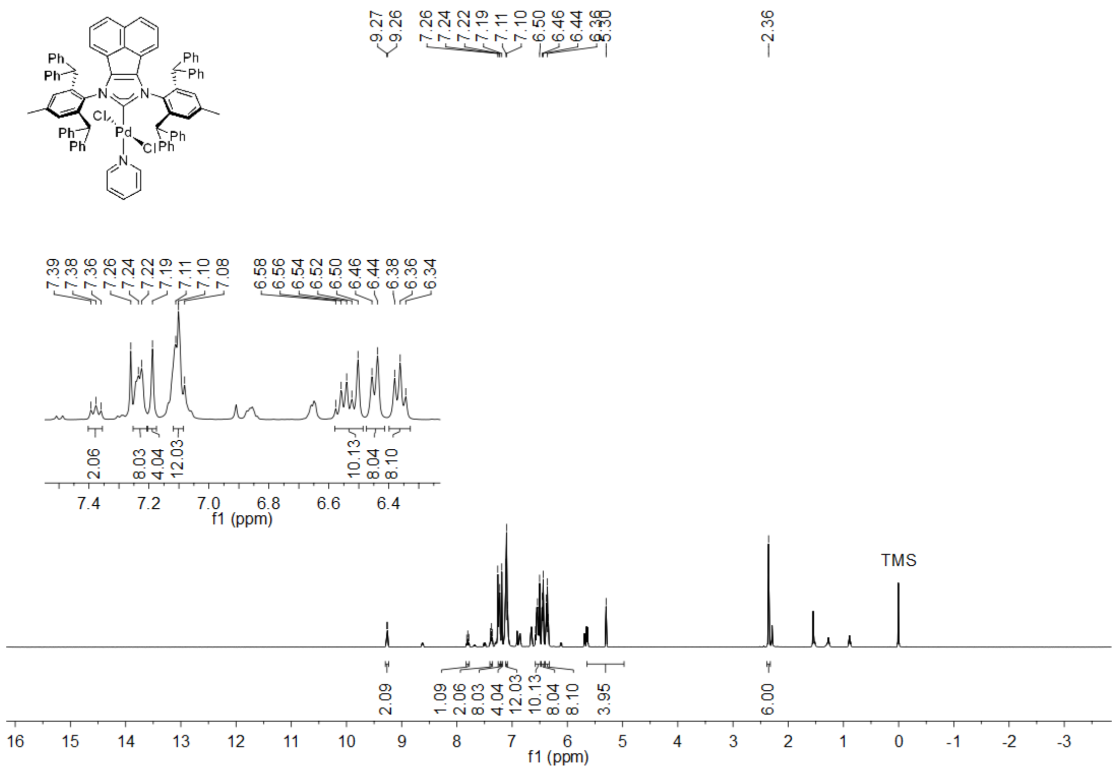


Figure S4. The NMR spectrum of **L2**



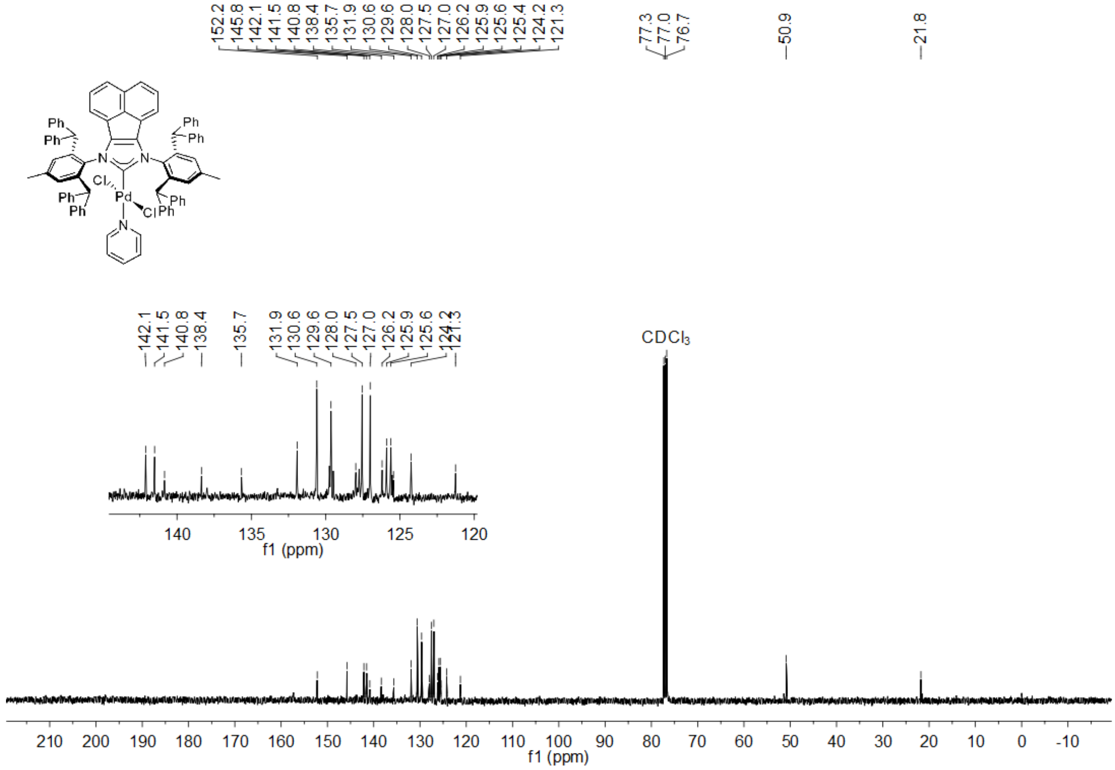


Figure S5. The NMR spectrum of **C1**

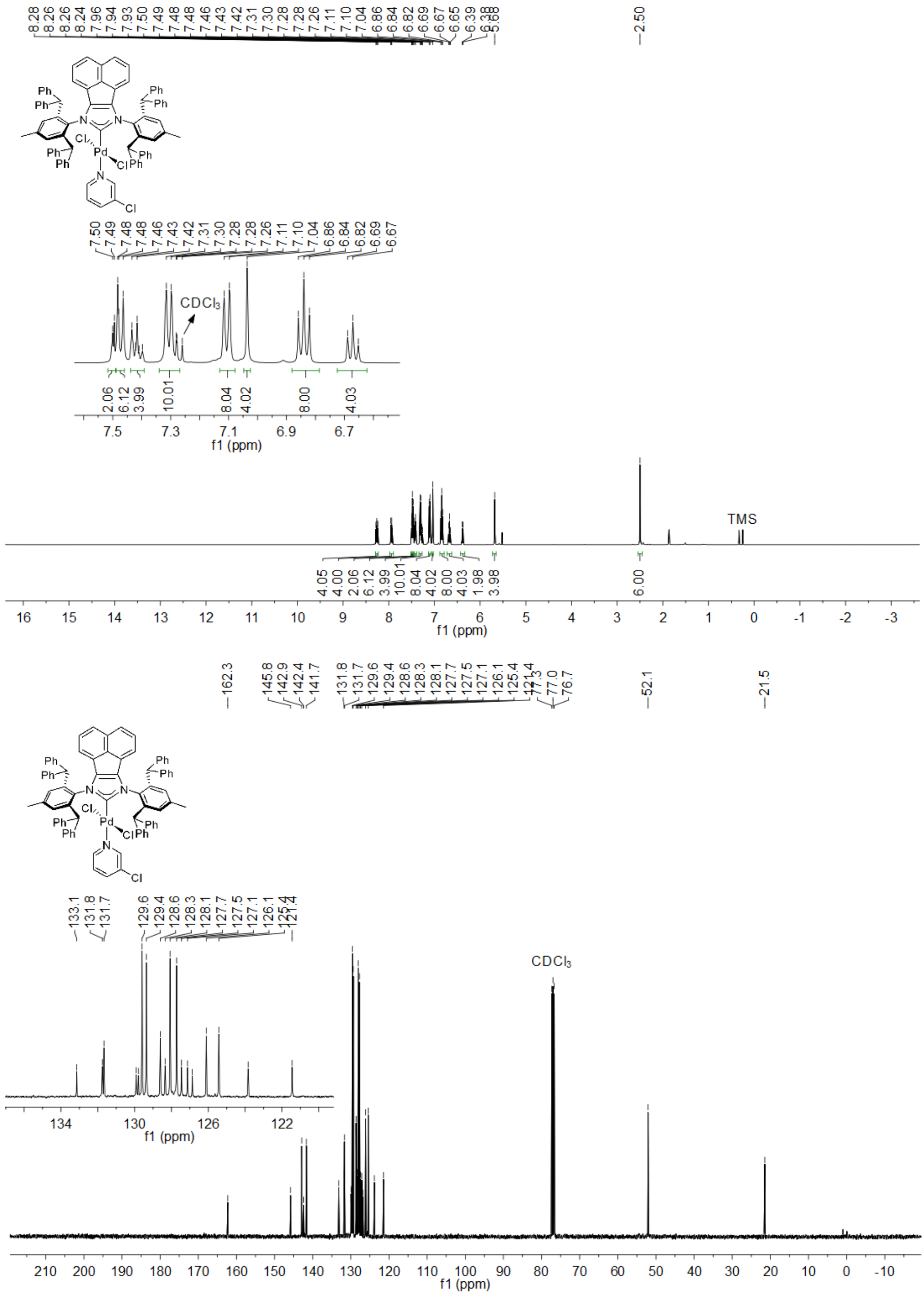
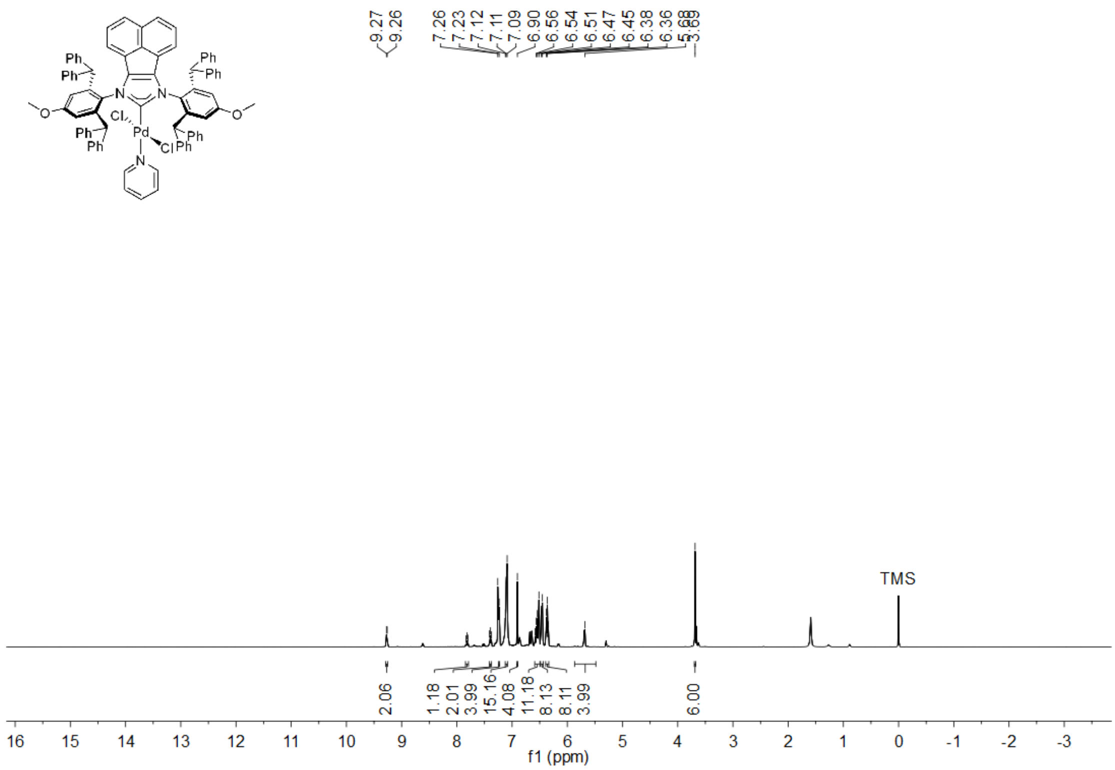


Figure S6. The NMR spectrum of **C2**



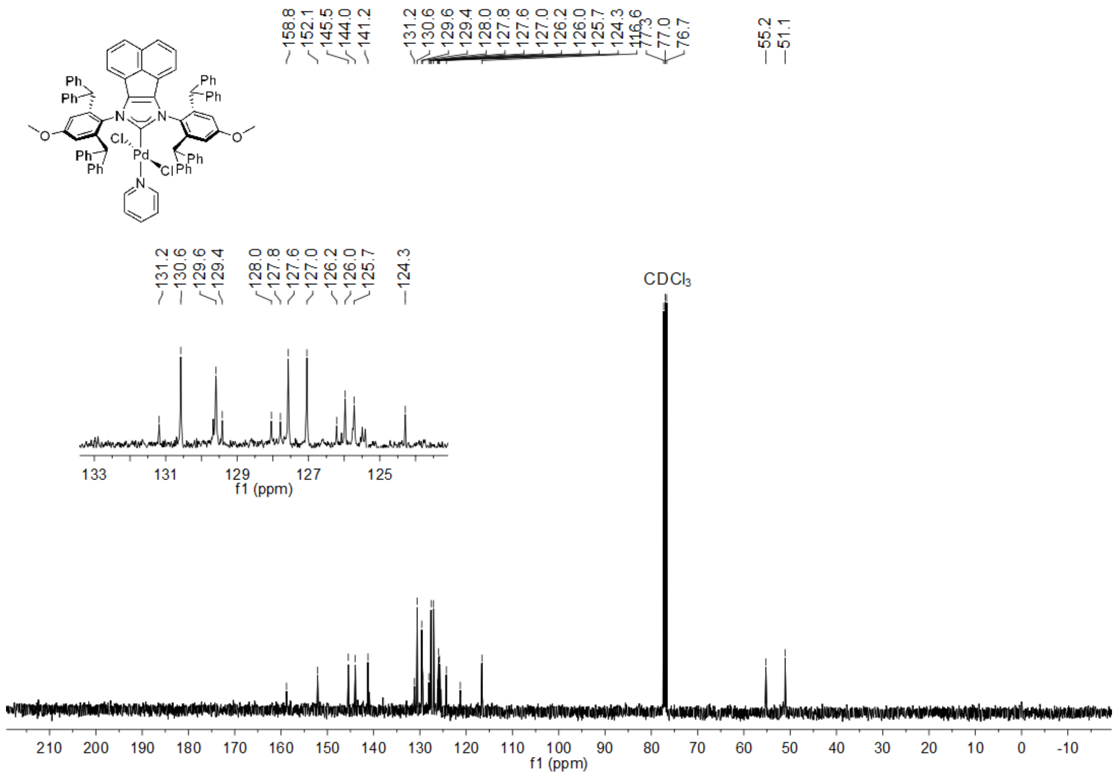
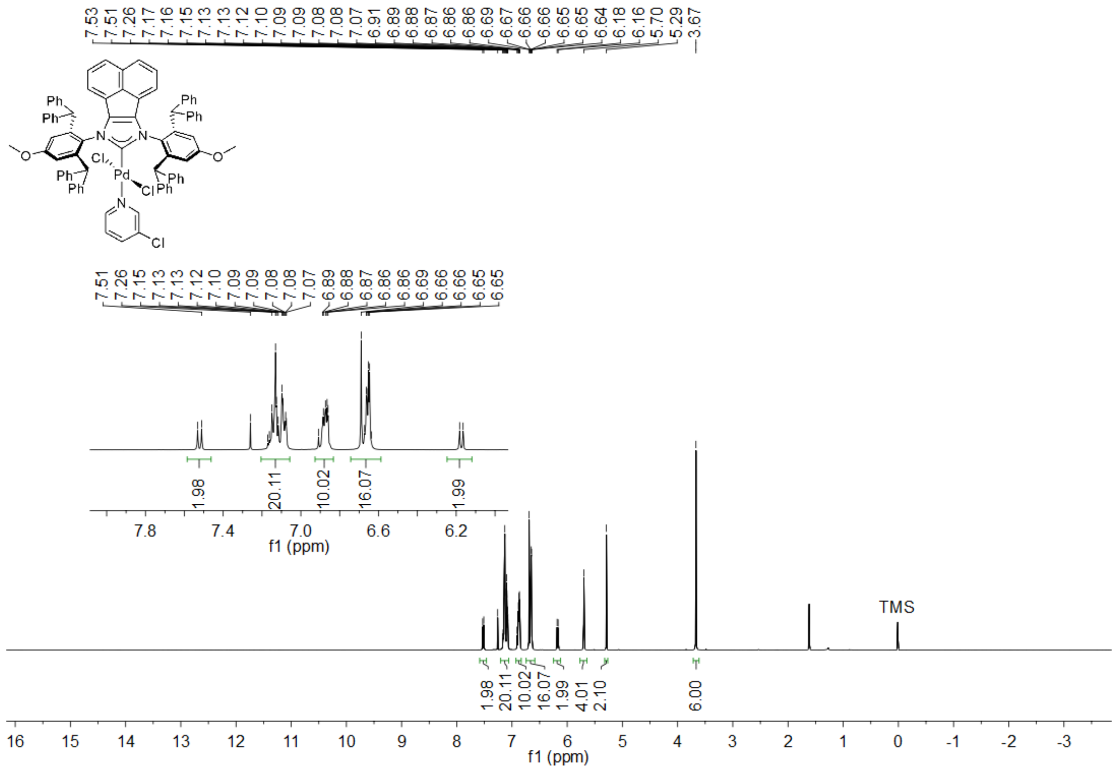


Figure S7. The NMR spectrum of **C3**



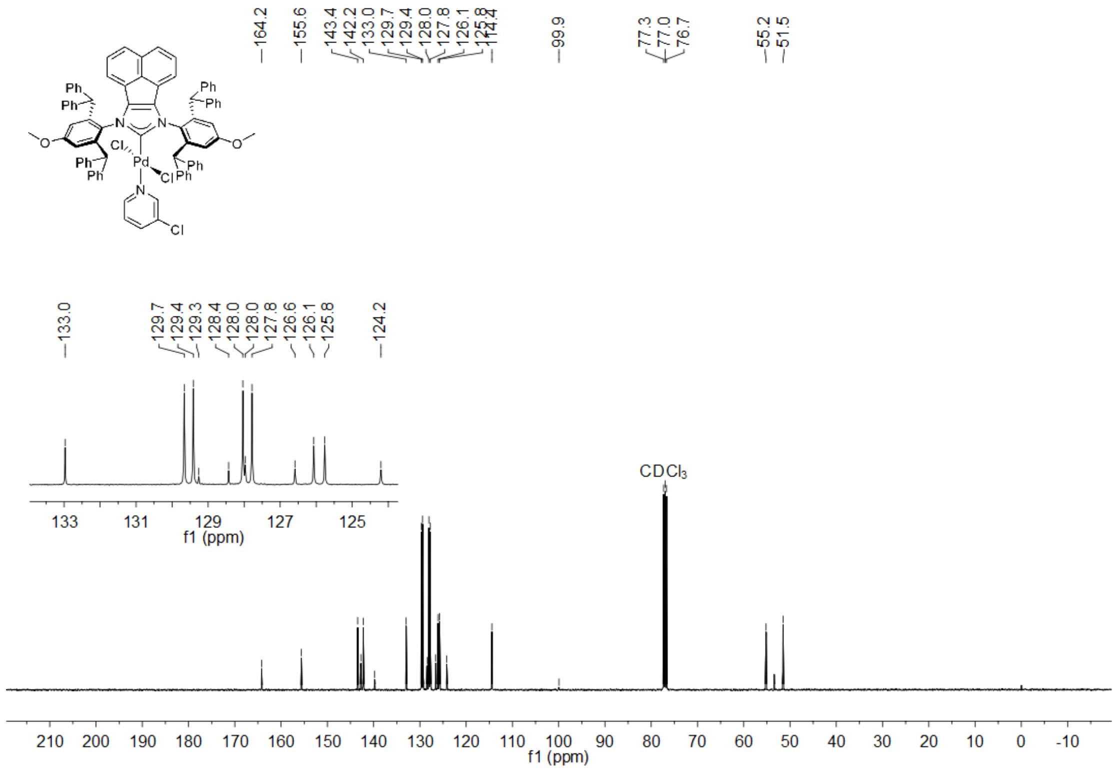


Figure S8. The NMR spectrum of **C4**

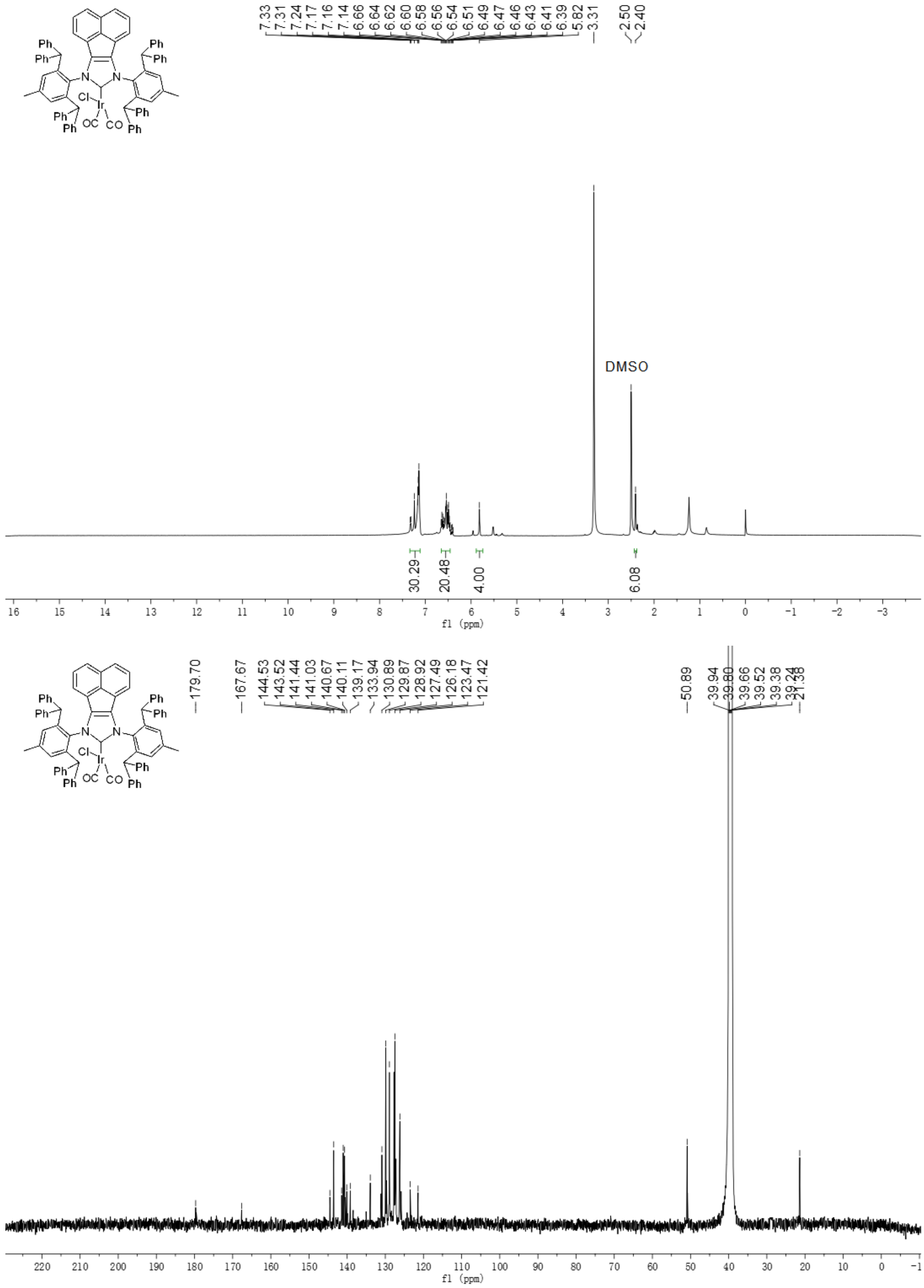
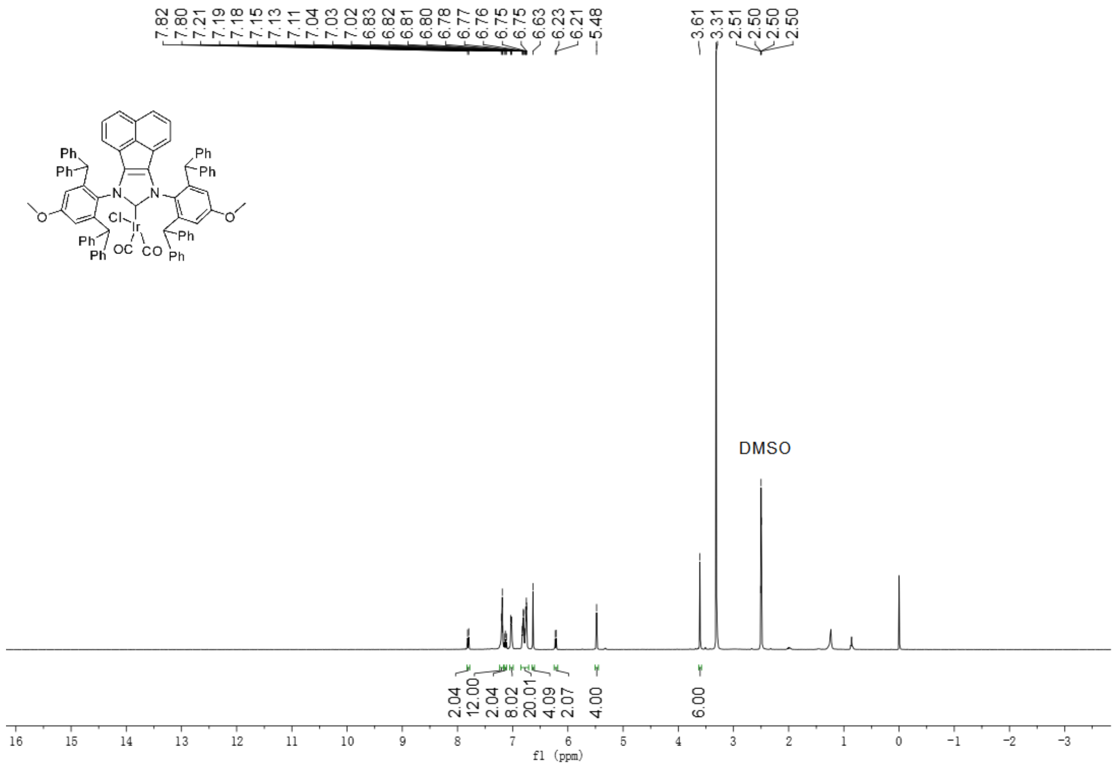


Figure S9. The NMR spectrum of **Ir-1**



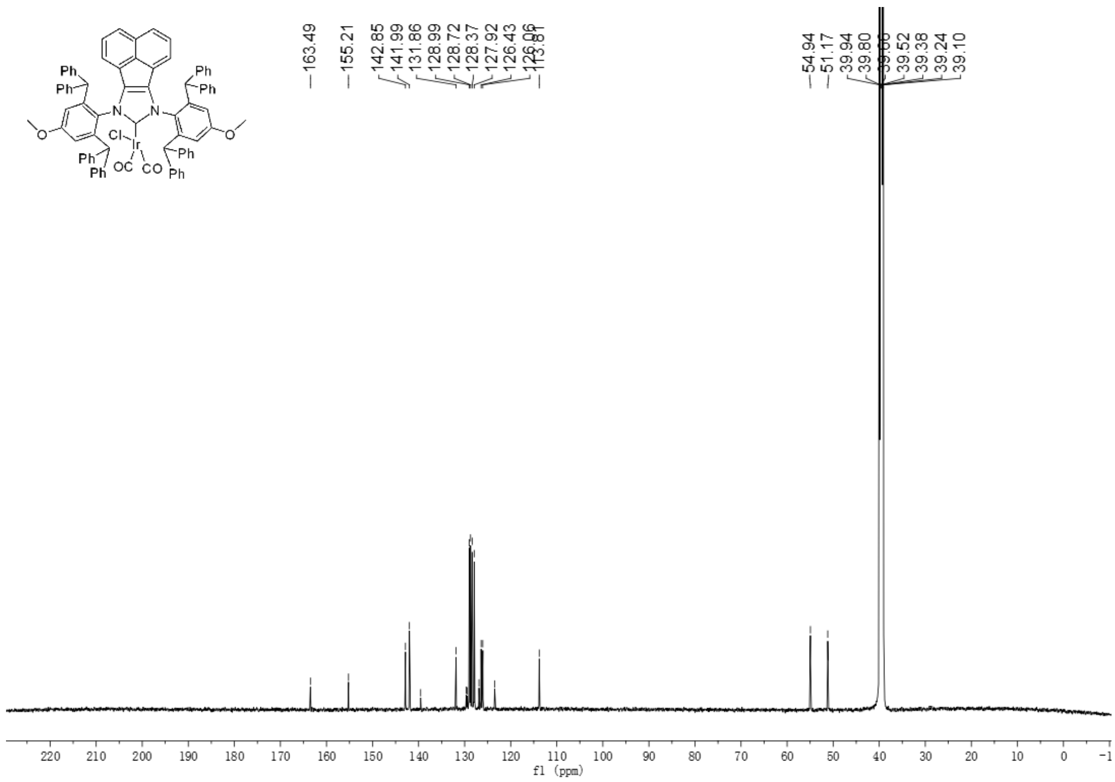
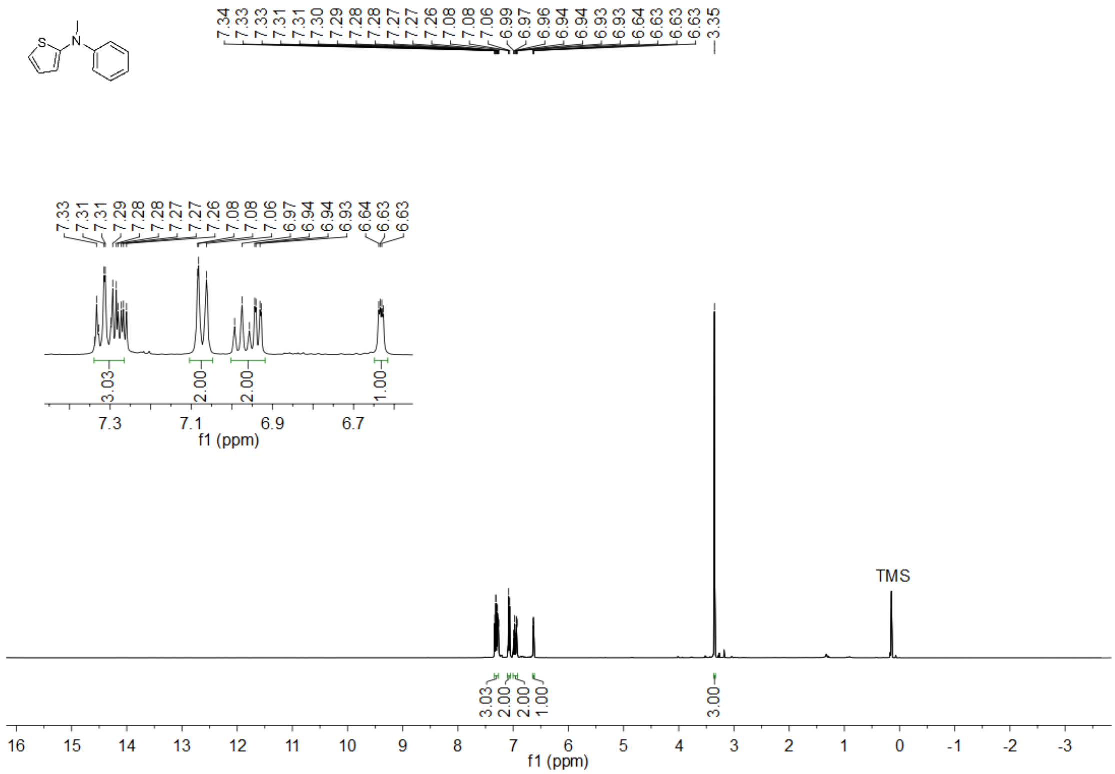


Figure S10. The NMR spectrum of **Ir-2**



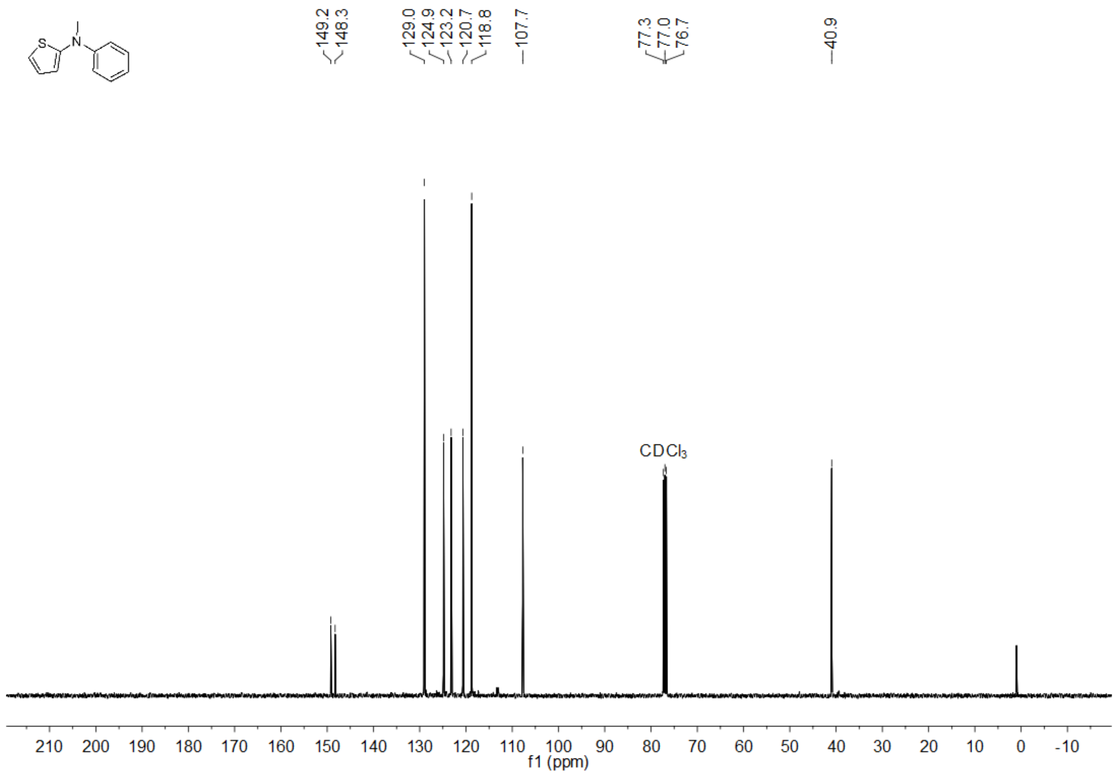
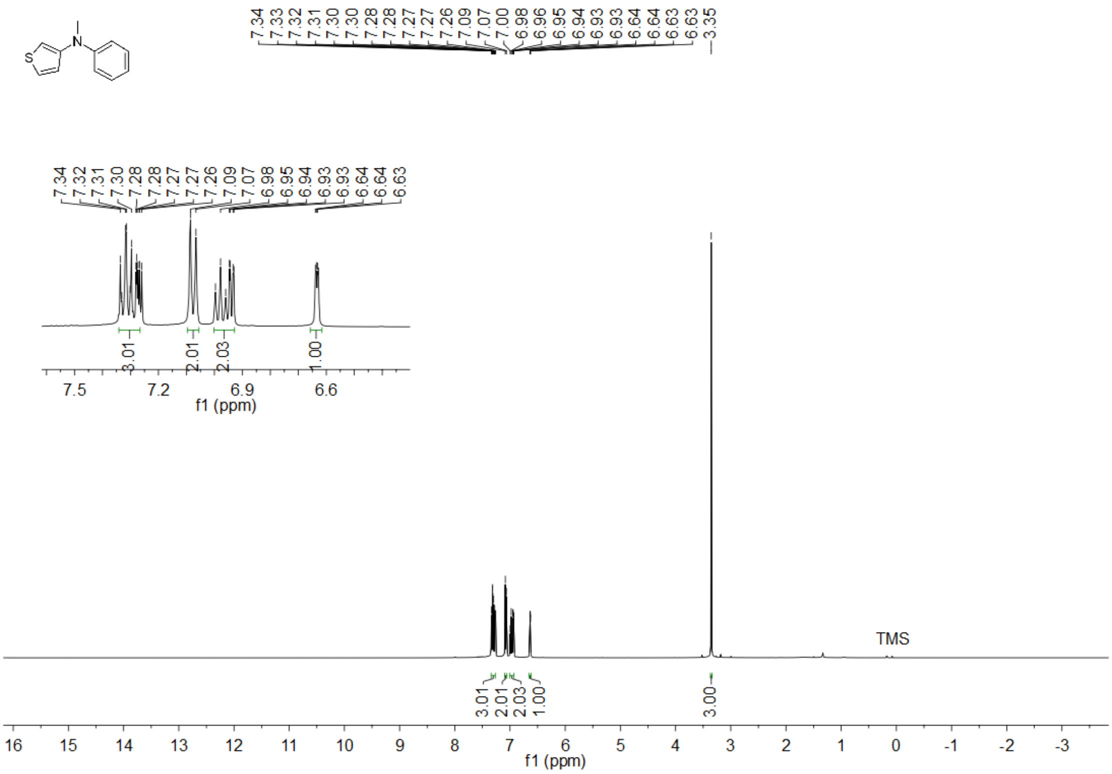


