Electronic Supplementary Information for

Dual anion and cation catalysis enabled by an ion-pairing photocatalyst

Xi-Xian Chen,[a,b] Xiang Chen,[a,b] Feng Lan,[a] Teng Zeng,[a] Hao Cui,*[a] and Xiao Zhang*[a]

[a]Fujian Key Laboratory of Polymer Materials, Fujian Provincial Key Laboratory of Advanced Materials Oriented Chemical Engineering, College of Chemistry and Materials Science, Fujian Normal University, Fuzhou 350117, China.

E-mail: cuihao@fjnu.edu.cn (H.C.); zhangxiao@fjnu.edu.cn (X.Z.)

[b]These authors contributed equally to this work.

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1. General methods

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. ^{19}F NMR spectra were recorded on an Bruker instrument (375 MHz). Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectrometry (HRMS) was recorded on a Q-TOF (AB SCIEX X500R with ESI source, and Agilent 7250 with EI source), which combines quadrupole precursor ion selection and a high-resolution accurate-mass (HR/AM) Time of Flight mass analyzer to deliver mass accuracy. Fourier Transform Infrared spectra were recorded on a Nicolet IS50 FT-IR spectrophotometer.

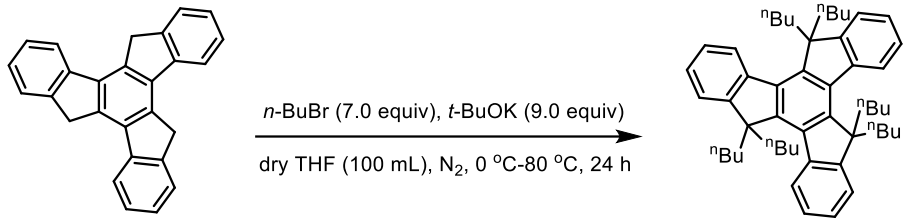
Substrates $^{n}Bu_4NPF_6$ were purchased from Energy-chemical, and solvents were purchased from Aladdin, and used without further purification.

2. Synthesis and characterization of $[TX\text{-}TPY]^{3+}\cdot 3Br^-$

The substrates **TX**, **TX-3Br** and **TX-TPr** were known compounds. The synthesis of **TX**, **TX-3Br** and **TX-TPr** were accomplished following the reported procedures[1-3].

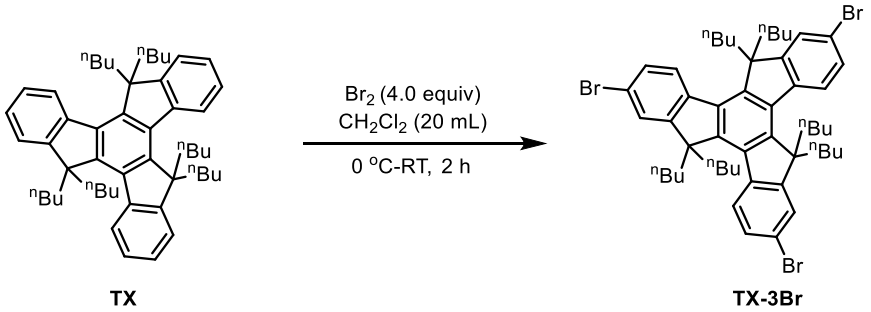
1) Synthesis of TX, TX-3Br, TX-TPr and $[TX\text{-}TPY]^{3+}\cdot 3Br^-$

Synthesis of TX:



Following the reported procedure[1], to a flame-dried Schlenk flask equipped with a magnetic stir bar were added **Truxene** (6.0 g, 17.5 mmol) and THF (100 mL) under nitrogen atmosphere. Then, *t*-BuOK (17.7 g, 157.5 mmol) was added, and the suspension was stirred at 0 °C for 30 minutes. Finally, 1-bromobutane (13.2 mL, 122.5 mmol) was added in one portion. The resulting mixture was stirred at 80 °C for 24 h (monitored by TLC) and cooled to room temperature. The reaction mixture was quenched by the addition of water. After the removal of THF, the residue was dissolved in CH_2Cl_2 and extracted with CH_2Cl_2 for three times, and the organic fractions were combined and washed with water. The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residues were purified by flash column chromatography on silica gel (PE) to provide the product **TX**[2] (9.88 g, 83% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 6.8 Hz, 3H), 7.47 (dd, *J* = 6.8, 2.0 Hz, 3H), 7.42-7.35 (m, 6H), 3.01-2.94 (m, 6H), 2.13-2.06 (m, 6H), 0.96-0.82 (m, 12H), 0.56-0.42 (m, 30H).

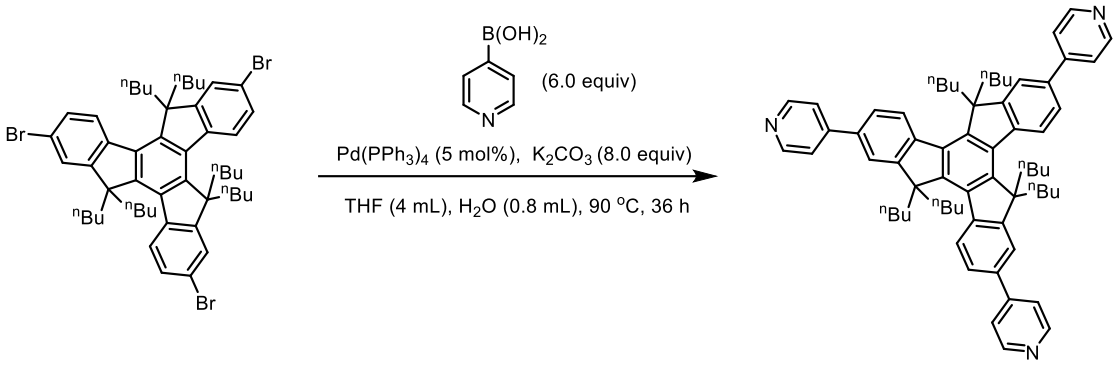
Synthesis of TX-3Br:



Following the reported procedure[3], to a stirred solution of **TX** (2.0 g, 2.95 mmol) in CH_2Cl_2 (20 mL) was slowly added bromine (0.6 mL, 11.8 mmol) at 0 °C. The reaction mixture was stirred for 2 h before the excess bromine was removed by bubbling N_2 through the solution and quenched with a cold aqueous saturated sodium sulfite solution. Then, the mixture was extracted with CH_2Cl_2 for three times, and the organic fractions were combined and washed with water. The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residues were

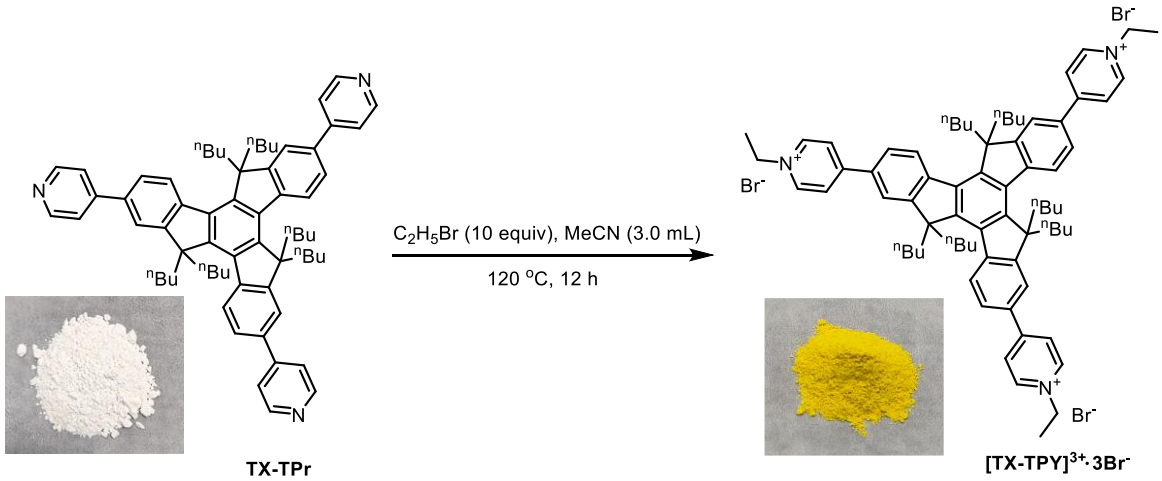
purified by flash column chromatography on silica gel (PE) to provide the product **TX-3Br**[2] (2.17 g, 80% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 3H), 7.57 (d, *J* = 2.0 Hz, 3H), 7.52 (dd, *J* = 8.4, 2.0 Hz, 3H), 2.90-2.83 (m, 6H), 2.07-2.00 (m, 6H), 0.99-0.79 (m, 12H), 0.58-0.33 (m, 30H).

Synthesis of TX-TPr:



Following the reported procedure[4], to a 25 mL Schlenk flask were added **TX-3Br** (400 mg, 0.44 mmol), 4-pyridine boronic acid (320 mg, 2.64 mmol), K_2CO_3 (480 mg, 3.52 mmol), $Pd(PPh_3)_4$ (32 mg, 5 mol%), THF (4 mL) and H_2O (0.8 mL). Then the mixture was stirred at 90 ℃ for about 36 h. After being cooled to room temperature, the reaction mixture was diluted with H_2O and extracted with EtOAc for three times, and the organic fractions were combined and washed with water. The organic phase was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residues were purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 15/1) to obtain **TX-TPr**[4] as a white solid (259.0 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 5.2 Hz, 6H), 8.53 (d, *J* = 8.4 Hz, 3H), 7.79 (s, 3H), 7.78 (d, *J* = 8.4 Hz, 3H), 7.71 (d, *J* = 5.2 Hz, 6H), 3.10-3.03 (m, 6H), 2.27-2.19 (m, 6H), 1.03-0.88 (m, 12H), 0.67-0.47 (m, 30H).

Synthesis of $[TX\text{-}TPY]^{3+}\cdot 3Br^-$:



To a 25 mL Schlenk flask were added **TX-TPr** (500 mg, 0.55 mmol), bromoethane (0.41 mL, 5.5 mmol) and MeCN (3.0 mL), then the reaction mixture was stirred at 120 °C for 12 h. After being cooled to room temperature, the resulting precipitate was collected by filtration, and washed with a small amount of CH_2Cl_2 and acetone to

provide **[TX-TPY]$^{3+}$·3Br^{-}** as a yellow solid (637.8 mg, 94% yield). m.p. = 266.6-268.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (d, J = 6.4 Hz, 6H), 8.84 (d, J = 6.8 Hz, 6H), 8.68 (d, J = 8.4 Hz, 3H), 8.58 (s, 3H), 8.37 (d, J = 8.0 Hz, 3H), 4.77 (q, J = 7.2 Hz, 6H), 3.10-3.03 (m, 6H), 2.56-2.50 (m, 6H), 1.67 (t, J = 7.2 Hz, 9H), 0.97-0.79 (m, 12H), 0.63-0.39 (m, 30H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.0, 154.5, 148.0, 145.0, 143.2, 138.1, 132.4, 127.5, 125.7, 124.8, 122.8, 56.5, 55.8, 36.0, 26.9, 22.7, 17.0, 14.1. IR (thin film): νmax (cm^{-1}) = 3390, 2953, 2928, 1635, 1602, 1522, 1479, 1435, 1301, 1227, 1198, 1176, 1042, 906, 808, 424, 409. HRMS (ESI) calcd for $C_{72}H_{90}BrN_3$ [M-Br^{-}]$^{2+}$: m/z = 537.8154. Found: 537.8149.

2) UV/Vis absorption spectra of TX and [TX-TPY]$^{3+}$·3Br^{-}

UV/vis absorption spectra of **TX** and **[TX-TPY]$^{3+}$·3Br^{-}** (0.01 mM in acetone) were recorded in 1 cm path quartz cuvettes using Pgeneral TU-1901 UV/Vis spectrometer.

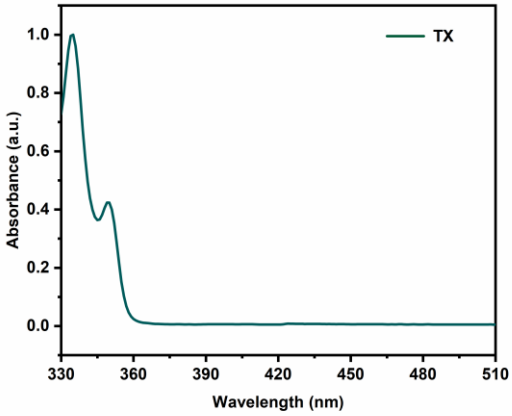


Fig. S1 UV/vis absorption spectrum of **TX** in acetone.

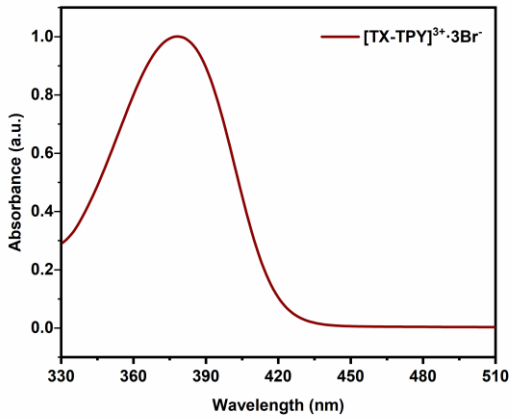


Fig. S2 UV/vis absorption spectrum of **[TX-TPY]$^{3+}$·3Br^{-}** in acetone.

3) Emission spectrum of [TX-TPY]$^{3+}$·3Br^{-}

Fluorescence spectrum was recorded on Edinburgh Instruments FS5 Spectrofluorometer in 1 cm quartz cuvettes. **[TX-TPY]$^{3+}$·3Br^{-}** was prepared as a 0.01 mM solution in acetone and used freshly for the measurements.

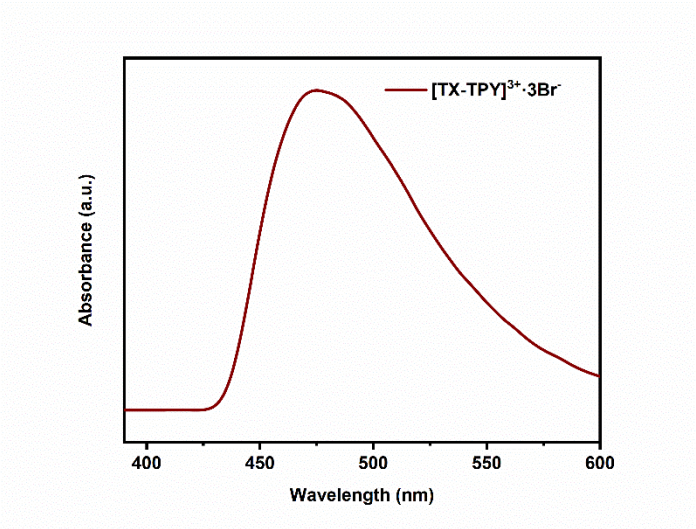


Fig. S3 Emission spectrum of **[TX-TPY]$^{3+}$·3Br^{-}** in acetone.

4) Fluorescence decay curve of [TX-TPY]$^{3+}$·3Br^{-}

Estimating lifetime of excited state of **[TX-TPY]$^{3+}$·3Br^{-}** was based on the ultrafast transient absorption spectroscopic techniques. The luminescence decays were measured on a Japan horiba Instruments FluoroMax-4 spectrometer. The sample compartment was home-built and designed as 10×10 mm cuvettes in 90° geometry between excitation and detection. The solution of **[TX-TPY]$^{3+}$·3Br^{-}** in acetone (0.01 mM) was excited at 430 nm. The decay trace was fitted by iterative reconvolution with an experimental instrument response function recorded directly after decay acquisition.

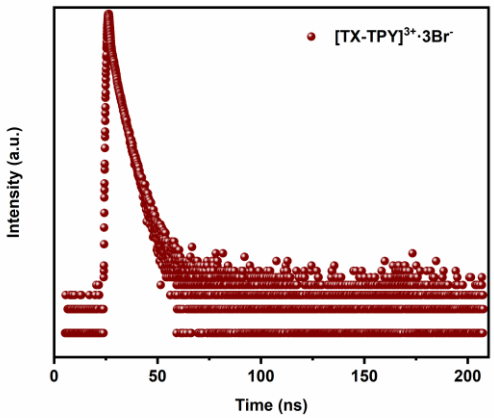


Fig. S4 Fluorescence decay curve of **[TX-TPY]$^{3+}$·3Br^{-}** in acetone, t = 3.039 ns.

5) UV/Vis absorption and emission spectra of [TX-TPY]$^{3+}$·3Br^{-}

The zero-zero vibrational state excitation energy $E_{0,0}$ was estimated by the corresponding energy of the wavelength at which emission and absorption overlap. This wavelength was determined setting the intensity of emission λ_{max} to the absorbance of **[TX-TPY]$^{3+}$·3Br^{-}** at excitation wavelength.

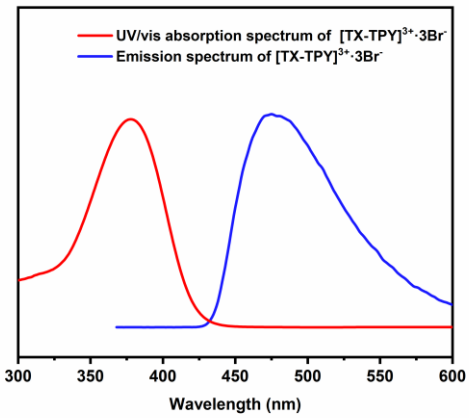


Fig. S5 UV/Vis absorption and emission spectra of **[TX-TPY]$^{3+}$·3Br^{-}** in acetone (0.01 mM). Cross point λ: 432 nm. $E_{0\text{-}0}$: 2.87 eV.

6) Cyclic voltammograms of [TX-TPY]$^{3+}$·3Br^{-}

Voltammetric experiments were conducted with a computer-controlled Shanghai Chen Hua CHI660E containing glassy carbon electrode serving as the working electrode, saturated calomel reference electrode, Pt wire auxiliary electrode.