Figure S11. The NMR spectrum of 5a



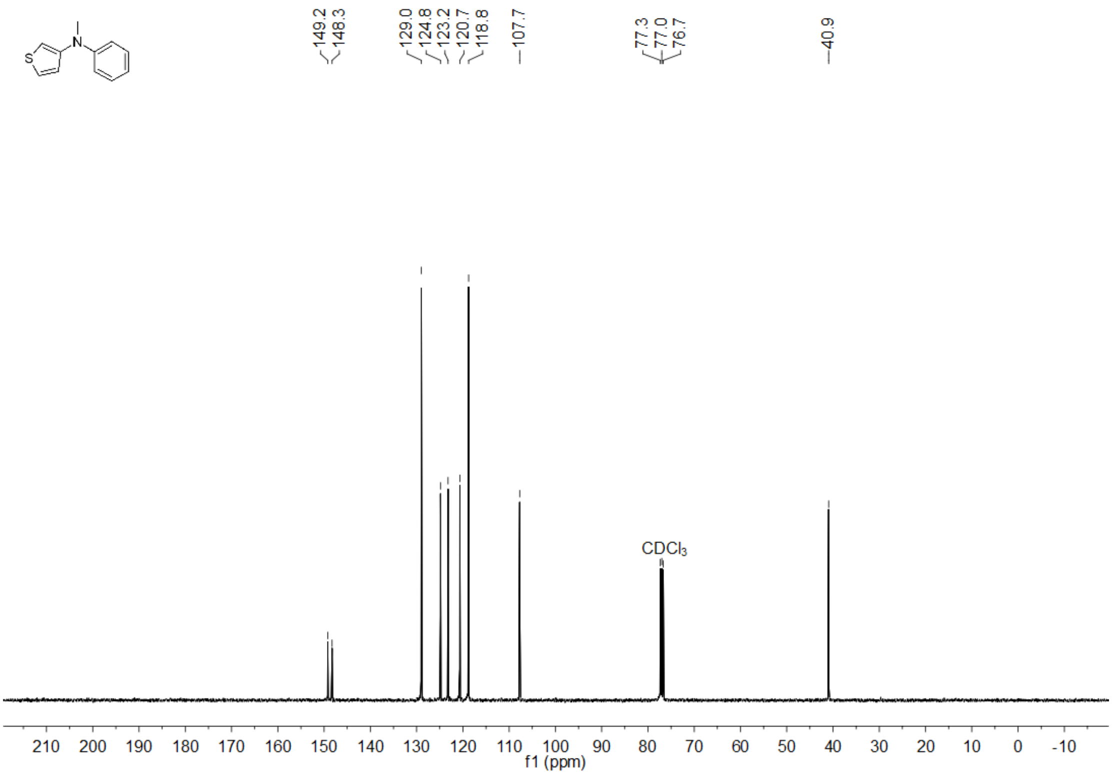


Figure S12. The NMR spectrum of 5b

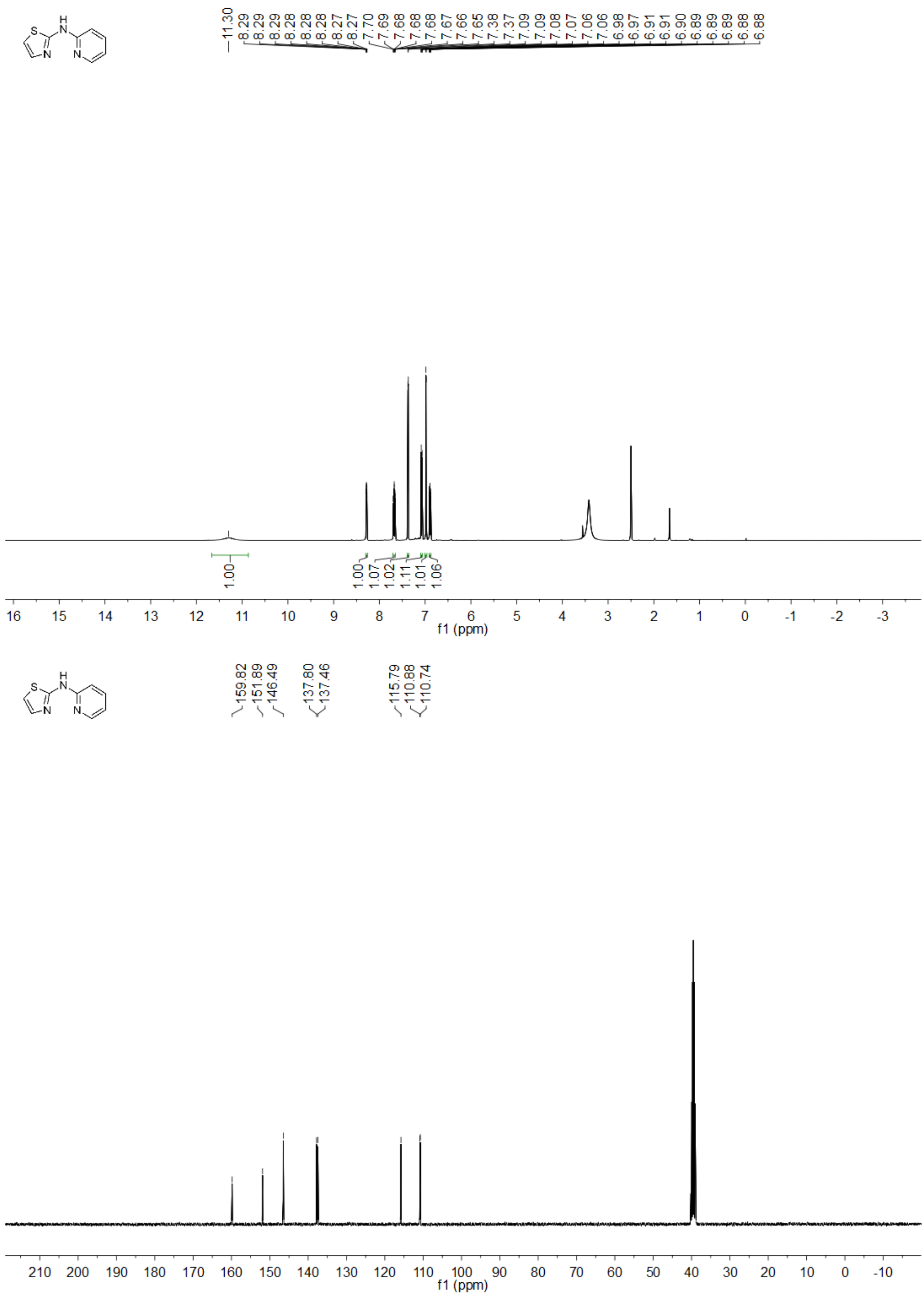


Figure S13. The NMR spectrum of 5c

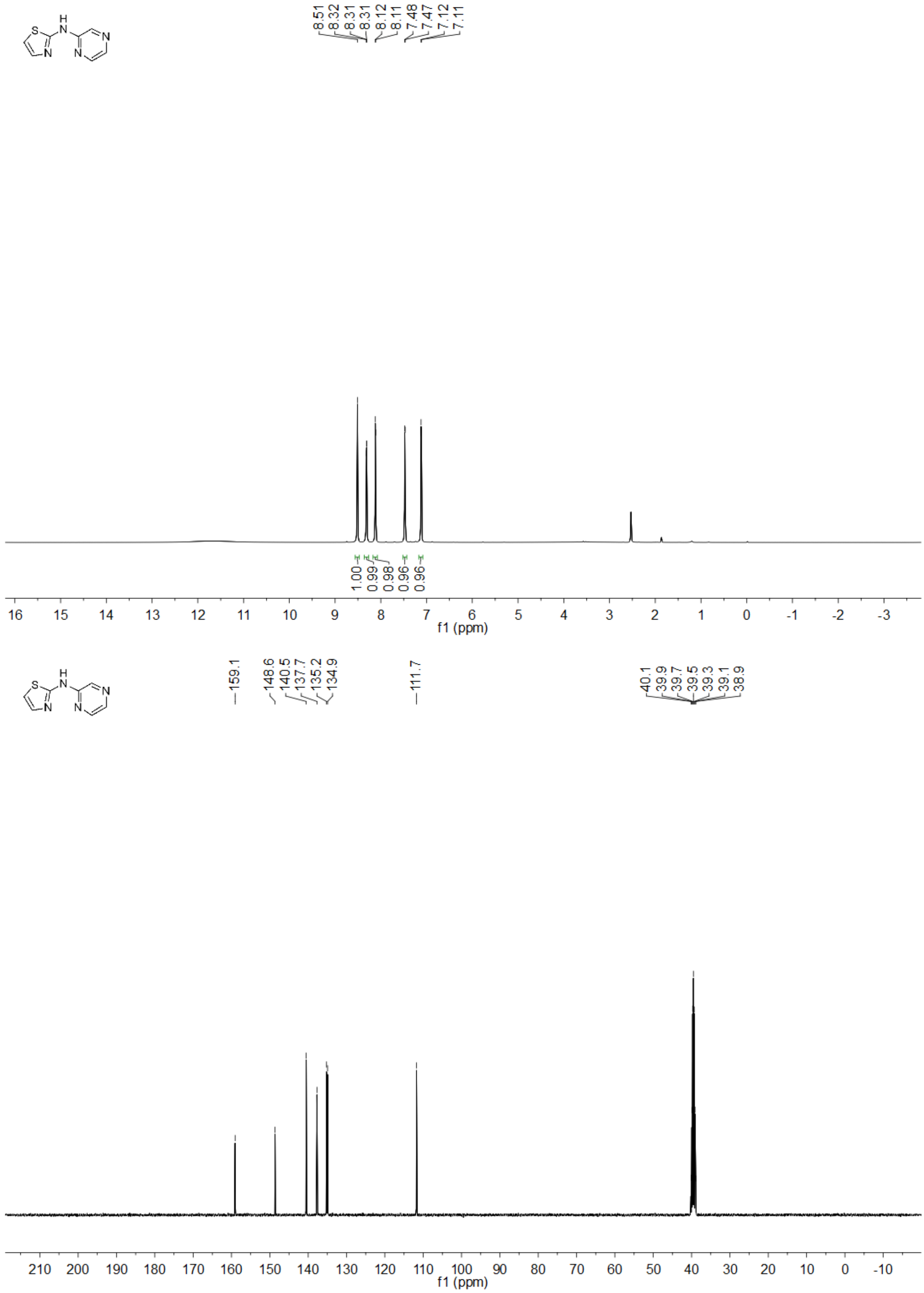
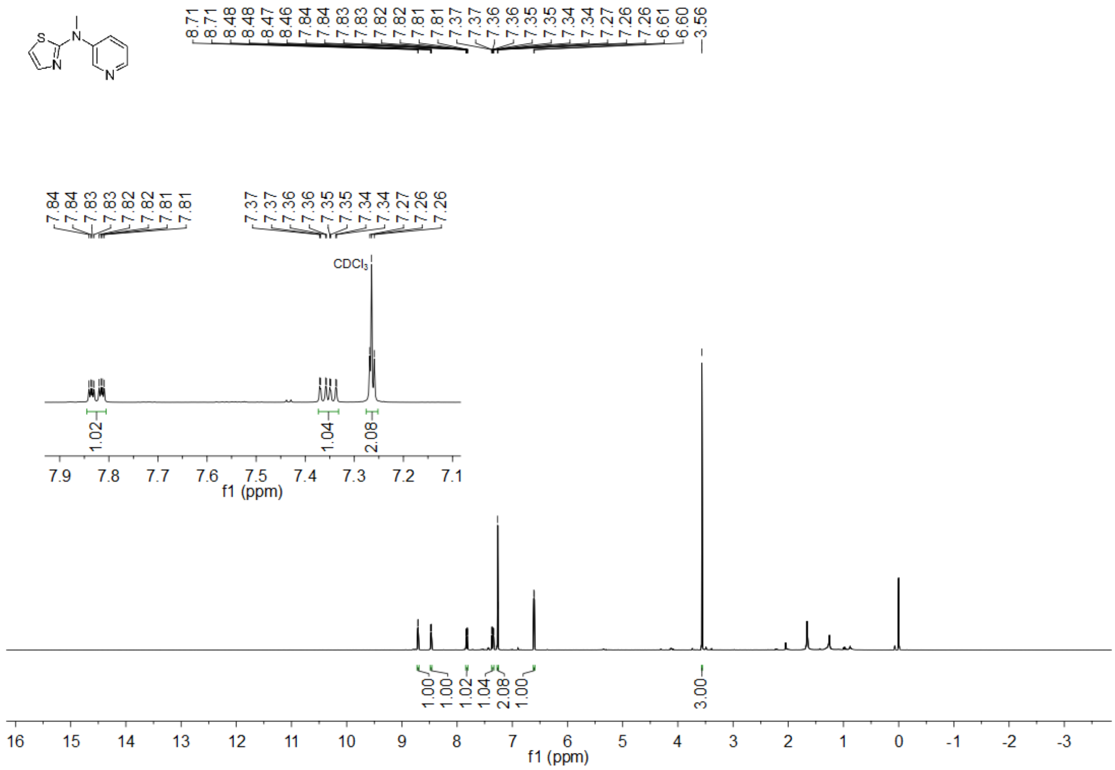


Figure S14. The NMR spectrum of 5d



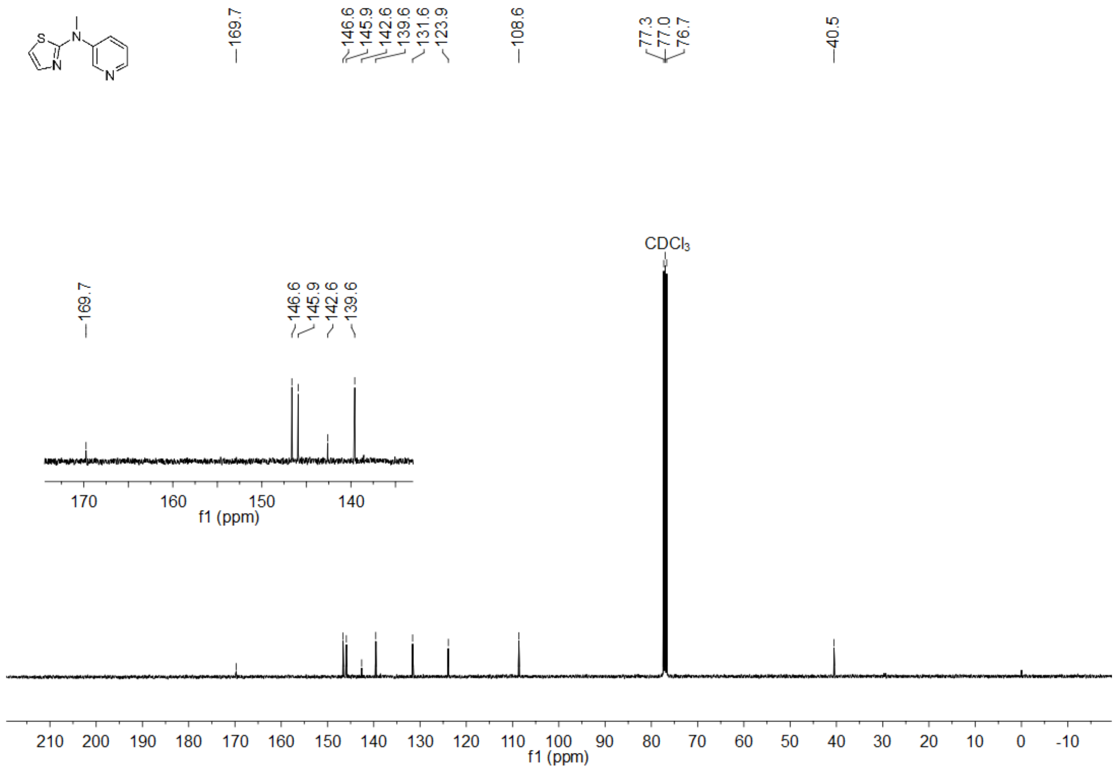


Figure S15. The NMR spectrum of 5e

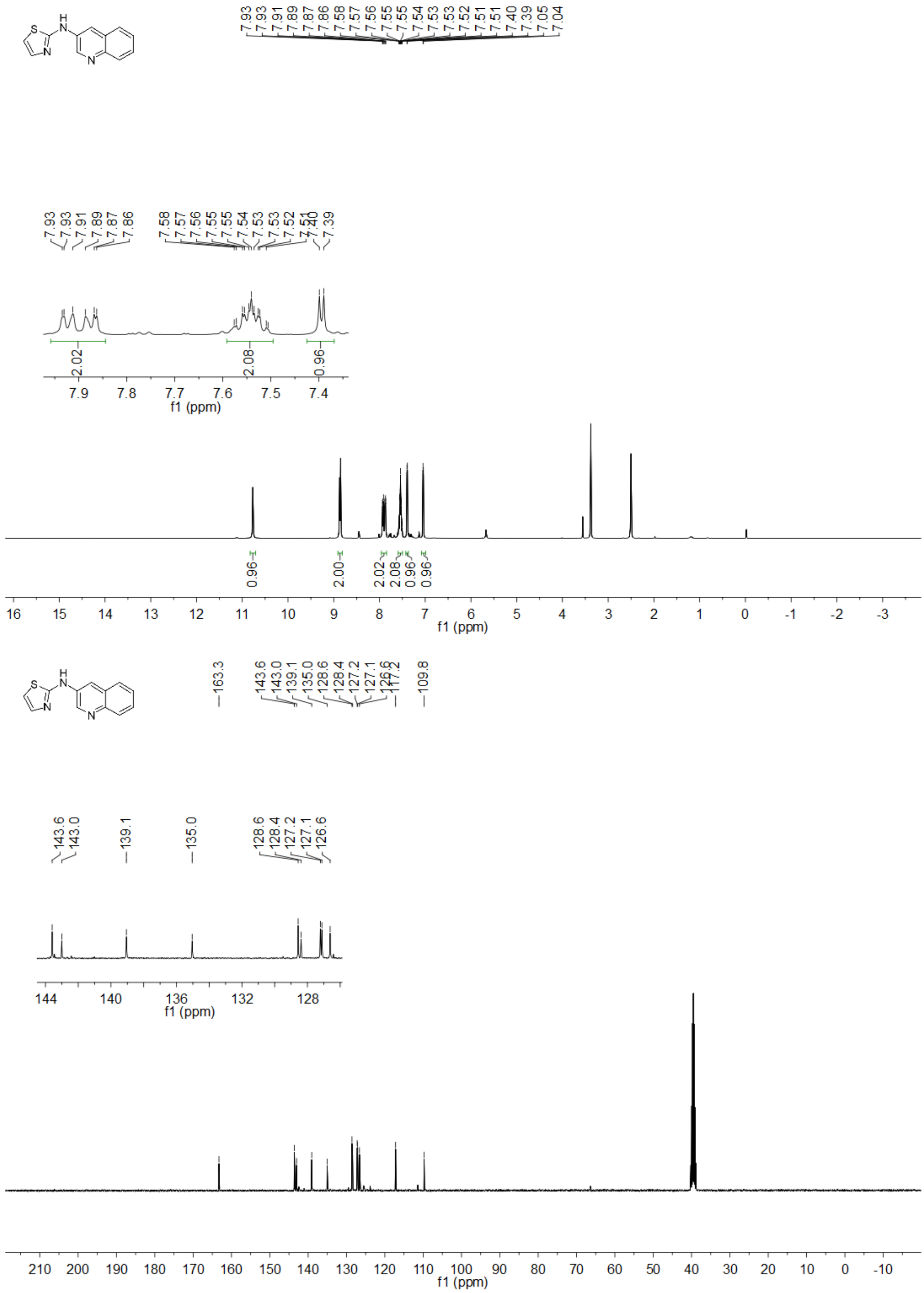


Figure S16. The NMR spectrum of 5f

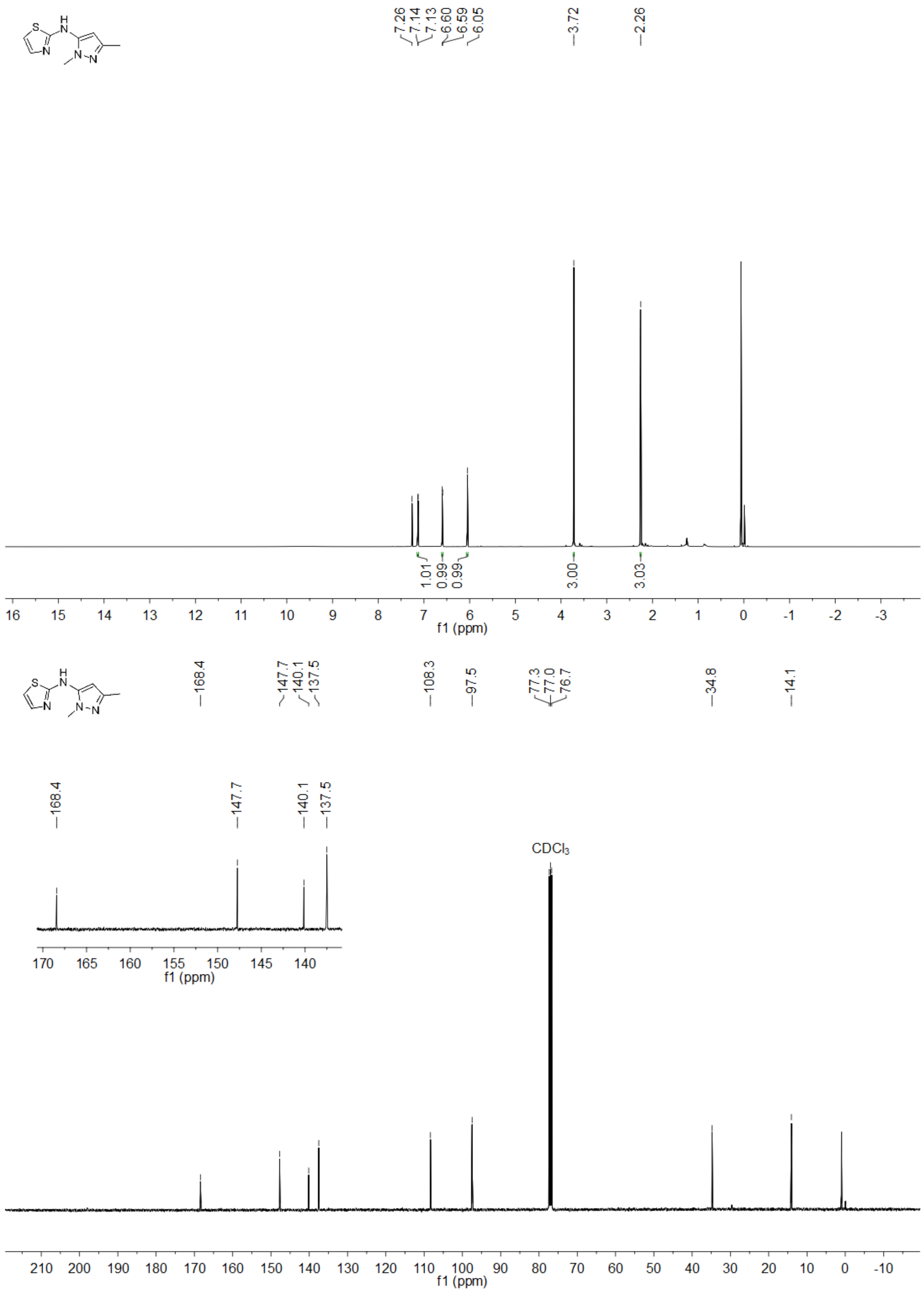


Figure S17. The NMR spectrum of 5g

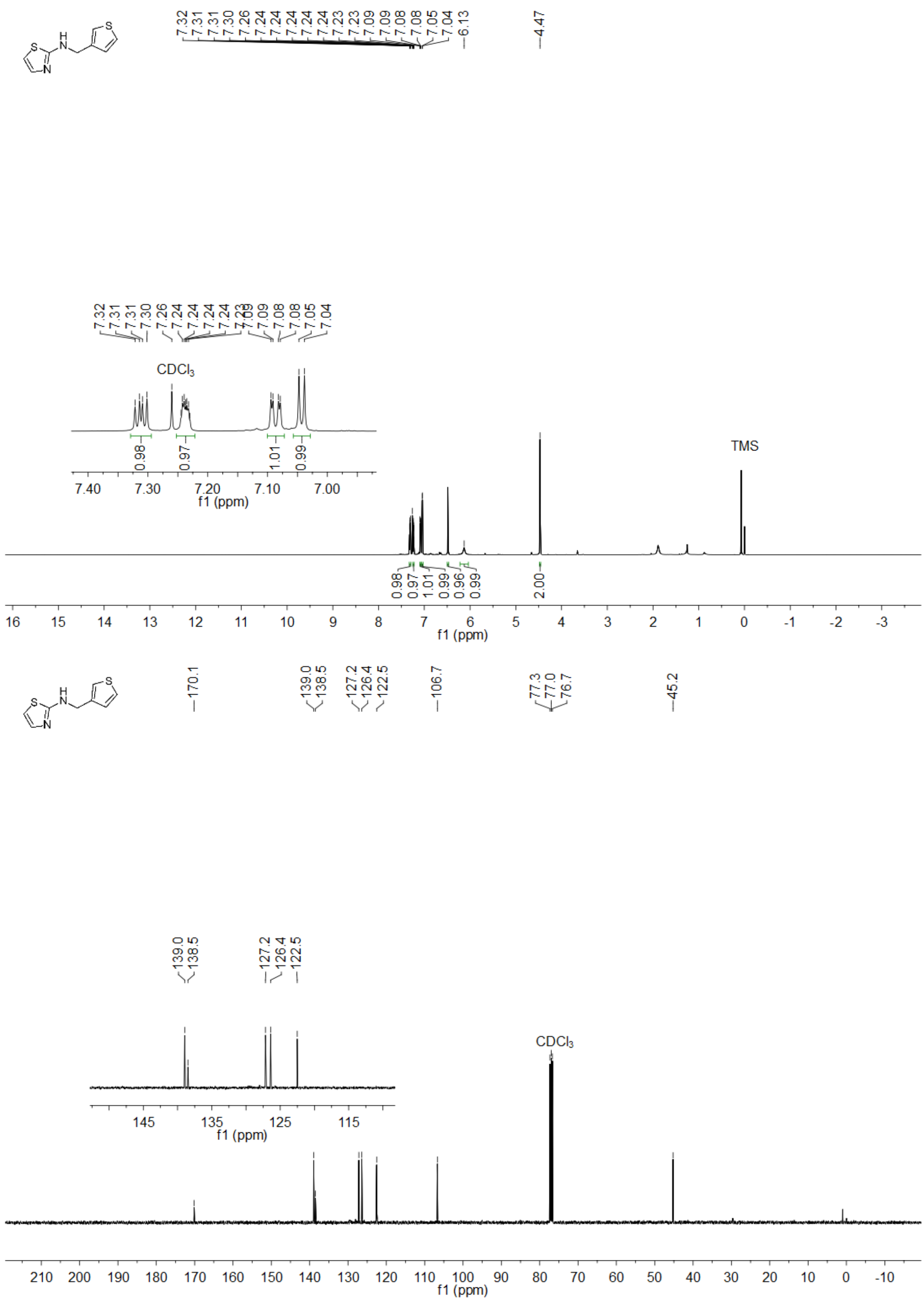
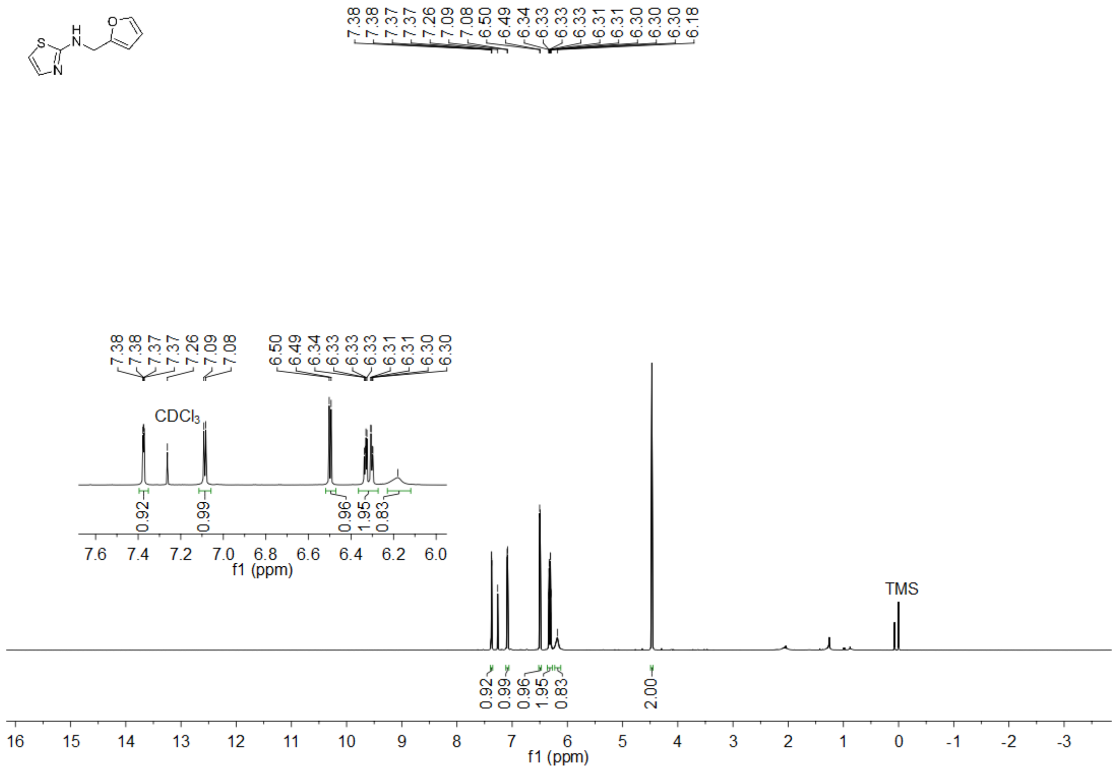


Figure S18. The NMR spectrum of 5h



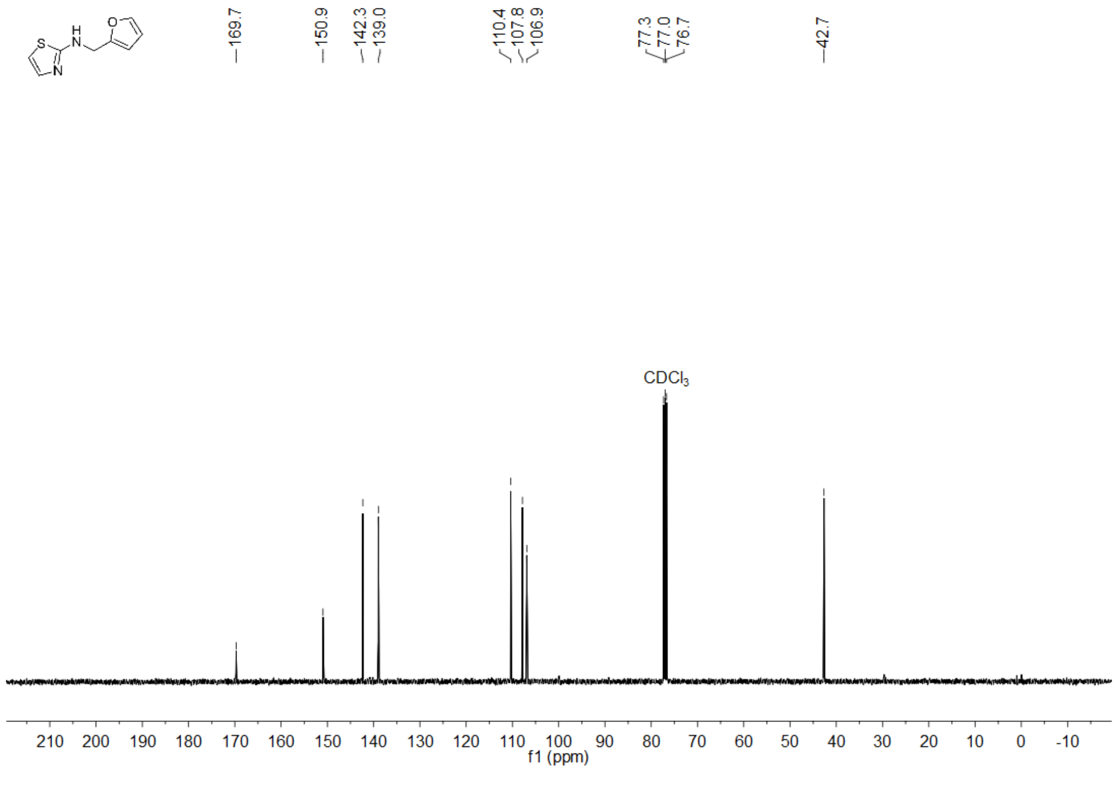
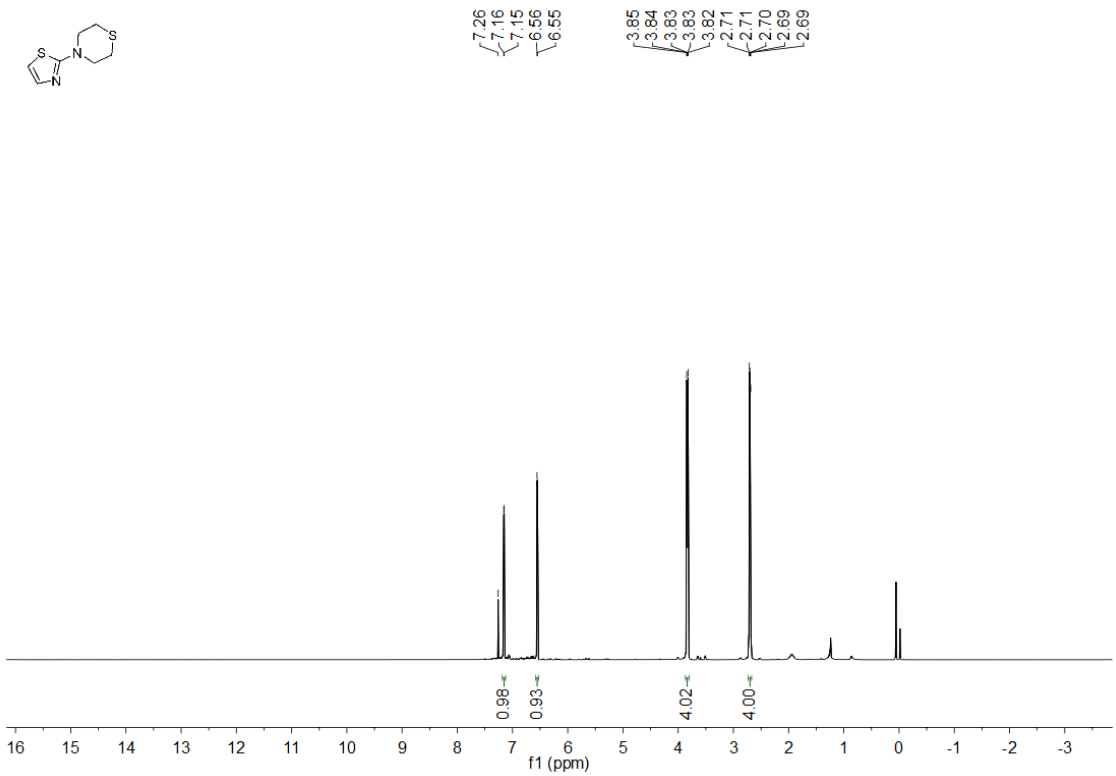


Figure S19. The NMR spectrum of 5i



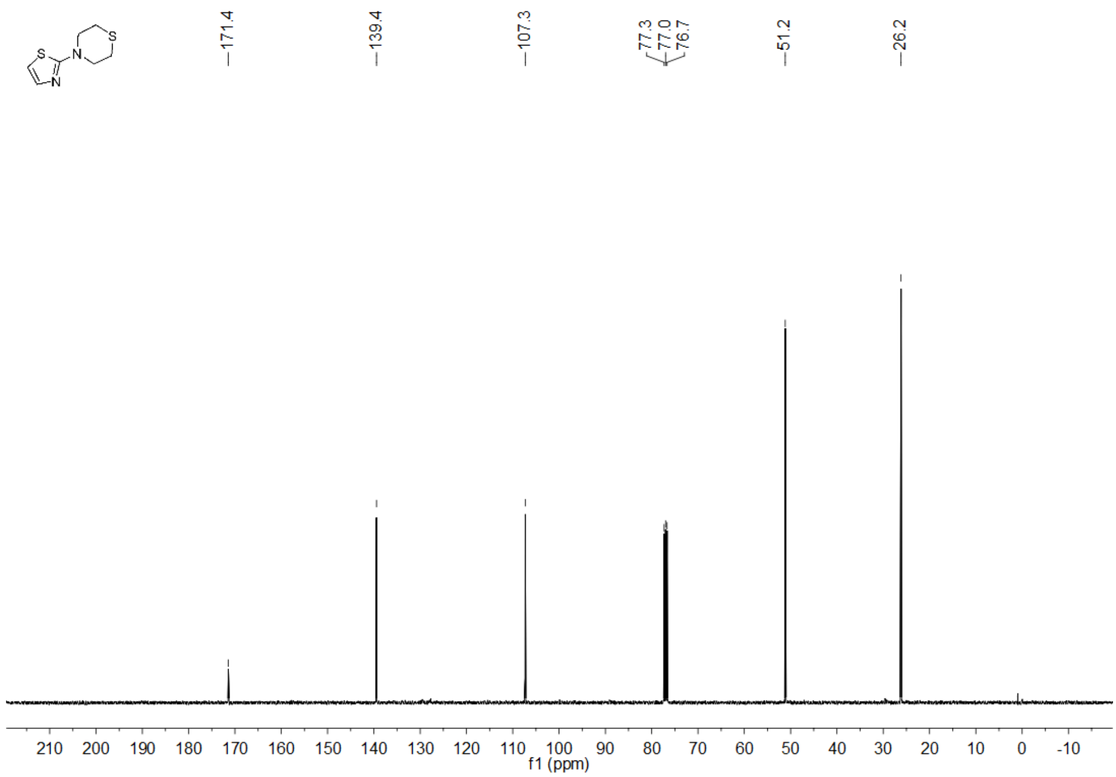
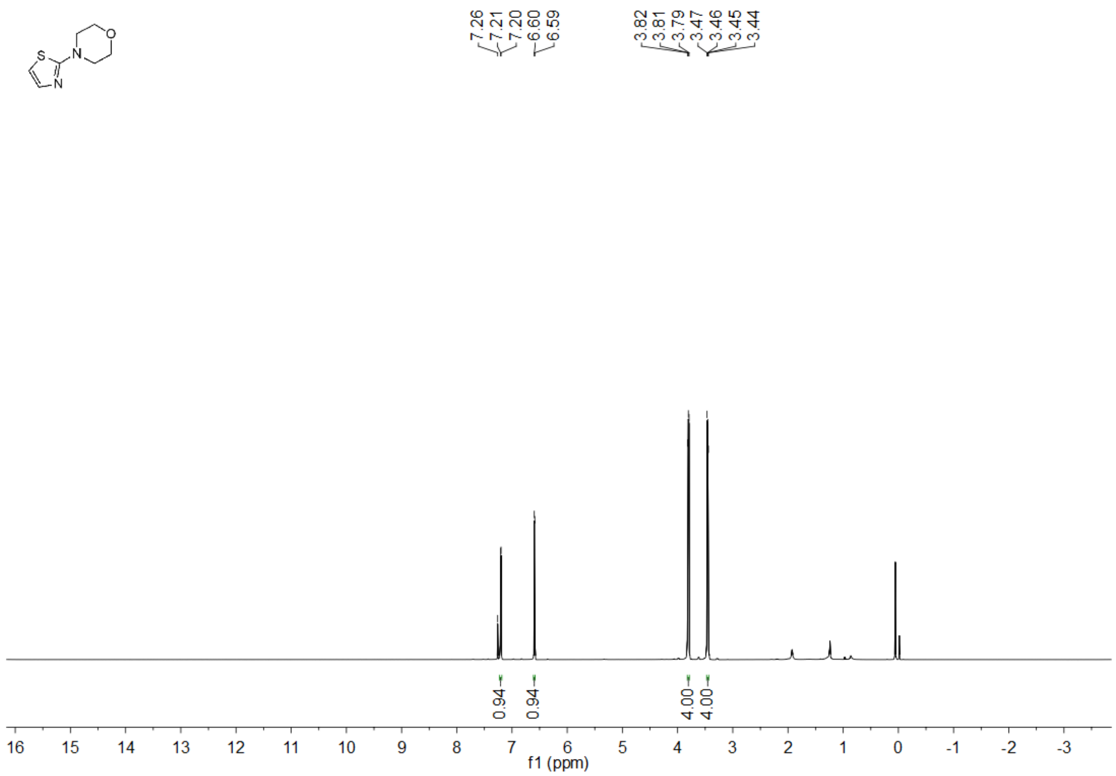


Figure S20. The NMR spectrum of 5j



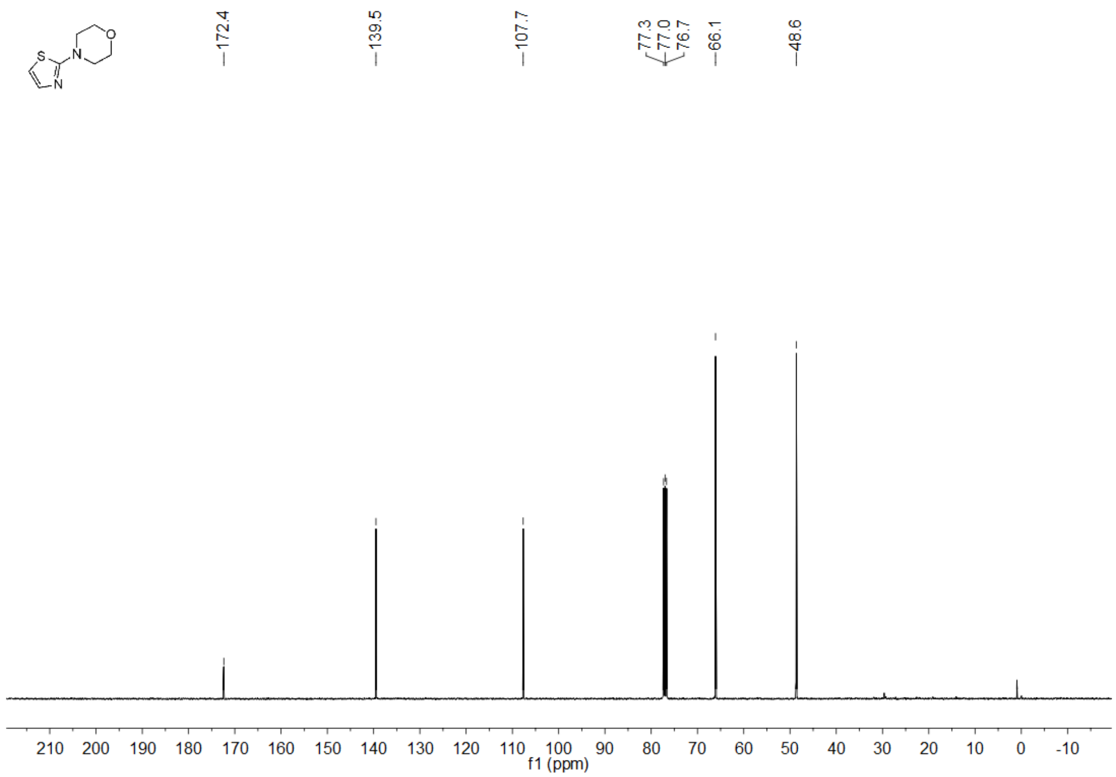
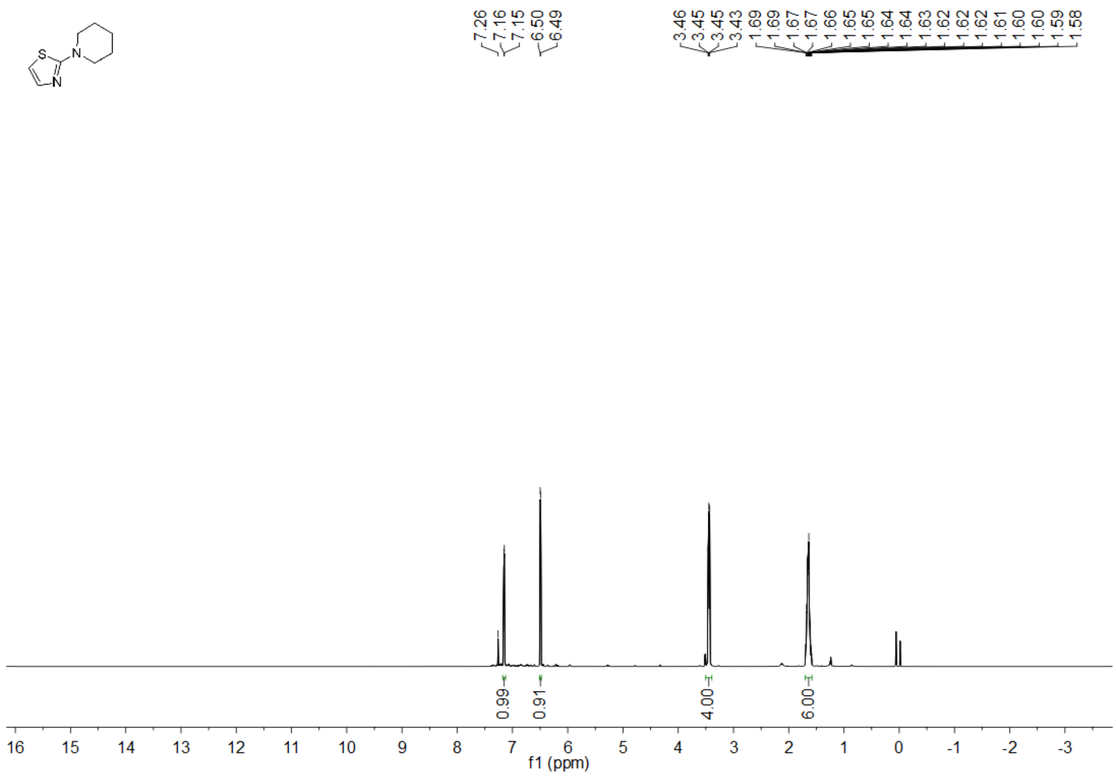


Figure S21. The NMR spectrum of 5k



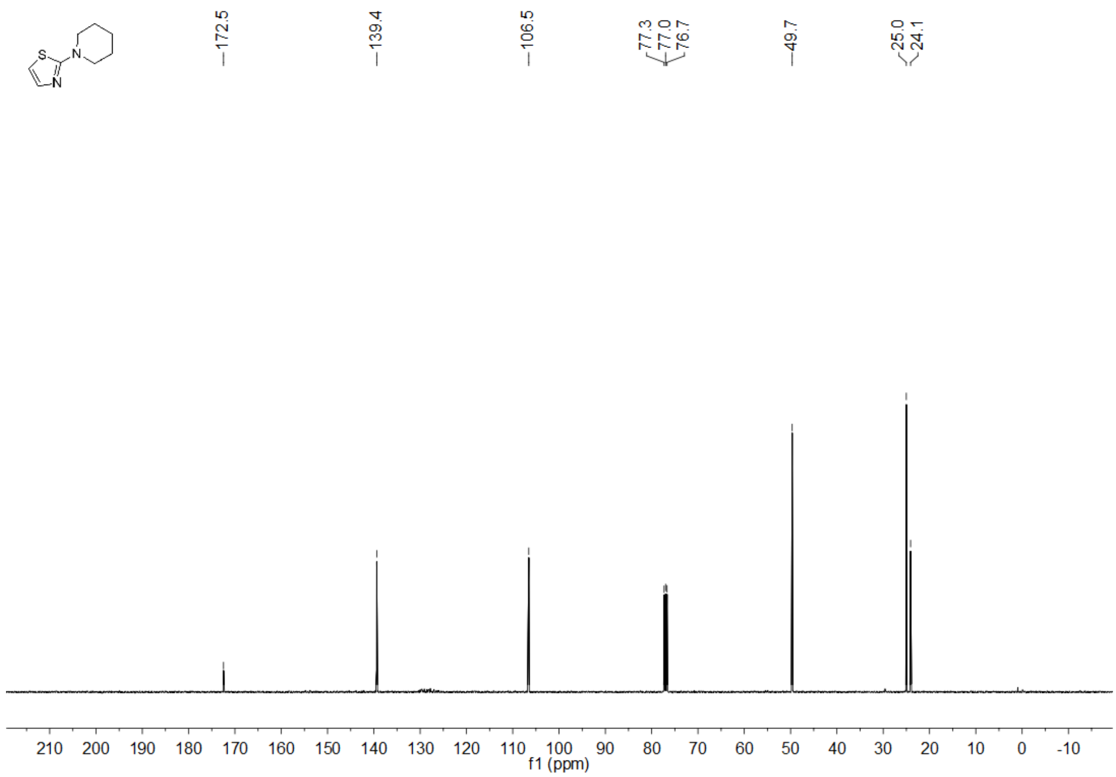
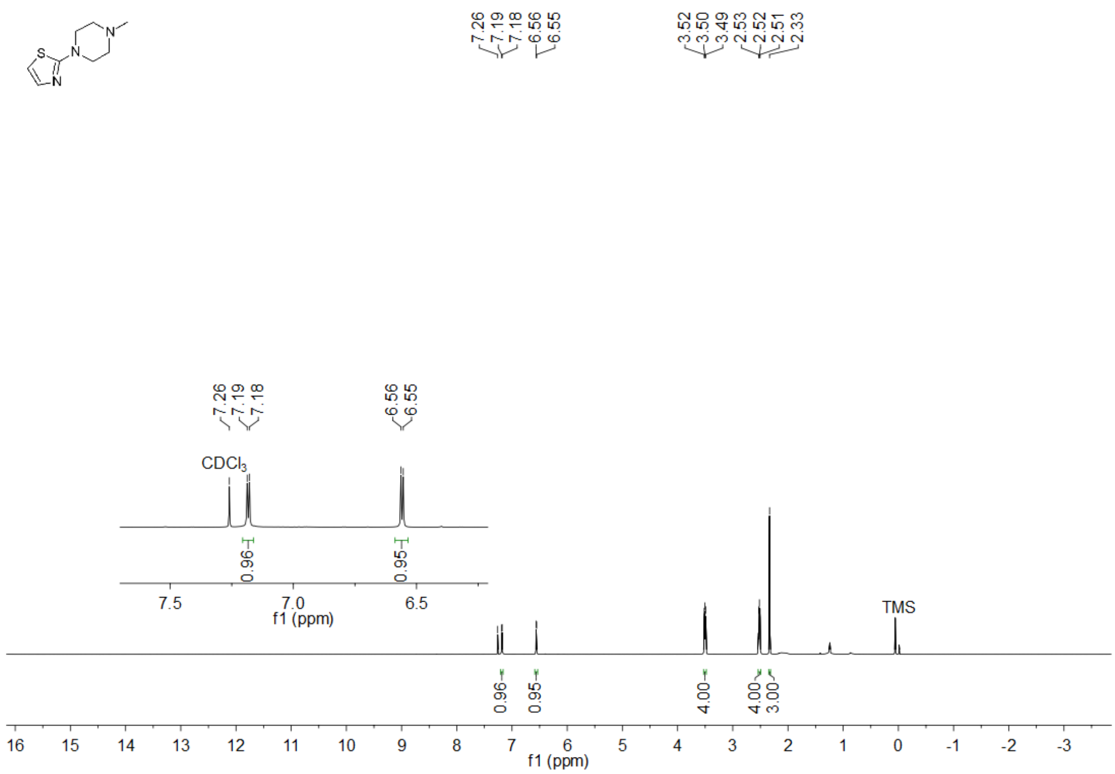


Figure S22. The NMR spectrum of 5l



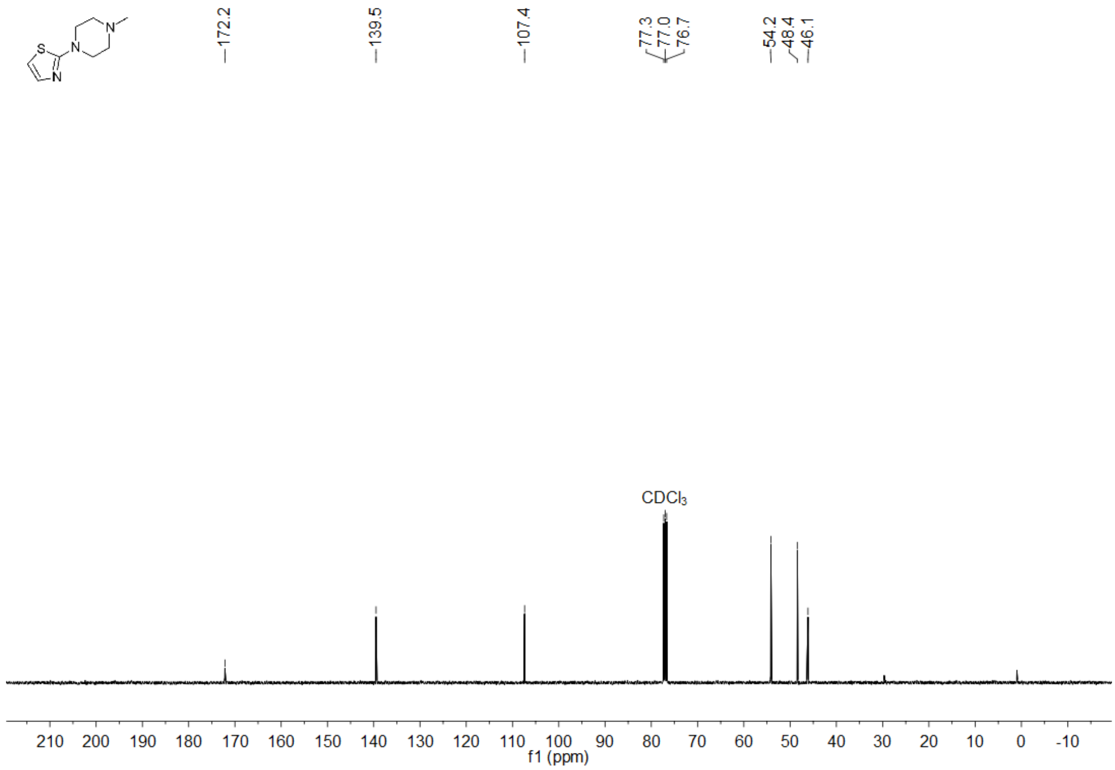


Figure S23. The NMR spectrum of 5m

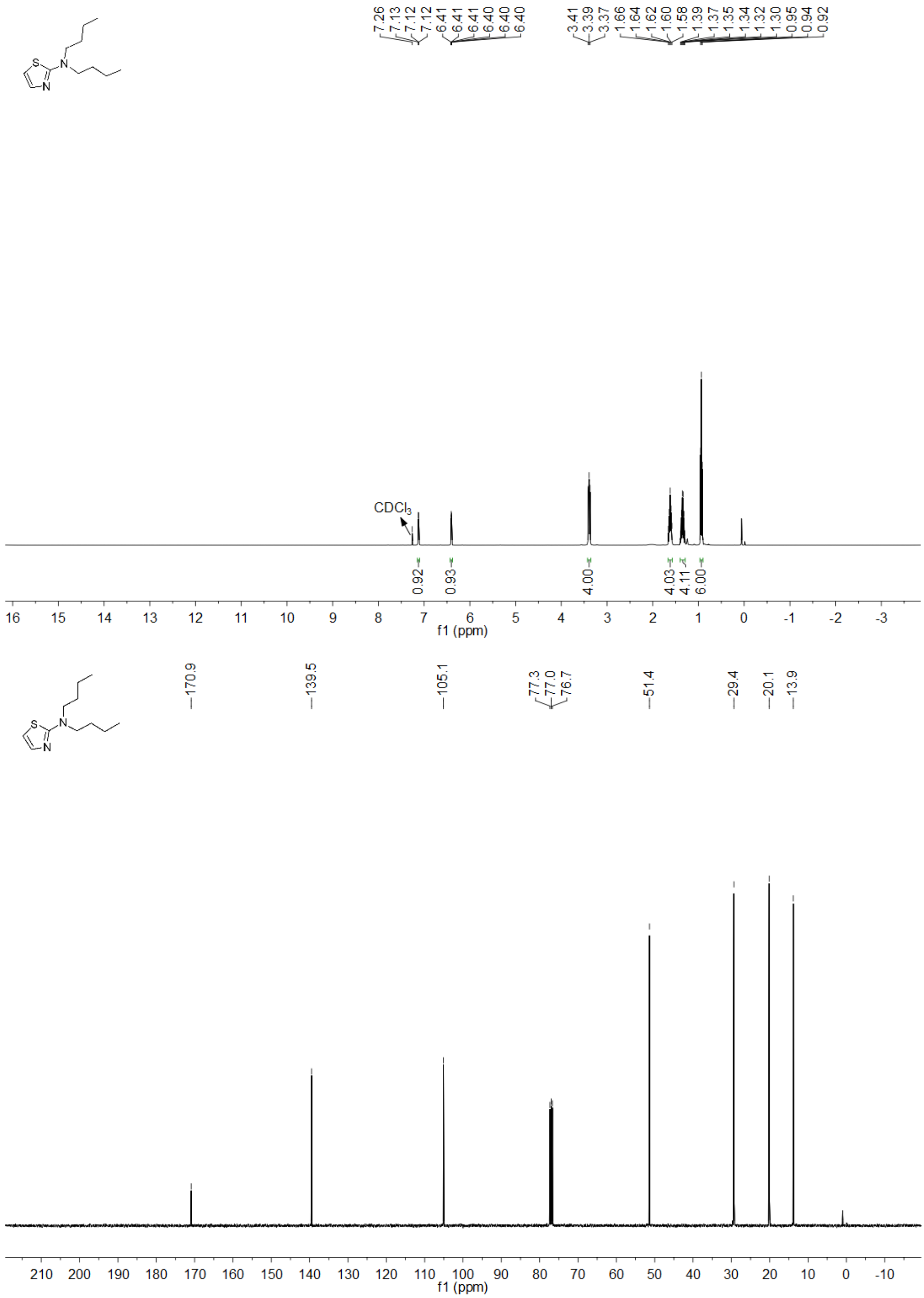
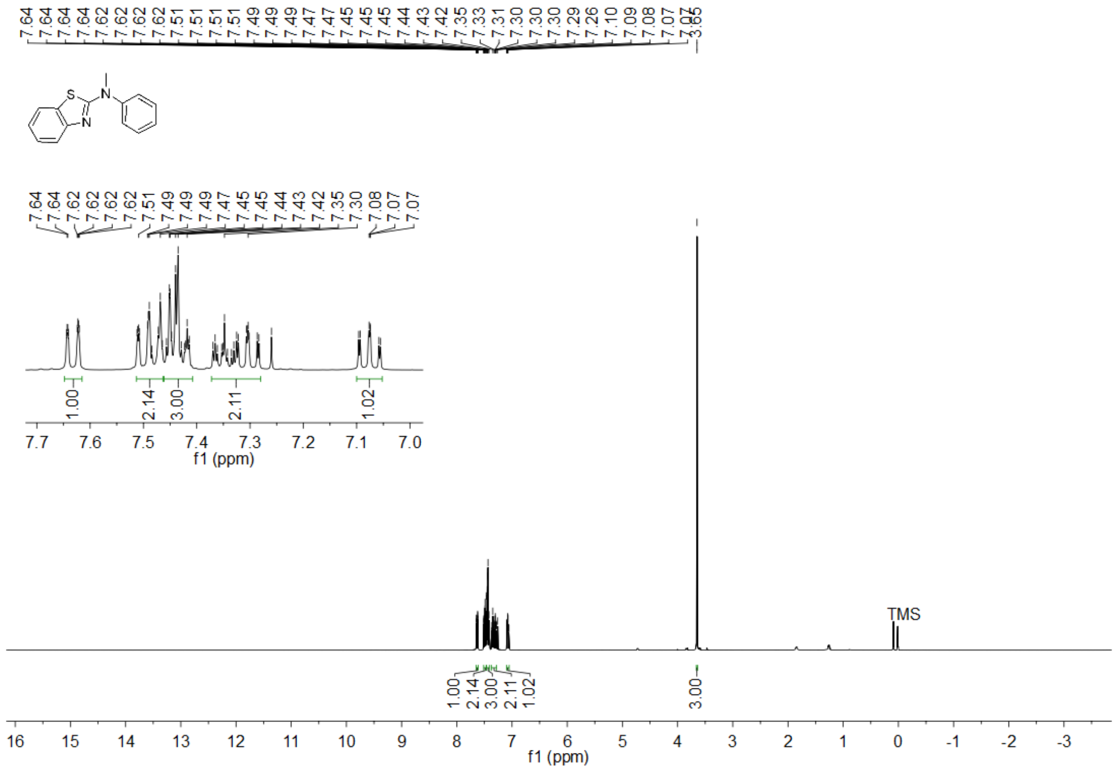


Figure S24. The NMR spectrum of 5n



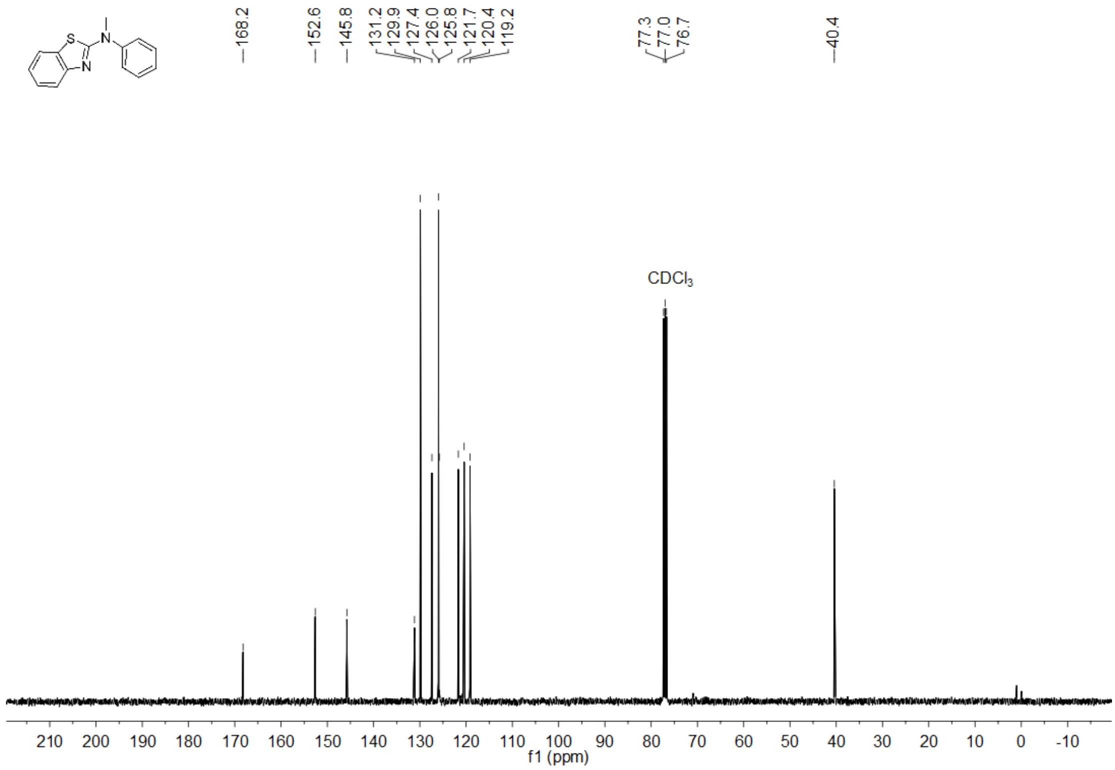
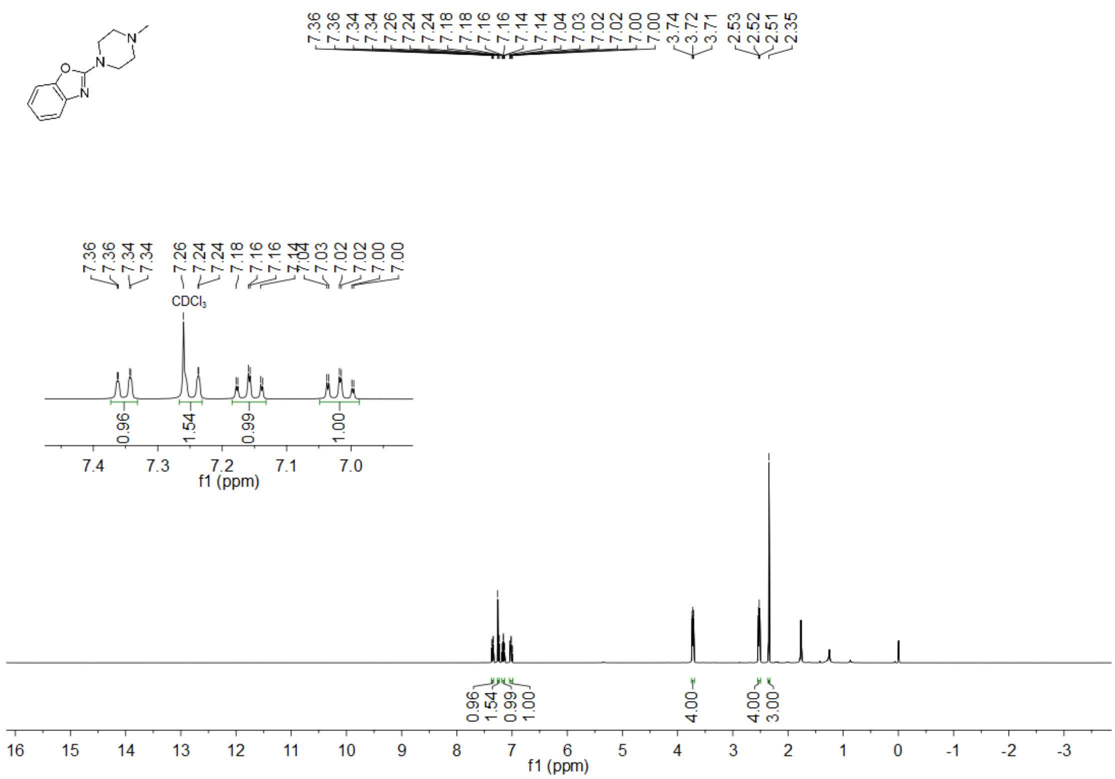


Figure S25. The NMR spectrum of 5o



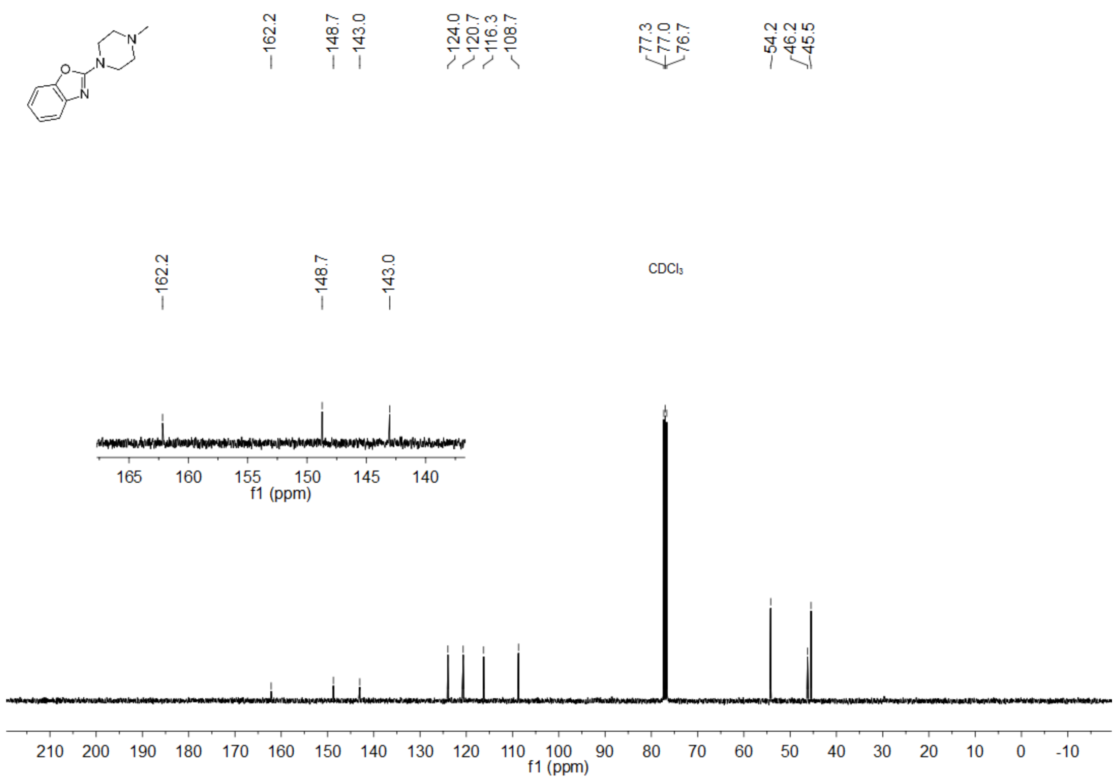


Figure S26. The NMR spectrum of 5p

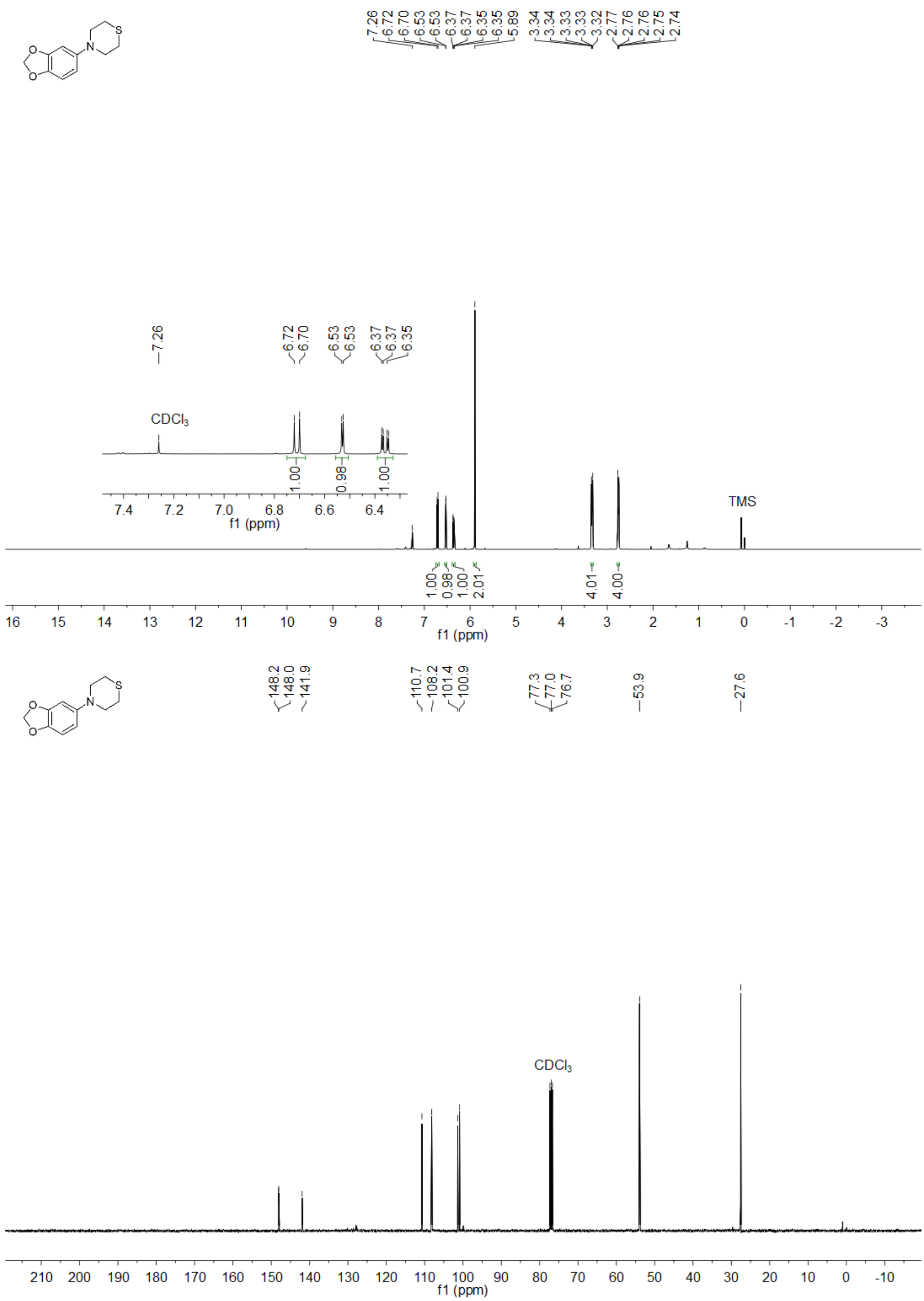
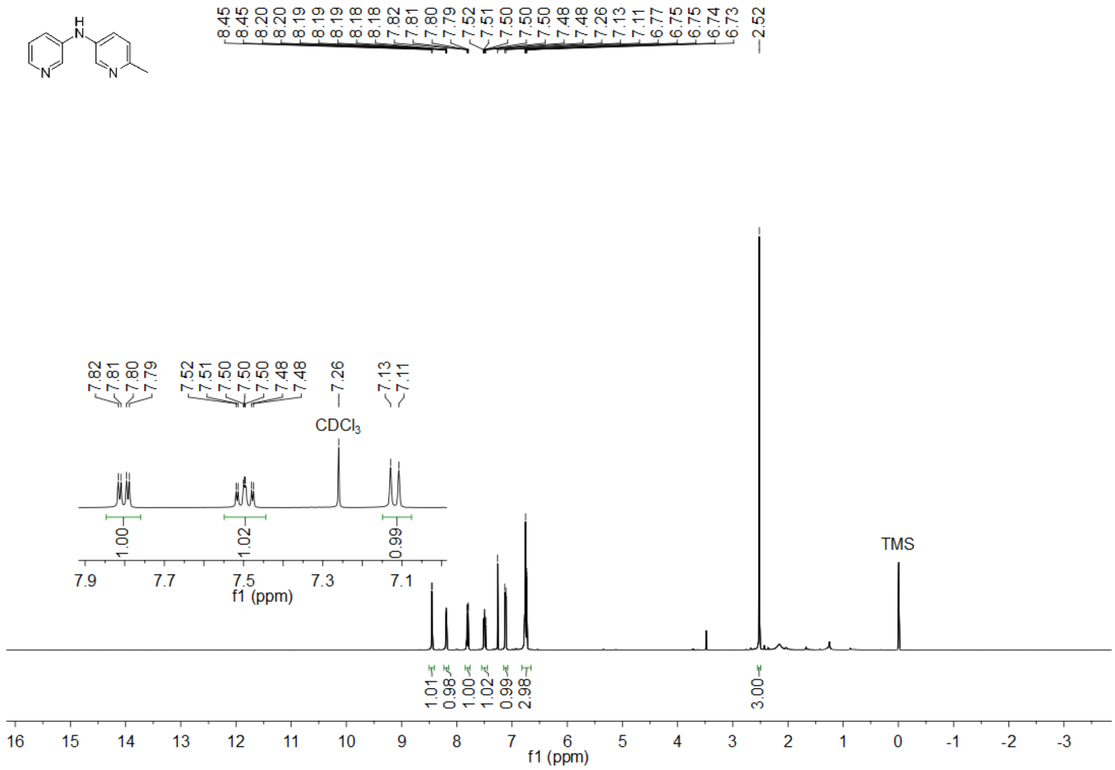