All solutions used for the voltammetric experiments were deoxygenated by purging with high purity nitrogen gas and measurements were performed in a electrolytic cell at room temperature.

Excited state oxidation and reduction potentials were calculated by the following approximating formulas: $E(PC^{*}/PC^{\bullet-}) = E(PC/PC^{\bullet-}) + E_{0,0}$ and $E(PC^{\bullet+}/PC^{*}) = E(PC^{\bullet+}/PC) - E_{0,0}$.

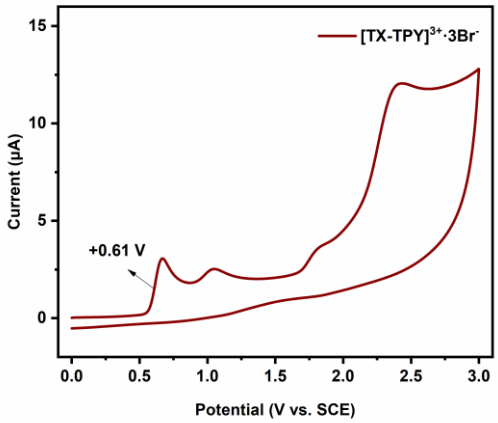


Fig. S6 Cyclic voltammogram of **[TX-TPY]$^{3+}$·3Br^{-}** in MeCN (1.0 mM) containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s. $E_{1/2}(Br^{\bullet}/Br^{-})$ = +0.61 V.

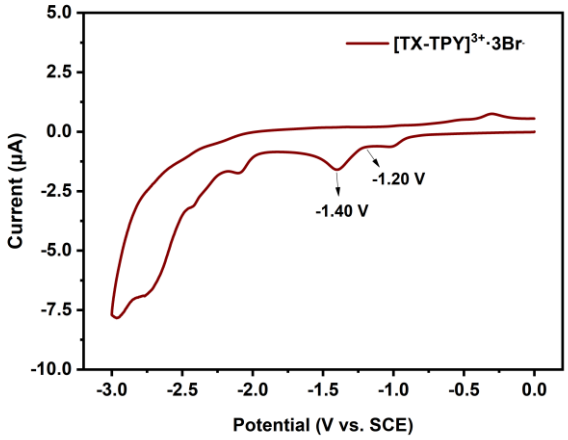
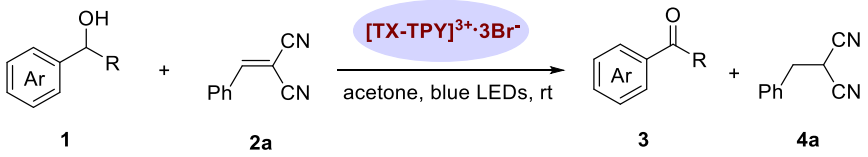


Fig. S7 Cyclic voltammogram of **[TX-TPY]$^{3+}$·3Br^{-}** in DMSO (1.0 mM) containing 0.1 M ^{n}Bu$_4$NPF$_6$. Scan rate: 0.1 V/s. E(PC/PC$^{\bullet-}$) = -1.20 ~ -1.40 V, E(PC*/PC$^{\bullet-}$) = +1.47 ~ +1.67 V.

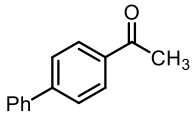
3. General procedure for photocatalytic hydrogen transfer

1) General procedure for photocatalytic hydrogen transfer between alcohols and 2a

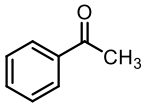


1 **2a** **3** **4a**

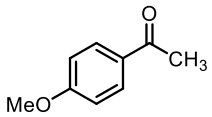
To a flame-dried sealed tube were added **[TX-TPY]$^{3+}$·3Br^{-}** (5.0 mol%), **1** (0.2 mmol), **2a** (0.6 mmol) and acetone (2.0 mL, 0.1 M). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from 30 W blue LEDs. Then the reaction mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 20/1) to afford the desired products **3**. The analytical data of the product **3a-3o** were summarized below.



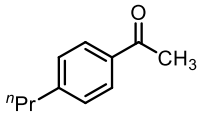
3a[5], 30.9 mg, white solid, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 6.8 Hz, 1H), 2.64 (s, 3H).



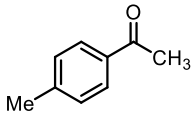
3b[6], 22.7 mg, colorless oil, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 2.62 (s, 3H).



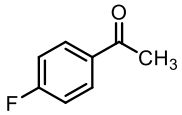
3c[6], 23.3 mg, colorless oil, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H).



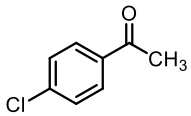
3d[7], 26.4 mg, colorless oil, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.58 (s, 3H), 1.72-1.62 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).



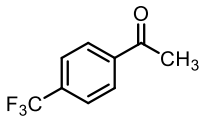
3e[7], 25.1 mg, colorless oil, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 2.58 (s, 3H), 2.41 (s, 3H).



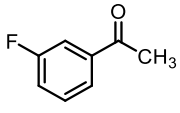
3f[6], 22.7 mg, colorless oil, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.13 (t, *J* = 8.4 Hz, 2H), 2.59 (s, 3H).



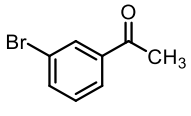
3g[7], 35.4 mg, colorless oil, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 2.59 (s, 3H).



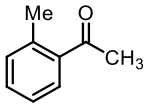
3h[6], 31.2 mg, colorless oil, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 2.66 (s, 3H).



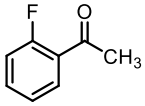
3i[6], 25.6 mg, yellow oil, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 1H), 7.66-7.62 (m, 1H), 7.48-7.42 (m, 1H), 7.30-7.24 (m, 1H), 2.61 (s, 3H).



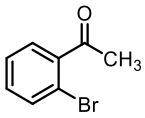
3j[6], 36.4 mg, yellow oil, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.69 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 2.60 (s, 3H).



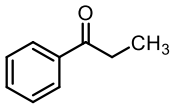
3k[8], 25.7 mg, colorless oil, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.2 Hz, 1H), 7.38 (td, *J* = 7.6, 1.6 Hz, 1H), 7.29-7.23 (m, 2H), 2.59 (s, 3H), 2.53 (s, 3H).



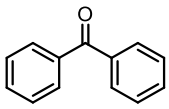
3l[6], 25.6 mg, yellow oil, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (td, *J* = 7.6, 2.0 Hz, 1H), 7.55-7.49 (m, 1H), 7.23 (td, *J* = 7.6, 1.2 Hz, 1H), 7.14 (ddd, *J* = 11.2, 8.0, 0.8 Hz, 1H), 2.65 (d, *J* = 5.2 Hz, 3H).



3m[6], 32.5 mg, yellow oil, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 7.30 (td, *J* = 8.0, 1.2 Hz, 1H), 2.64 (s, 3H).

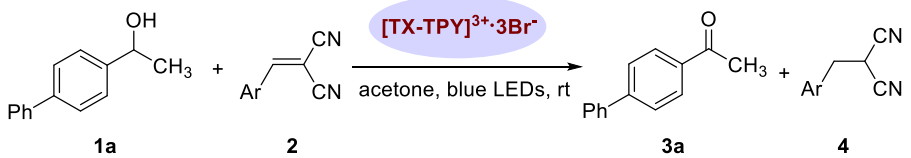


3n[5], 24.2 mg, yellow oil, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.01 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

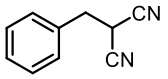


3o[5], 31.1 white, solid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 4H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 4 H).

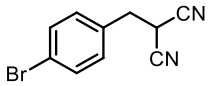
2) General procedure for photocatalytic hydrogen transfer between alkenes and 1a



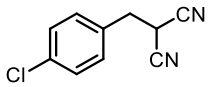
To a flame-dried sealed tube were added **[TX-TPY]$^{3+}$·3Br$^-$** (5.0 mol%), **1a** (0.6 mmol), **2** (0.2 mmol) and acetone (2.0 mL, 0.1 M). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from 30 W blue LEDs. Then the reaction mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 15/1) to afford the desired products **4**. The analytical data of the product **4a-4p** were summarized below.



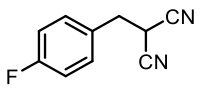
4a[9], 25.0 mg, white solid, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.38 (m, 3H), 7.33-7.31 (m, 2H), 3.91 (t, *J* = 6.8 Hz, 1H), 3.29 (d, *J* = 6.8 Hz, 2H).



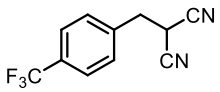
4b[10], 33.9 mg, white solid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.92 (t, *J* = 6.8 Hz, 1H), 3.24 (d, *J* = 6.8 Hz, 2H).



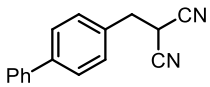
4c[10], 32.0 mg, white solid, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 3.91 (t, *J* = 6.8 Hz, 1H), 3.26 (d, *J* = 6.8 Hz, 2H).



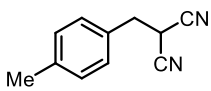
4d[10], 31.4 mg, white solid, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.13-7.08 (m, 2H), 3.91 (t, *J* = 6.8 Hz, 1H), 3.27 (d, *J* = 6.8 Hz, 2H).



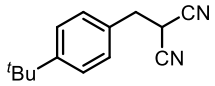
4e, 38.0 mg, yellow oil, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 3.98 (t, *J* = 6.8 Hz, 1H), 3.36 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 131.2 (q, *J* = 32.0 Hz), 129.8, 126.3 (q, *J* = 4.0 Hz), 123.8 (q, *J* = 271.0 Hz), 111.9, 36.2, 24.7. ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.81 (s). IR (thin film): νmax (cm^{-1}) = 2918, 2849, 1631, 1421, 1323, 1163, 1109, 1066, 1019, 800, 733, 599, 406. HRMS (EI) calcd for $C_{11}H_7F_3N_2$ $[M]^{\cdot+}$: 224.0556. Found: 224.0557.



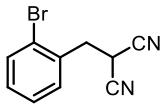
4f, 36.4 mg, white solid, 74% yield. m.p. = 131.8-133.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.40-7.34 (m, 3H), 3.93 (t, *J* = 6.8 Hz, 1H), 3.31 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 140.2, 131.9, 129.6, 128.9, 128.0, 127.8, 127.1, 112.2, 36.4, 25.0. IR (thin film): νmax (cm^{-1}) = 2926, 1485, 1442, 1025, 1005, 850, 808, 758, 726, 687, 568, 476. HRMS (EI) calcd for $C_{16}H_{12}N_2$ $[M]^{\cdot+}$: 232.0995. Found: 232.0995.



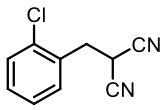
4g[9], 29.3 mg, white solid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.19 (m, 4H), 3.87 (t, *J* = 6.8 Hz, 1H), 3.24 (d, *J* = 6.8 Hz, 2H), 2.36 (s, 3H).



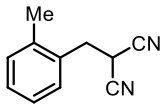
4h[9], 32.2 mg, white solid, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.88 (t, *J* = 6.8 Hz, 1H), 3.26 (d, *J* = 7.2 Hz, 2H), 1.32 (s, 9H).



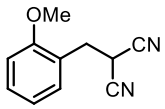
4i, 40.7 mg, colorless oil, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42-7.35 (m, 2H), 7.29-7.24 (m, 1H), 4.15 (t, *J* = 8.0 Hz, 1H), 3.45 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.5, 132.4, 132.1, 130.8, 128.5, 124.2, 112.0, 37.5, 22.7. IR (thin film): νmax (cm^{-1}) = 2909, 2257, 1569, 1471, 1443, 1028, 910, 750, 732, 660, 567, 441. HRMS (EI) calcd for $C_{10}H_7BrN_2$ $[M]^{\cdot+}$: 233.9787. Found: 233.9791.



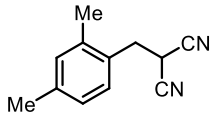
4j[9], 34.4 mg, colorless oil, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 1H), 7.41-7.38 (m, 1H), 7.37-7.30 (m, 2H), 4.11 (t, *J* = 8.0 Hz, 1H), 3.45 (d, *J* = 8.0 Hz, 2H).



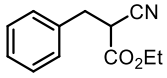
4k[9], 32.9 mg, white solid, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.21 (m, 4H), 3.85 (t, *J* = 7.6 Hz, 1H), 3.33 (d, *J* = 7.6 Hz, 2H), 2.39 (s, 3H).



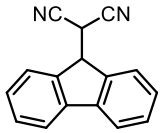
4l[11], 26.4 mg, colorless oil, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 4.17 (t, *J* = 7.6 Hz, 1H), 3.87 (s, 3H), 3.31 (d, *J* = 8.0 Hz, 2H).



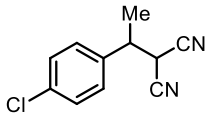
4m, 23.9 mg, colorless oil, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 3.82 (td, *J* = 8.0, 1.2 Hz, 1H), 3.30 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 136.1, 132.0, 129.9, 128.3, 127.6, 112.4, 33.7, 23.9, 21.1, 19.3. IR (thin film): νmax (cm^{-1}) = 2919, 2256, 1617, 1507, 1449, 1380, 1034, 832, 797, 732, 574, 450, 425. HRMS (EI) calcd for $C_{12}H_{12}N_2$ $[M]^{\cdot+}$: 184.0995. Found: 184.0994.



4n[10], 23.0 mg, yellow oil, 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.72 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.31-3.16 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H).

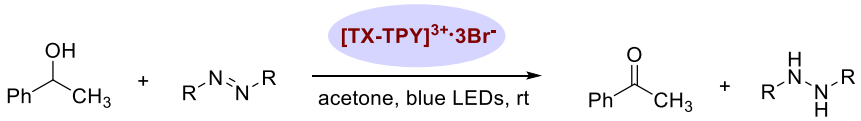


4o, 39.1 mg, yellow solid, 84% yield. m.p. = 155.2-156.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.38 (td, *J* = 7.6, 1.2 Hz, 2H), 4.38 (d, *J* = 7.6 Hz, 1H), 4.22 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 139.7, 129.8, 128.2, 124.7, 120.8, 111.6, 46.0, 27.7. IR (thin film): νmax (cm^{-1}) = 2920, 1477, 1449, 1314, 1031, 1002, 910, 764, 742, 727, 677, 648, 620. HRMS (ESI) calcd for $C_{16}H_{10}N_2$ $[M]^{\cdot+}$: 230.0838. Found: 230.0840.

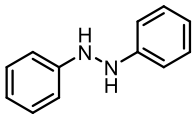


4p[12], 34.9 mg, yellow oil, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.84 (d, *J* = 6.4 Hz, 1H), 3.48-3.41 (m, 1H), 1.63 (d, *J* = 7.2 Hz, 3H).

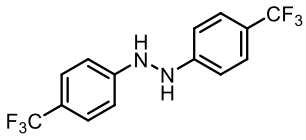
3) General procedure for photocatalytic hydrogen transfer between diazo compounds and 1b



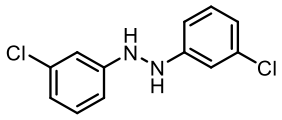
To a flame-dried sealed tube were added **[TX-TPY]$^{3+}$·3Br$^-$** (5.0 mol%), **1b** (0.6 mmol), **5** (0.2 mmol) and acetone (2.0 mL, 0.1 M). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from 40 W Kessil lamp. Then the reaction mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 20/1) to afford the desired products **6**. The analytical data of the product **6a-6o** were summarized below.



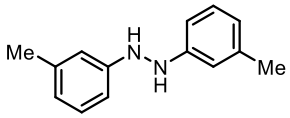
6a[13], 34.3 mg, yellow solid, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.6 Hz, 4H), 6.85-6.81 (m, 6H), 5.58 (s, 2H).



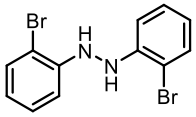
6b[13], 52.7 mg, yellow solid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 4H), 6.87 (d, *J* = 8.4 Hz, 4H), 5.93 (s, 2H).



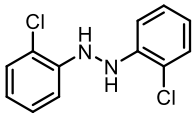
6c[13], 45.2 mg, yellow solid, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.6 Hz, 2H), 6.83-6.79 (m, 4H), 6.67 (dt, *J* = 8.0. 1.6 Hz, 2H), 5.62 (s, 2H).



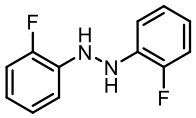
6d[13], 36.4 mg, yellow solid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.6 Hz, 2H), 6.68-6.63 (m, 6H), 5.50 (s, 2H), 2.27 (s, 6H).



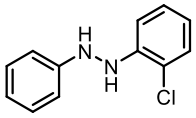
6e[13], 53.4 mg, yellow solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.16 (td, *J* = 8.0, 1.6 Hz, 2H), 6.92 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.73 (td, *J* = 8.0, 1.6 Hz, 2H), 6.22 (s, 2H).



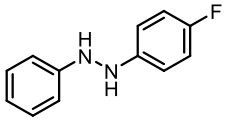
6f[13], 45.3 mg, yellow solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.12 (td, *J* = 8.0, 1.6 Hz, 2H), 6.94 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.78 (td, *J* = 8.0, 1.6 Hz, 2H), 6.19 (s, 2H).



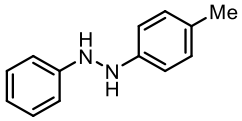
6g[14], 40.2 mg, yellow solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-6.97 (m, 6H), 6.81-6.75 (m, 2H), 5.86 (s, 2H).



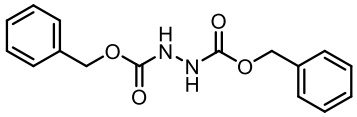
6h[15], 39.1 mg, yellow solid, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 7.01 (dt, *J* = 8.0, 1.2 Hz, 1H), 6.87-6.72 (m, 4H), 6.15 (s, 1H), 5.58 (s, 1H).