Figure S27. The NMR spectrum of 5q



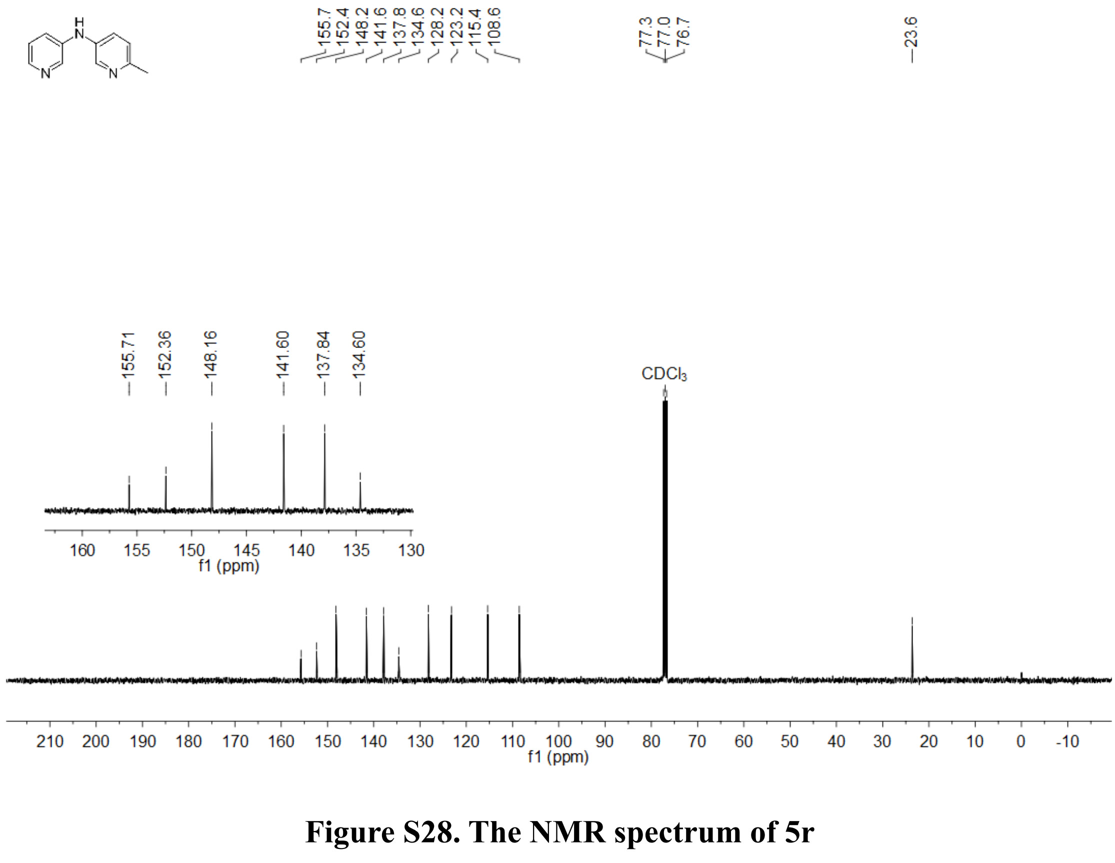
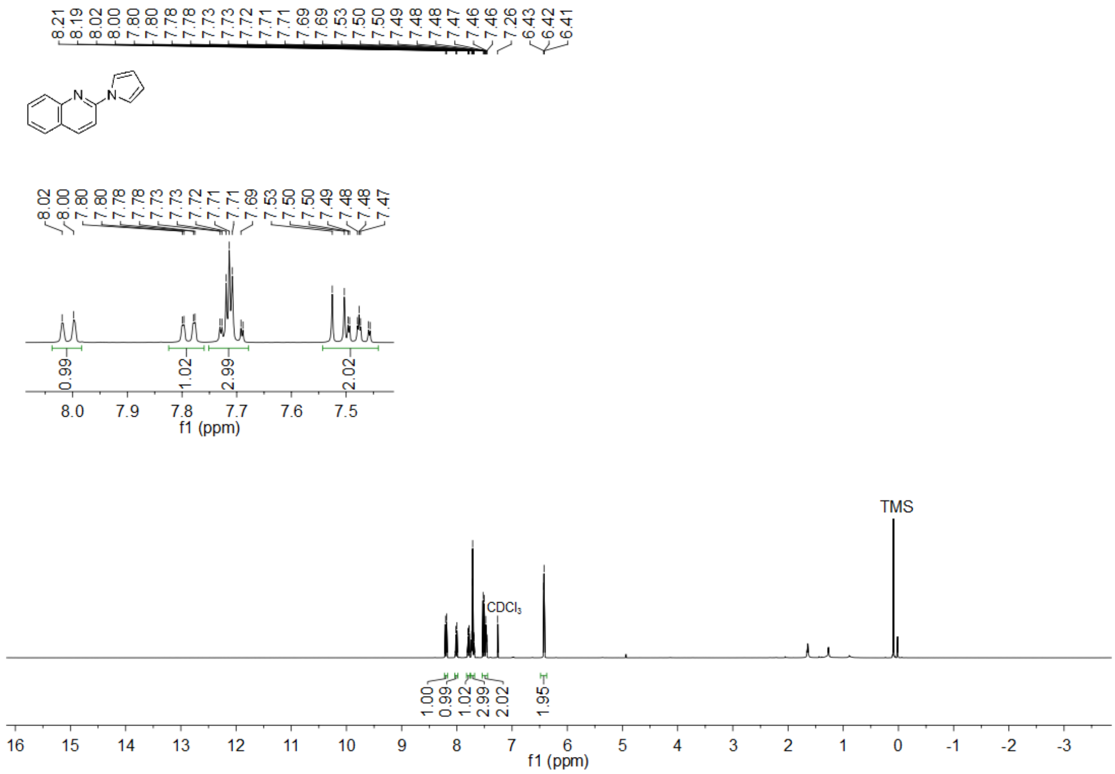


Figure S28. The NMR spectrum of 5r



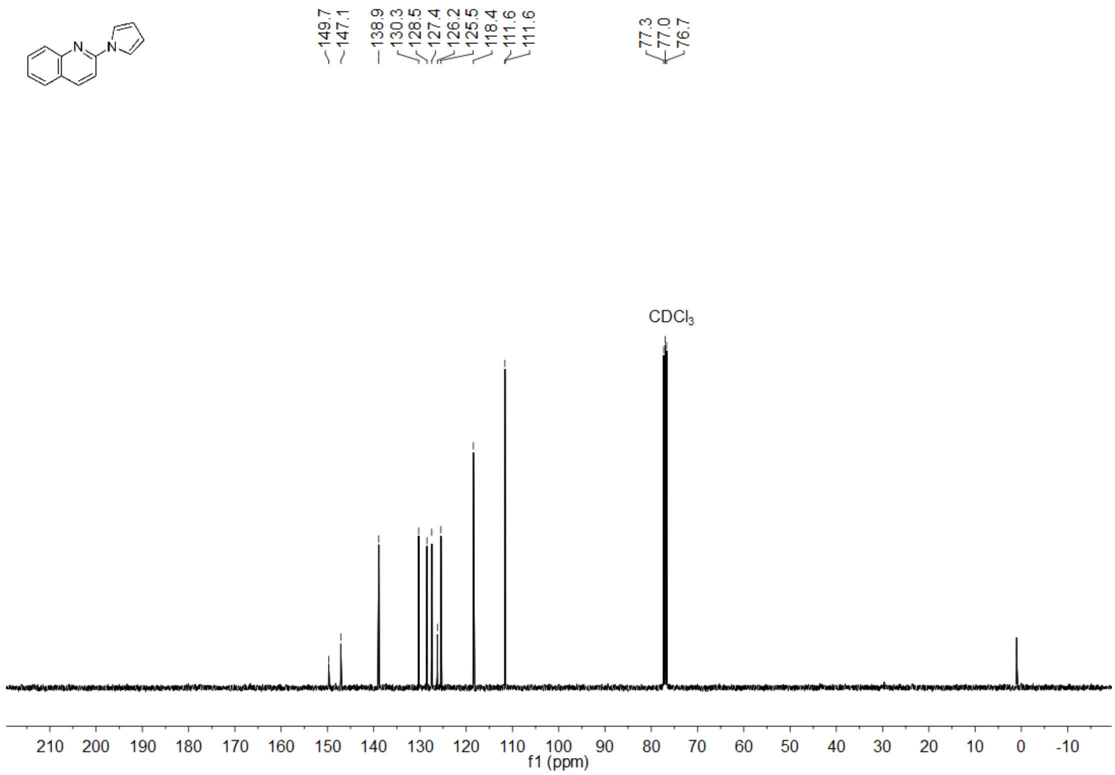
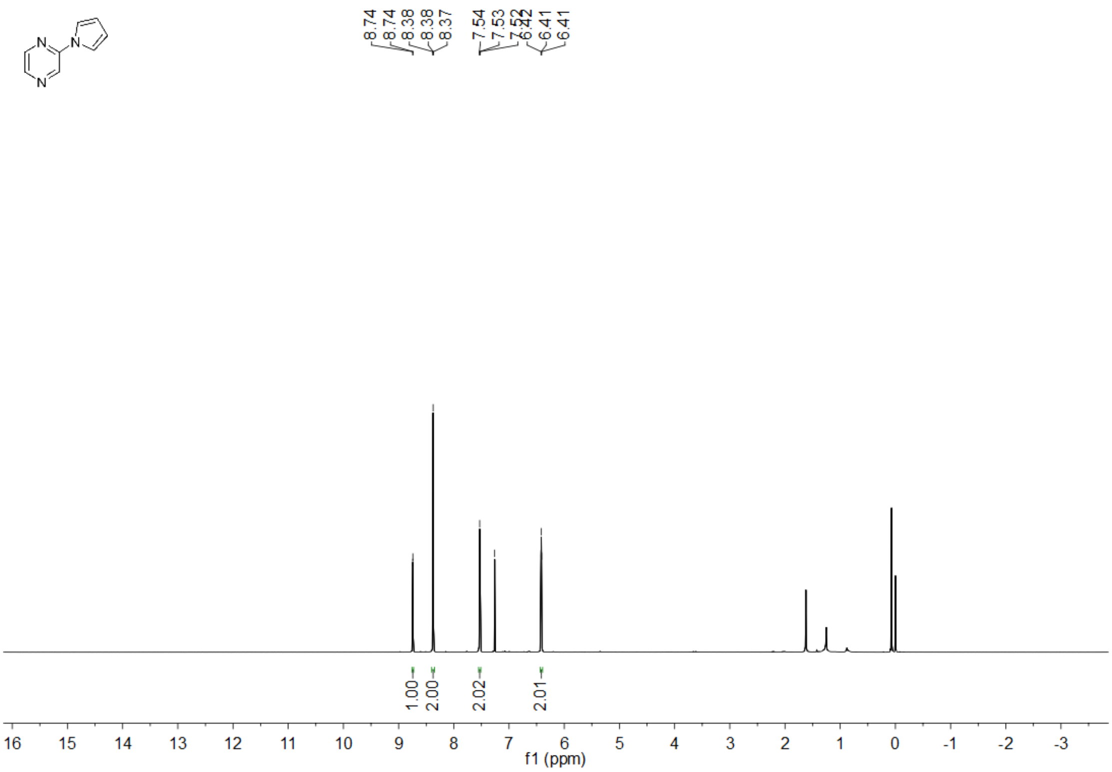


Figure S29. The NMR spectrum of 5s



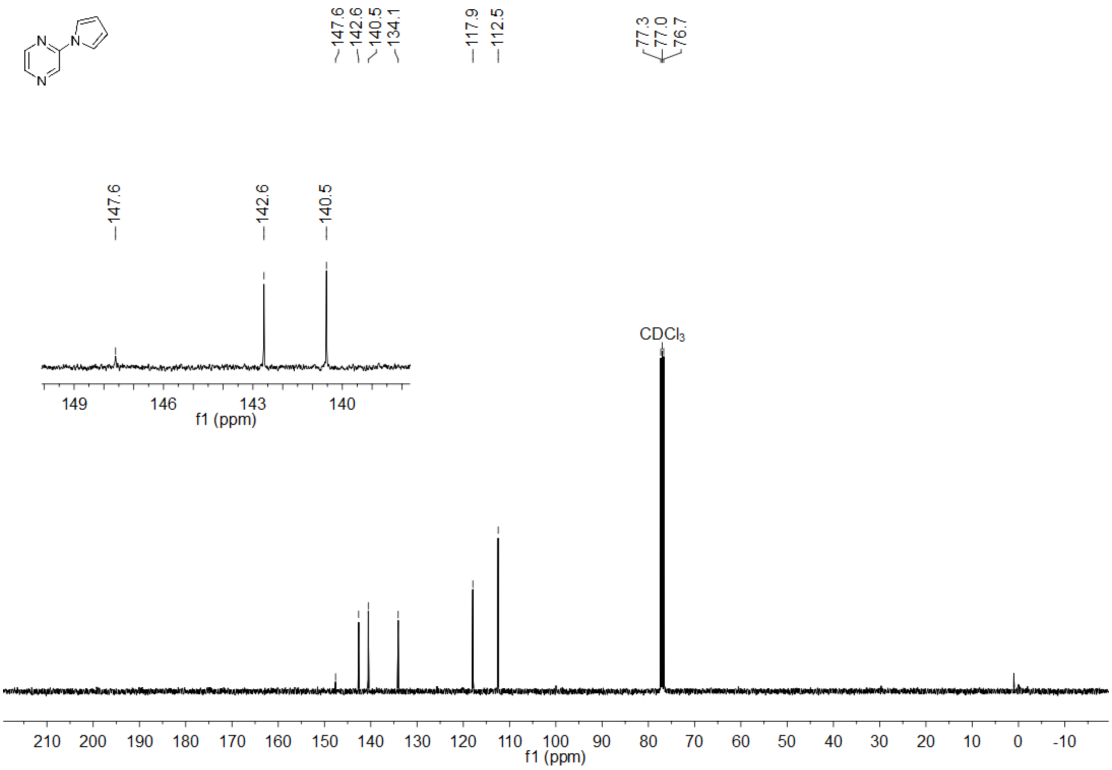
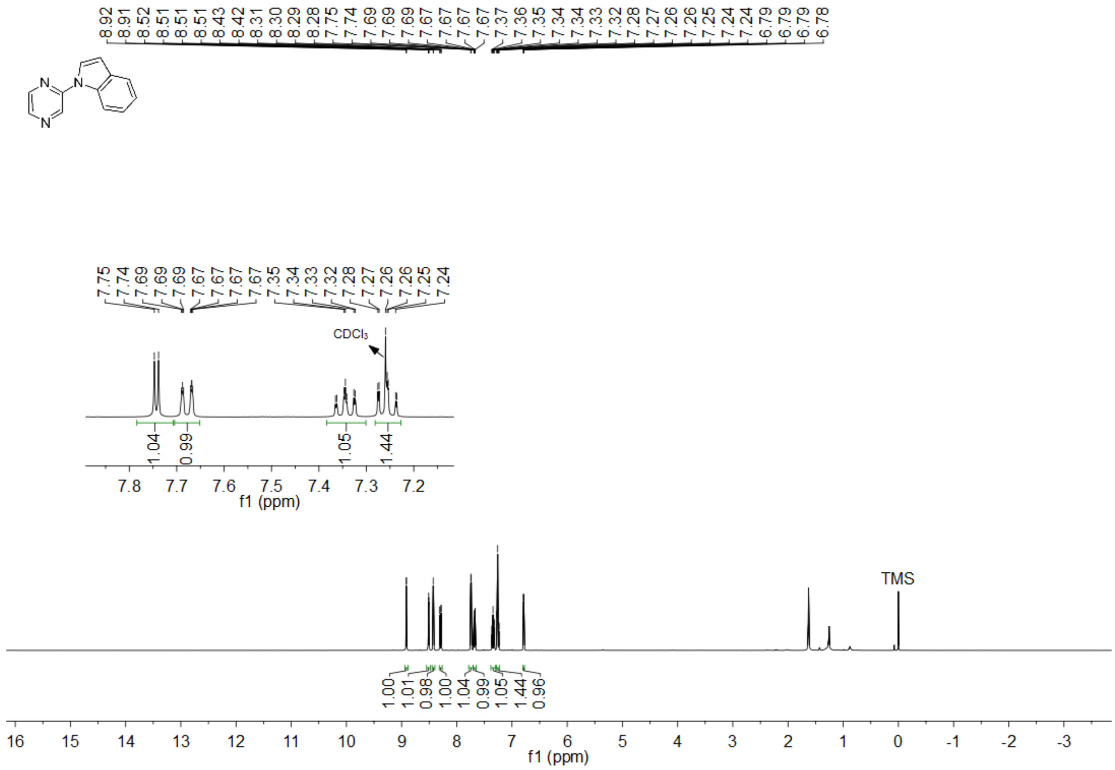


Figure S30. The NMR spectrum of 5t



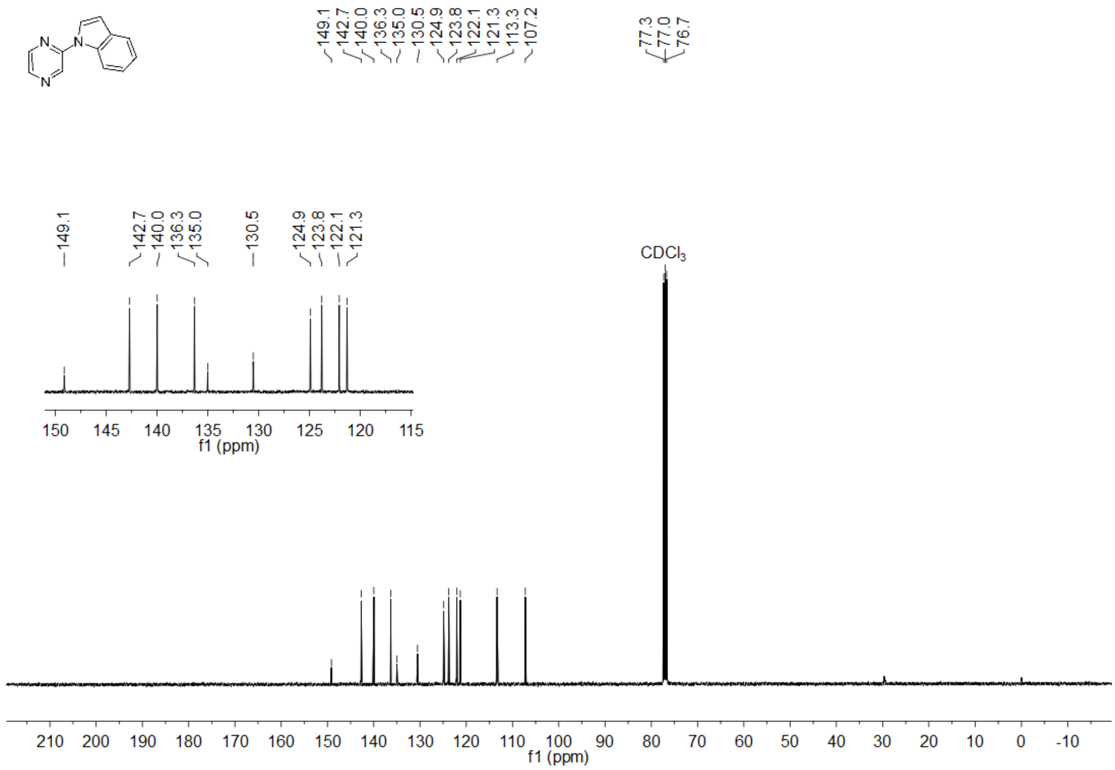
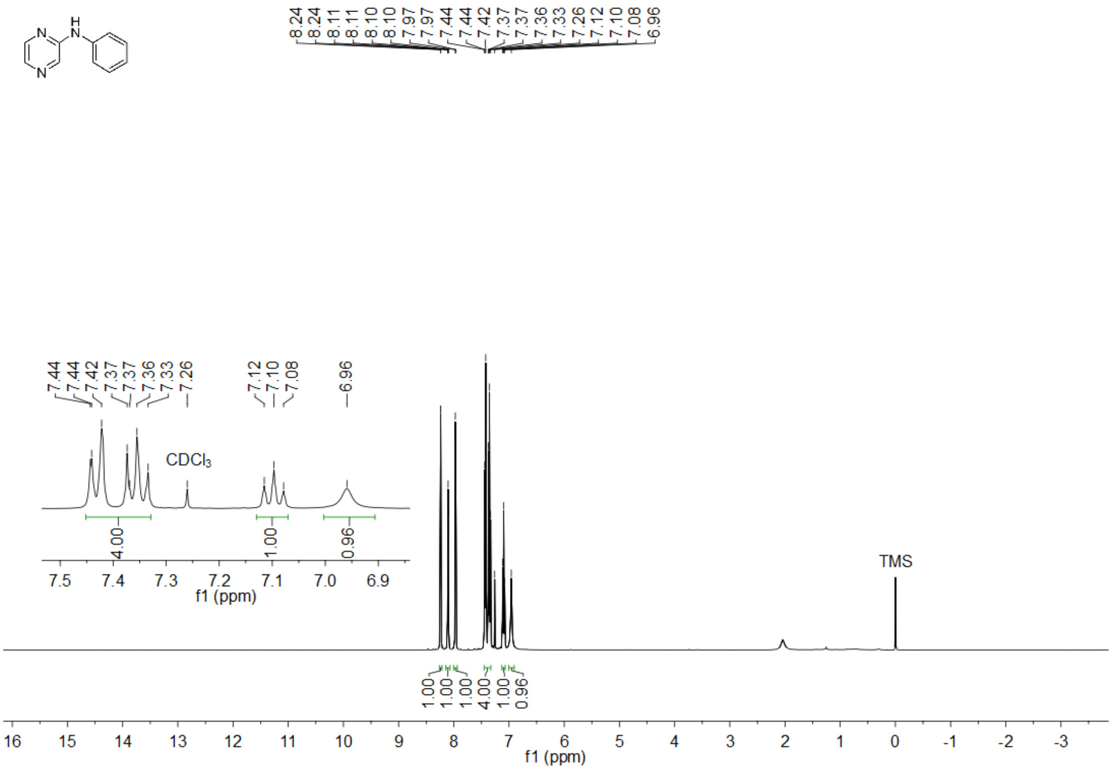


Figure S31. The NMR spectrum of 5u



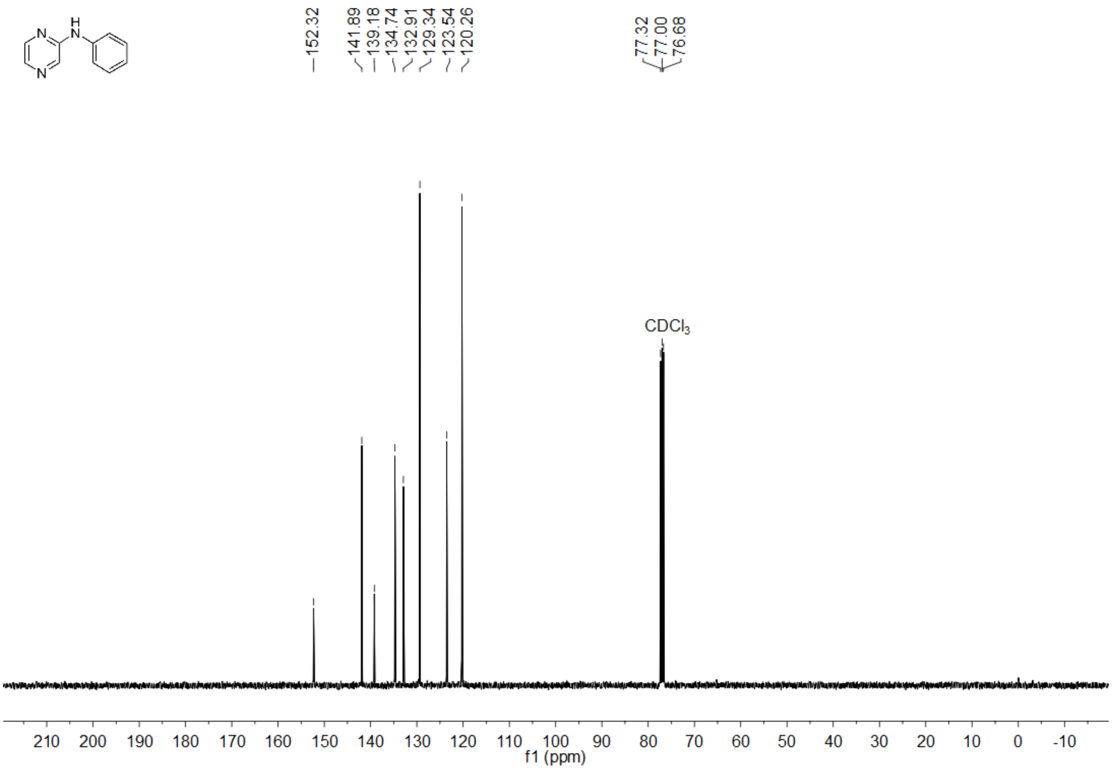
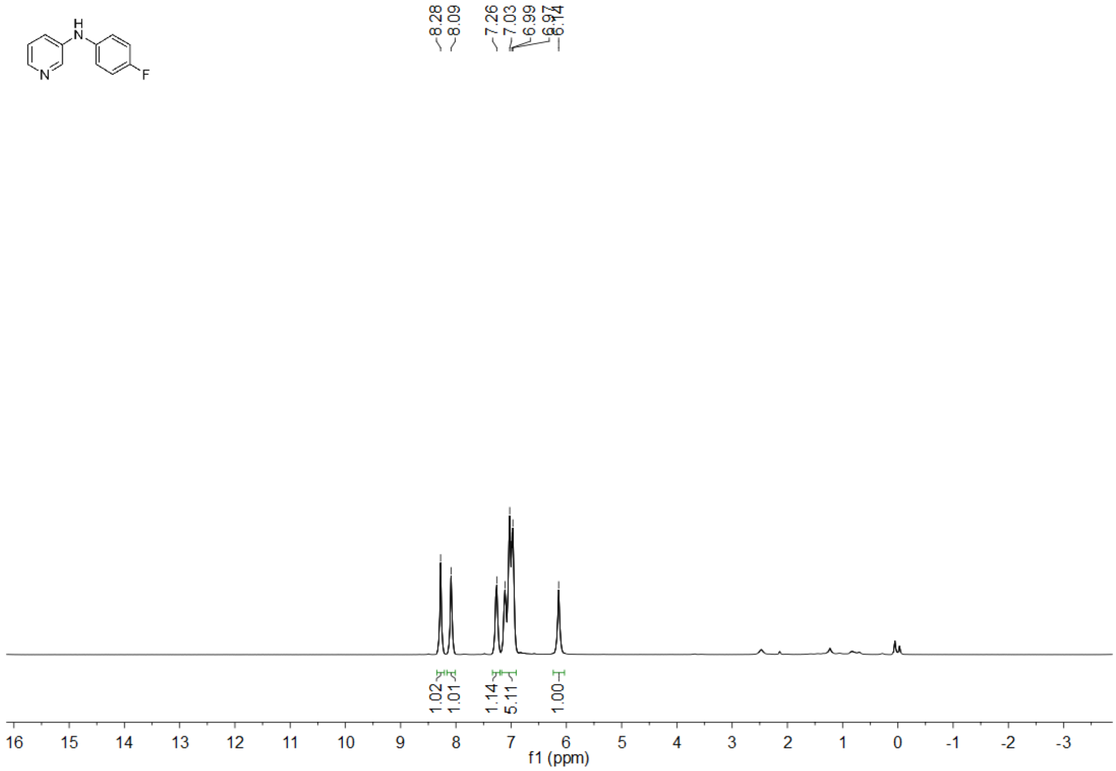


Figure S32. The NMR spectrum of 5v



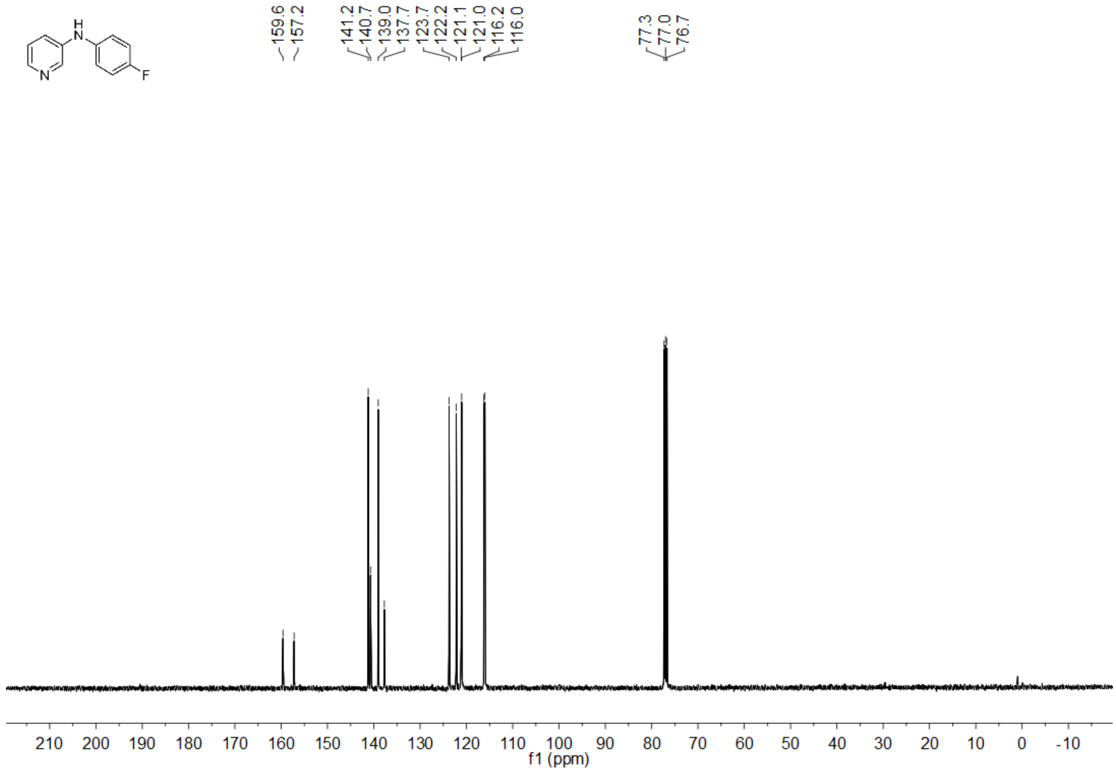


Figure S33. The NMR spectrum of 5w

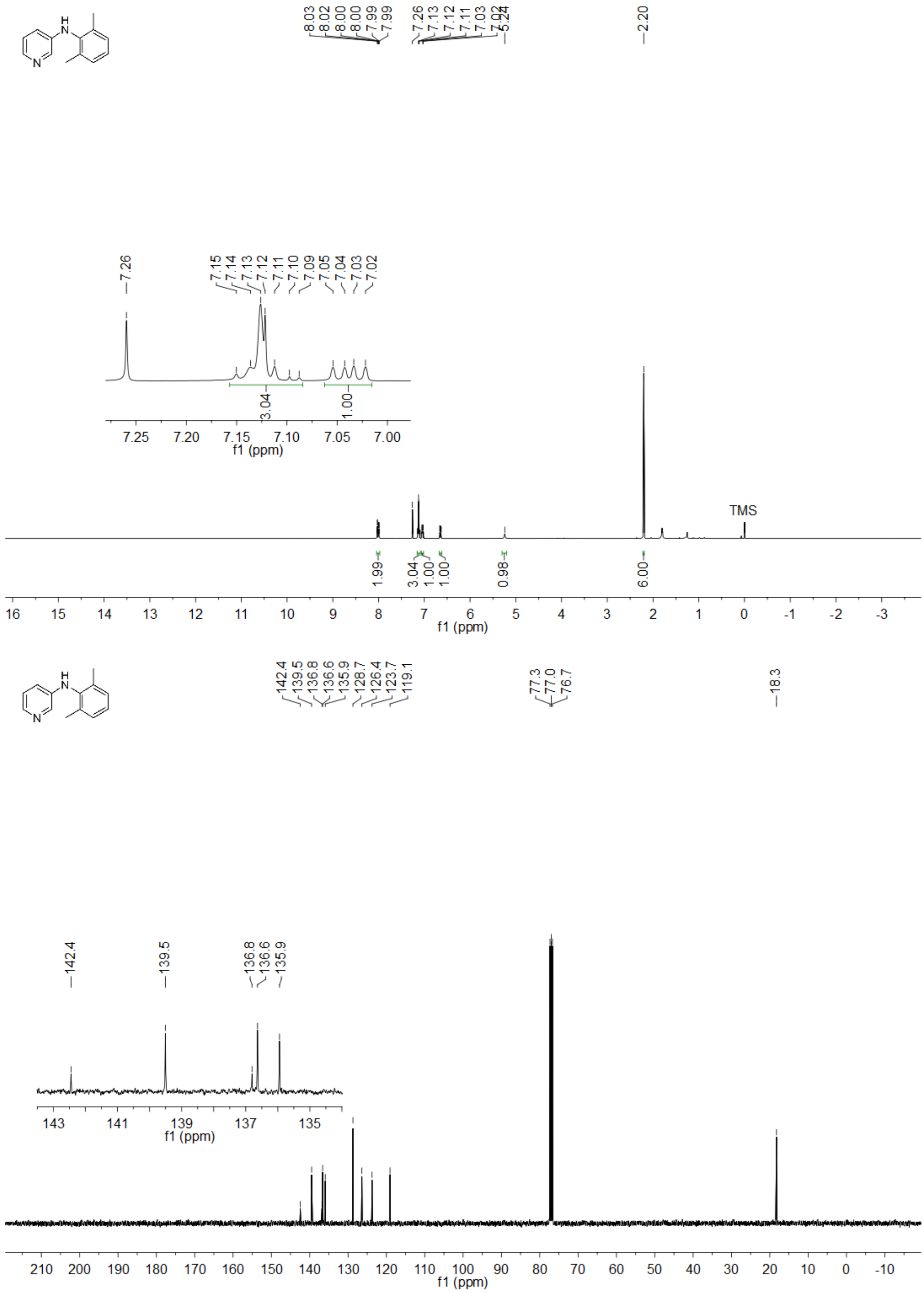


Figure S34. The NMR spectrum of 5x

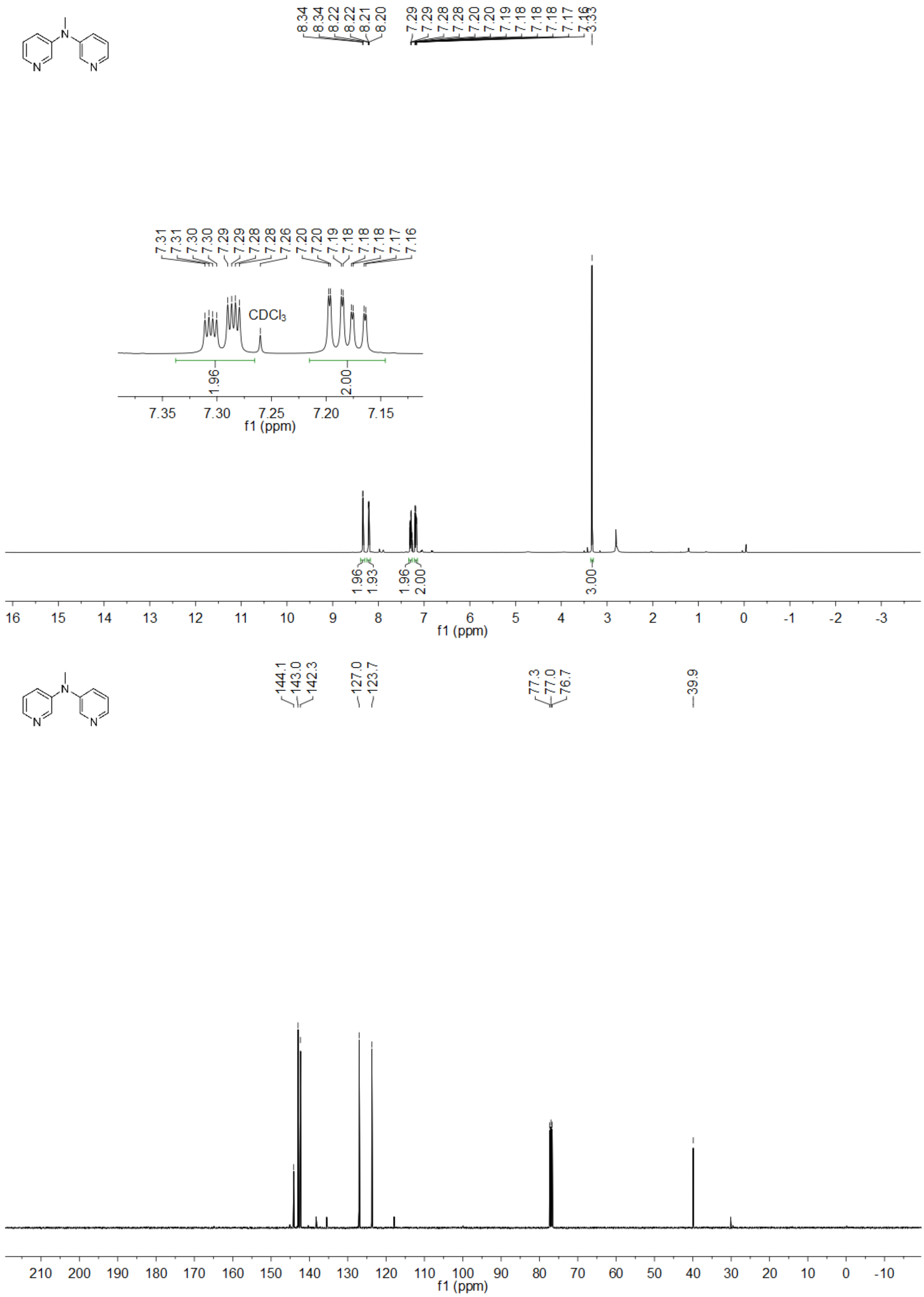


Figure S35. The NMR spectrum of 5y

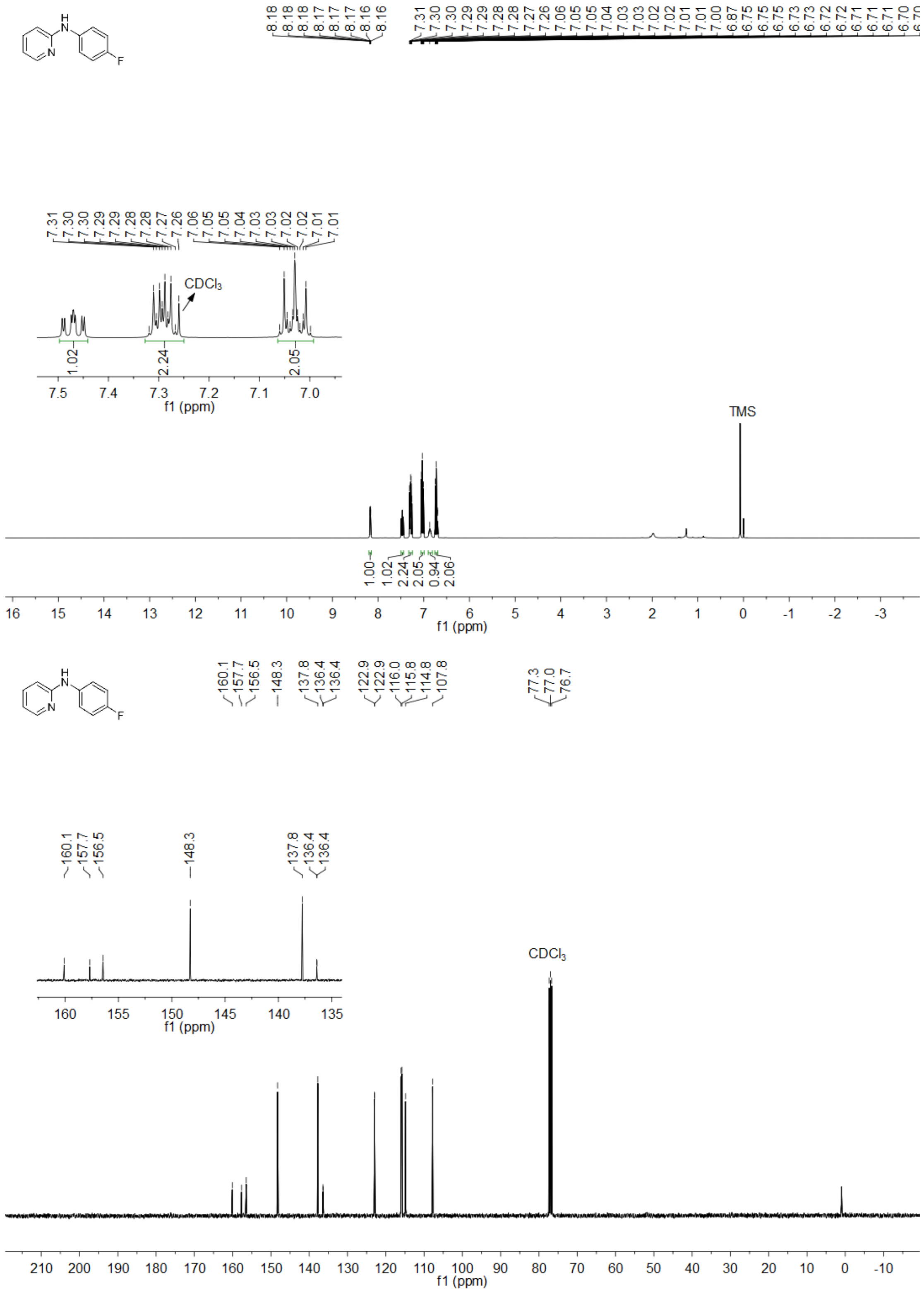
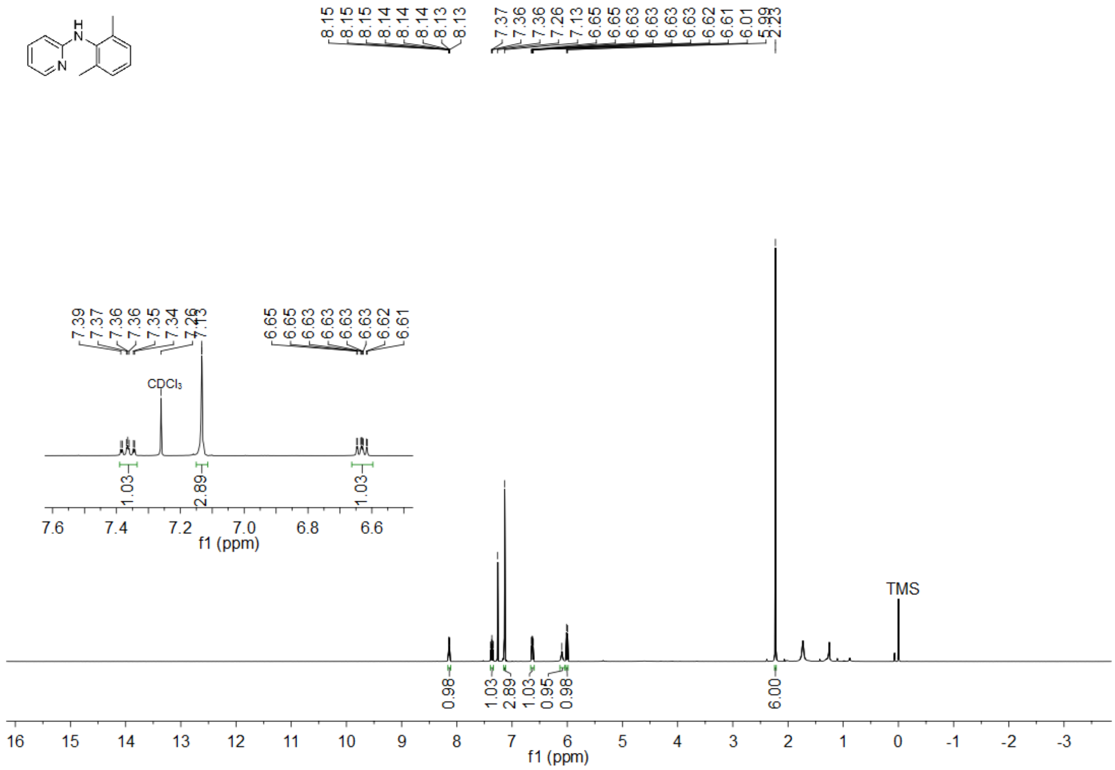


Figure S36. The NMR spectrum of 5z



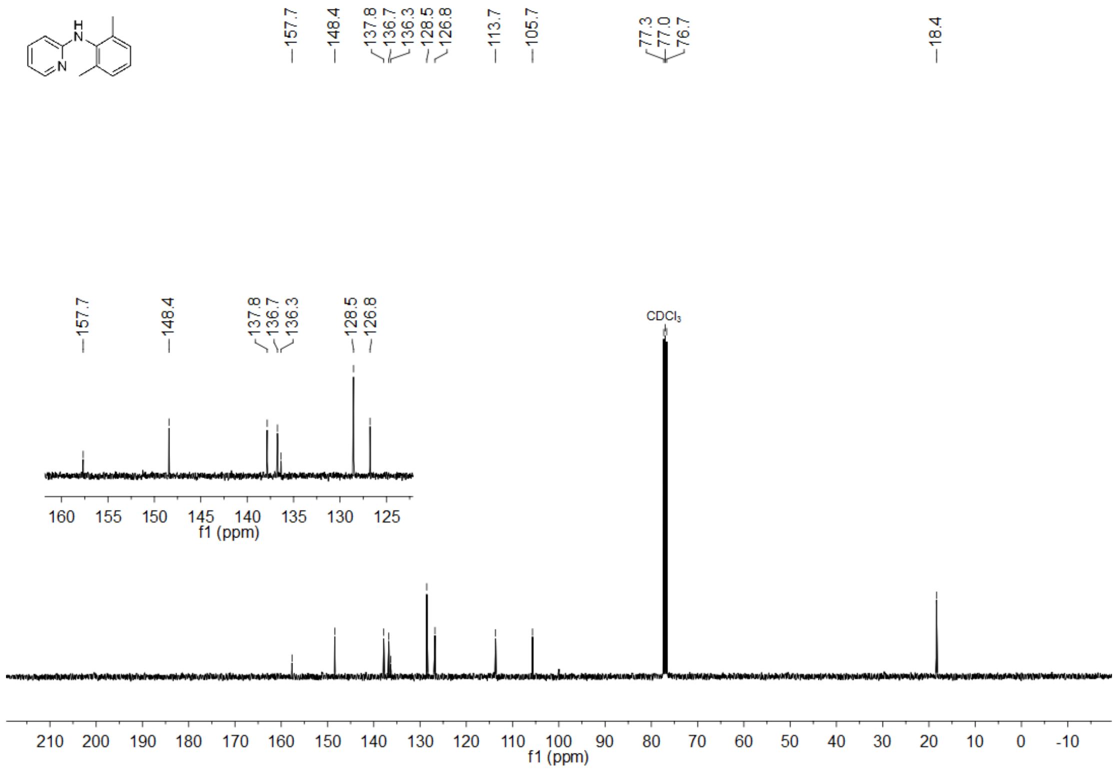
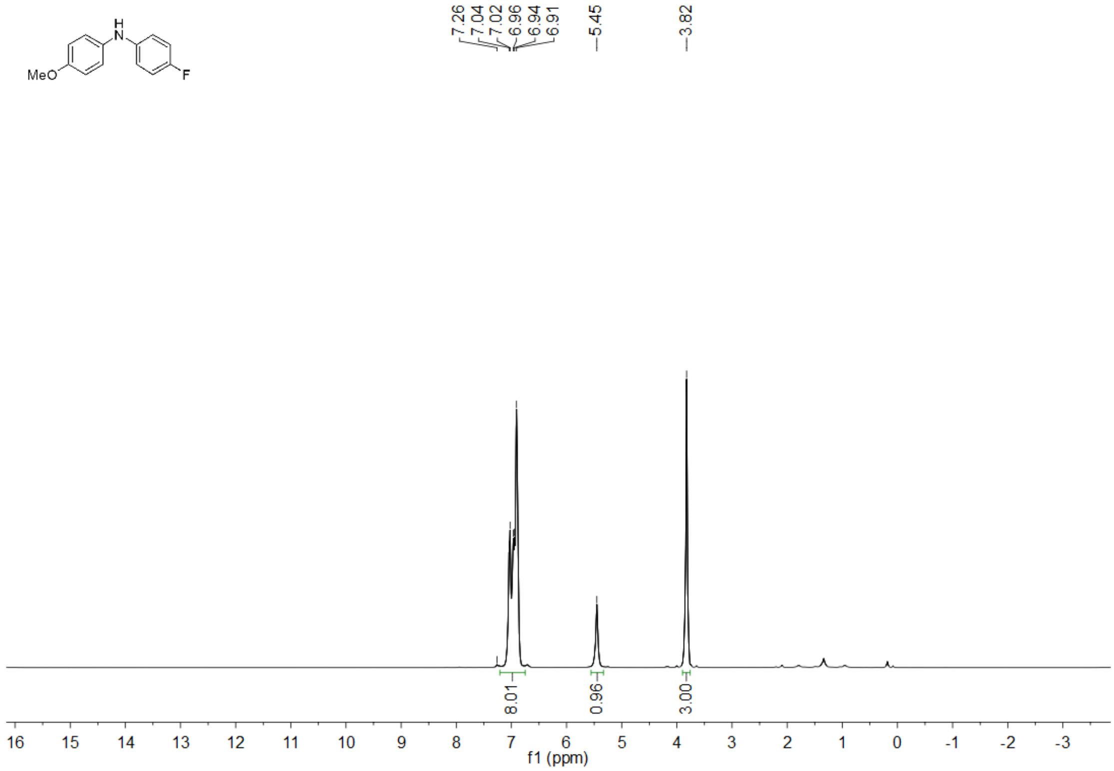


Figure S37. The NMR spectrum of 5aa



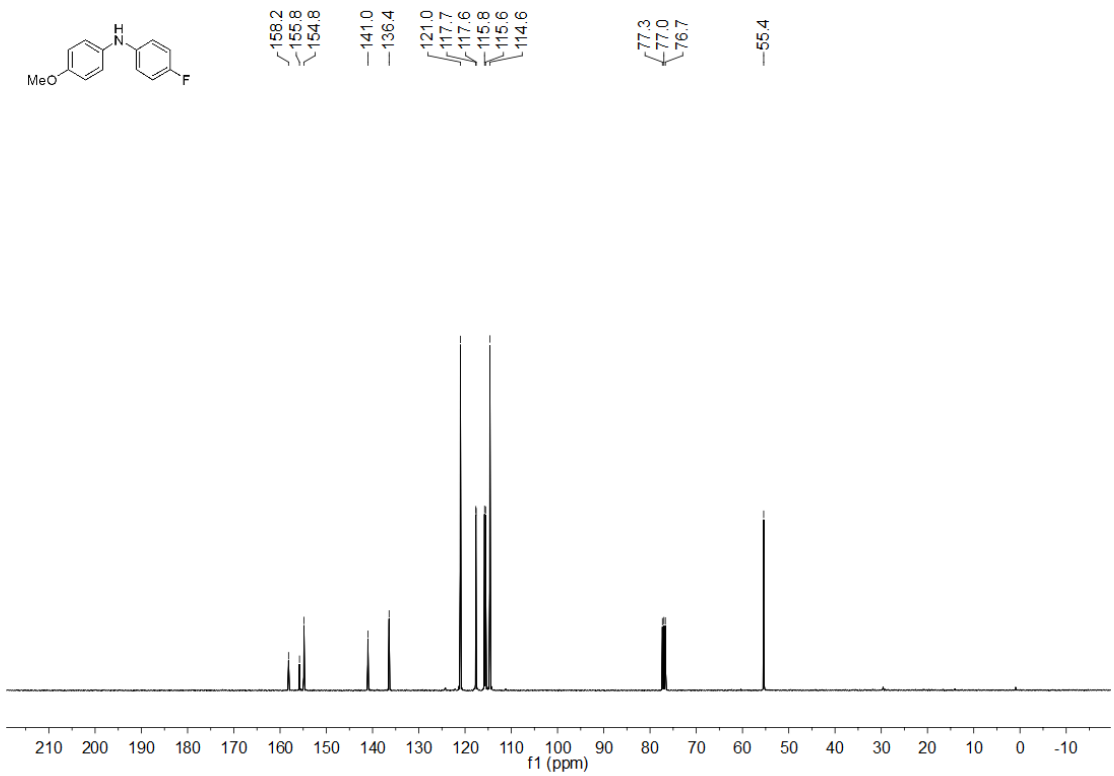
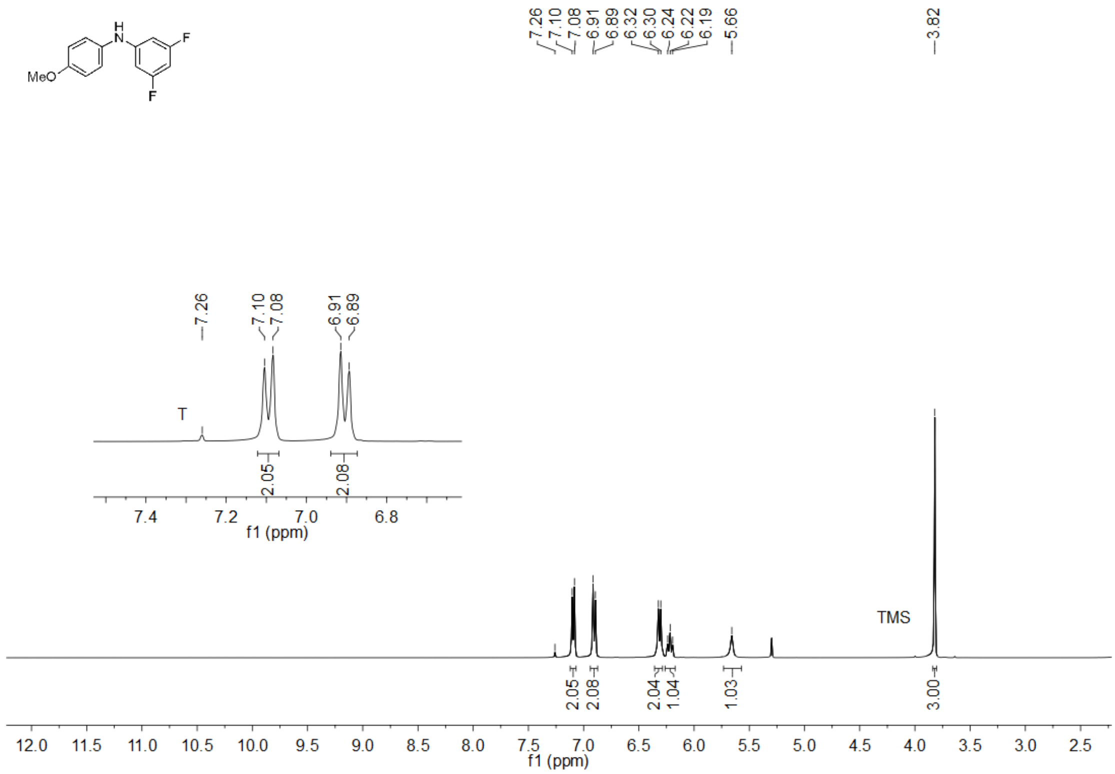


Figure S38. The NMR spectrum of **6a**



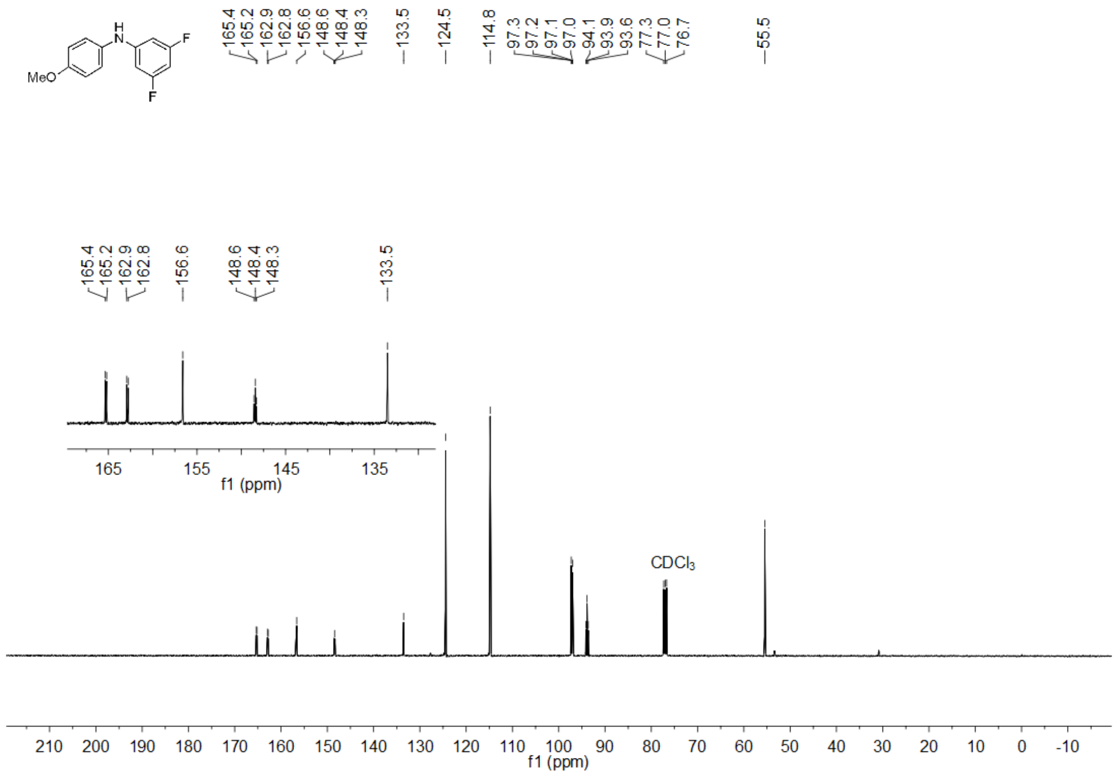
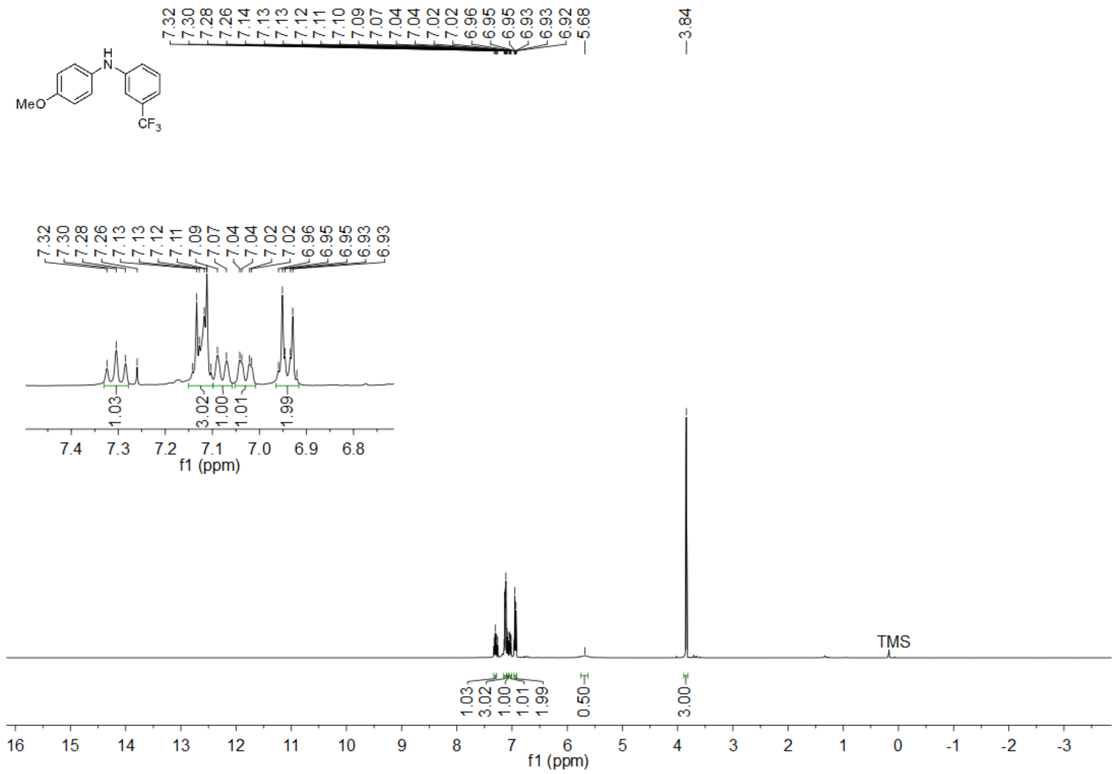


Figure S39. The NMR spectrum of **6b**



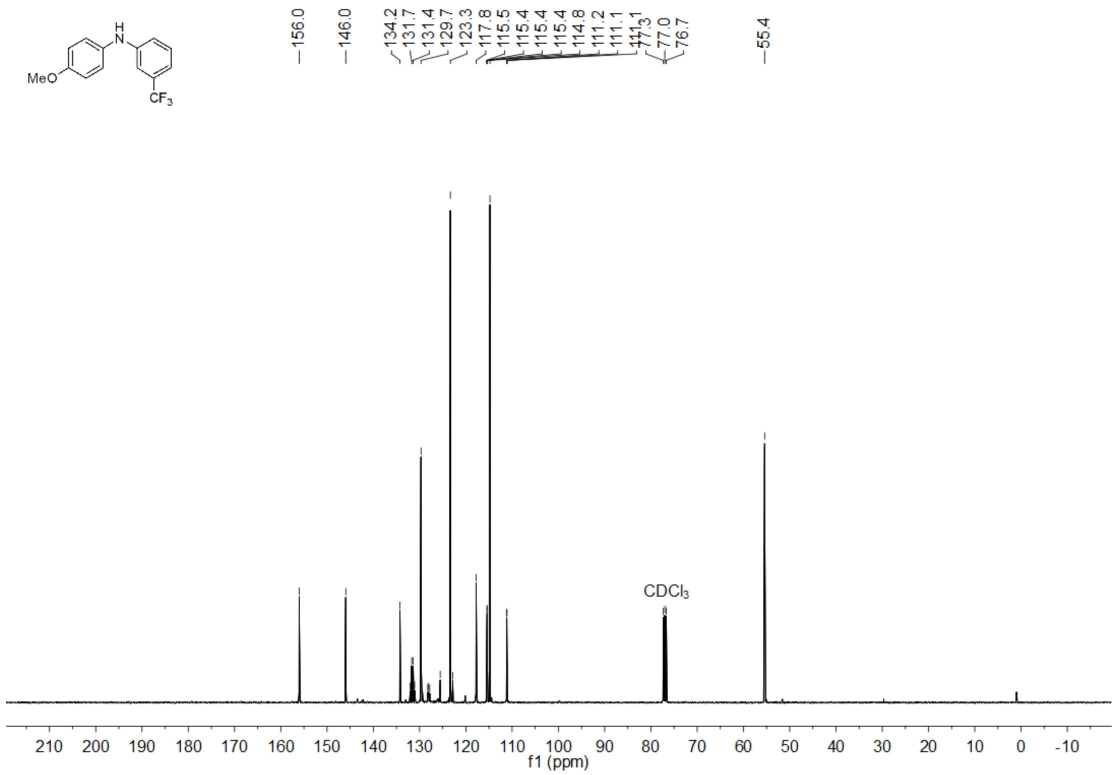
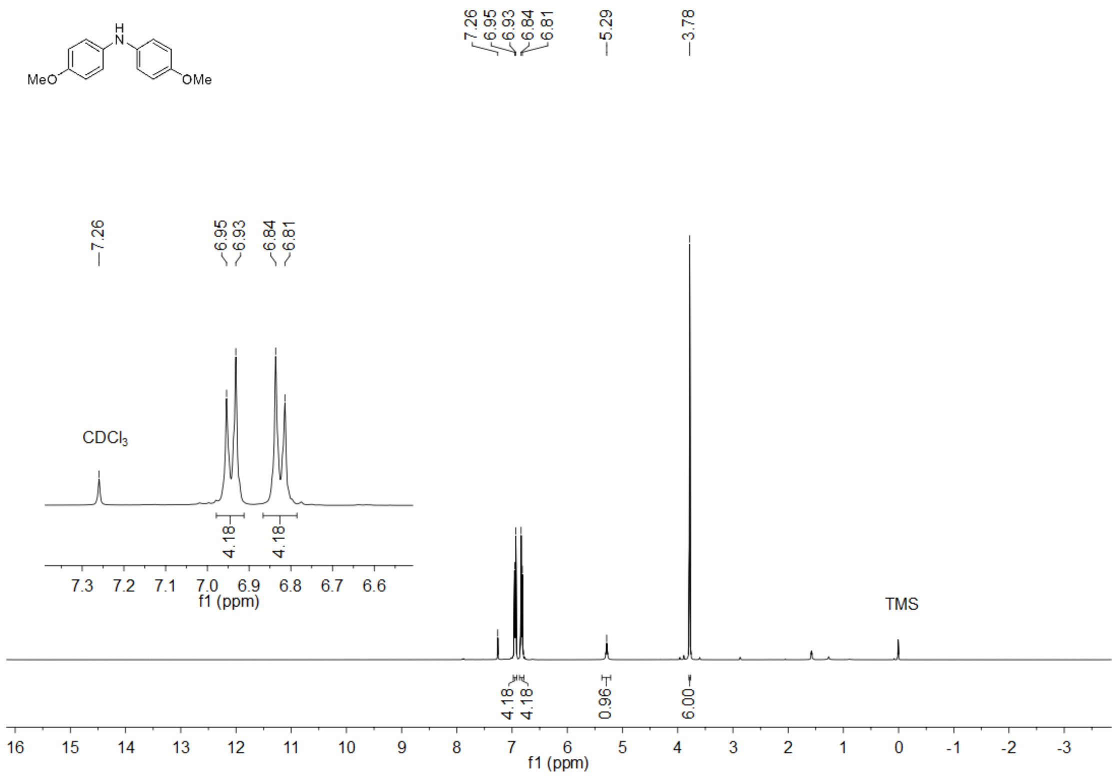


Figure S340. The NMR spectrum of **6c**



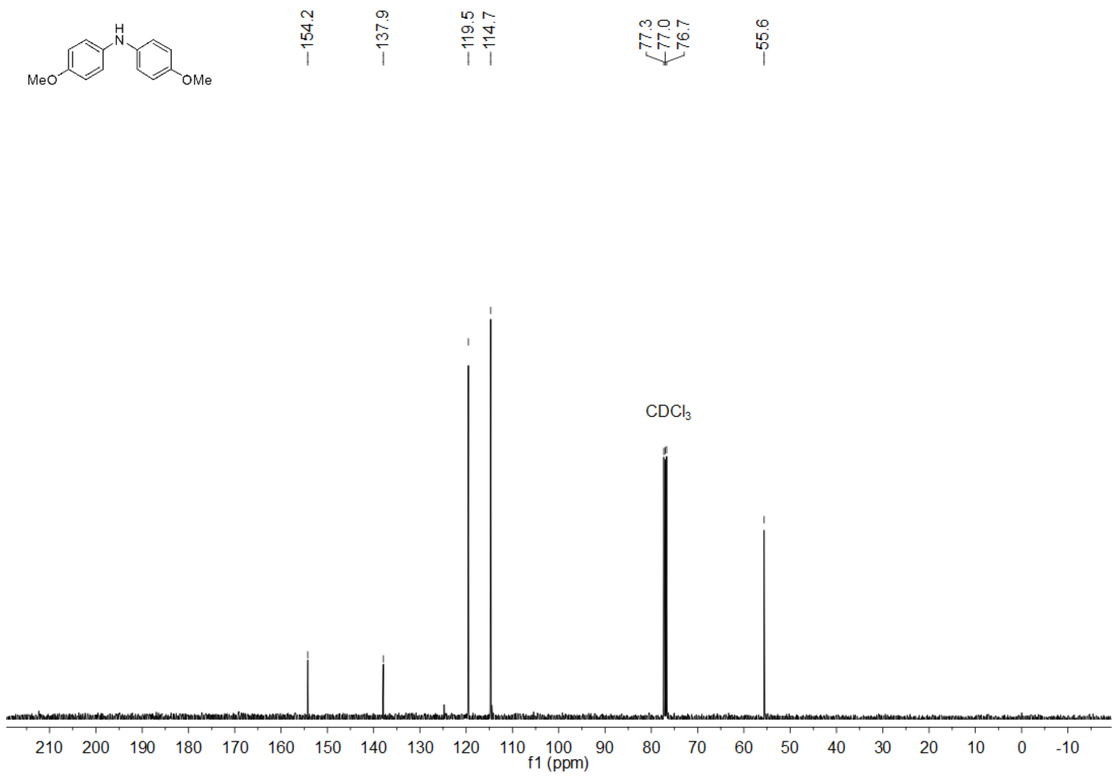
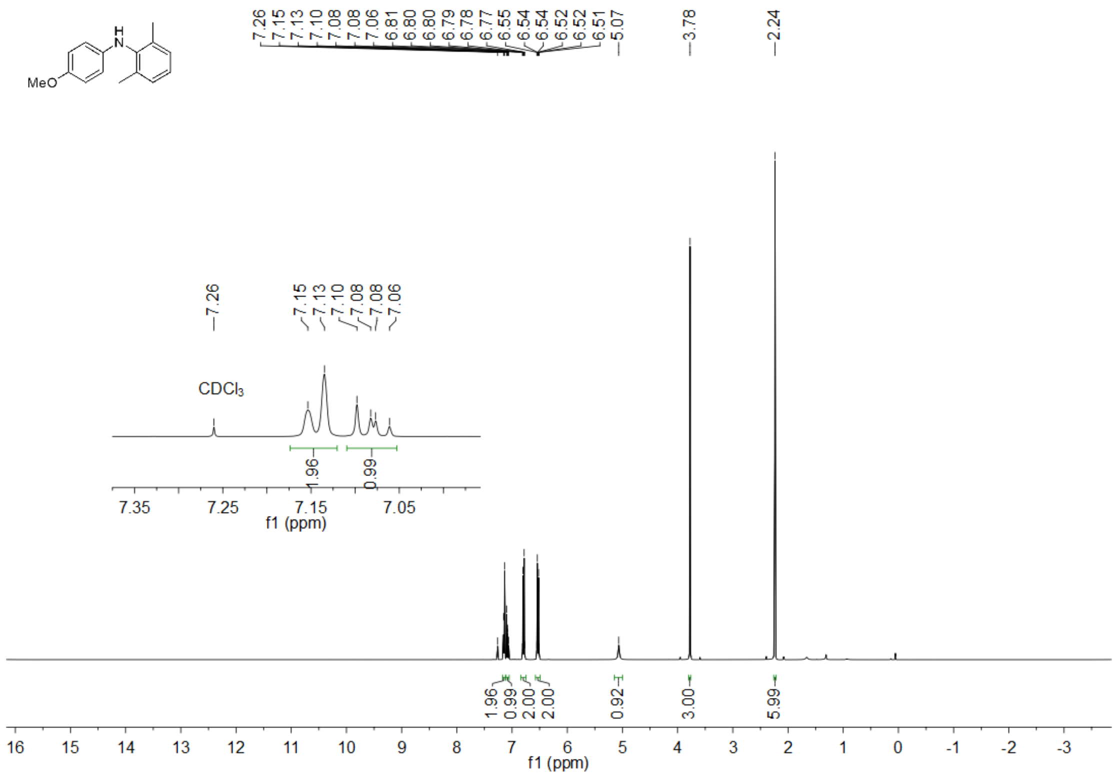


Figure S41. The NMR spectrum of **6d**



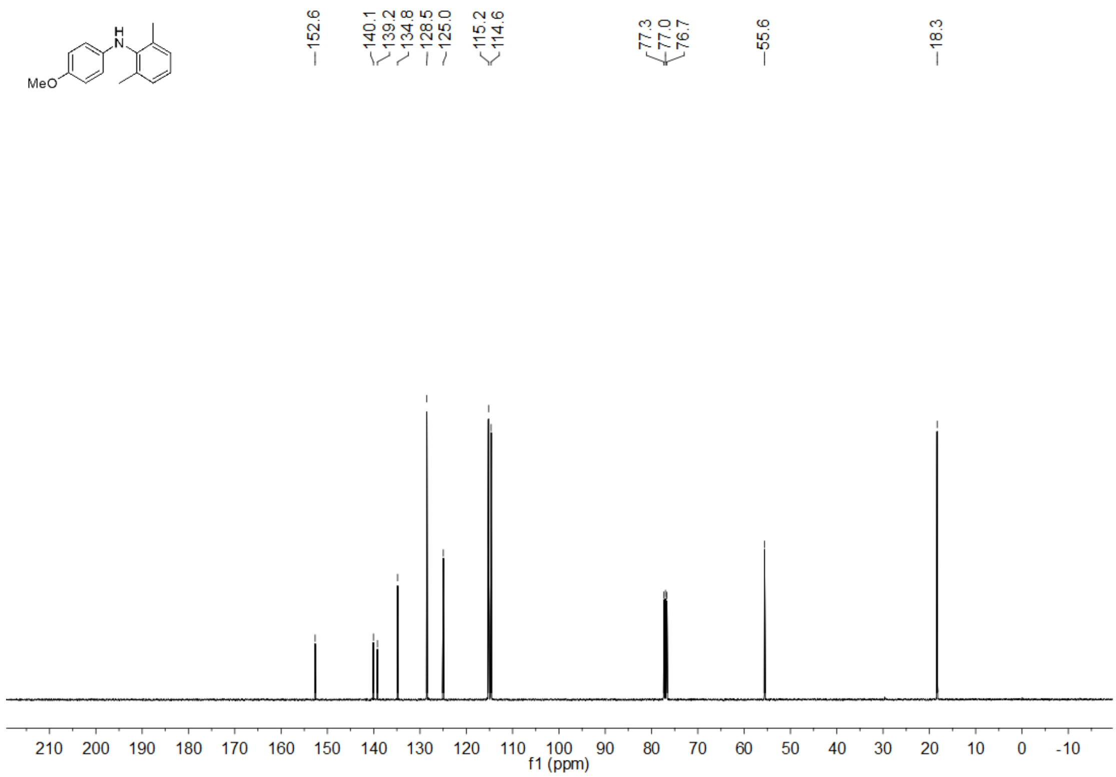
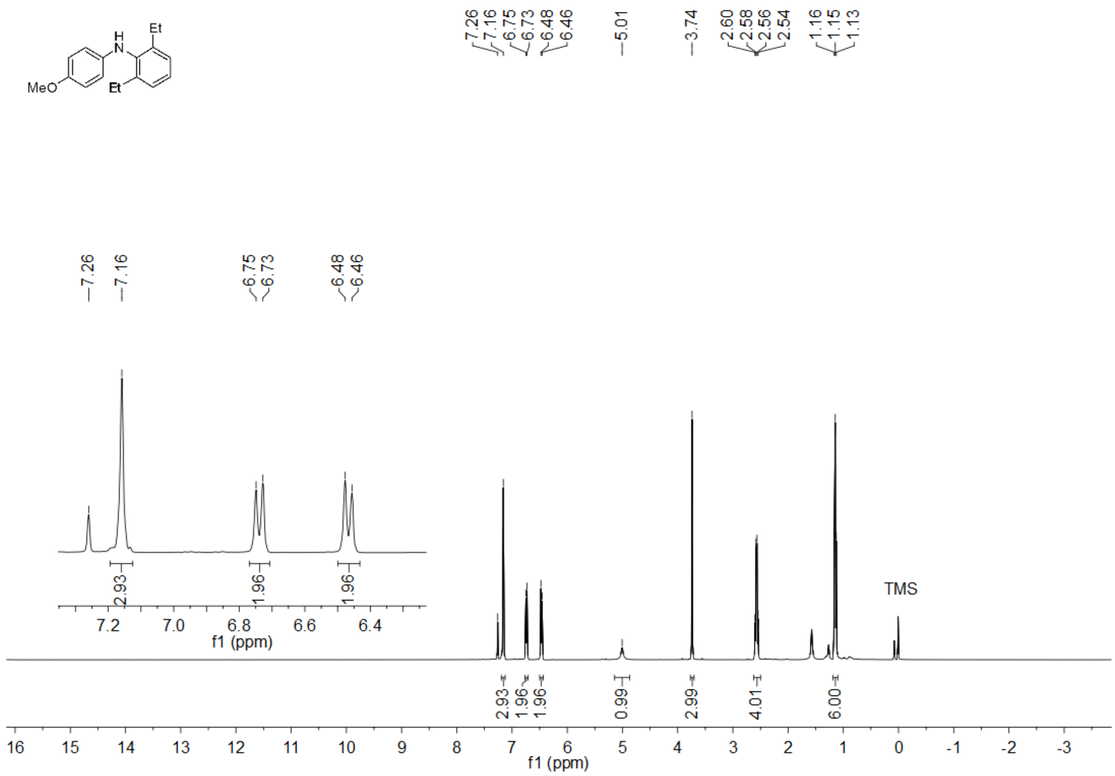