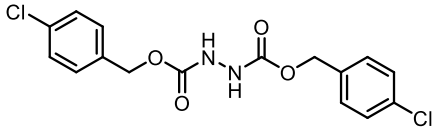
6i[13], 33.3 mg, yellow solid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.18 (m, 2H), 6.89 (t, *J* = 8.8 Hz, 2H), 6.85-6.74 (m, 5H), 5.56 (s, 1H), 5.48 (s, 1H).



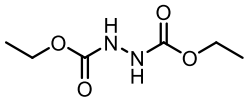
6j[13], 33.6 mg, yellow solid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.17 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.84-6.79 (m, 3H), 6.74 (d, *J* = 8.4 Hz, 2H), 5.54 (s, 1H), 5.48 (s, 1H), 2.45 (s, 3H).



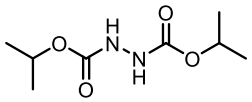
6k[16], 51.6 mg, colorless oil, 84% yield. The ^{1}H NMR spectrum was appeared as a mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 10H), 6.96 and 6.62 (br, 2H), 5.18-5.11 (m, 4H).



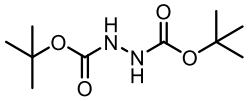
6l[17], 51.7 mg, white solid, 88% yield. The ^{1}H NMR spectrum was appeared as a mixture of rotamers. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.38-8.93 (m, 2H), 7.46-7.30 (m, 8H), 5.18-5.02 (m, 4H).



6m[18], 29.4 mg, colorless oil, 84% yield. The ^{1}H NMR spectrum was appeared as a mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 and 6.73 (br, 2H), 4.30-4.18 (m, 4H), 1.34-1.24 (m, 6H).



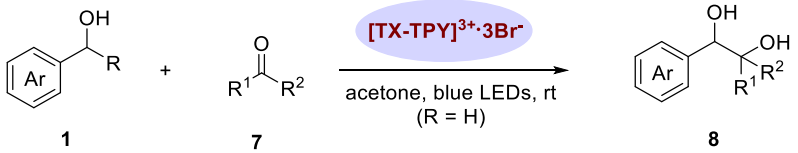
6n[18], 45.9 mg, white solid, 96% yield. The ^{1}H NMR spectrum was appeared as a mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 and 6.55 (br, 2H), 5.02-4.91 (m, 2H), 1.31-1.25 (m, 12H).



6o[18], 40.3 mg, colorless oil, 83% yield. The ^{1}H NMR spectrum was appeared as a mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 and 6.84 (br, 2H), 1.48 (s, 18H).

4. General procedure for photocatalytic cross-coupling

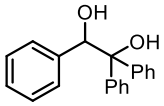
1) General procedure for photocatalytic cross-coupling of benzylic alcohols with aryl ketones



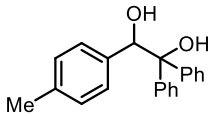
1 **7** **8**

To a flame-dried sealed tube were added **[TX-TPY]$^{3+}$·3Br$^-$** (5.0 mol%), **1** (0.6 mmol), **7** (0.2 mmol) and acetone (2.0 mL, 0.1 M). The reaction mixture was degassed

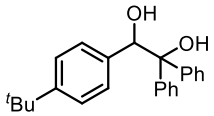
via freeze-pump-thaw for 3 cycles. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from 40 W Kessil lamp. Then the reaction mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford the desired products **8**. The analytical data of the product **8a-8m** were summarized below.



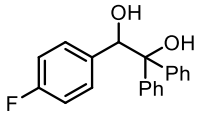
8a[19]**,** 36.3 mg, white solid, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 6.8 Hz, 1H), 7.18-7.05 (m, 10H), 5.64 (d, *J* = 2.8 Hz, 1H), 3.14 (s, 1H), 2.42 (d, *J* = 3.2 Hz, 1H).



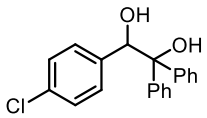
8b[19]**,** 37.1 mg, white solid, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 6.8 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.18-7.08 (m, 5H), 6.96-9.94 (m, 4H), 5.62 (d, *J* = 3.2 Hz, 1H), 3.12 (s, 1H), 2.37 (d, *J* = 3.2 Hz, 1H), 2.26 (s, 3H).



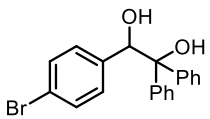
8c[19]**,** 37.2 mg, white solid, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.17-7.09 (m, 7H), 6.99 (d, *J* = 8.4 Hz, 2H), 5.62 (d, *J* = 3.2 Hz, 1H), 3.13 (s, 1H), 2.37 (d, *J* = 3.2 Hz, 1H), 1.25 (s, 9H).



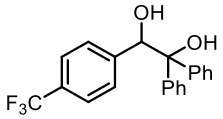
8d[19]**,** 40.5 mg, white solid, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.74 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.12-7.09 (m, 5H), 7.01 (dd, *J* = 8.8, 6.0 Hz, 2H), 6.81 (t, *J* = 8.4 Hz, 2H), 5.60 (d, *J* = 3.2 Hz, 1H), 3.12 (s, 1H), 2.45 (d, *J* = 3.2 Hz, 1H).



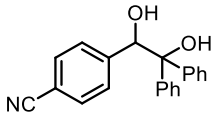
8e[20]**,** 48.9 mg, white solid, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.13-7.08 (m, 7H), 6.97 (d, *J* = 8.4 Hz, 2H), 5.61 (d, *J* = 2.8 Hz, 1H), 3.08 (s, 1H), 2.44 (d, *J* = 3.2 Hz, 1H).



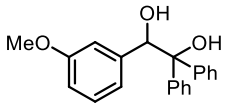
8f[20]**,** 49.0 mg, white solid, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 5.6 Hz, 2H), 7.14-7.10 (m, 5H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.59 (s, 1H), 3.06 (s, 1H), 2.43 (s, 1H).



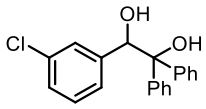
8g[20]**,** 51.7 mg, white solid, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.14-7.10 (m, 7H), 5.67 (s, 1H), 3.10 (s, 1H), 2.54 (s, 1H).



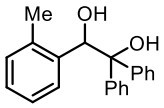
8h[20]**,** 47.3 mg, white solid, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.14-7.07 (m, 7H), 5.66 (s, 1H), 3.08 (s, 1H), 2.54 (br, 1H).



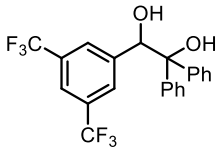
8i[19]**,** 33.1 mg, white solid, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 6.8 Hz, 2H), 7.30 (t, *J* = 6.8 Hz, 1H), 7.18-7.05 (m, 6H), 6.74-6.67 (m, 2H), 6.53 (s, 1H), 5.62 (s, 1H), 3.60 (s, 3H), 3.09 (s, 1H), 2.43 (br, 1H).



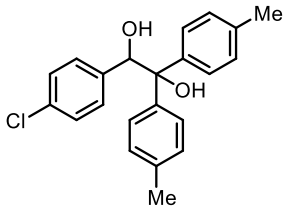
8j[20]**,** 45.8 mg, white solid, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 6.4 Hz, 1H), 7.16-7.09 (m, 7H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 5.59 (s, 1H), 3.08 (s, 1H), 2.48 (br, 1H).



8k[19]**,** 36.2 mg, white solid, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.09-7.00 (m, 3H), 6.95 (d, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 5.84 (d, *J* = 2.4 Hz, 1H), 3.35 (s, 1H), 2.29 (d, *J* = 2.8 Hz, 1H), 1.72 (s, 3H).

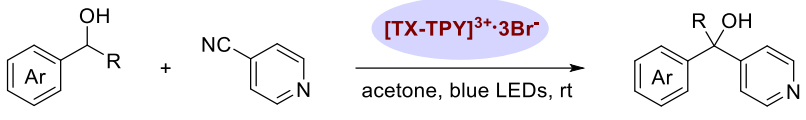


8l[20]**,** 55.7 mg, white solid, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 6.8 Hz, 2H), 7.36-7.33 (m, 3H), 7.17-7.13 (m, 3H), 7.07-7.04 (m, 2H), 5.68 (d, *J* = 3.6 Hz, 1H), 3.05 (s, 1H), 2.71 (d, *J* = 3.6 Hz, 1H).



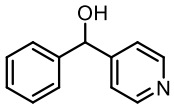
8m[20]**,** 53.8 mg, white solid, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 6.8 Hz, 2H), 6.96 (d, *J* = 6.8 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.52 (s, 1H), 2.99 (s, 1H), 2.48 (s, 1H), 2.35 (s, 3H), 2.22 (s, 3H).

2) General procedure for photocatalytic cross-coupling of benzylic alcohols with 4-cyanopyridine

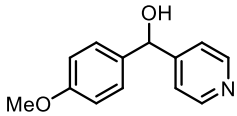


1 **9** **10**

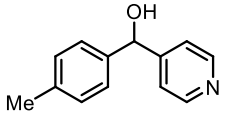
To a flame-dried sealed tube were added **[TX-TPY]$^{3+}$·3Br$^-$** (5.0 mol%), **1** (0.6 mmol), **9** (0.2 mmol) and acetone (2.0 mL, 0.1 M). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from 40 W Kessil lamp. Then the reaction mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 3/1) to afford the desired products **10**. The analytical data of the product **10a-10o** were summarized below.



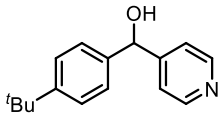
10a[21], 29.6 mg, white solid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 6.0 Hz, 2H), 7.34 -7.27 (m, 7H), 5.77 (s, 1H), 4.12 (br, 1H).



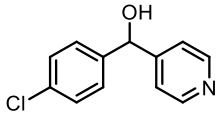
10b[21], 30.8 mg, white solid, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 6.0 Hz, 2H), 7.30 (d, *J* = 6.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.75 (s, 1H), 3.79 (s, 3H), 3.43 (br, 1H).



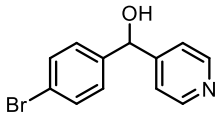
10c[21], 29.8 mg, white solid, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 6.0 Hz, 2H), 7.31 (d, *J* = 6.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.76 (s, 1H), 3.11 (br, 1H), 2.34 (s, 3H).



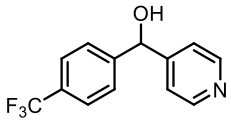
10d[21], 40.1 mg, white solid, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 6.0 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 5.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.75 (s, 1H), 3.72 (br, 1H), 1.29 (s, 9H).



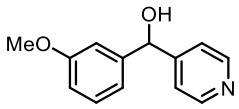
10e[21], 32.4 mg, white solid, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 6.0 Hz, 2H), 7.32 - 7.26 (m, 6H), 5.76 (s, 1H), 4.08 (br, 1H).



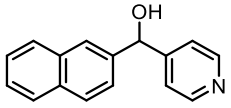
10f[21], 38.1 mg, white solid, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 6.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 6.0 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.75 (s, 1H), 3.84 (br, 1H).



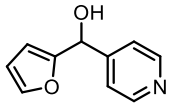
10g[21], 41.2 mg, white solid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 6.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 6.0 Hz, 2H), 5.84 (s, 1H), 4.31 (br, 1H).



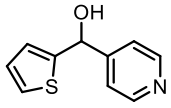
10h[21], 30.8 mg, white solid, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.2 Hz, 2H), 7.32 (d, *J* = 4.8 Hz, 2H), 7.26 (t, *J* = 5.2 Hz, 1H), 6.93 - 6.90 (m, 2H), 6.84 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.76 (s, 1H), 3.78 (s, 3H), 3.34 (br, 1H).



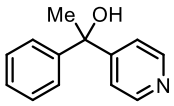
10i[21], 39.2 mg, white solid, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 6.4 Hz, 2H), 7.81 - 7.77 (m, 4H), 7.48 - 7.46 (m, 2H), 7.36 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.31 (d, *J* = 6.0 Hz, 2H), 5.89 (s, 1H), 4.51 (br, 1H).



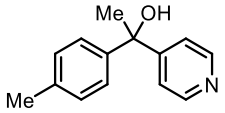
10j[21], 25.1 mg, white solid, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 6.0 Hz, 2H), 7.39 - 7.37 (m, 3H), 6.33 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.16 (d, *J* = 3.2 Hz, 1H), 5.83 (s, 1H), 4.21 (br, 1H).



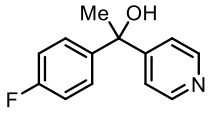
10k[21], 30.3 mg, white solid, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 5.2 Hz, 2H), 7.37 (d, *J* = 5.2 Hz, 2H), 7.28 (d, *J* = 5.6 Hz, 1H), 6.96 - 6.90 (m, 2H), 6.03 (s, 1H), 4.79 (br, 1H).



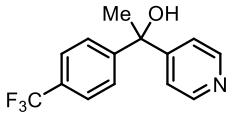
10l[21], 27.2 mg, white solid, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 6.0 Hz, 2H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.35 - 7.31 (m, 4H), 7.29 - 7.25 (m, 1H), 3.33 (br, 1H), 1.93 (s, 3H).



10m[22], 29.4 mg, white solid, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.2 Hz, 2H), 7.32 (d, *J* = 6.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.0 (br, 1H), 2.33 (s, 3H), 1.92 (s, 3H).



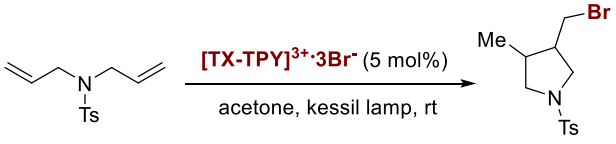
10n[22], 31.2 mg, white solid, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.2 Hz, 2H), 7.40 - 7.36 (m, 2H), 7.32 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.02 (t, *J* = 8.8 Hz, 2H), 2.82 (br, 1H), 1.93 (s, 3H).



10o[21], 39.7 mg, white solid, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 6.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 6.0 Hz, 2H), 4.21 (br, 1H), 1.95 (s, 3H).

5. Mechanistic studies

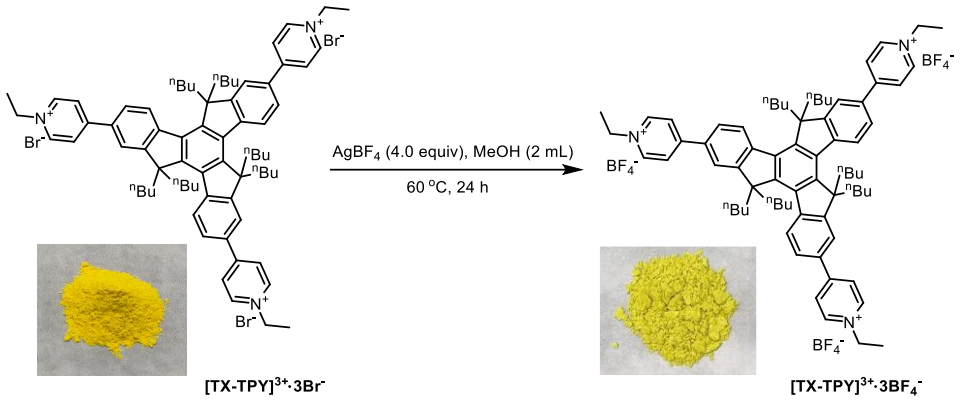
1) Bromine radical trapping experiment



11 **12**, 4.8% yield

To a flame-dried sealed tube were added **[TX-TPY]$^{3+}$·3Br$^-$** (5.0 mol%), **11** (0.2 mmol) and acetone (2.0 mL, 0.1 M). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the reaction mixture was thoroughly degassed, the vial was sealed and positioned approximately 2~3 cm from 40 W Kessil lamp. Then the reaction mixture was stirred at room temperature for 8 h under nitrogen atmosphere. Afterwards, the reaction mixture was concentrated by rotary evaporation. The yield of **12** was determined by crude ^{1}H NMR using triphenylmethane as an internal standard.

2) Synthesis and characterization of [TX-TPY]$^{3+}$·3BF$_4^-$



2.1) Synthesis of [TX-TPY]$^{3+}$·3BF$_4^-$

The synthesis of **[TX-TPY]$^{3+}$·3BF$_4^-$** was following the reported procedure[23], to a solution of **[TX-TPY]$^{3+}$·3Br$^-$** (500 mg, 0.404 mmol) in MeOH (2.0 mL) was added $AgBF_4$ (316 mg, 1.62 mmol), and the mixture was stirred at 60 °C for 24 h. After being cooled to room temperature, the reaction mixture was filtered and washed with a small amount of methanol. The filtrate was combined and evaporated in vacuo to obtain the product **[TX-TPY]$^{3+}$·3BF$_4^-$** (500 mg, 98% yield) as a yellow solid. m.p. = 237.6-240.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.15 (d, J = 6.4 Hz, 6H), 8.74 (d, J = 6.4 Hz, 6H), 8.66 (d, J = 8.4 Hz, 3H), 8.49 (s, 3H), 8.31 (d, J = 8.0 Hz, 3H), 4.68 (q, J = 7.6 Hz, 6H), 3.10-3.01 (m, 6H), 2.48-2.42 (m, 6H), 1.62 (t, J = 7.2 Hz, 9H), 0.91-0.79 (m, 12H), 0.57-0.37 (m, 30H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.0, 154.6, 148.0, 144.8, 143.3, 138.0, 132.3, 127.4, 125.8, 124.7, 122.6, 56.4, 56.0, 36.0, 26.9, 22.6, 16.7, 14.1. IR (thin film): νmax (cm^{-1}) = 3449, 2956, 1637, 1604, 1466, 1299, 1034, 836, 533, 521. HRMS (ESI) calcd for $C_{72}H_{90}BF_4N_3$ [M-BF$_4^-$]$^{2+}$: m/z = 541.8577. Found: 541.8584.