Figure S42. The NMR spectrum of **6e**



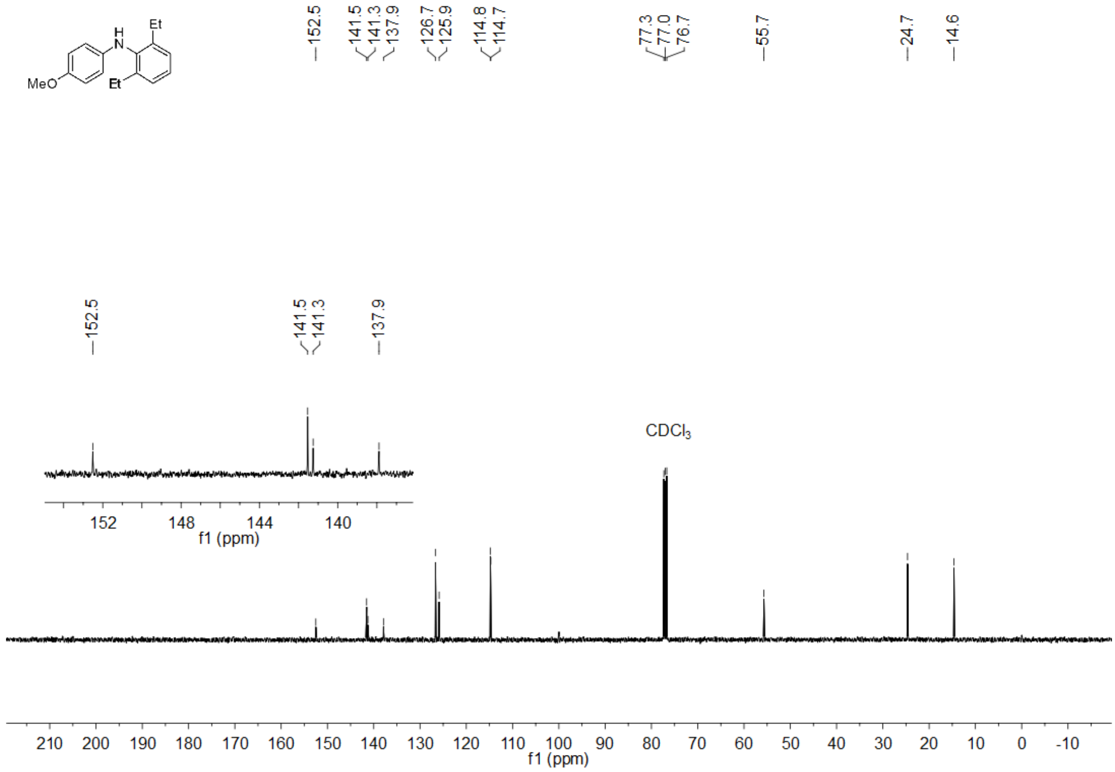


Figure S43. The NMR spectrum of **6f**

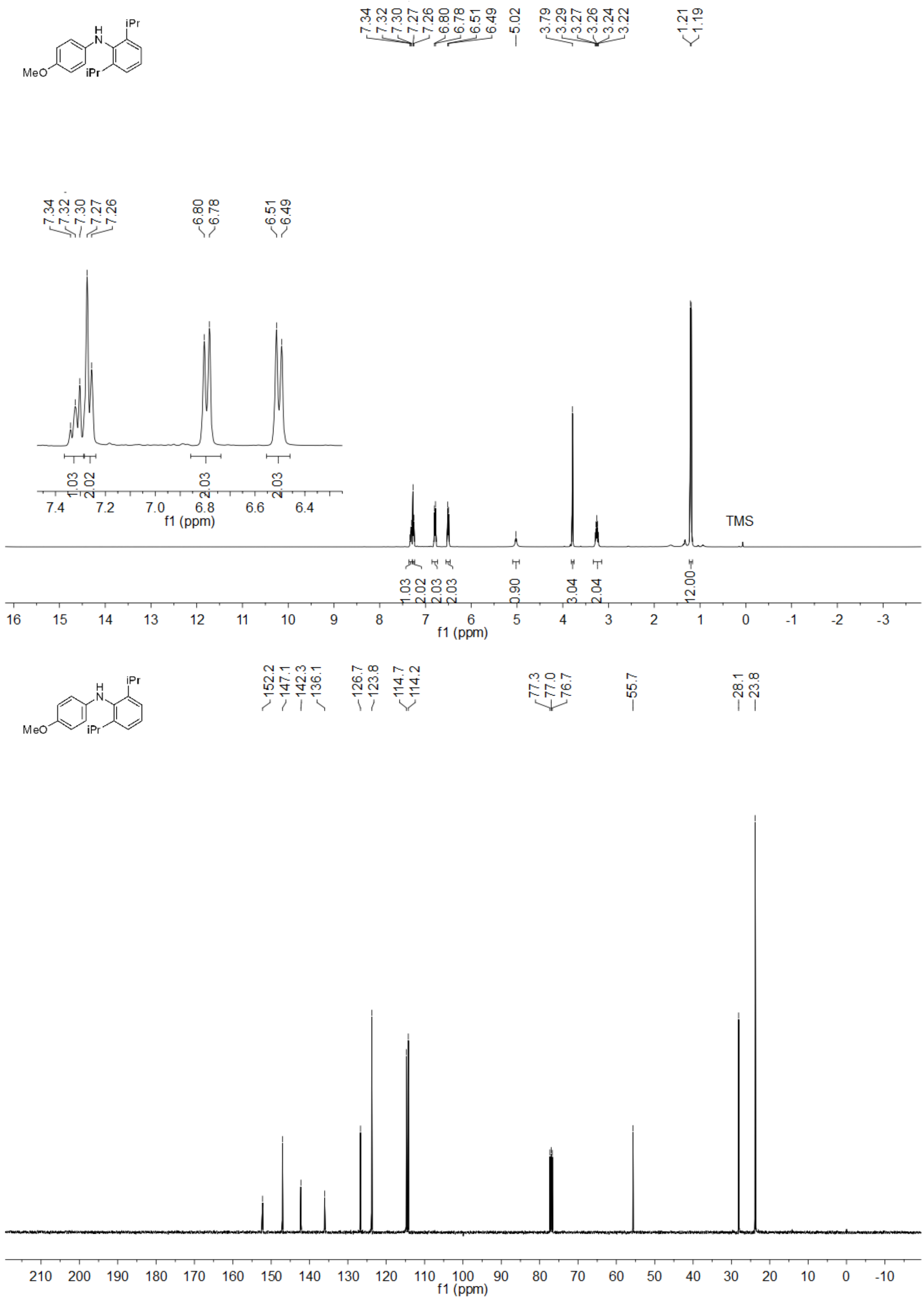
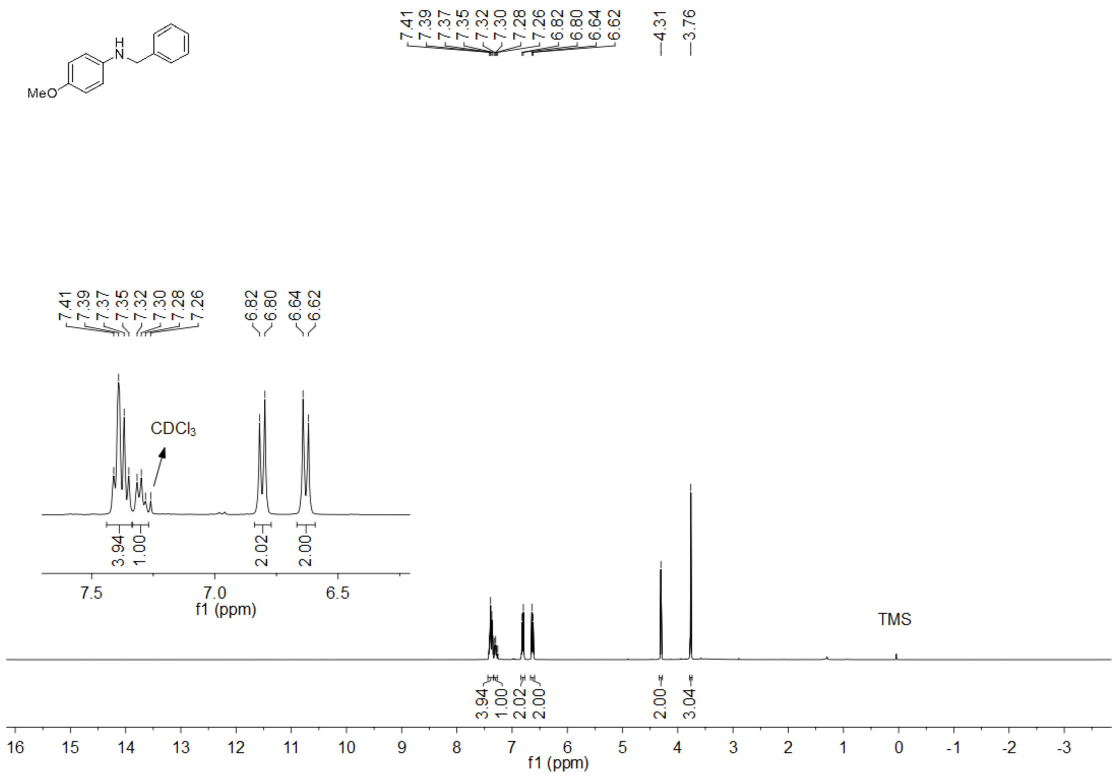


Figure S44. The NMR spectrum of **6g**



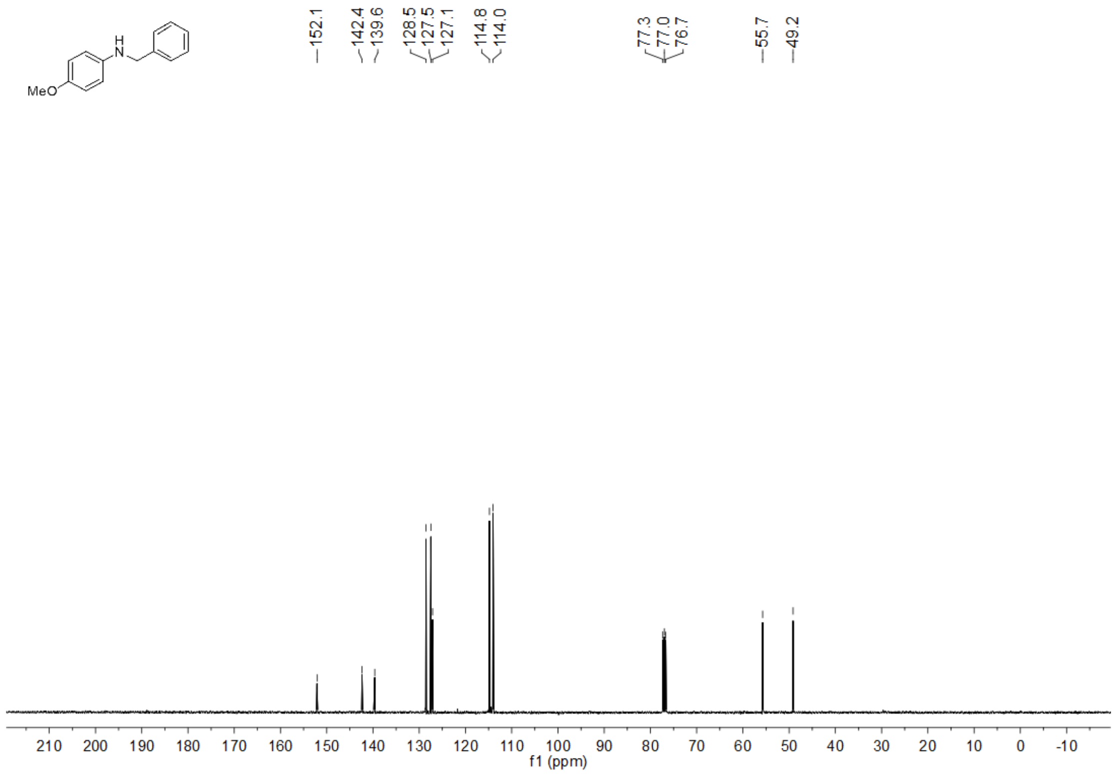
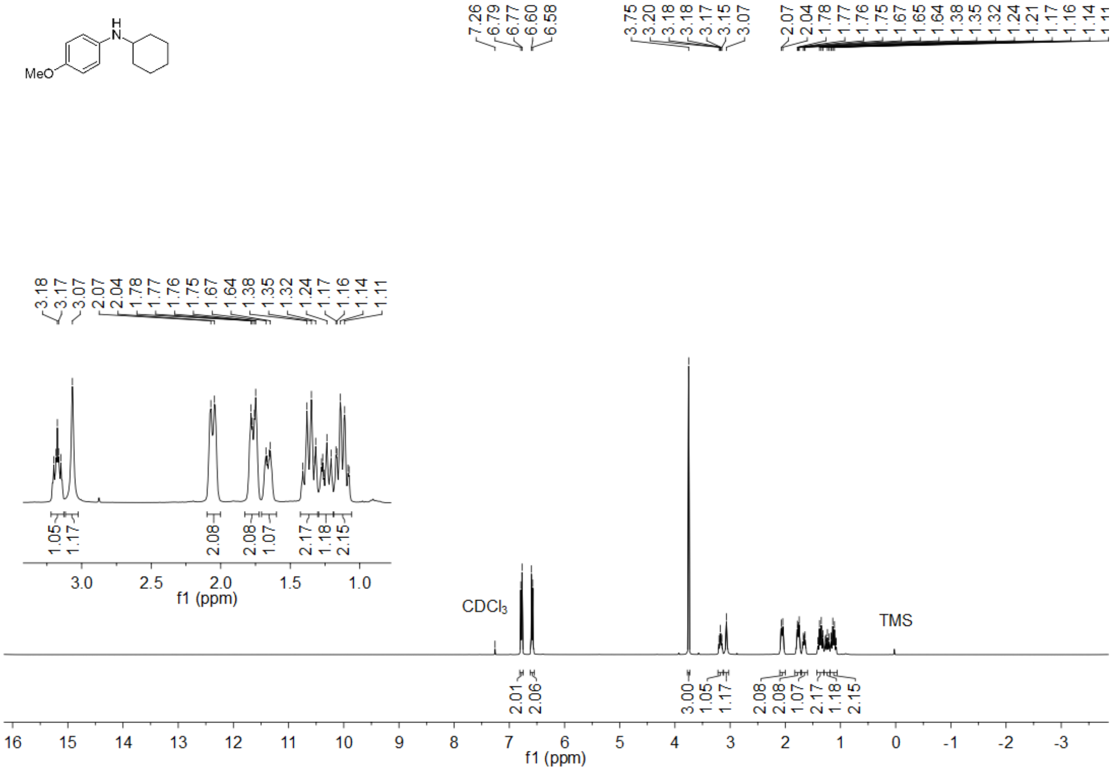


Figure S45. The NMR spectrum of **6h**



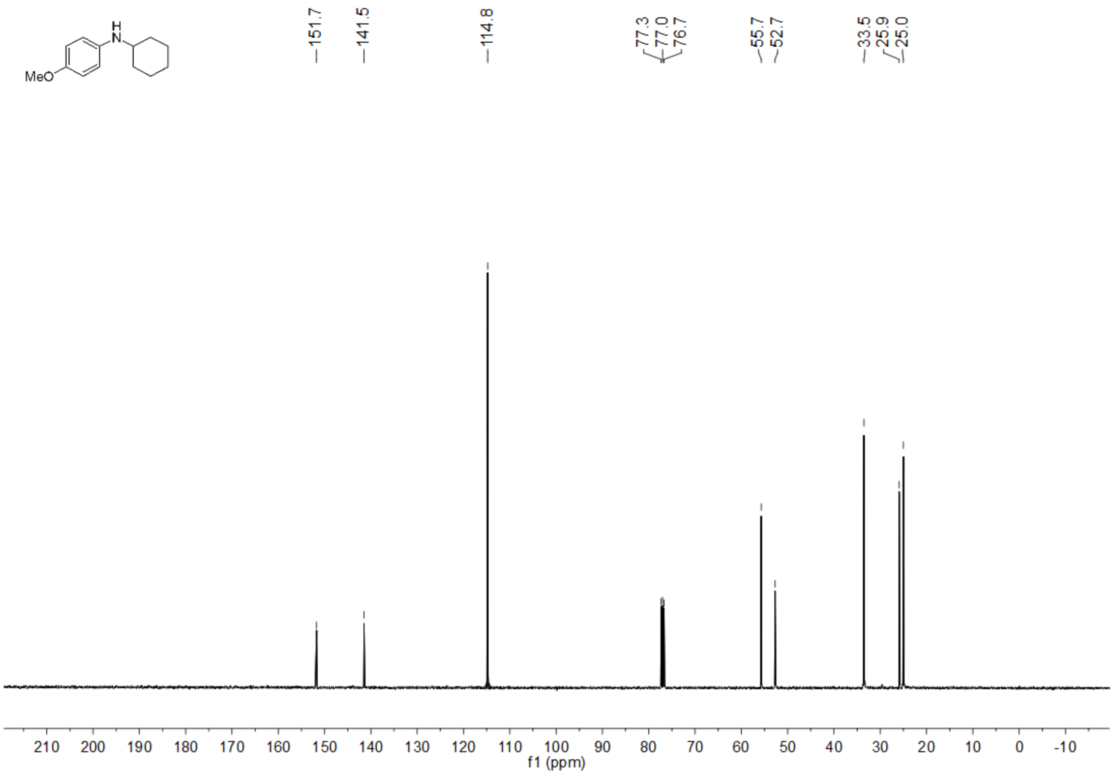
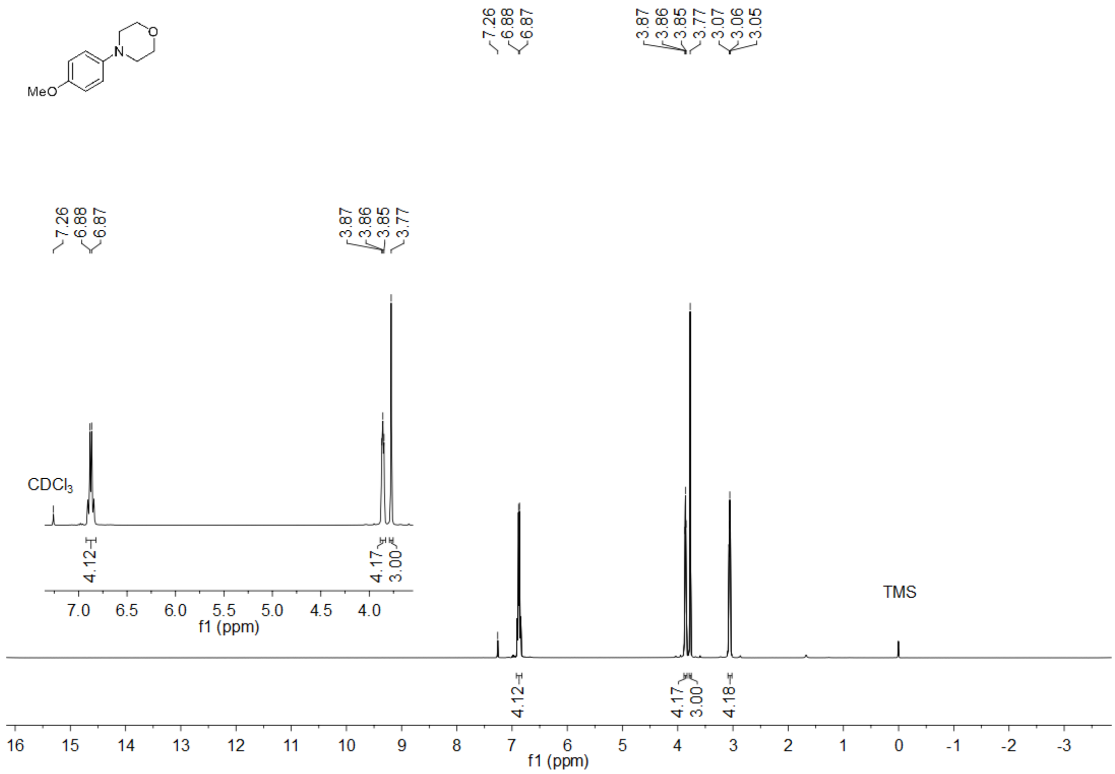


Figure S46. The NMR spectrum of **6i**



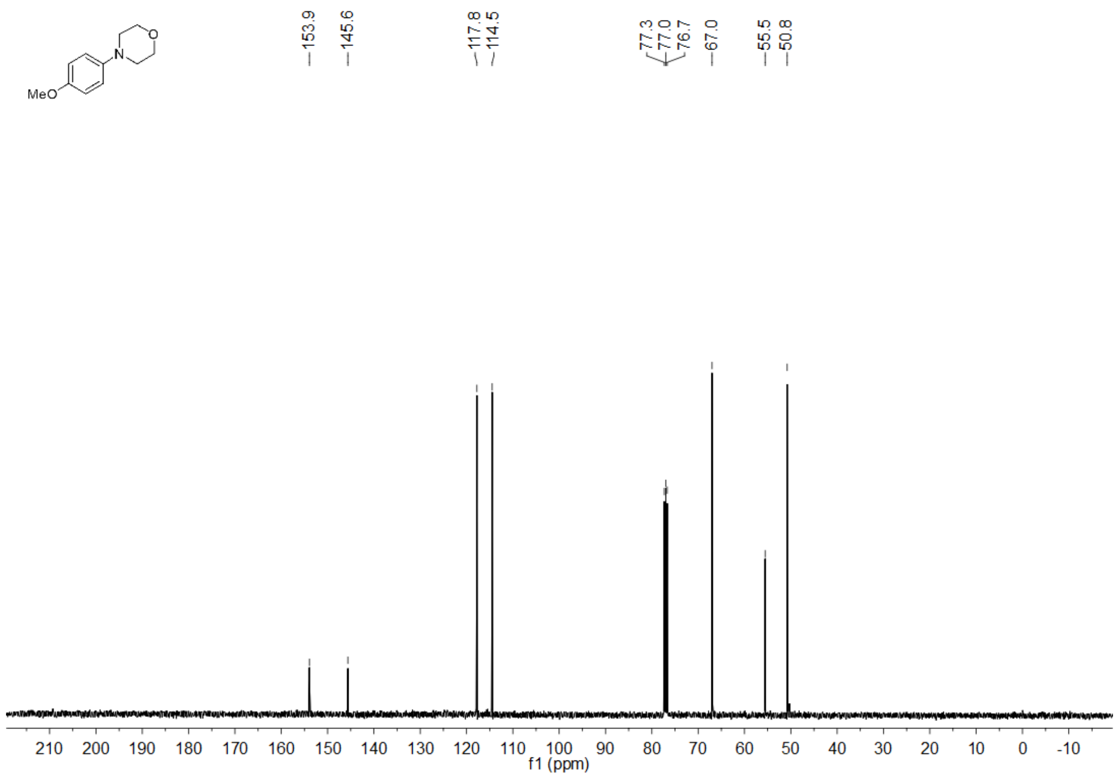
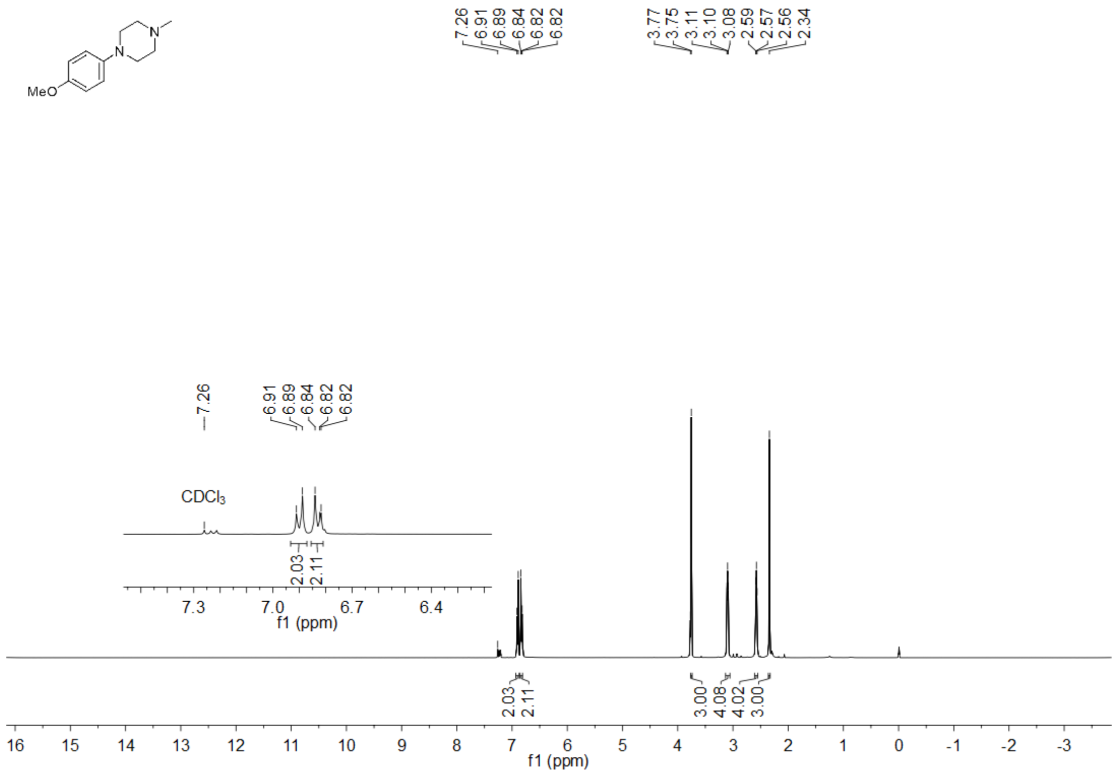


Figure S47. The NMR spectrum of **6j**



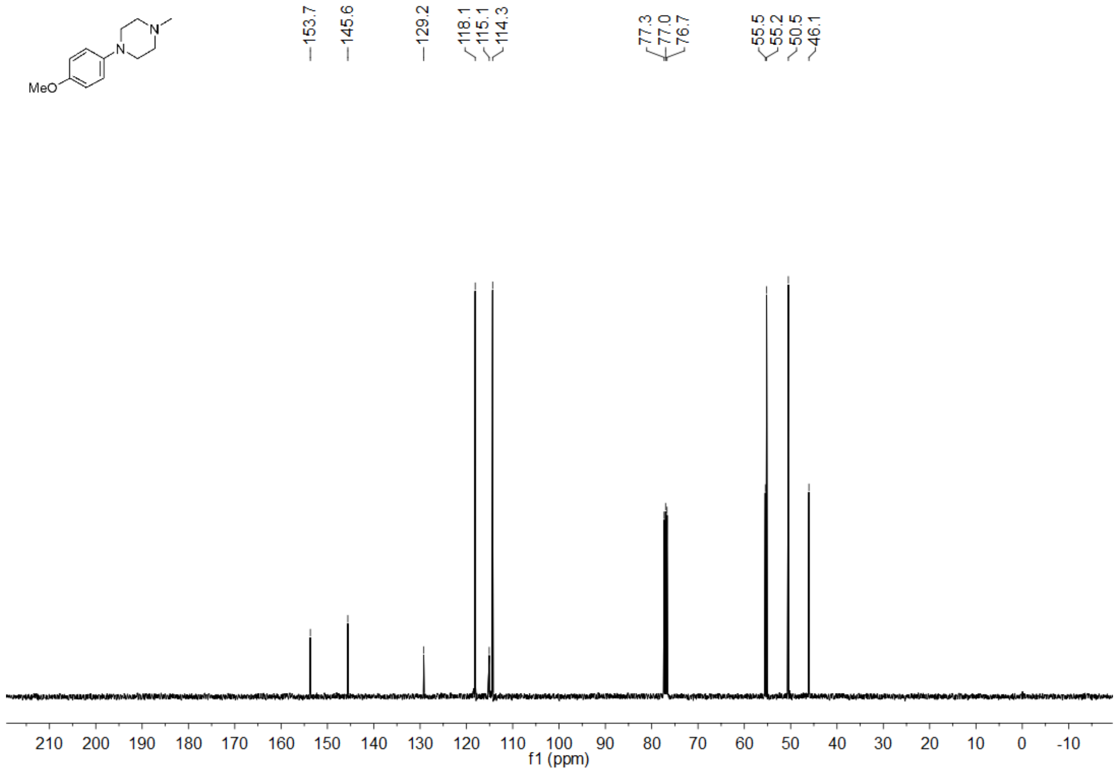


Figure S48. The NMR spectrum of **6k**

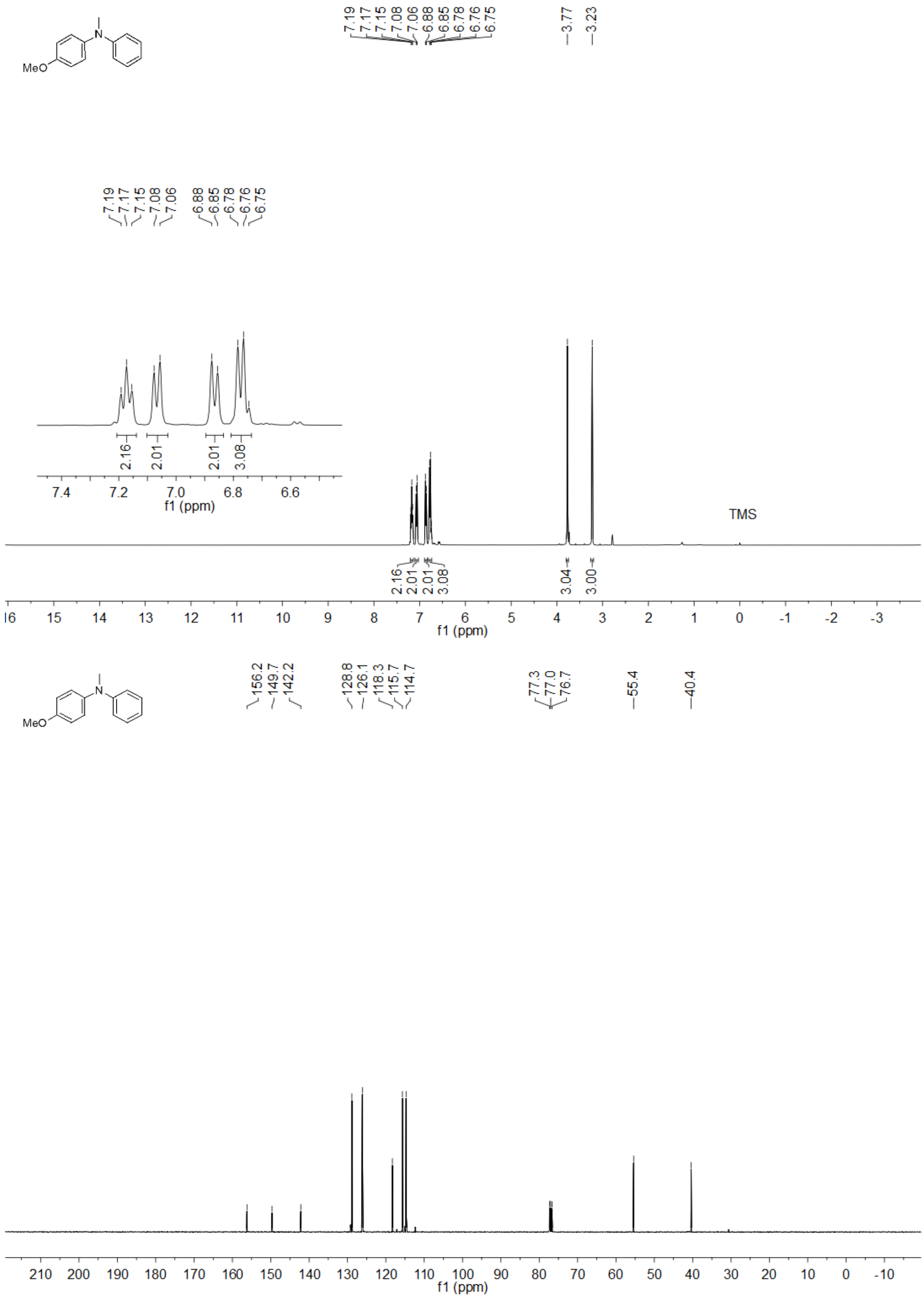


Figure S49. The NMR spectrum of **6l**

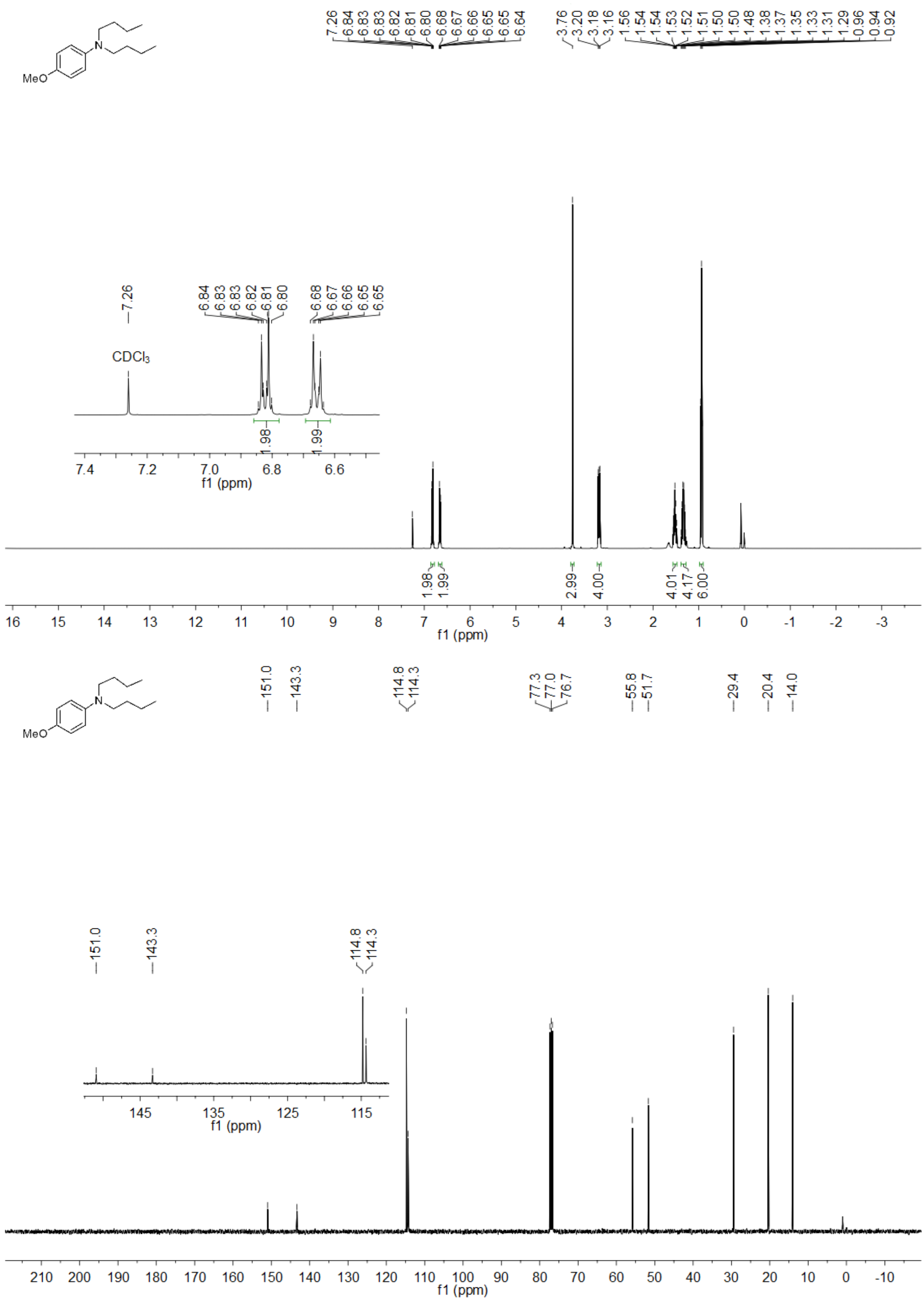


Figure S50. The NMR spectrum of 6m

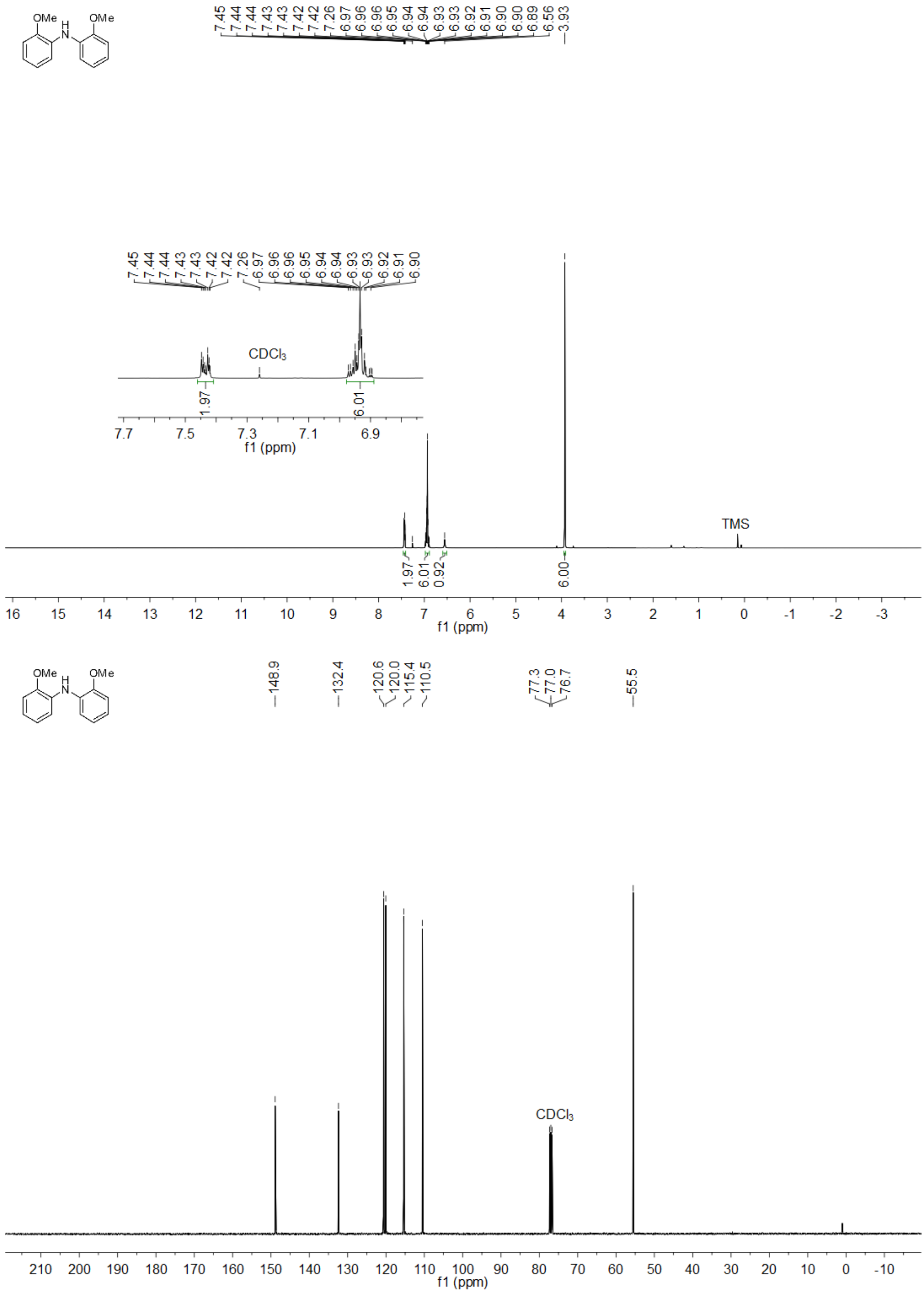
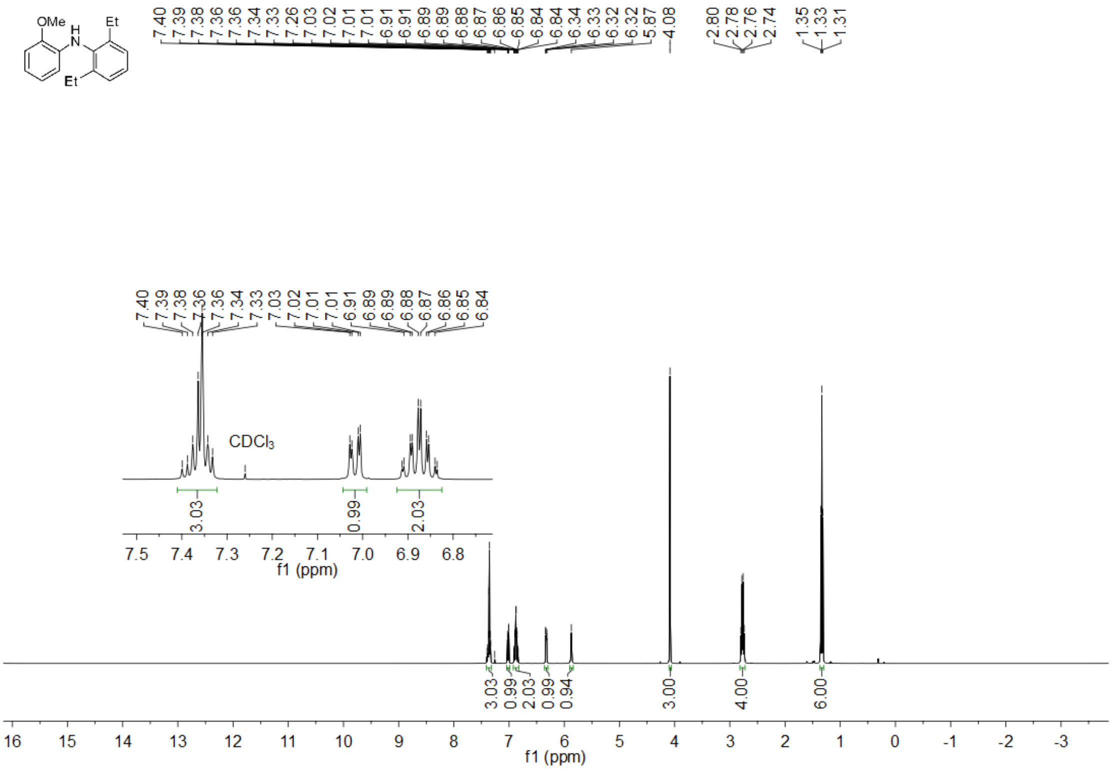


Figure S51. The NMR spectrum of 6n



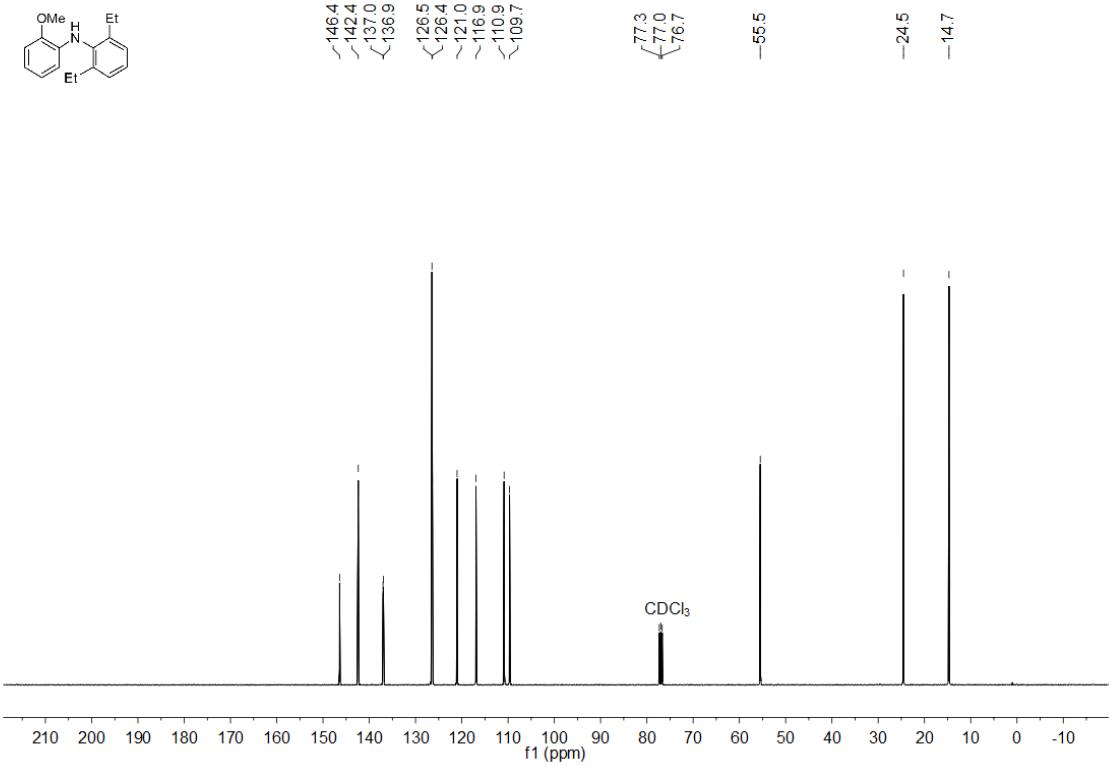
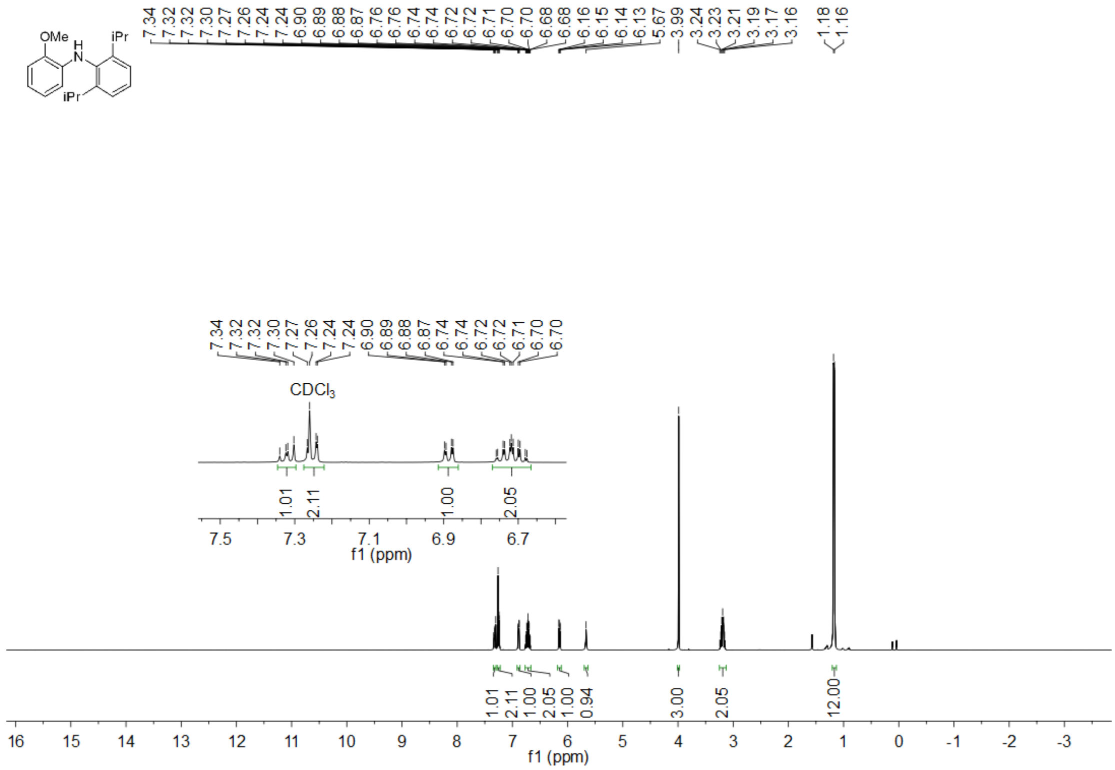


Figure S52. The NMR spectrum of 6o



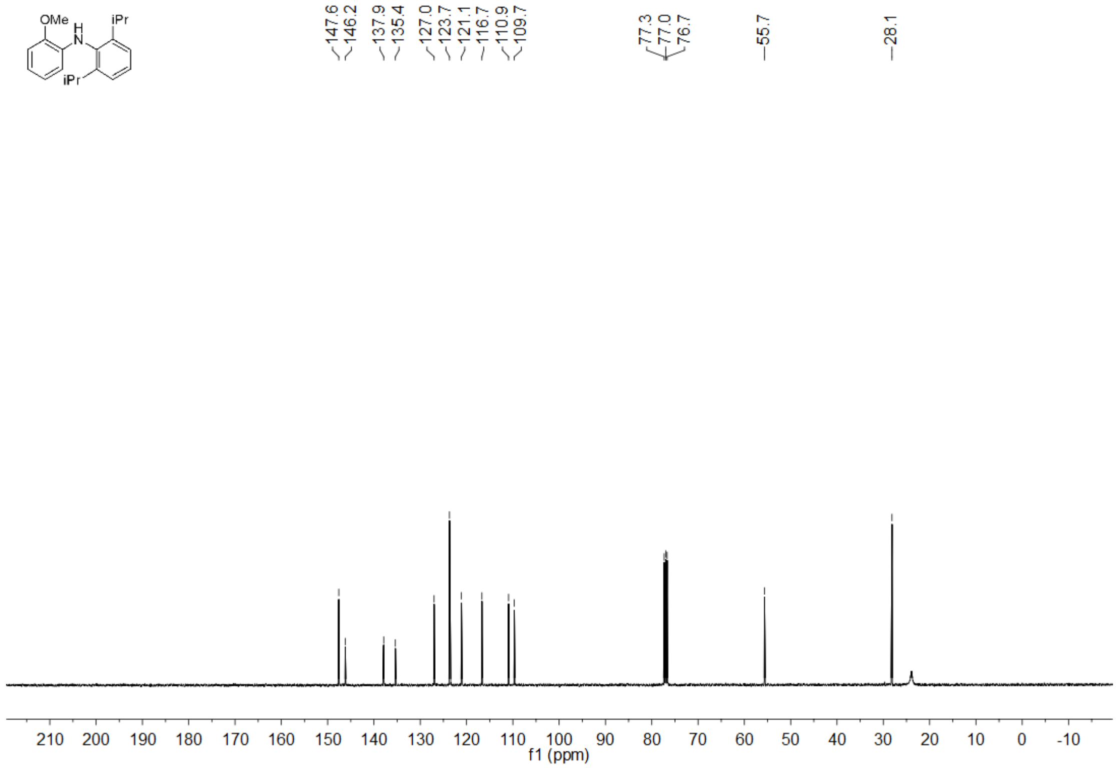
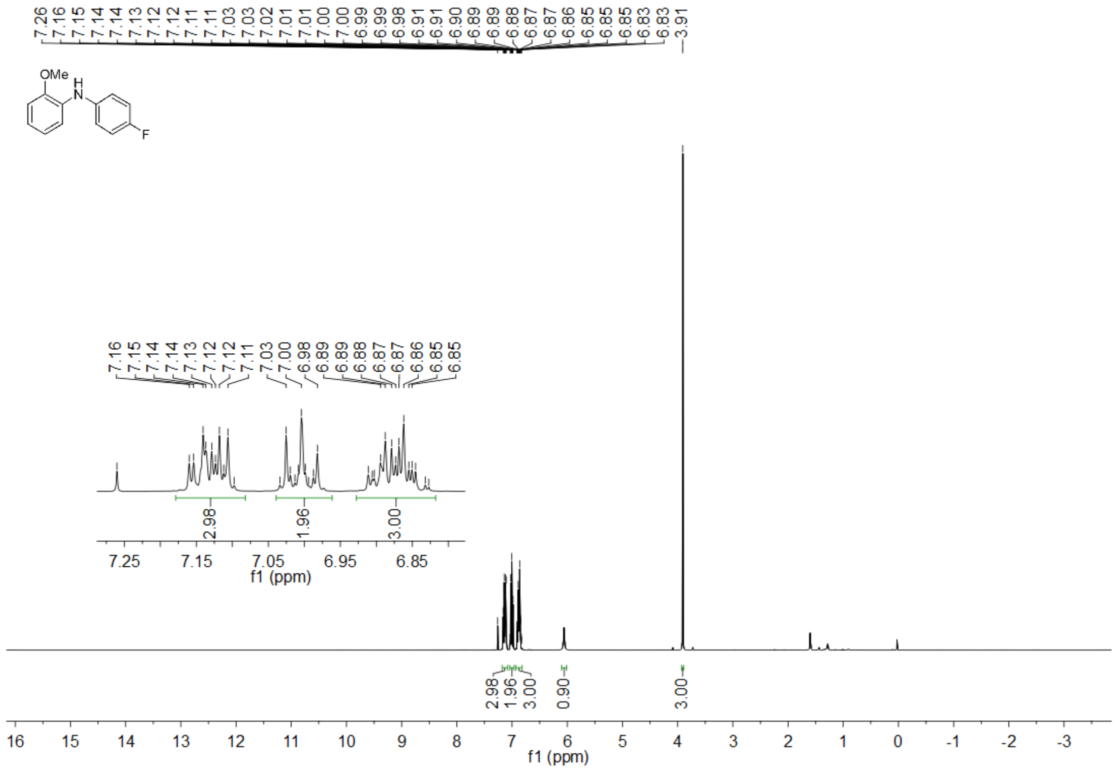


Figure S53. The NMR spectrum of 6p



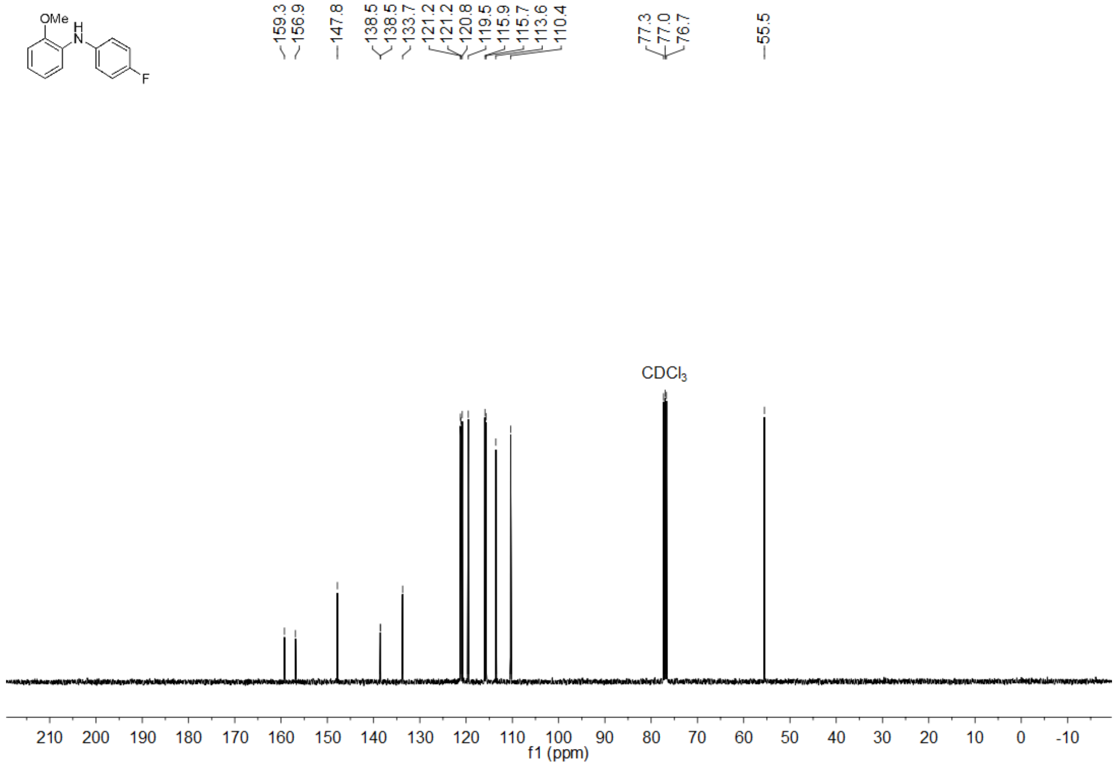
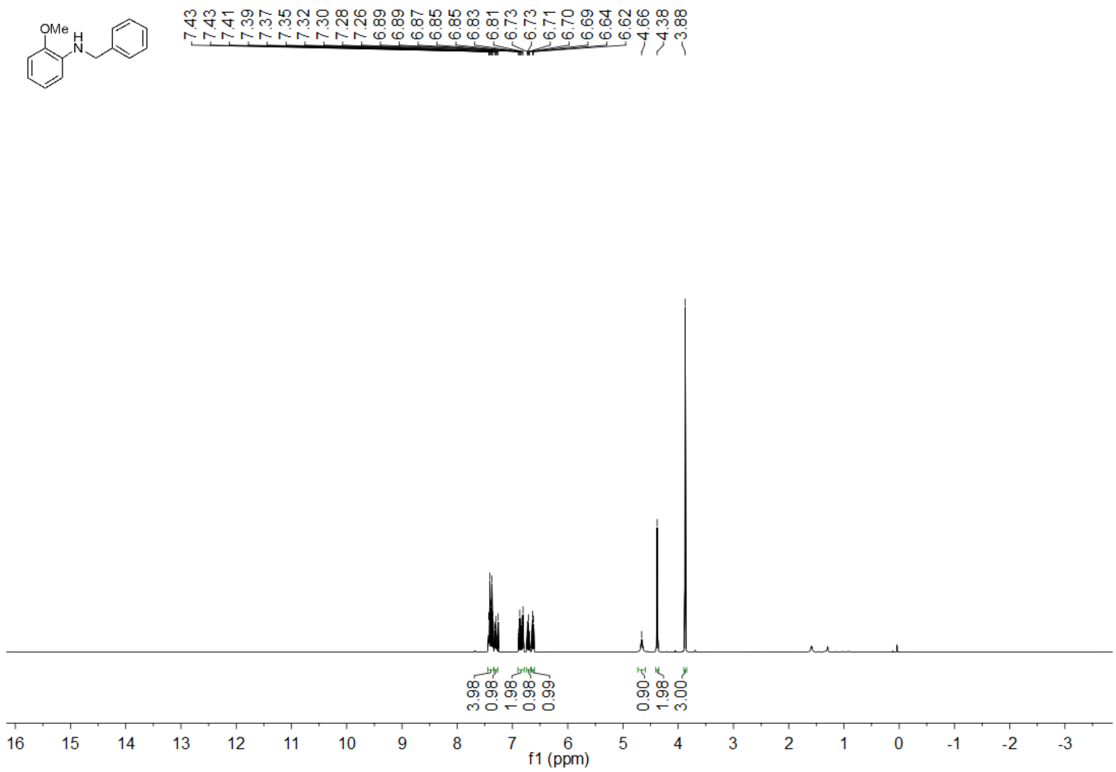


Figure S54. The NMR spectrum of 6q



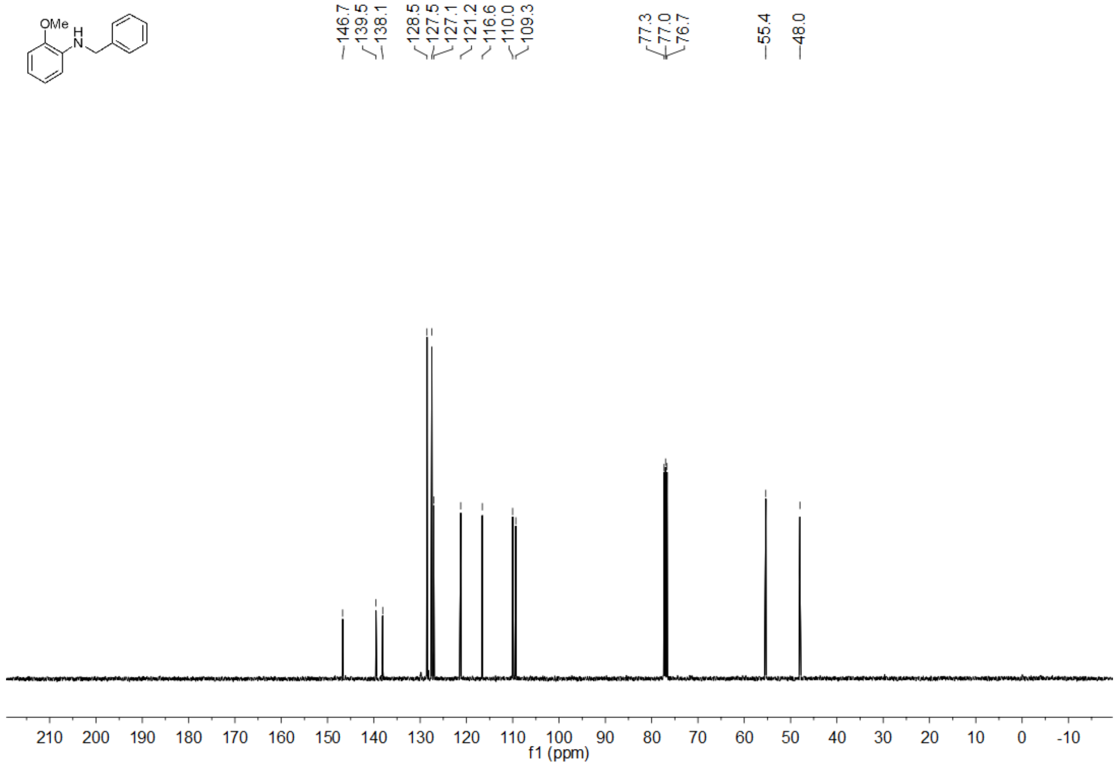
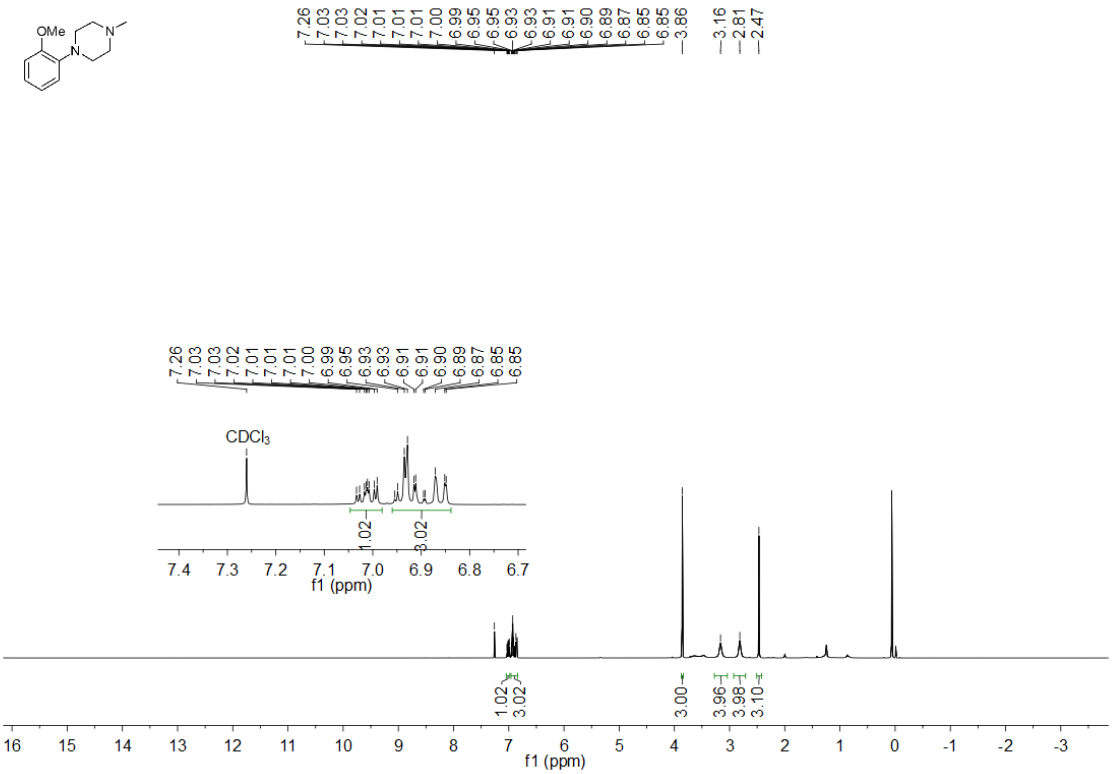


Figure S55. The NMR spectrum of 6r



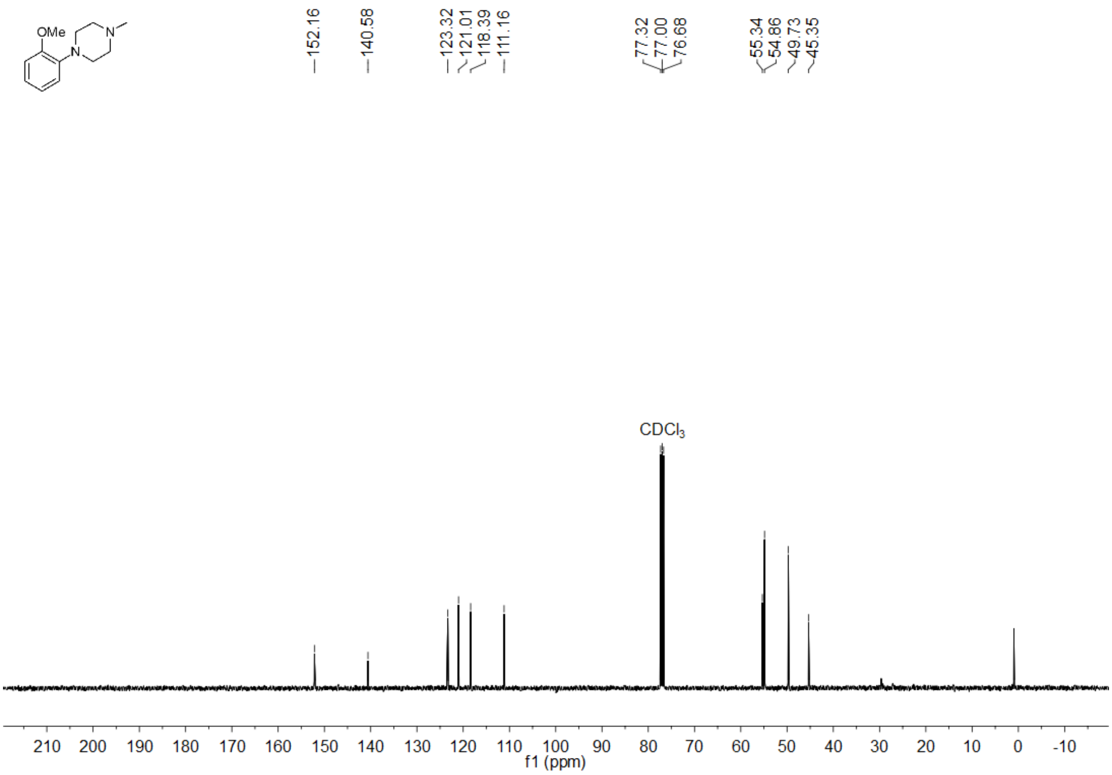
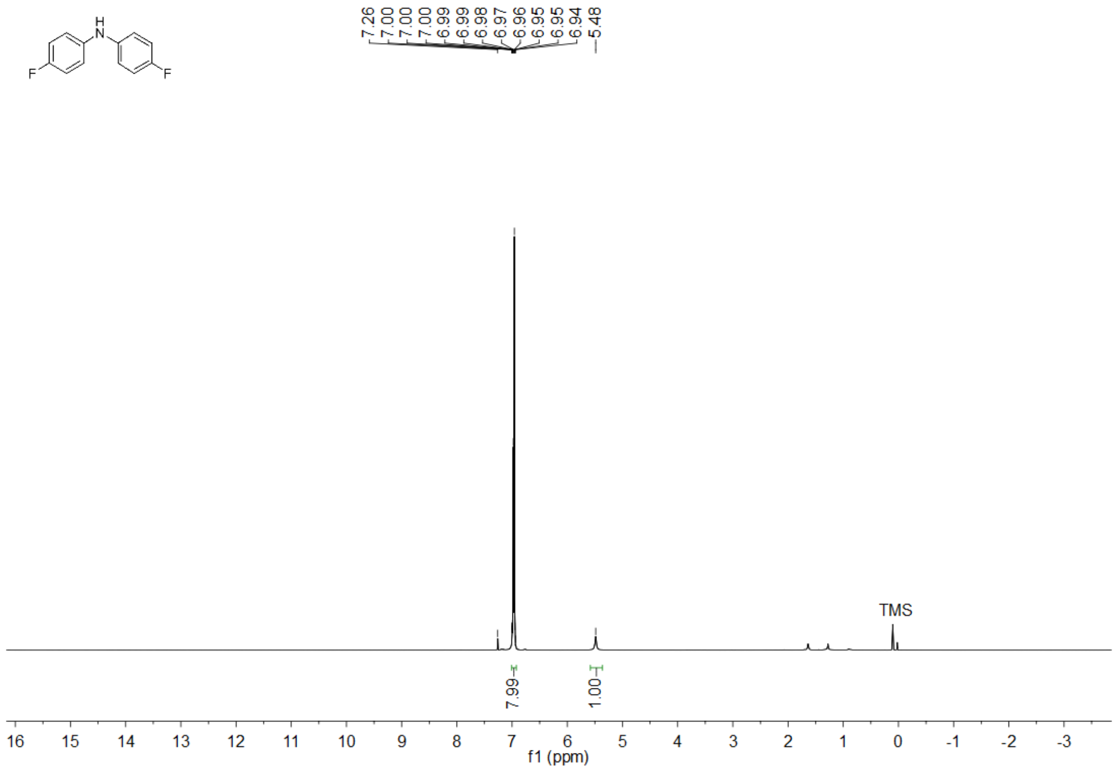


Figure S56. The NMR spectrum of 6s



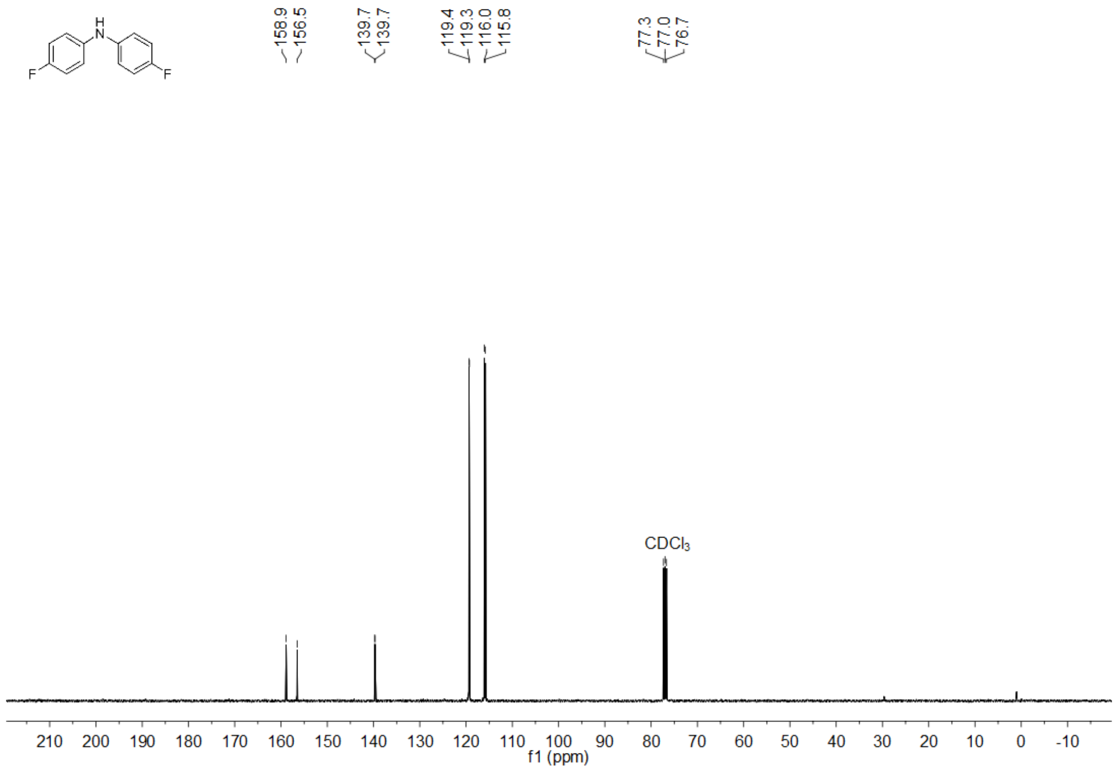
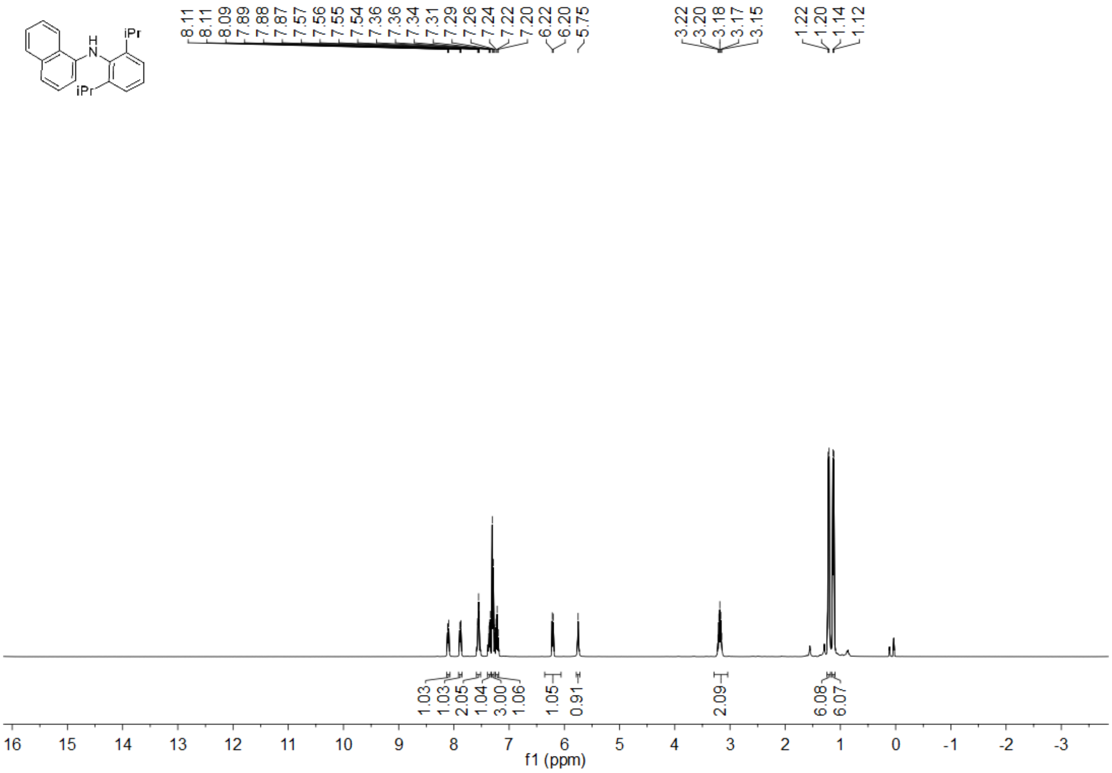