2.2) UV/Vis absorption spectrum of [TX-TPY]$^{3+}$·3BF$_4^-$

UV/vis absorption spectrum of **[TX-TPY]$^{3+}$·3BF$_4^-$** (0.01 mM in acetone) was recorded in 1 cm path quartz cuvettes using Pgeneral TU-1901 UV/Vis spectrometer.

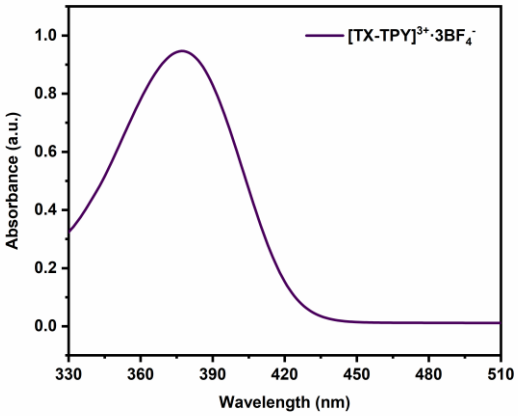


Fig. S8 UV/vis absorption spectrum of **[TX-TPY]$^{3+}$·3BF$_4^-$** in acetone.

2.3) Emission spectrum of [TX-TPY]$^{3+}$·3BF$_4^-$

Fluorescence spectrum was recorded on Edinburgh Instruments FS5 Spectrofluorometer in 1 cm quartz cuvettes. **[TX-TPY]$^{3+}$·3BF$_4^-$** was prepared as a 0.01 mM solution in acetone and used freshly for the measurement.

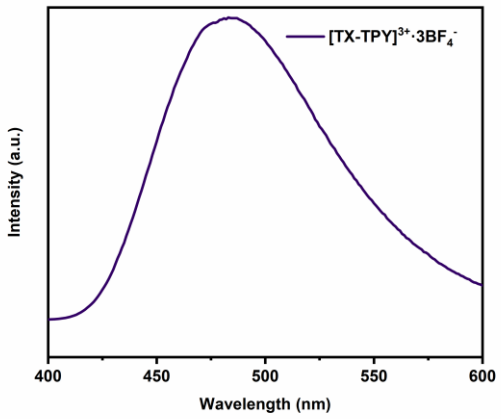


Fig. S9 Emission spectrum of **[TX-TPY]$^{3+}$·3BF$_4^-$** in acetone.

2.4) UV/Vis absorption and emission spectra of [TX-TPY]$^{3+}$·3BF$_4^-$

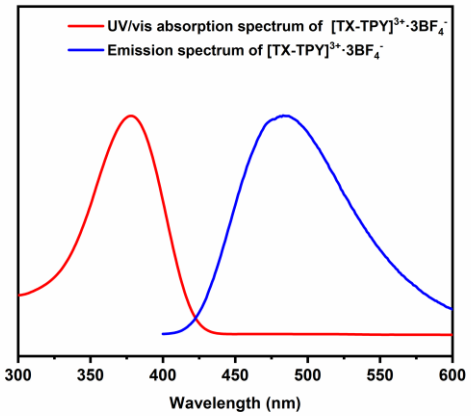


Fig. S10 UV/Vis absorption and emission spectra of **[TX-TPY]$^{3+}$·3BF$_4^-$** in acetone (0.01 mM). Cross point λ: 423 nm. $E_{0\text{-}0}$: 2.93 eV.

2.5) Cyclic voltammograms of [TX-TPY]$^{3+}$·3BF$_4^-$

Voltammetric experiments were conducted with a computer-controlled Shanghai Chen Hua CHI660E containing glassy carbon electrode serving as the working electrode, saturated calomel reference electrode, Pt wire auxiliary electrode.

All solutions used for the voltammetric experiments were deoxygenated by purging with high purity nitrogen gas and measurements were performed in a electrolytic cell at room temperature.

Excited state oxidation and reduction potentials were calculated by the following approximating formulas: $E(PC^*/PC^{\bullet-}) = E(PC/PC^{\bullet-}) + E_{0,0}$ and $E(PC^{\bullet+}/PC^*) = E(PC^{\bullet+}/PC) - E_{0,0}$.

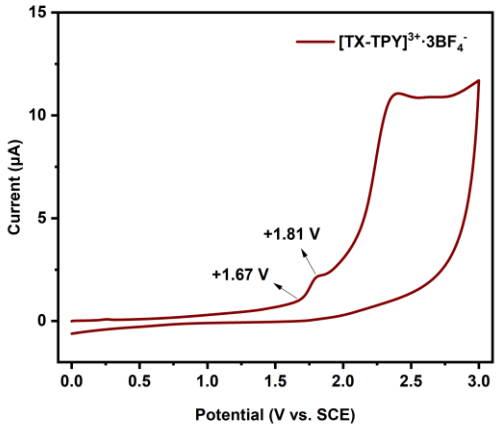


Fig. S11 Cyclic voltammogram of **[TX-TPY]$^{3+}$·3BF$_4^-$** in MeCN (1.0 mM) containing 0.1 M ^{n}Bu$_4$NPF$_6$. Scan rate: 0.1 V/s. E (PC$^{\bullet+}$/PC) = +1.67 ~ +1.81 V, E (PC$^{\bullet+}$/PC*) = -1.12 ~ -1.26 V

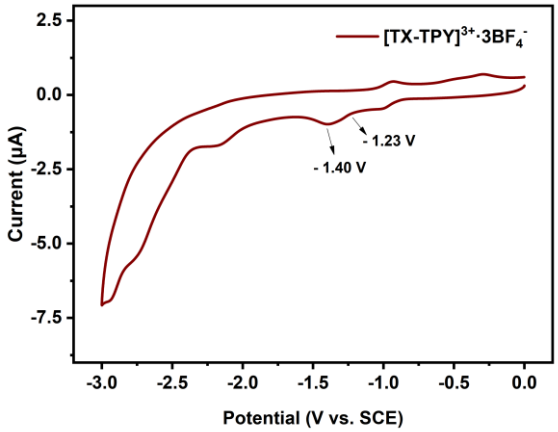


Fig. S12 Cyclic voltammogram of **[TX-TPY]$^{3+}$·3BF$_4^-$** in DMSO (1.0 mM) containing 0.1 M ^{n}Bu$_4$NPF$_6$. Scan rate: 0.1 V/s. E (PC/PC$^{\bullet-}$) = -1.23 ~ -1.40 V, E (PC*/PC$^{\bullet-}$) = +1.53 ~ +1.70 V

3) Cyclic voltammograms of TBABr

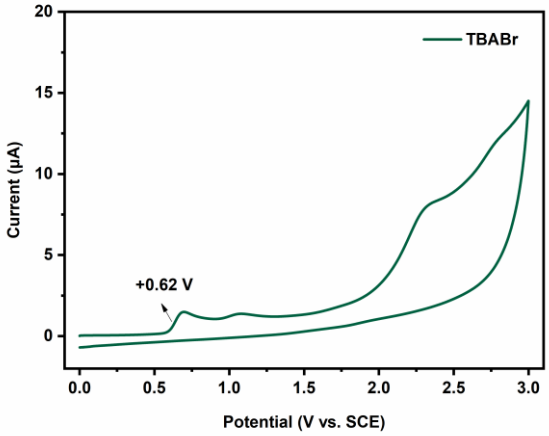


Fig. S13 Cyclic voltammogram of **TBABr** in MeCN (1.0 mM) containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s. $E_{1/2}(Br^{\bullet}/Br^{-})$ = +0.62 V.

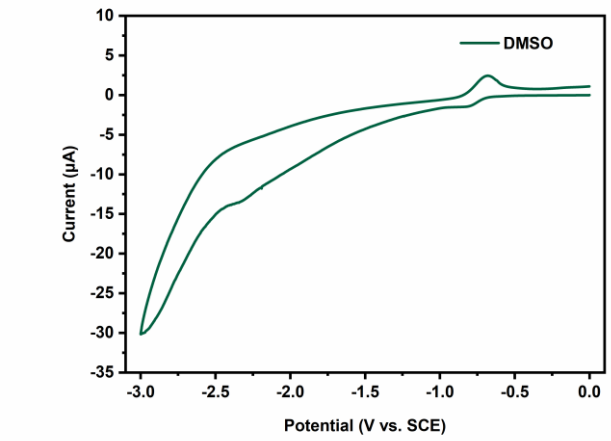
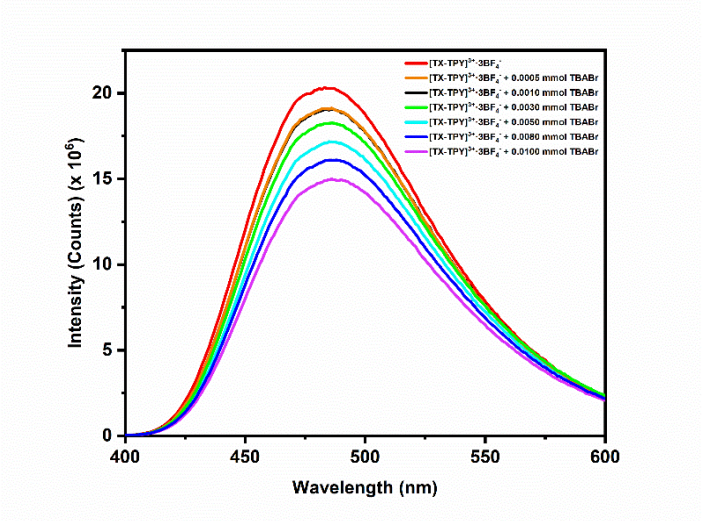


Fig. S14 Cyclic voltammogram of DMSO containing 0.1 M $^{n}Bu_4NPF_6$. Scan rate: 0.1 V/s.

4) Fluorescence quenching experiments

The concentration of **[TX-TPY]$^{3+}$·3BF$_4^-$** was 0.01 mM in MeOH. The concentration of the quencher (**TBABr**) was 0.1 M in MeOH. For each quenching experiment, the quencher was titrated to a solution (10 mL) of **[TX-TPY]$^{3+}$·3BF$_4^-$** in a quartz glass bottle, respectively. The addition of the quencher refers to an increase of the quencher concentration of 5×10^{-4} M, 1×10^{-3} M, 3×10^{-3} M, 5×10^{-3} M, 8×10^{-3} M, 1×10^{-2} M. Then the emission intensity of **[TX-TPY]$^{3+}$·3BF$_4^-$** was collected respectively.



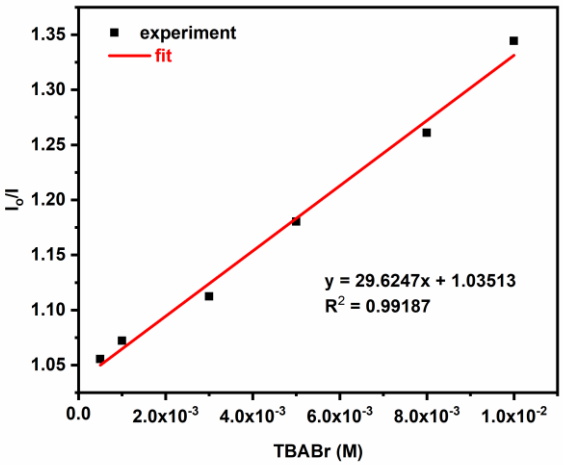


Fig. S15 Stern-Volmer quenching experiments.

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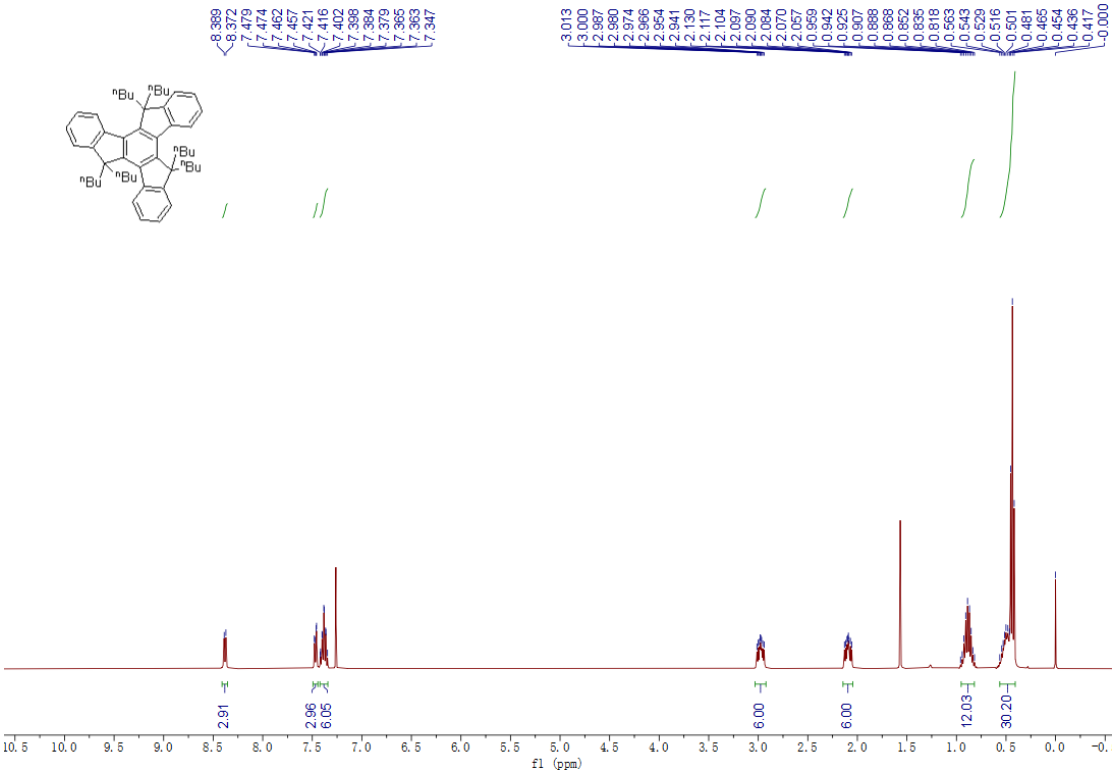
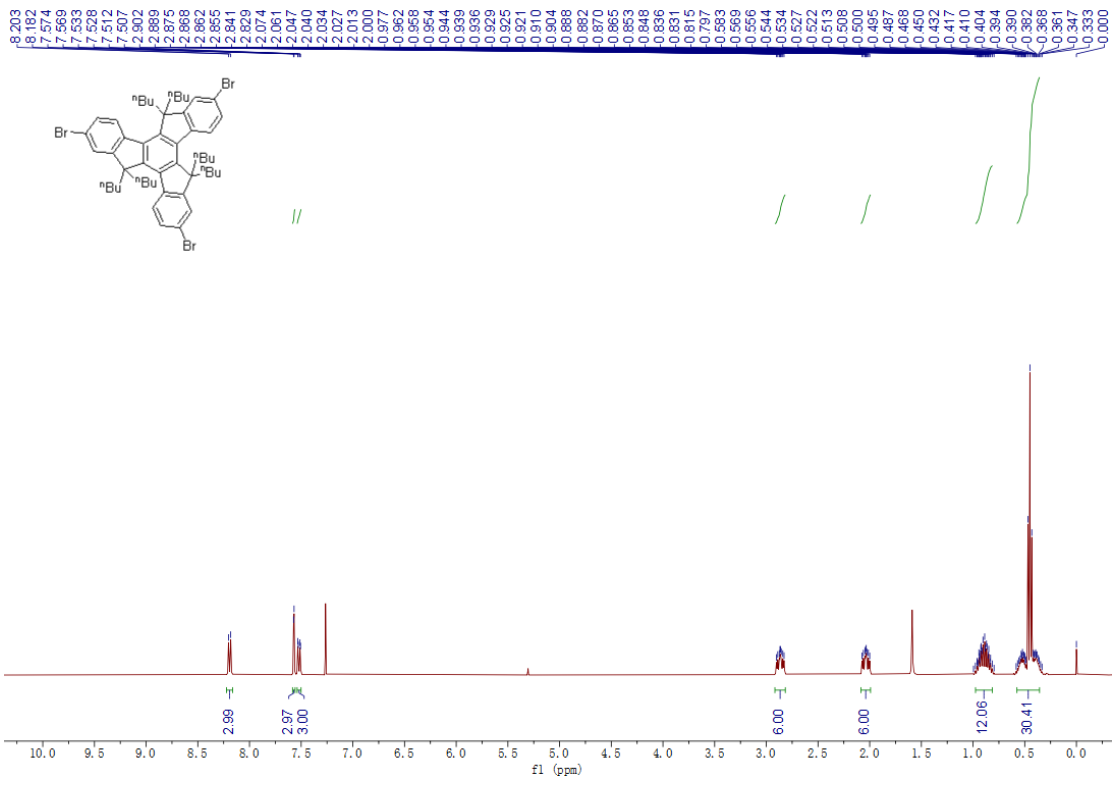
7. Copies of NMR spectra

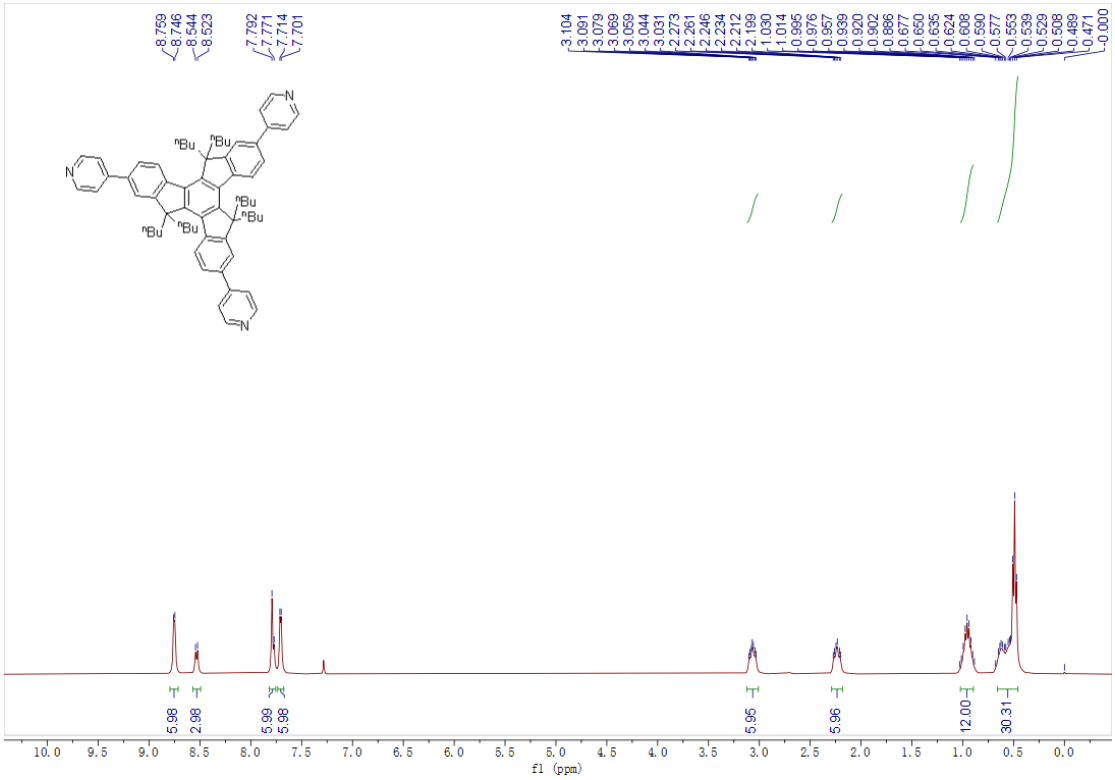
^{1}H NMR Spectrum of **TX**



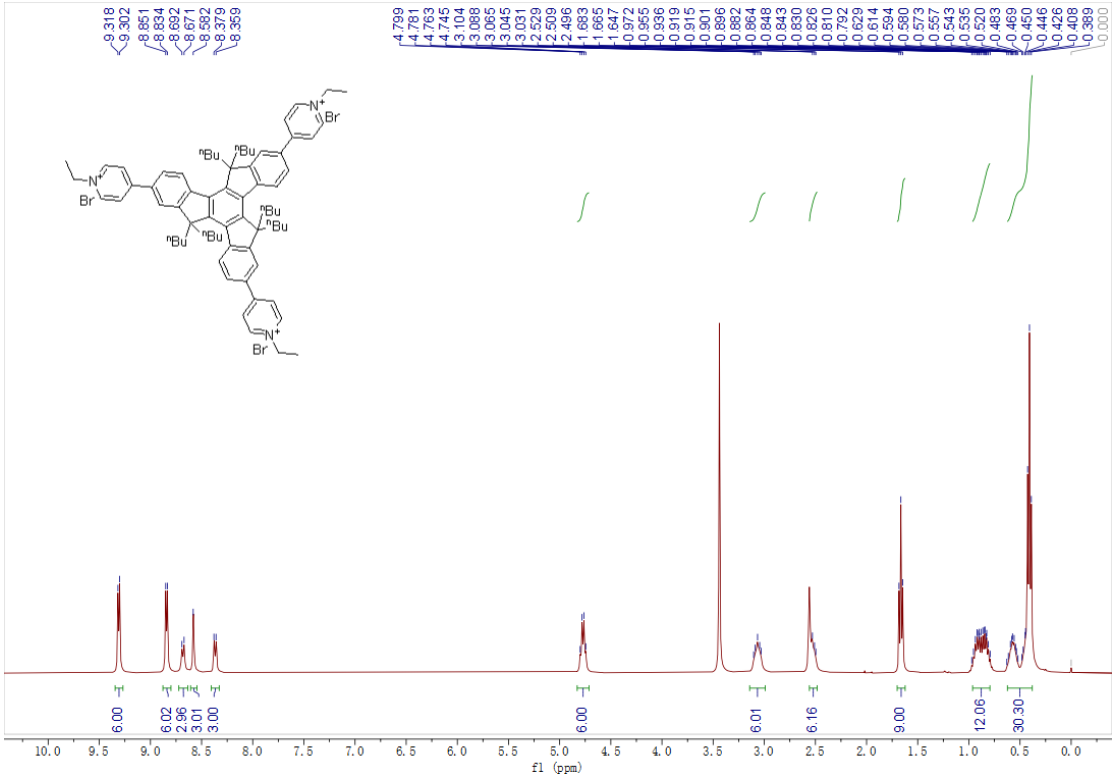
^{1}H NMR Spectrum of **TX-3Br**



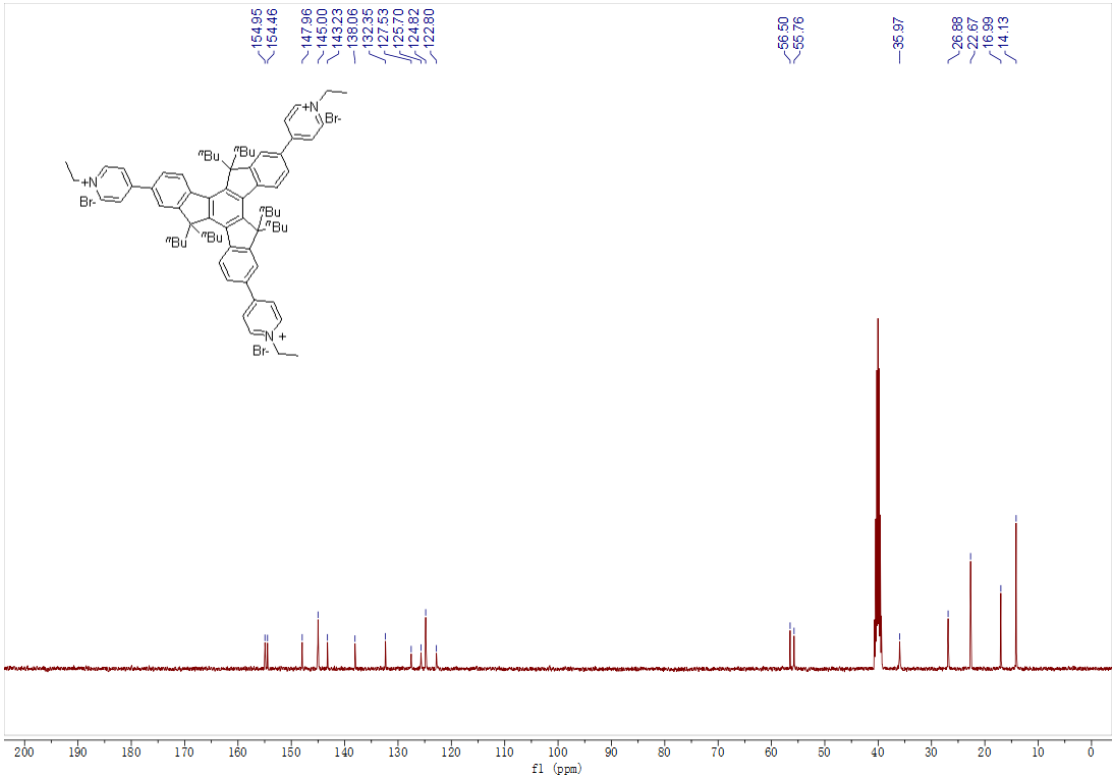
^{1}H NMR Spectrum of **TX-TPr**



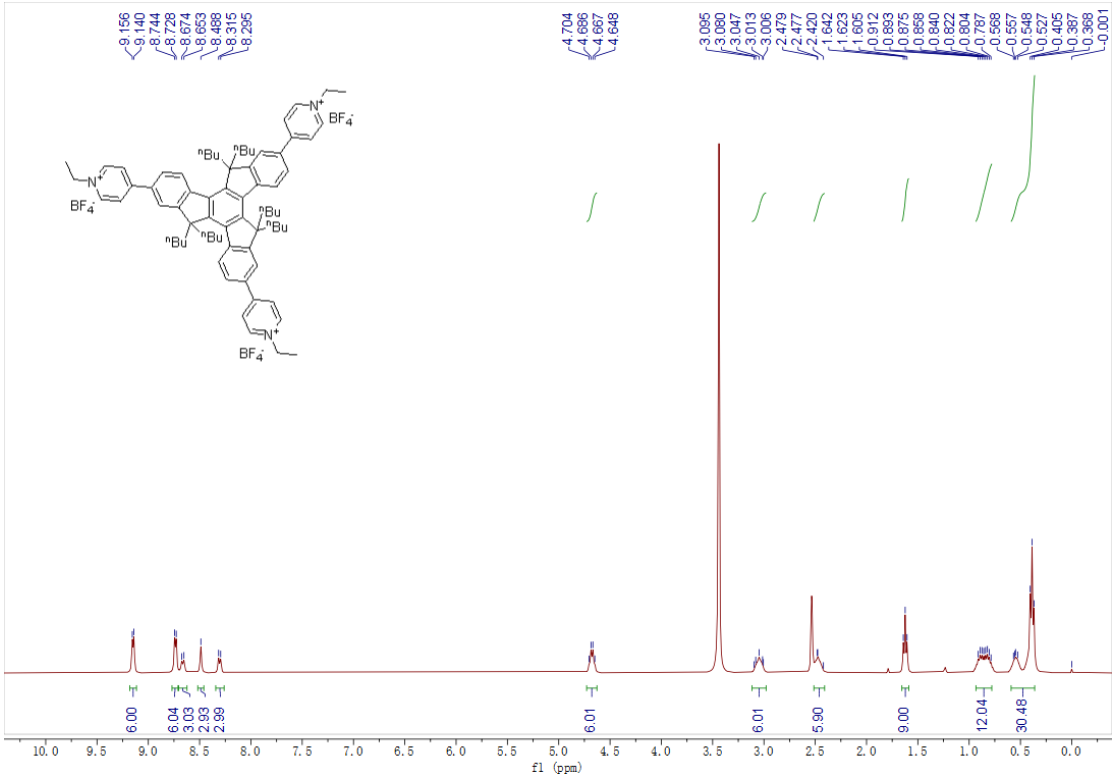
^{1}H NMR Spectrum of **[TX-TPY]$^{3+}$·3Br$^-$**



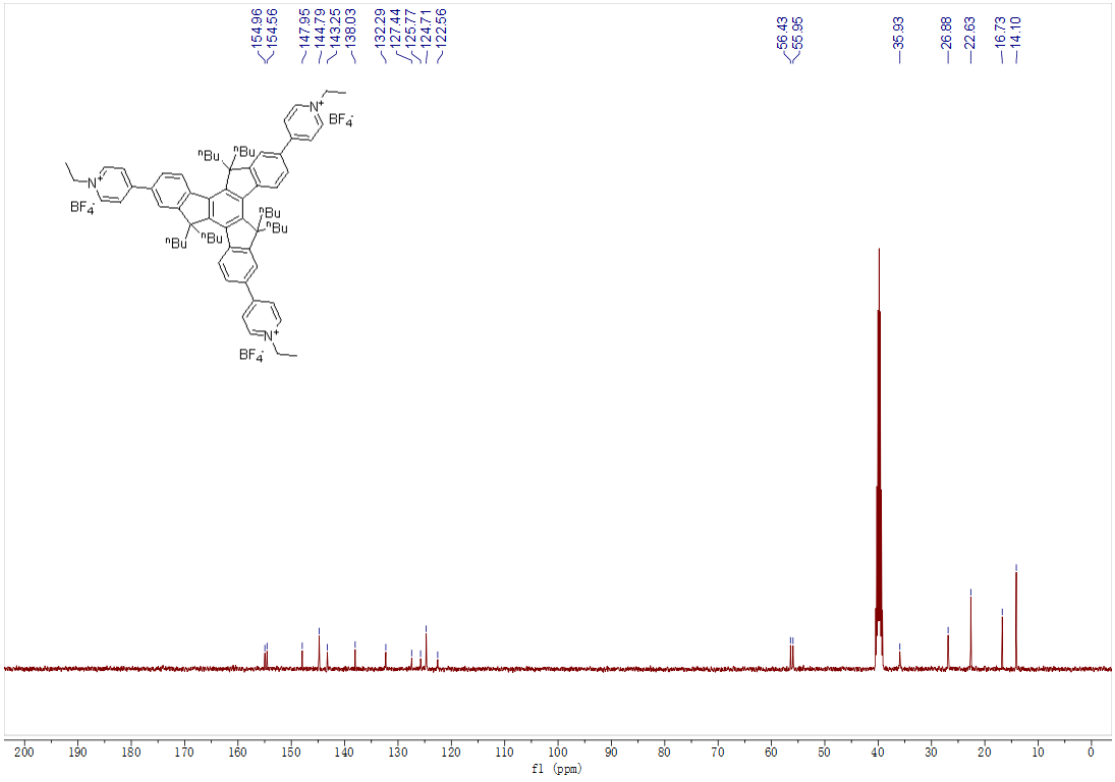
^{13}C NMR Spectrum of **[TX-TPY]$^{3+}$·3Br^{-}**



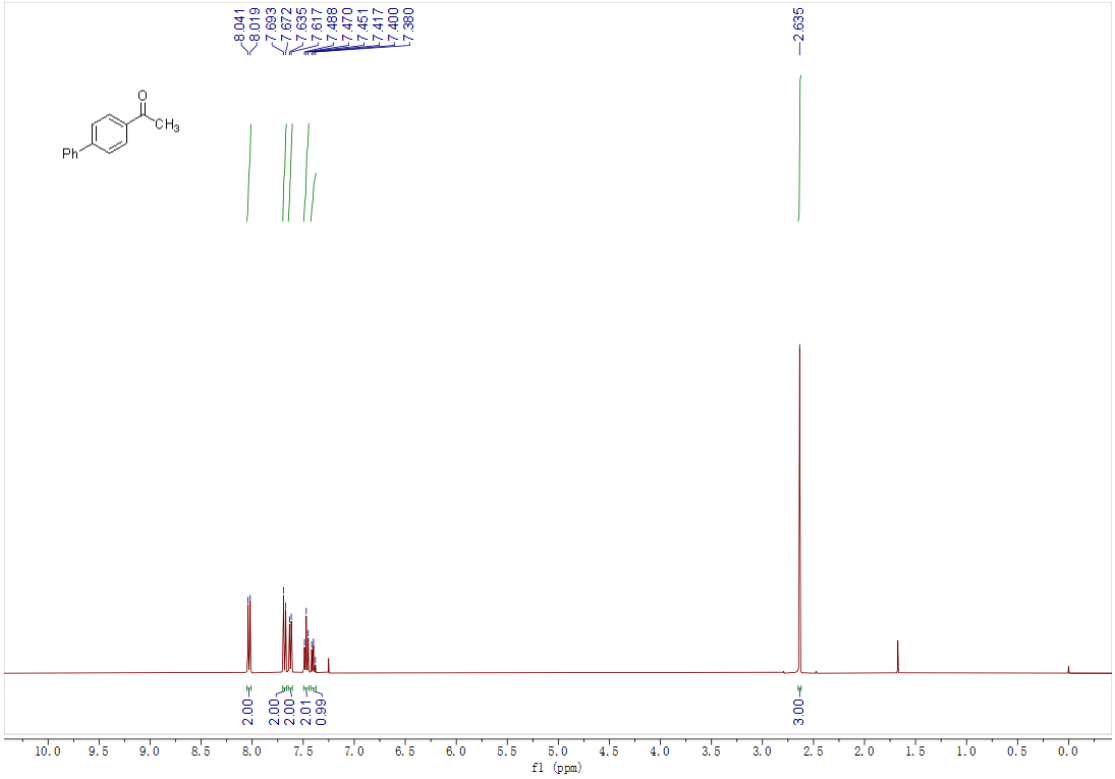
^{1}H NMR Spectrum of **[TX-TPY]$^{3+}$·3BF$_4^{-}$**



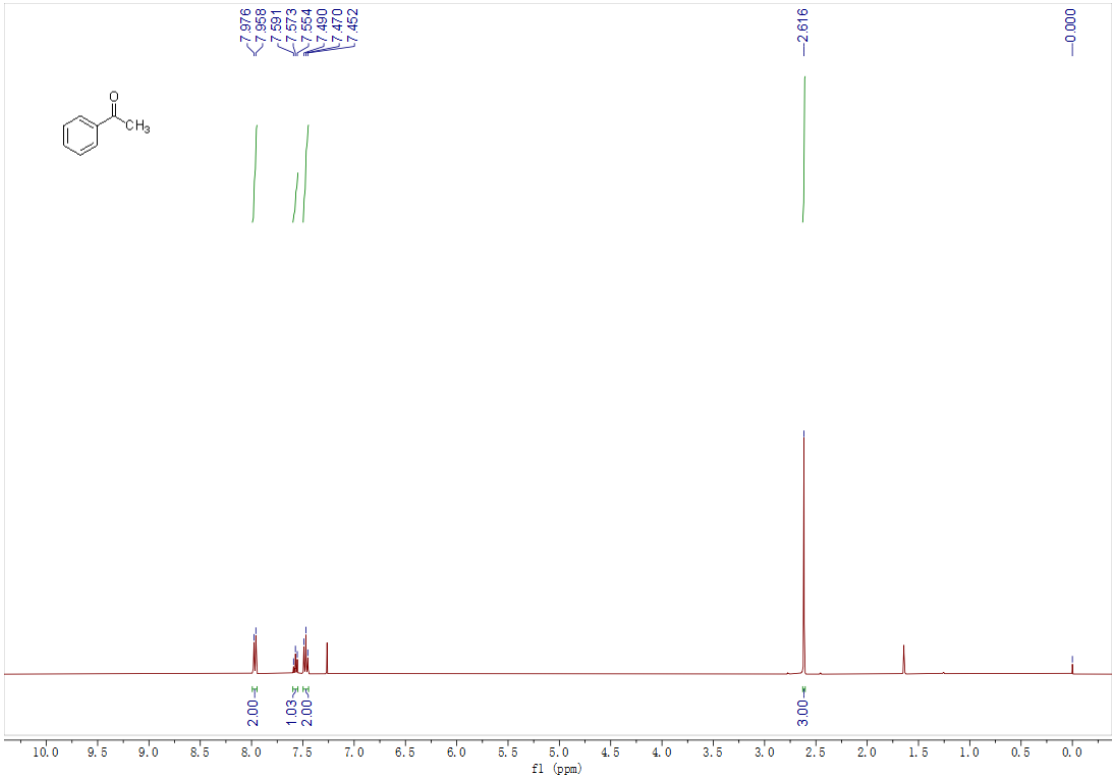
^{13}C NMR Spectrum of **[TX-TPY]$^{3+}$·3BF$_4^-$**