Figure S57. The NMR spectrum of 6t



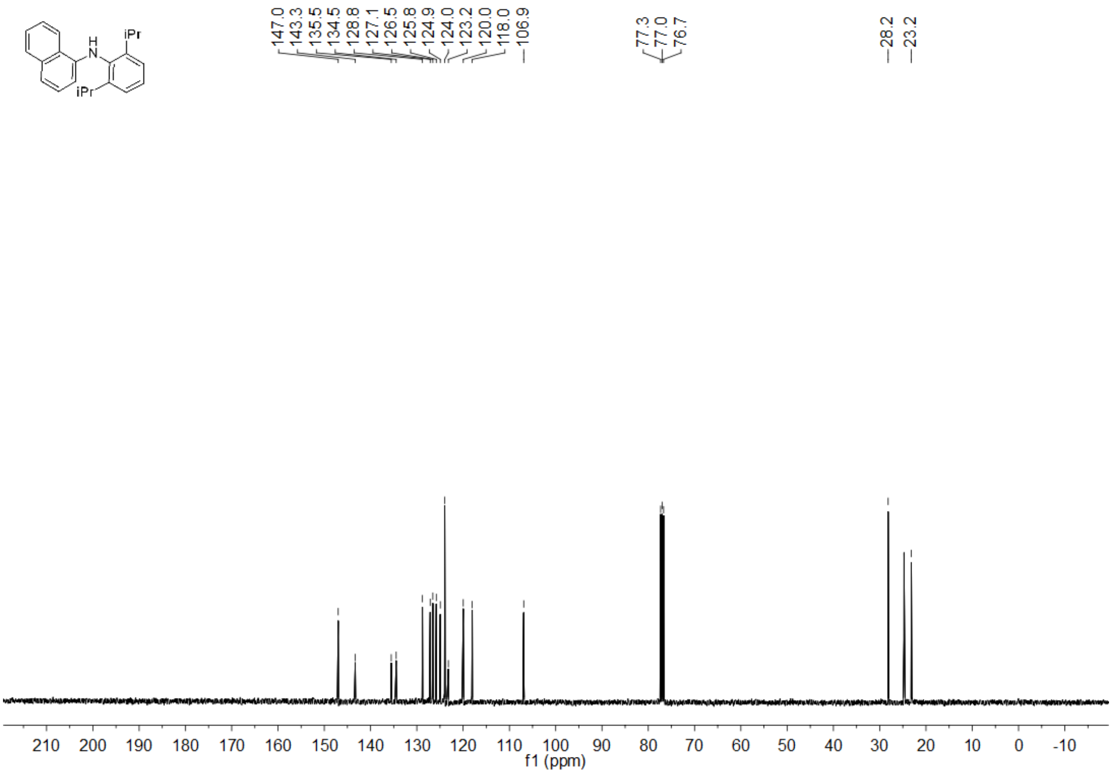


Figure S58. The NMR spectrum of 6u

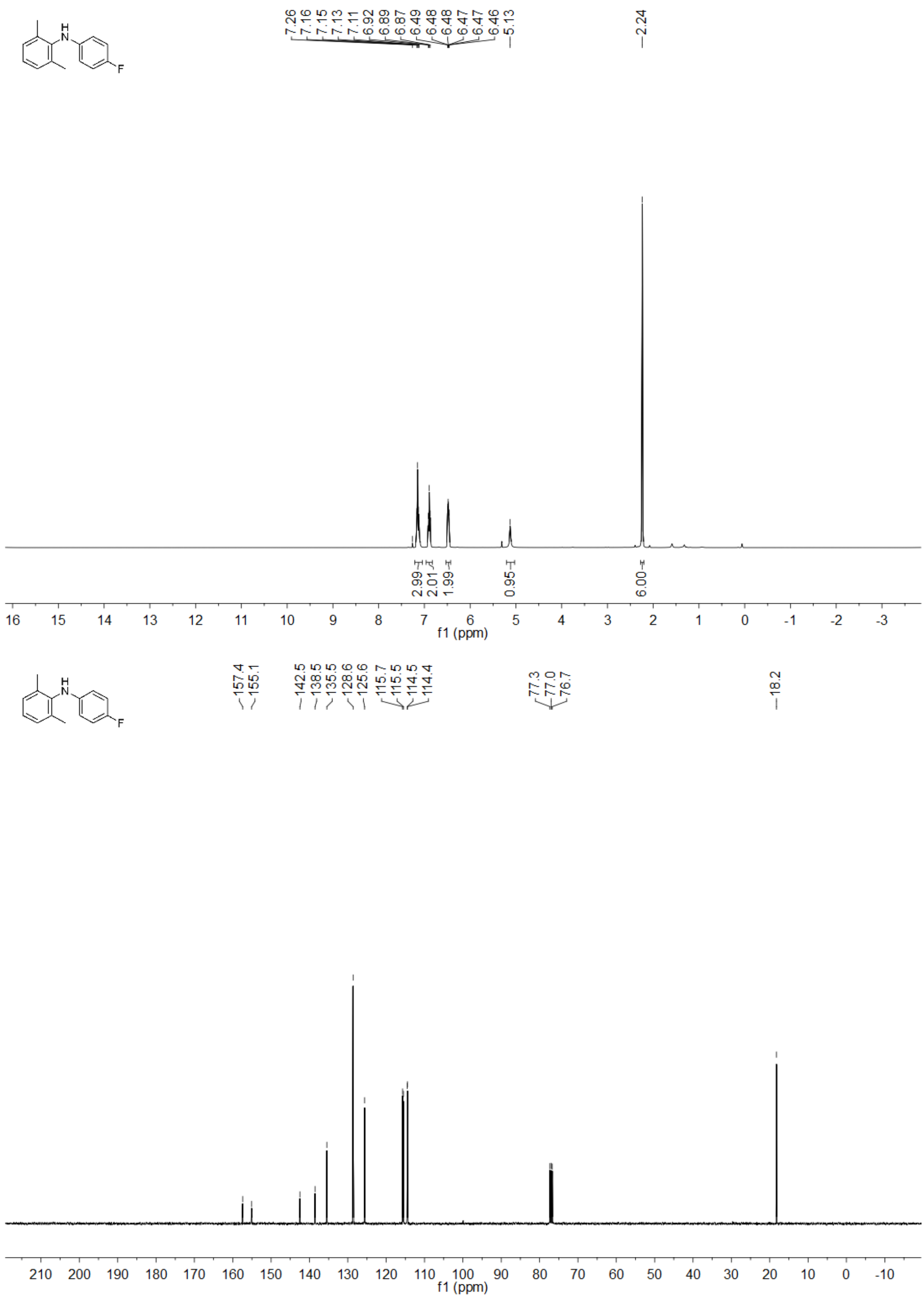
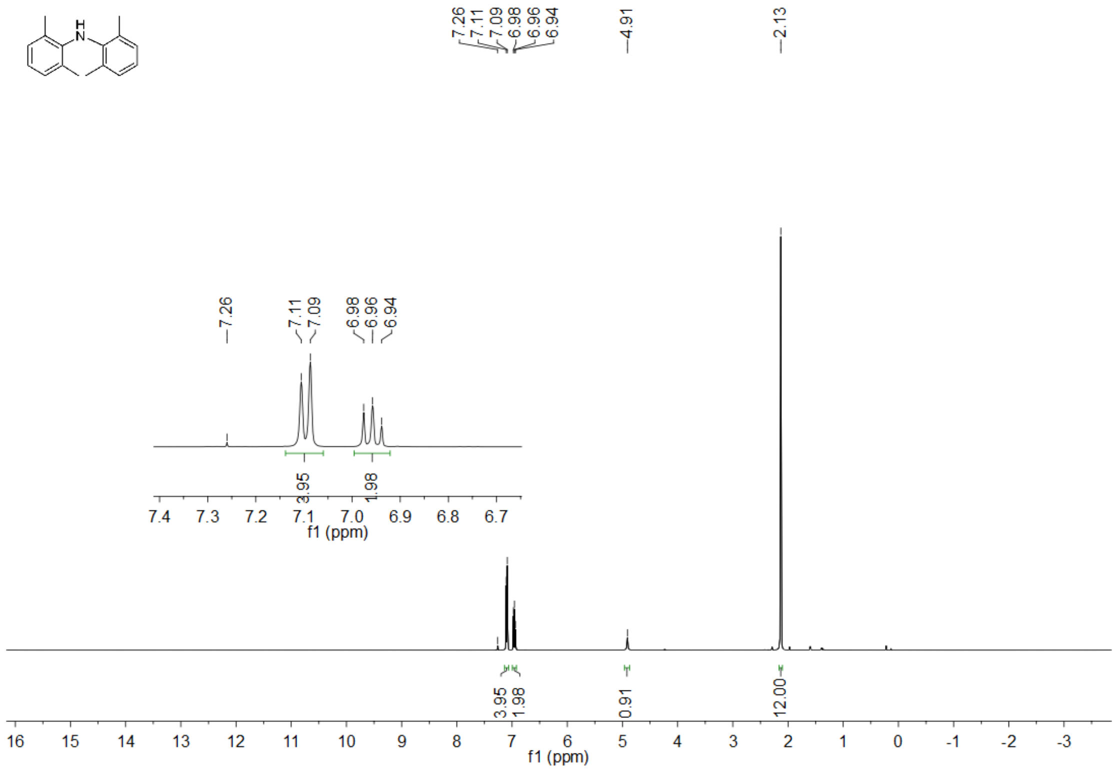


Figure S59. The NMR spectrum of 6v



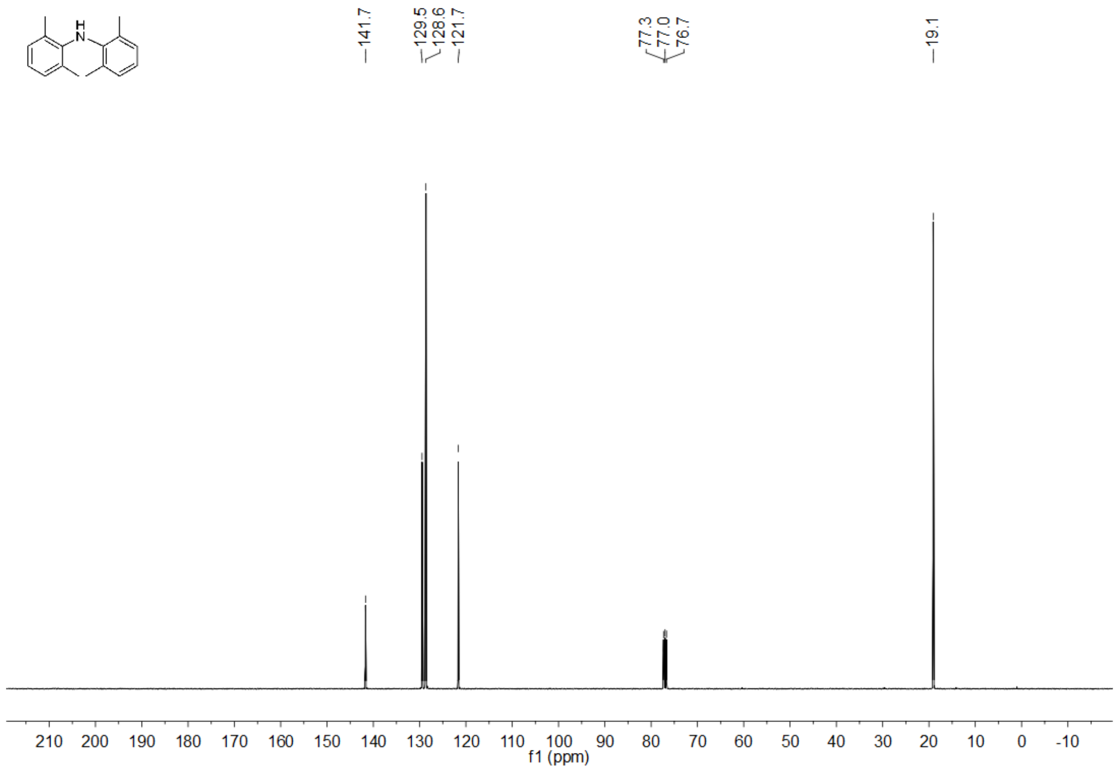
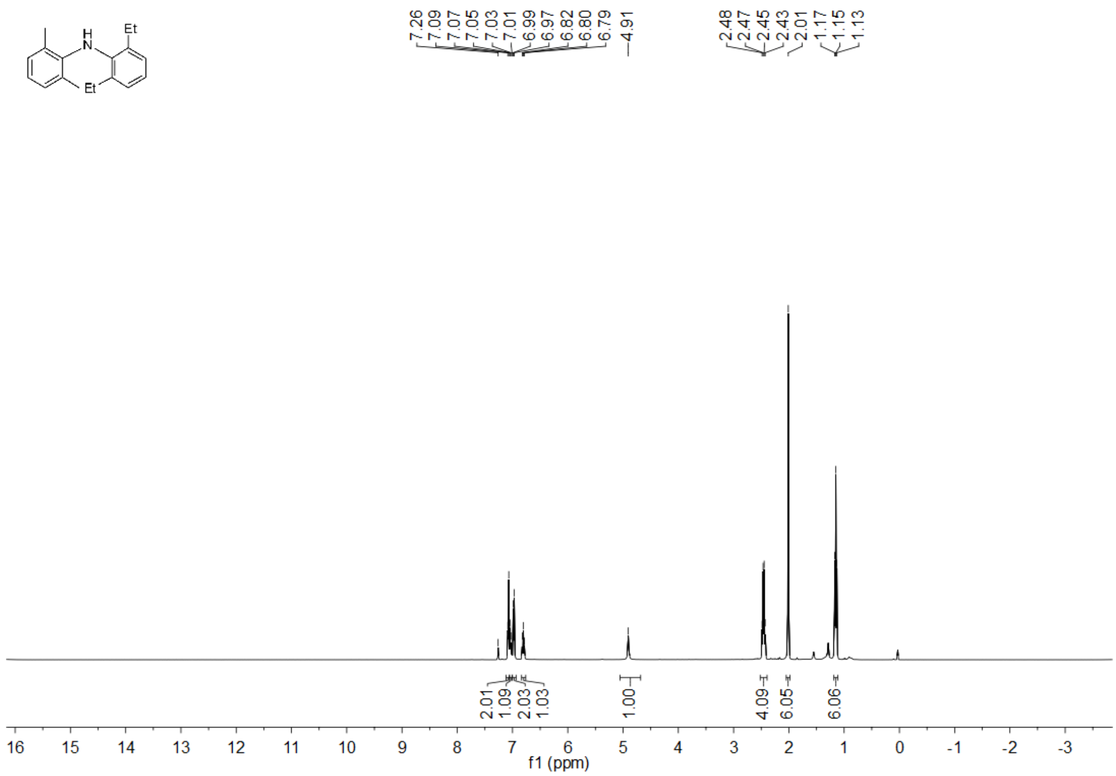


Figure S60. The NMR spectrum of 6w



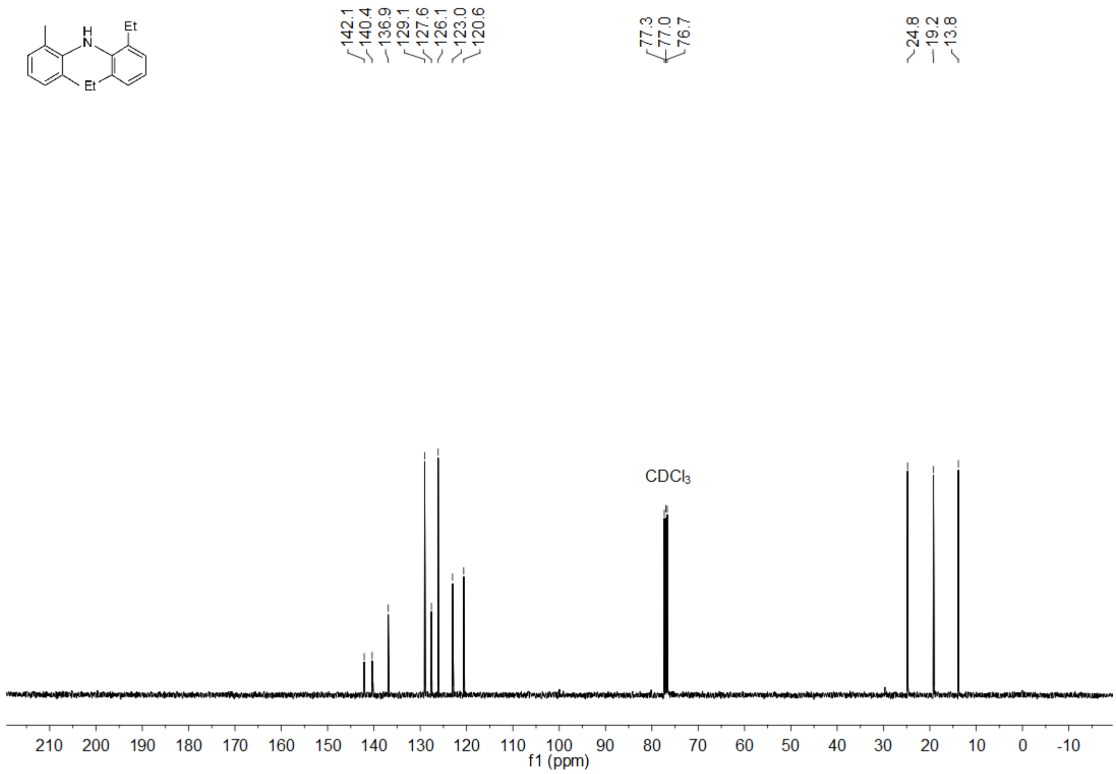
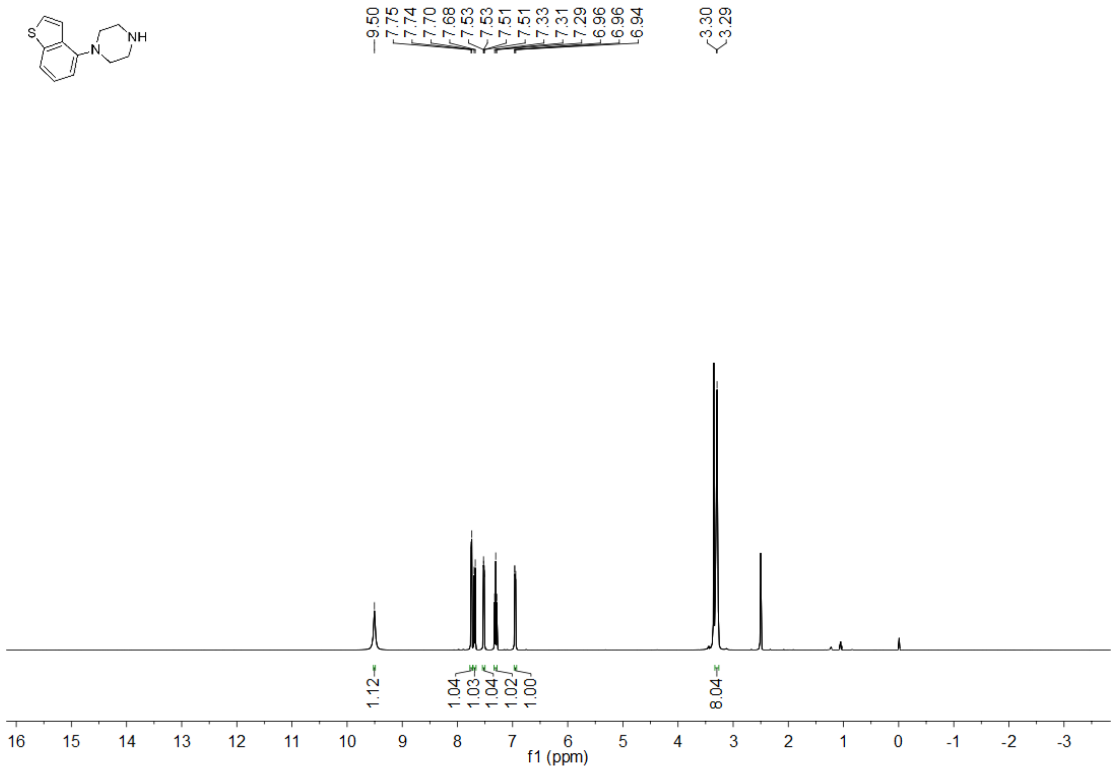


Figure S61. The NMR spectrum of 6x



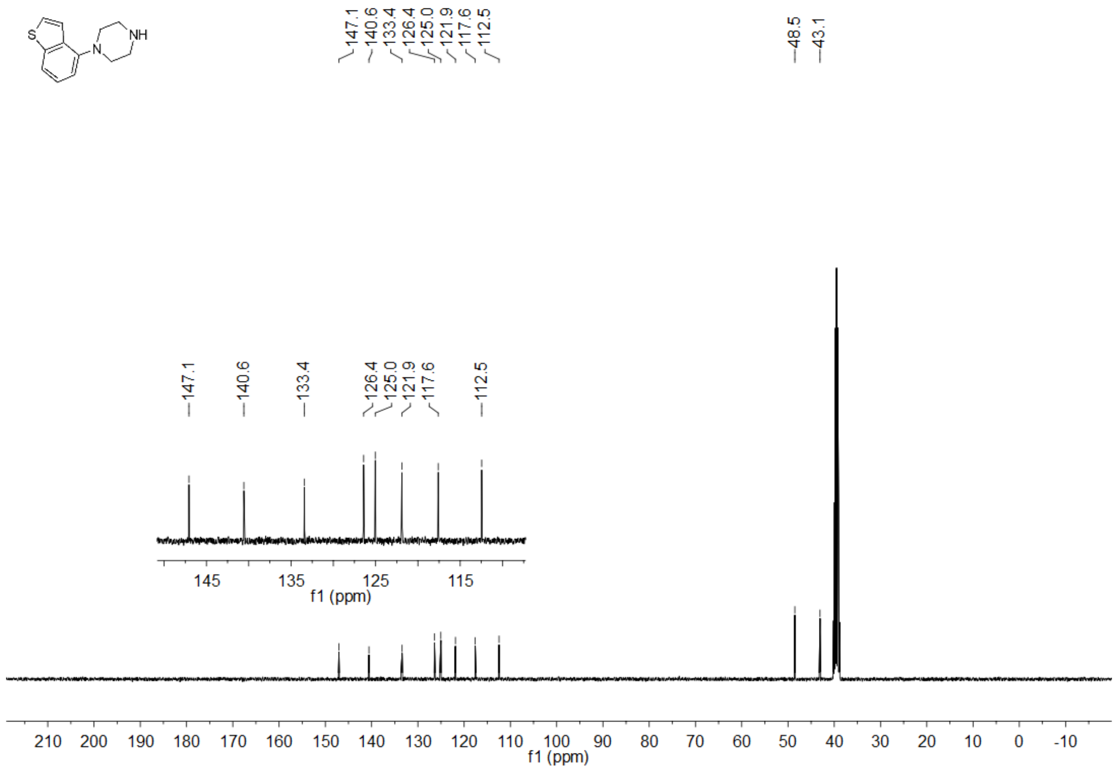
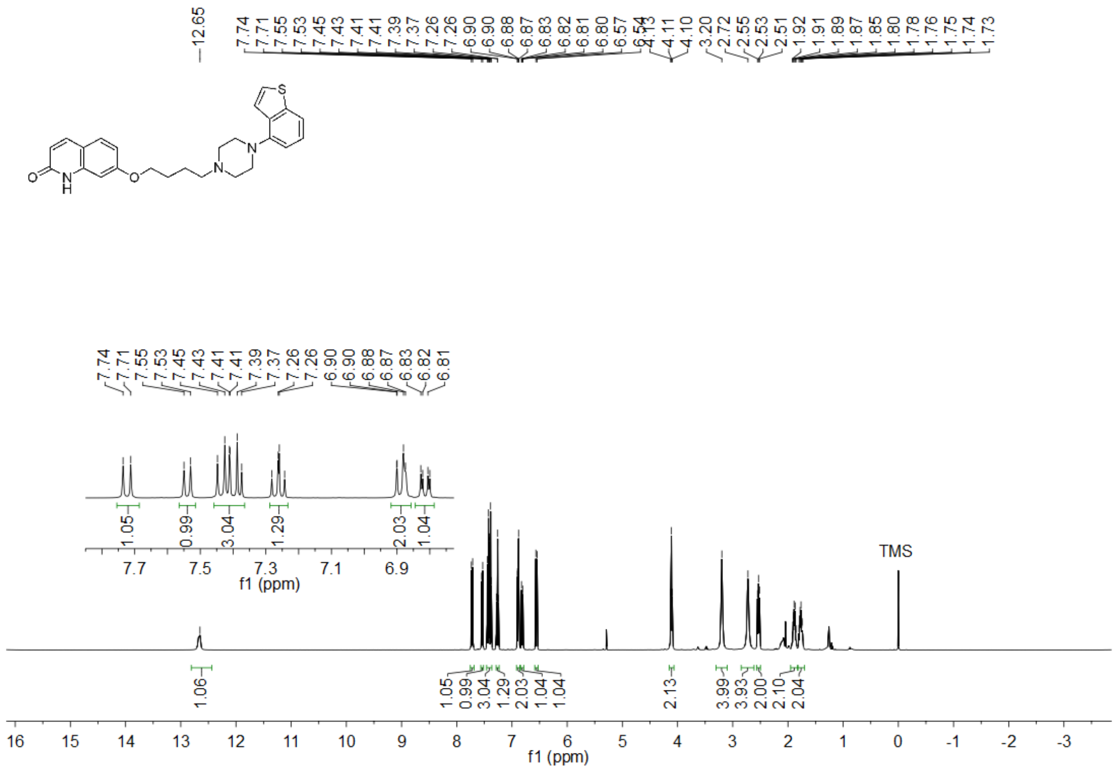


Figure S62. The NMR spectrum of 8a



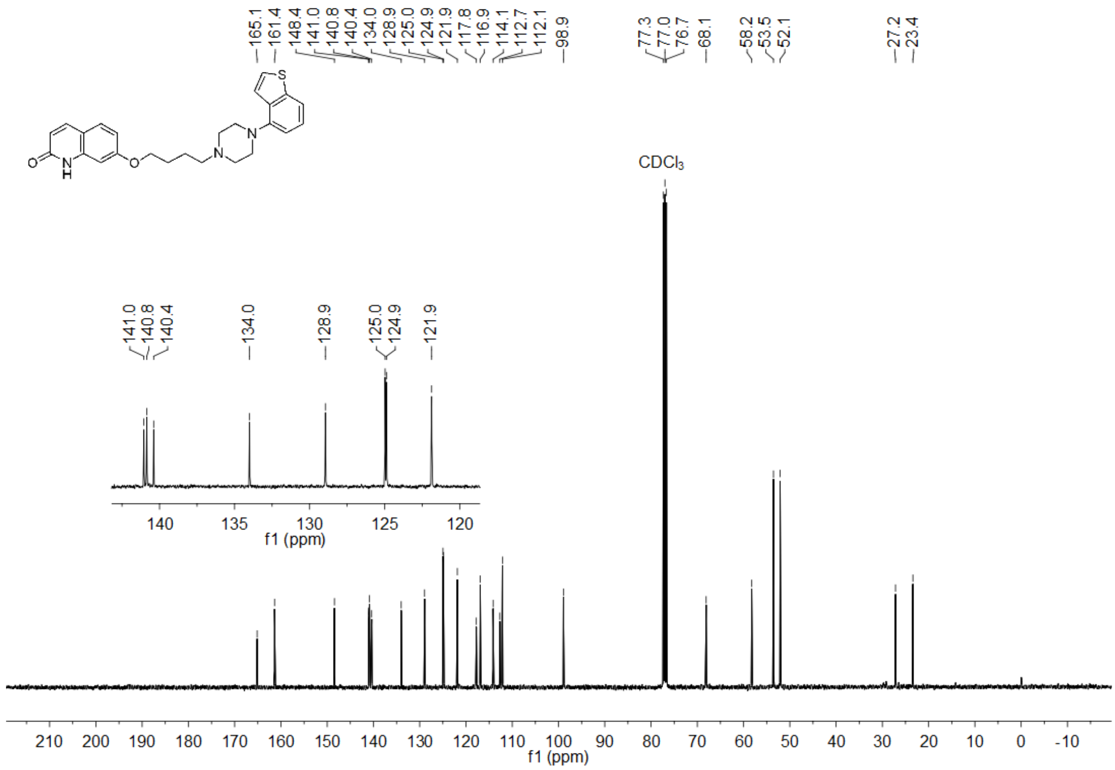


Figure S63. The NMR spectrum of 9a

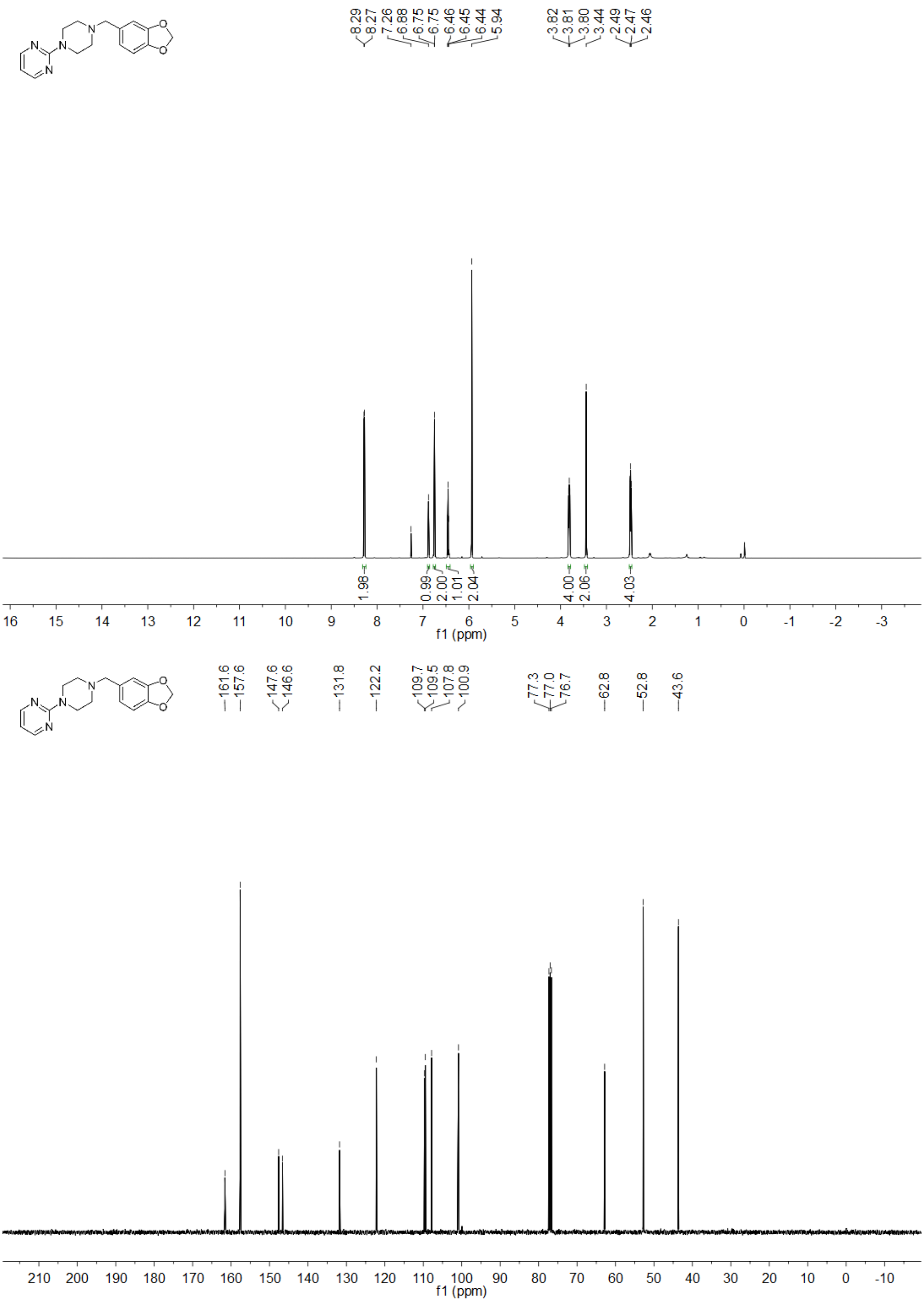


Figure S64. The NMR spectrum of 10a

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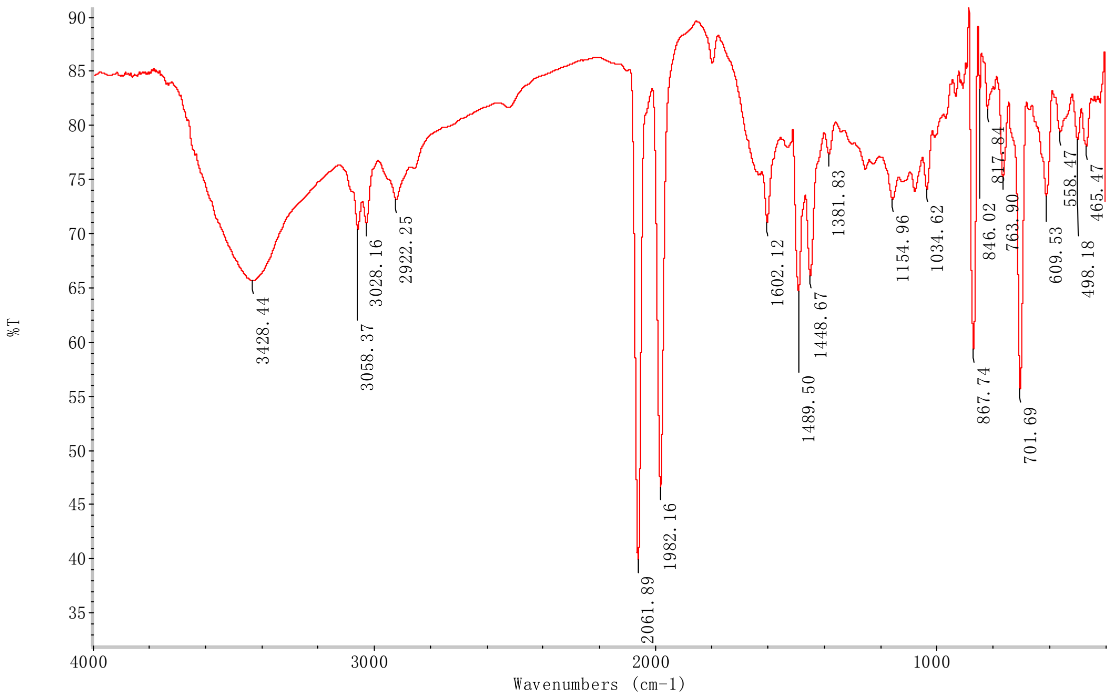

Figure S65. IR spectrum for Ir-1 [Ir(IPr*An)(Cl)(CO)2] compound.

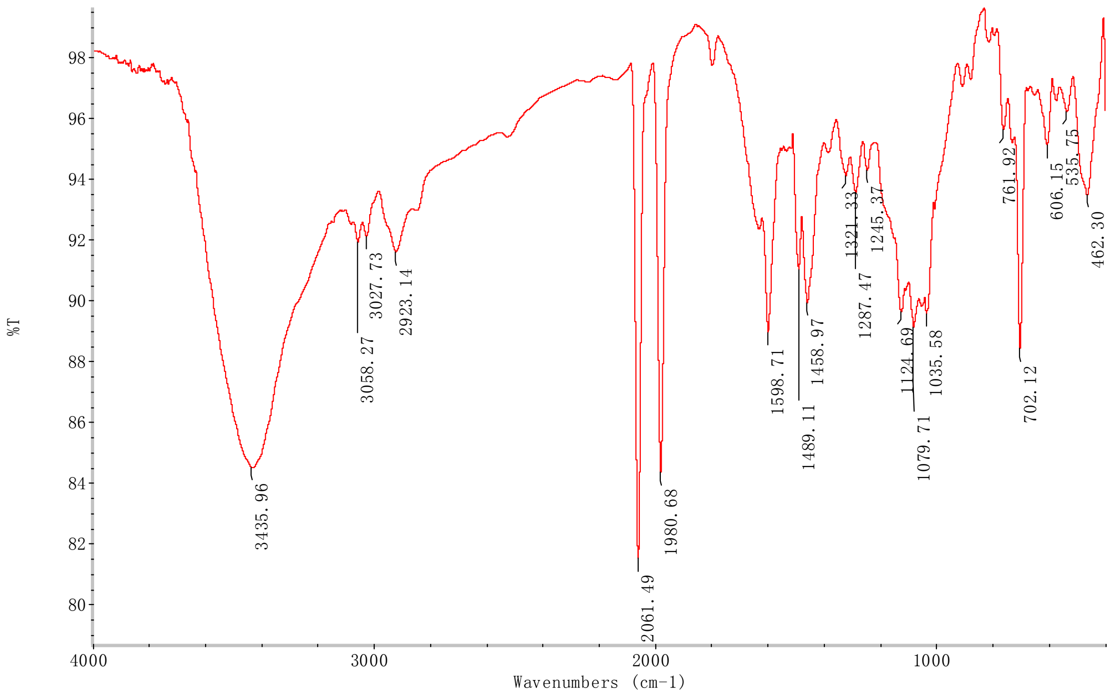

Figure S66. IR spectrum for Ir-2 [Ir(IPrOMe*An)(Cl)(CO)2] compound.