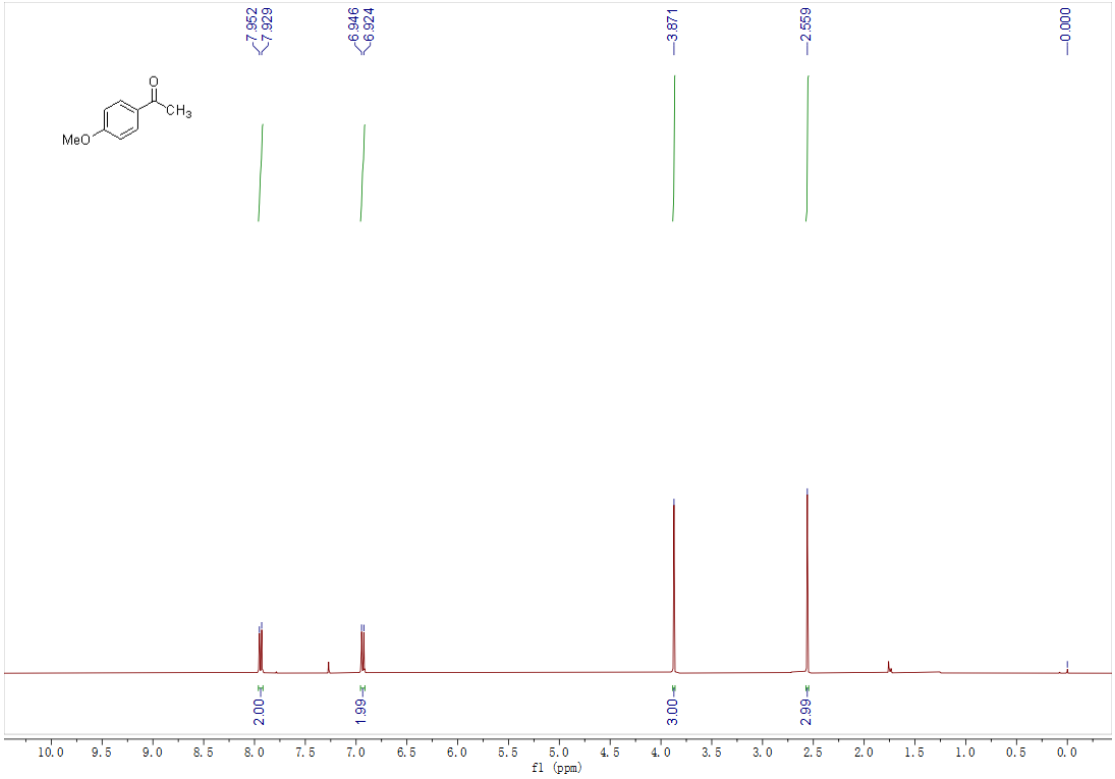
^{1}H NMR Spectrum of **3a**



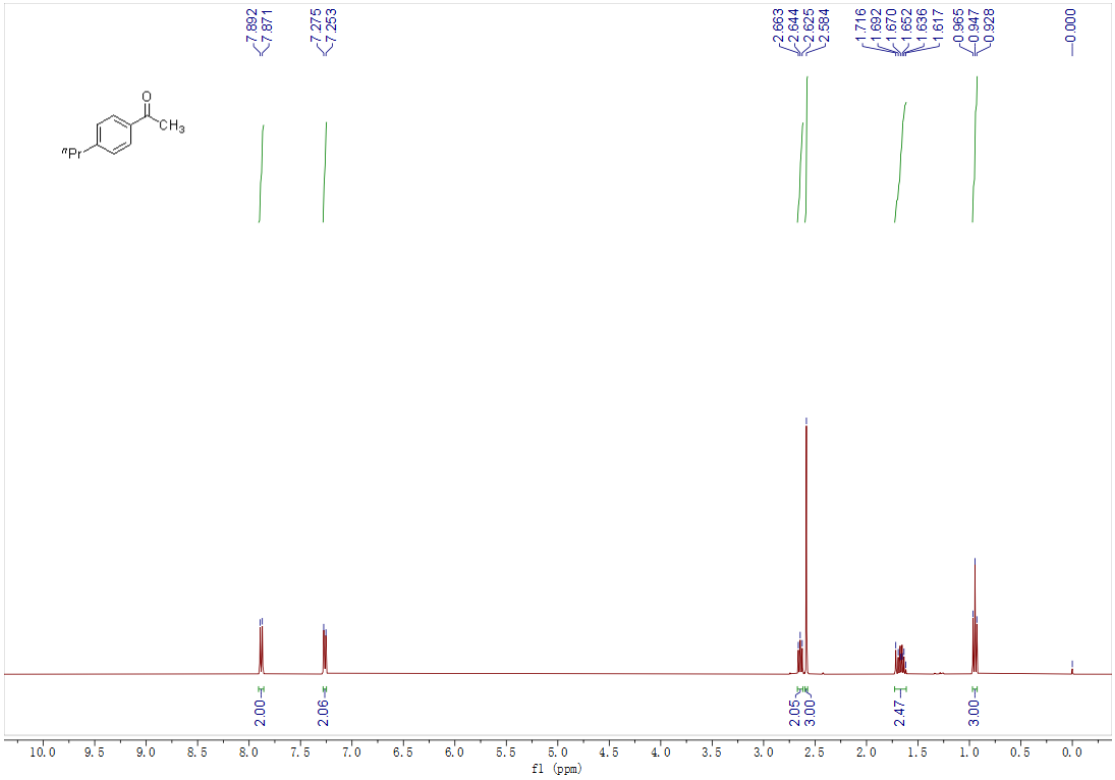
^{1}H NMR Spectrum of **3b**



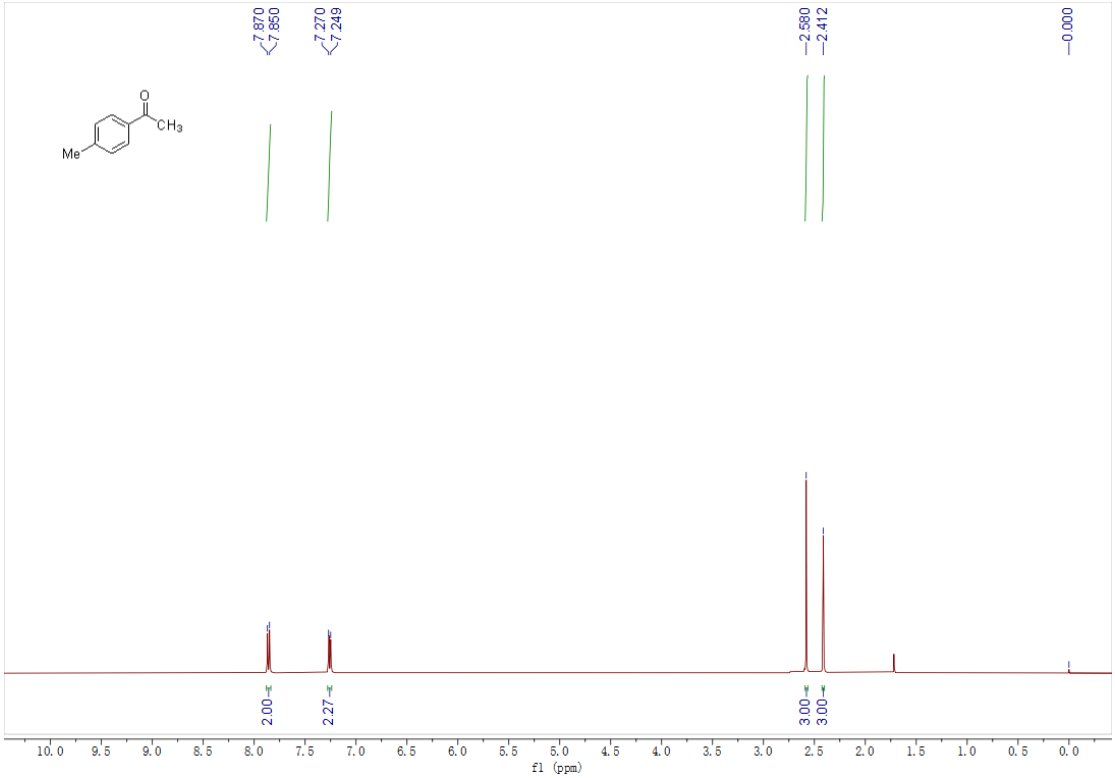
^{1}H NMR Spectrum of **3c**



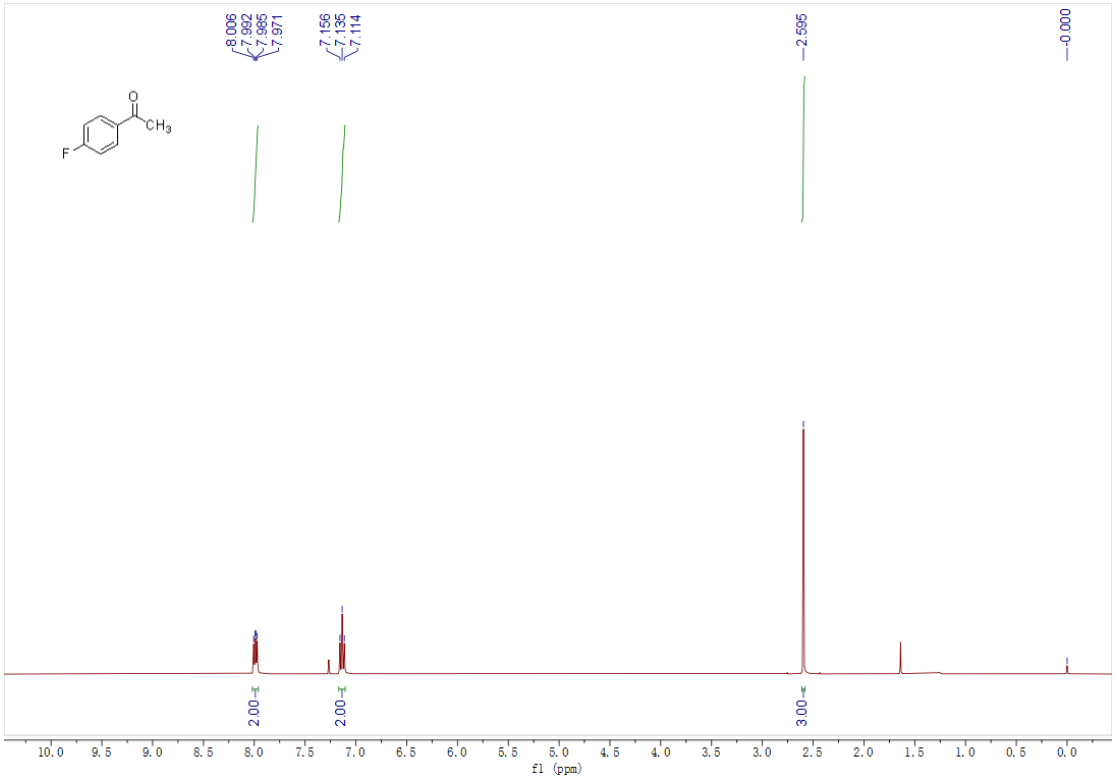
^{1}H NMR Spectrum of **3d**



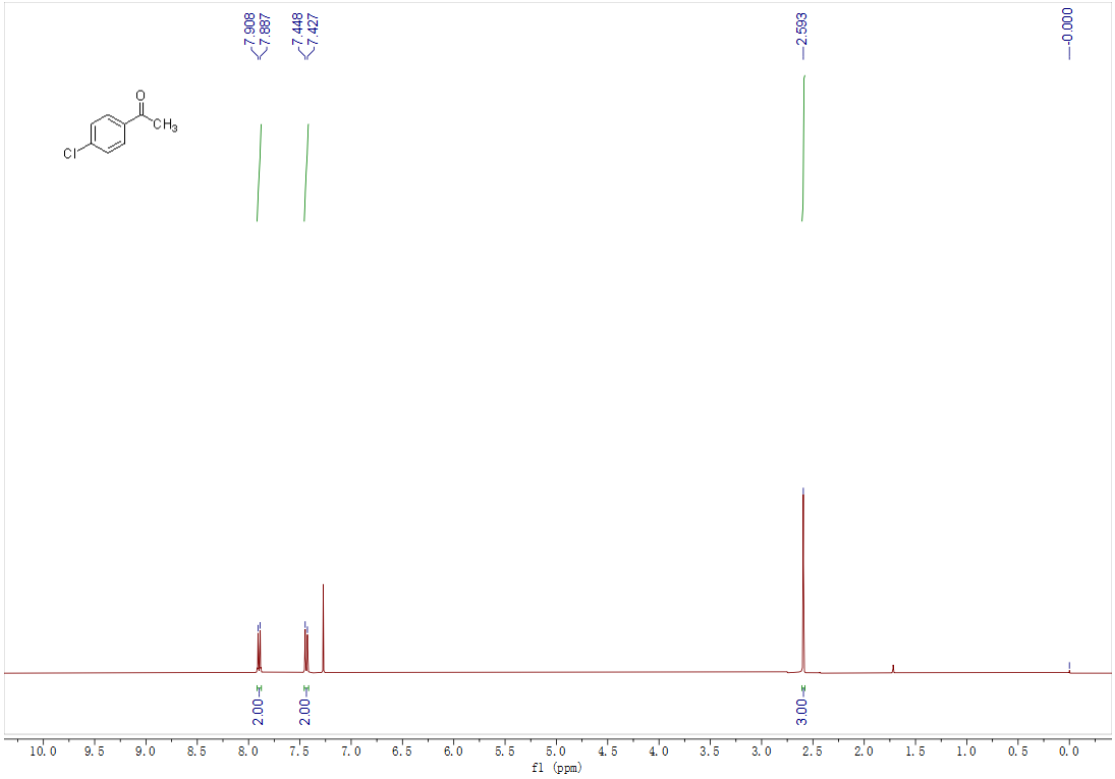
^{1}H NMR Spectrum of **3e**



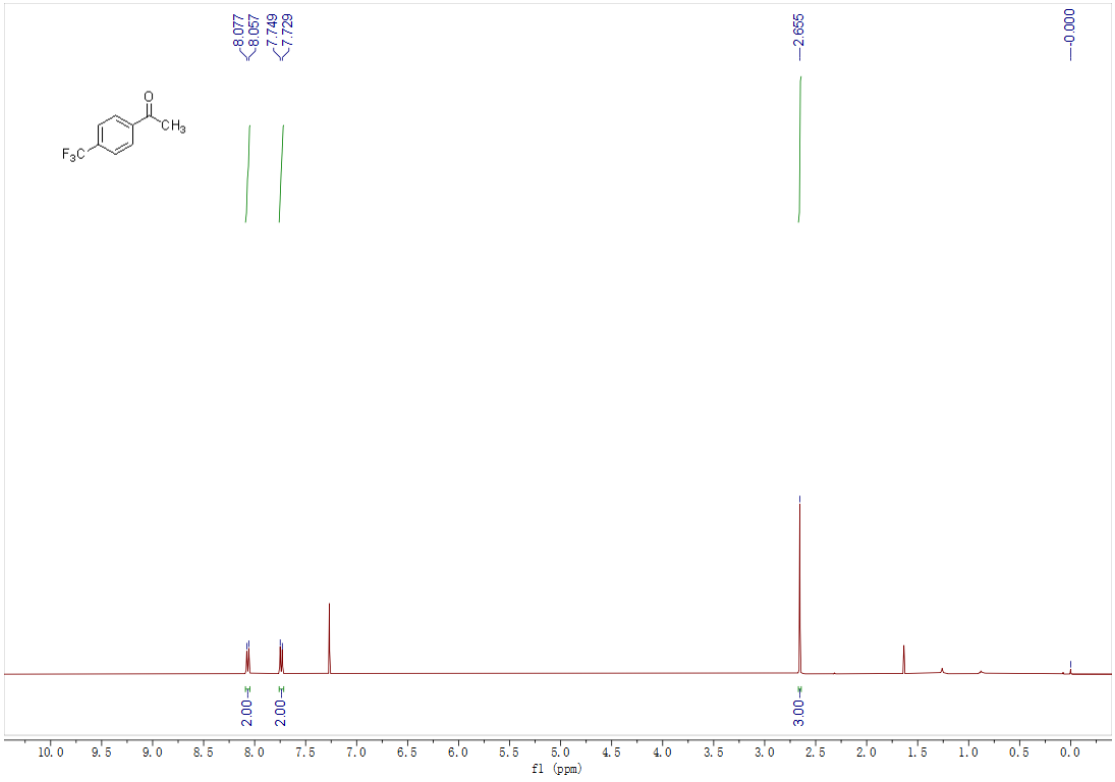
^{1}H NMR Spectrum of **3f**



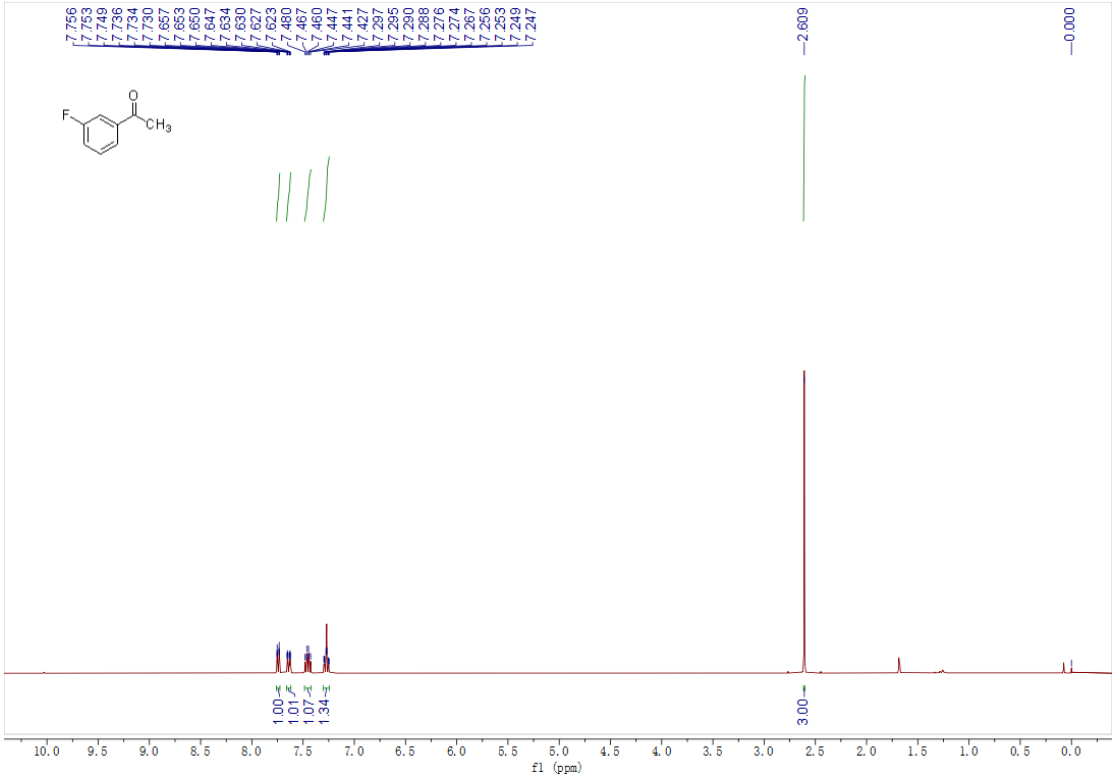
^{1}H NMR Spectrum of **3g**



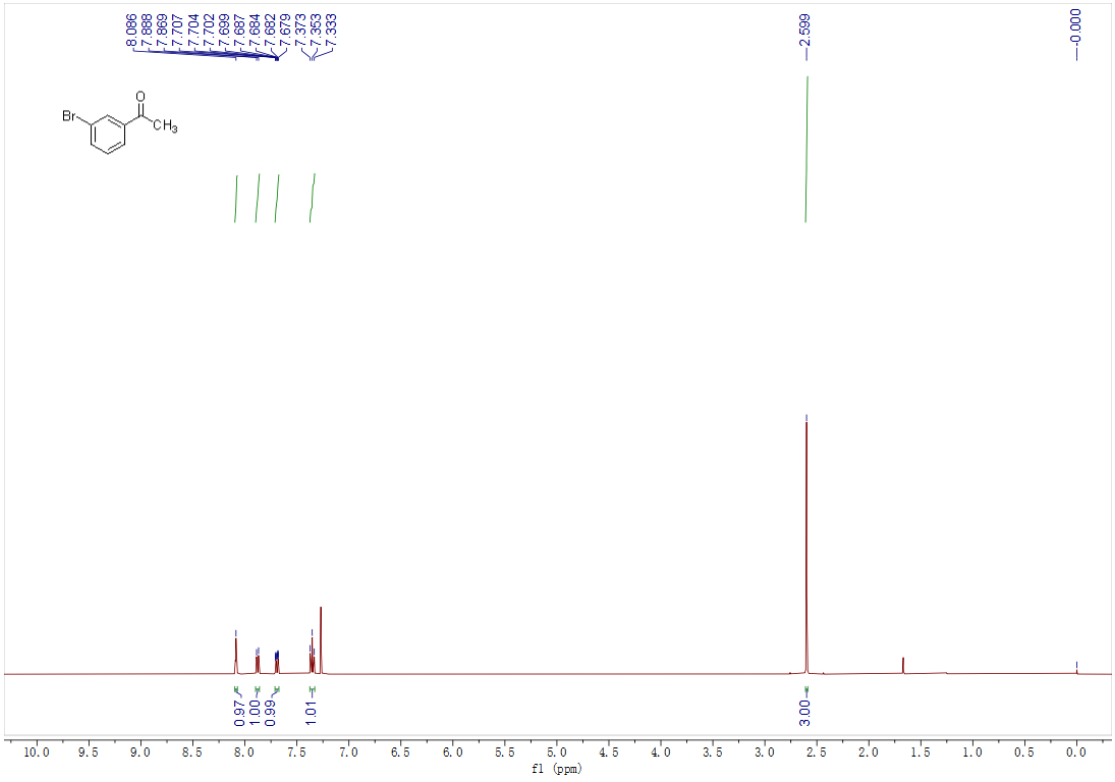
^{1}H NMR Spectrum of **3h**



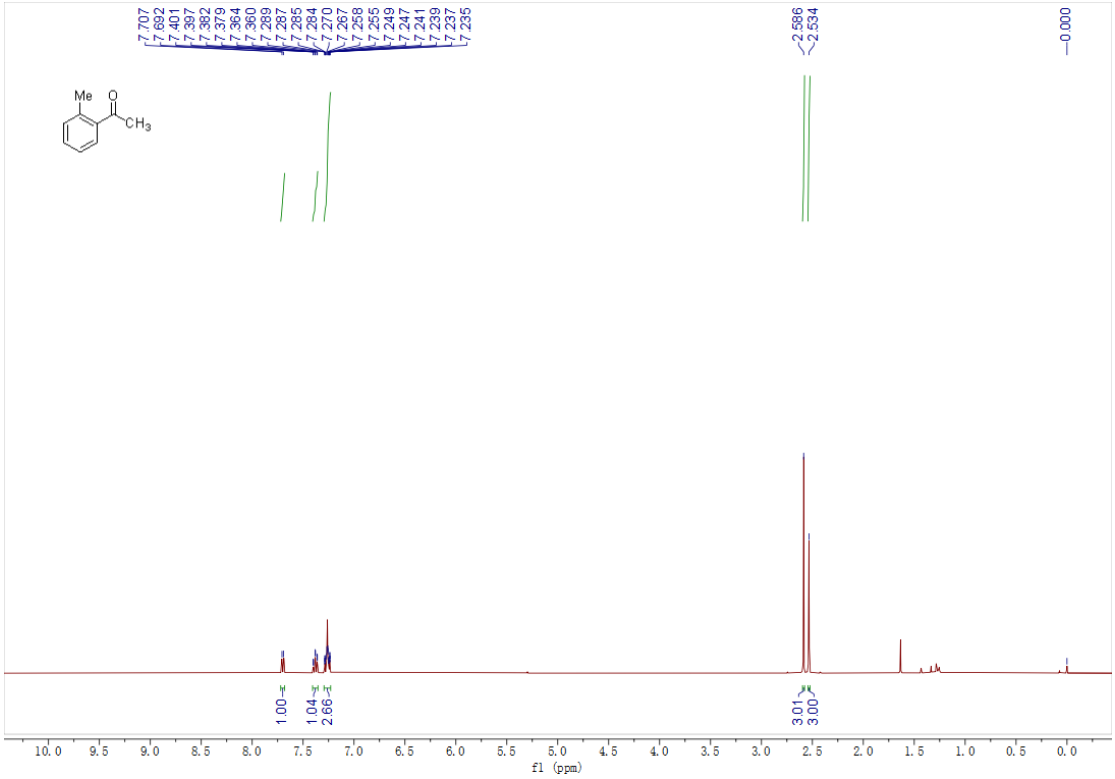
^{1}H NMR Spectrum of **3i**



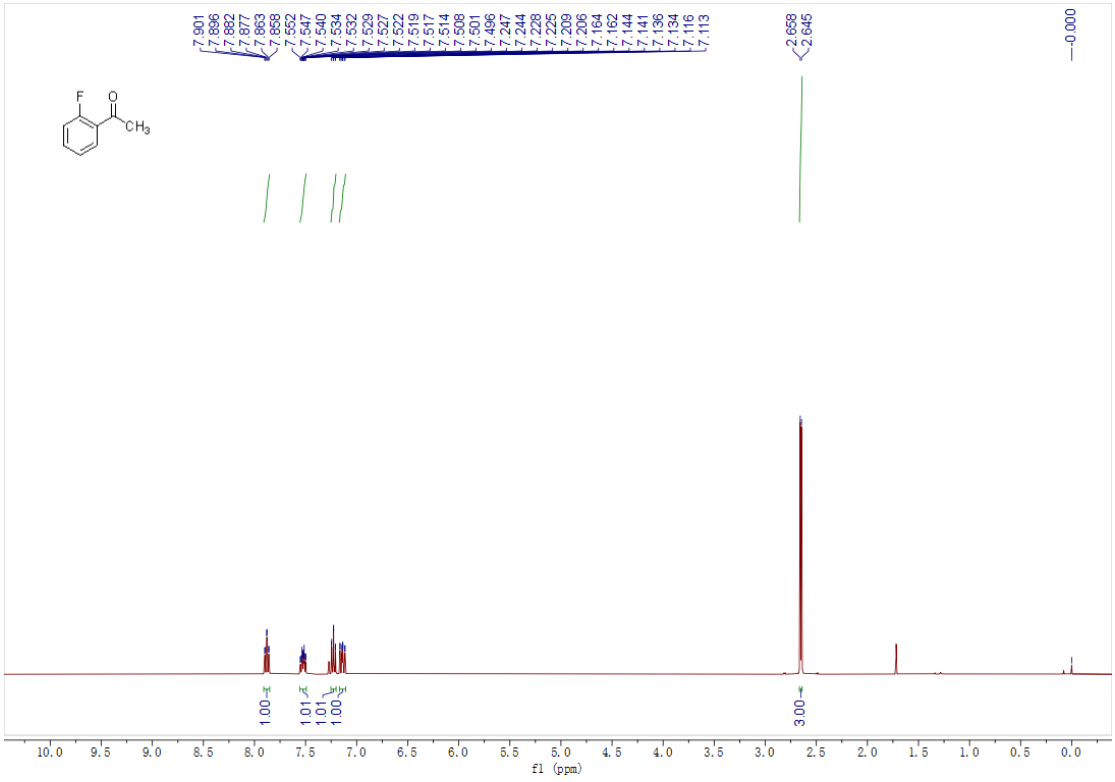
^{1}H NMR Spectrum of **3j**



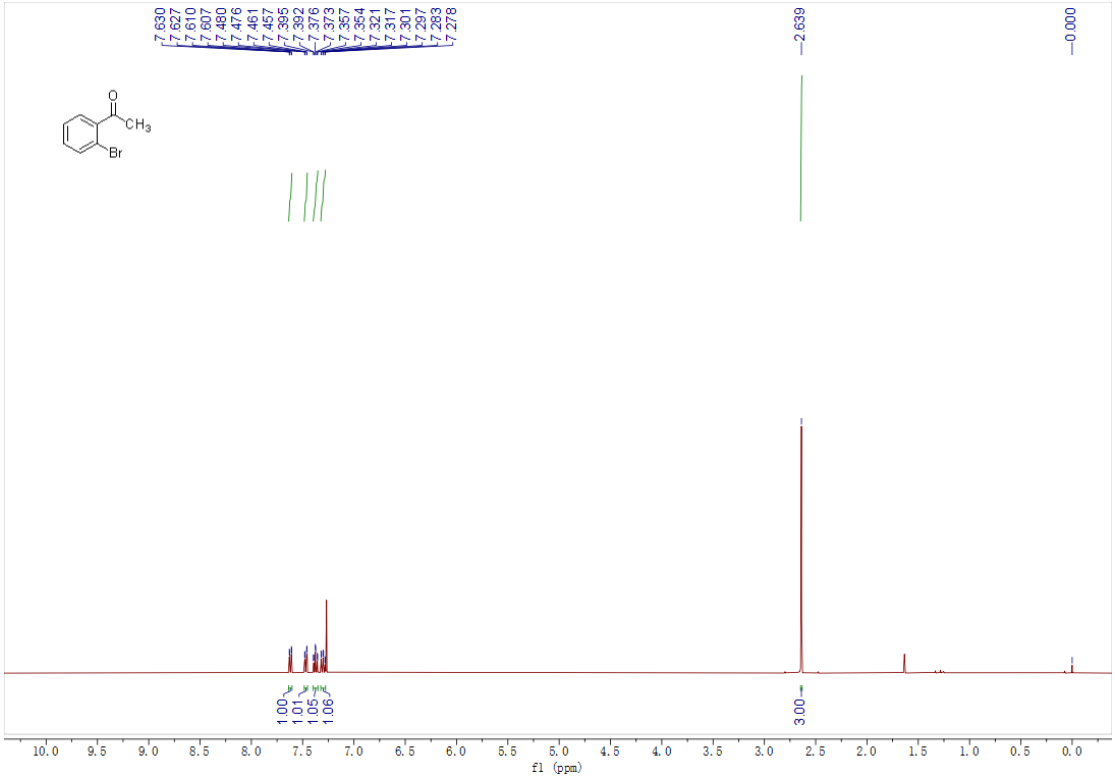
^{1}H NMR Spectrum of **3k**



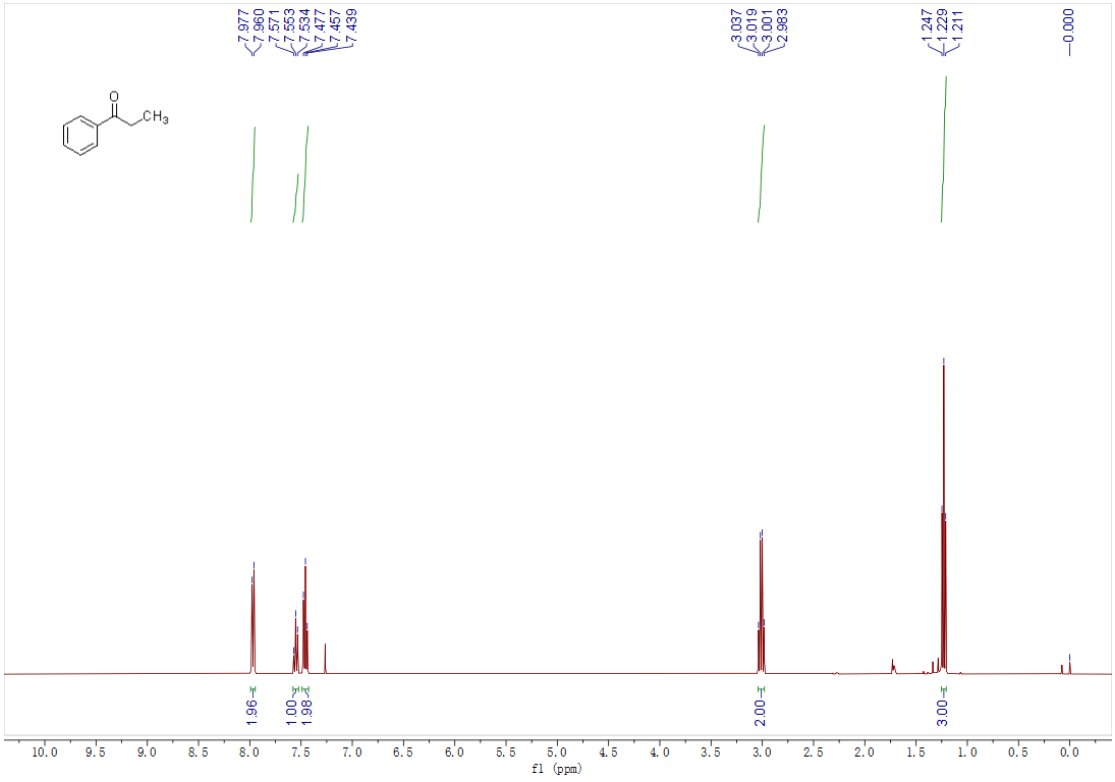
^{1}H NMR Spectrum of **3l**



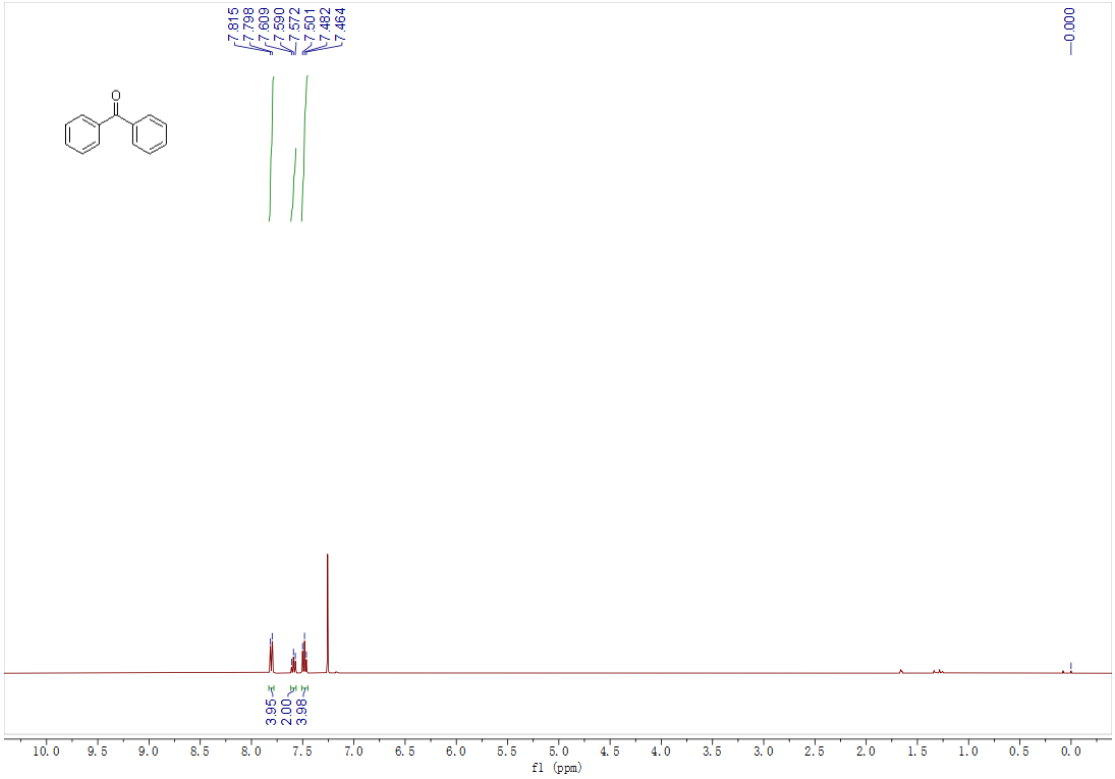
^{1}H NMR Spectrum of **3m**



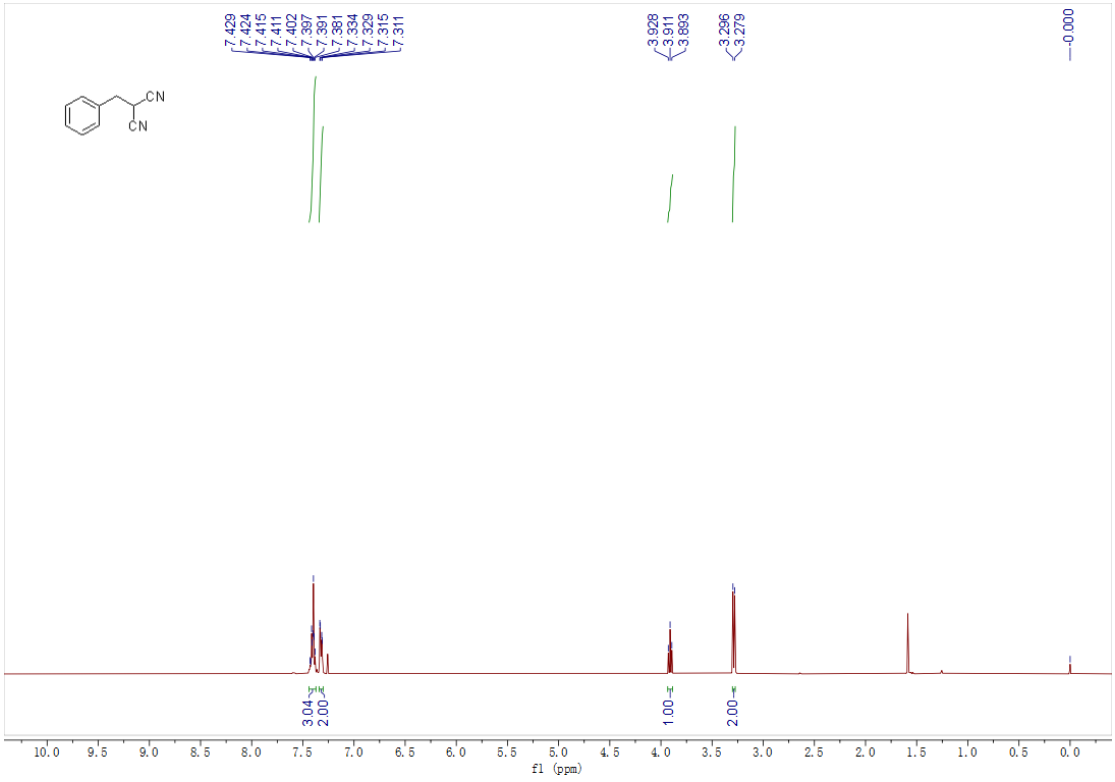
^{1}H NMR Spectrum of **3n**



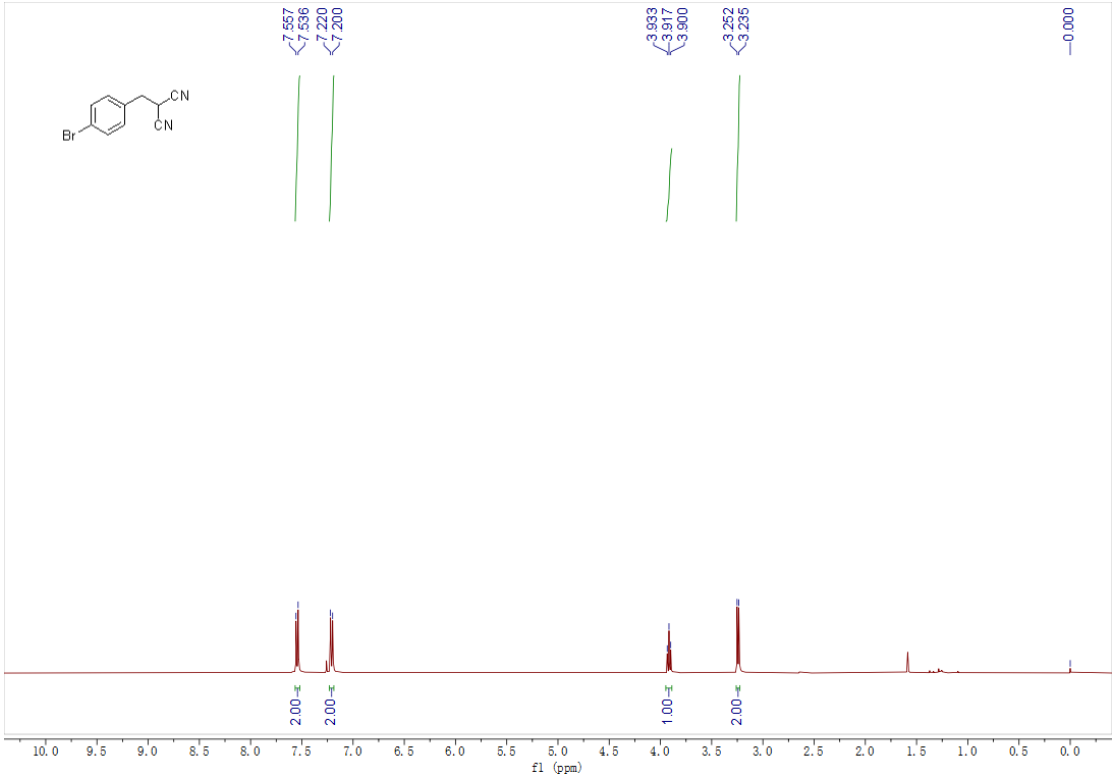
^{1}H NMR Spectrum of **3o**



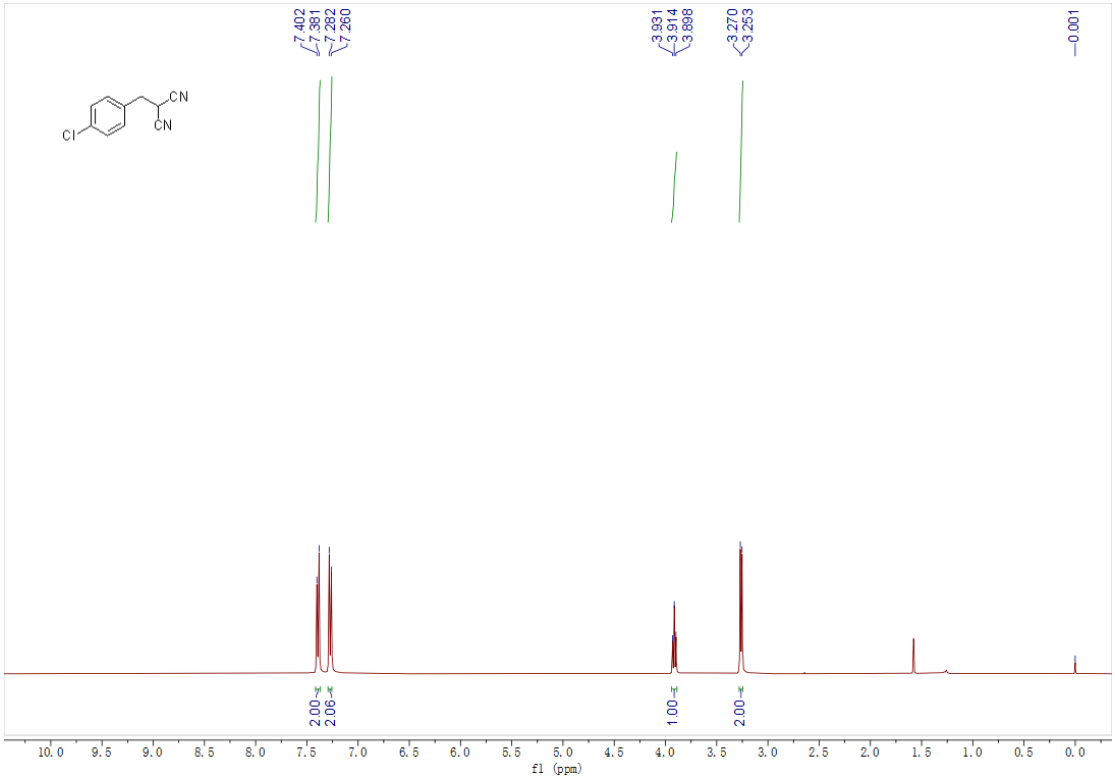
^{1}H NMR Spectrum of **4a**



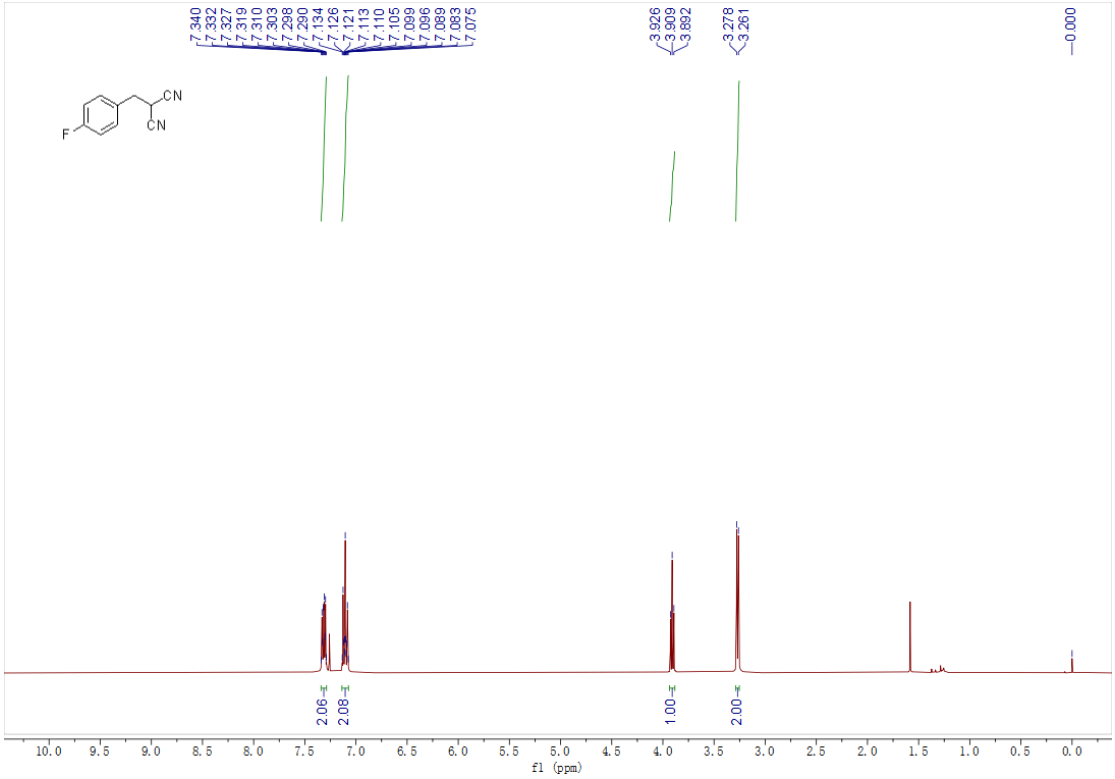
^{1}H NMR Spectrum of **4b**



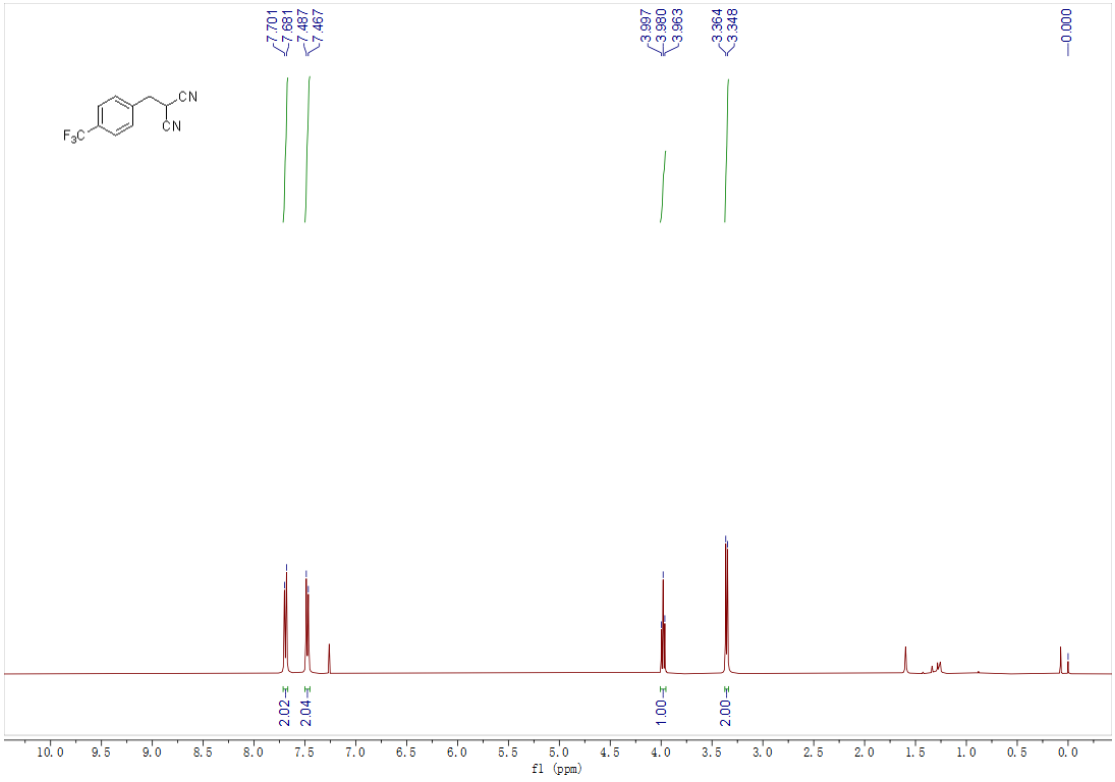
^{1}H NMR Spectrum of **4c**



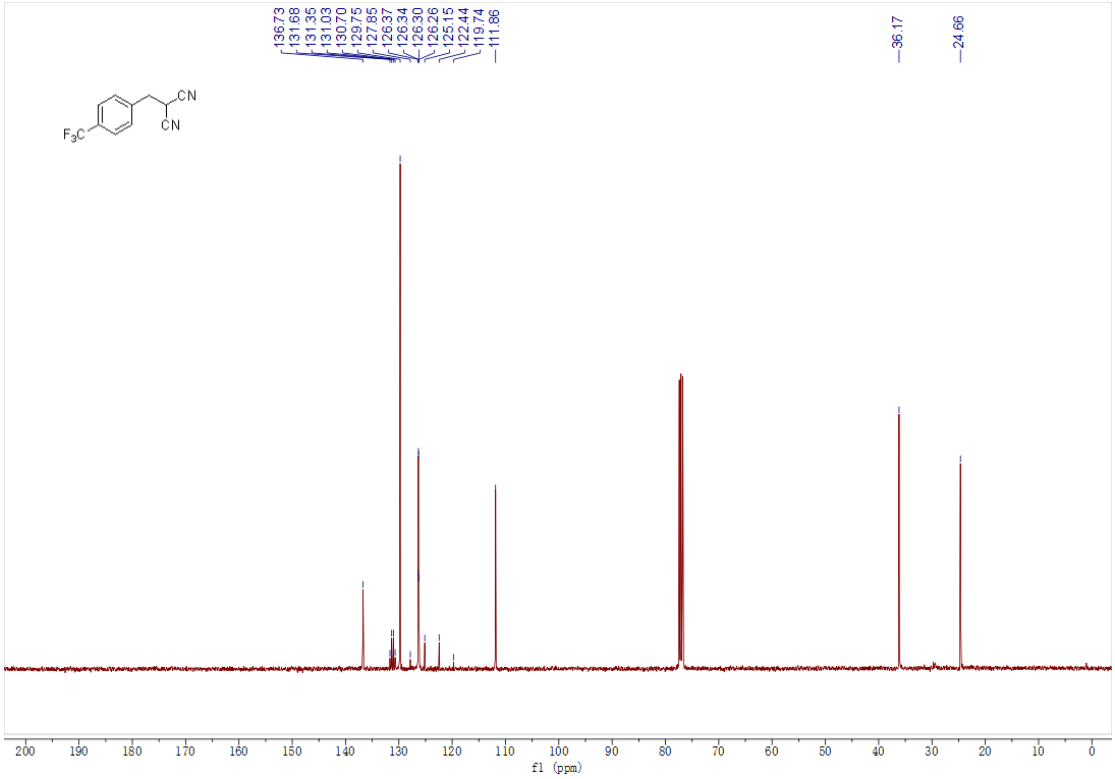
^{1}H NMR Spectrum of **4d**



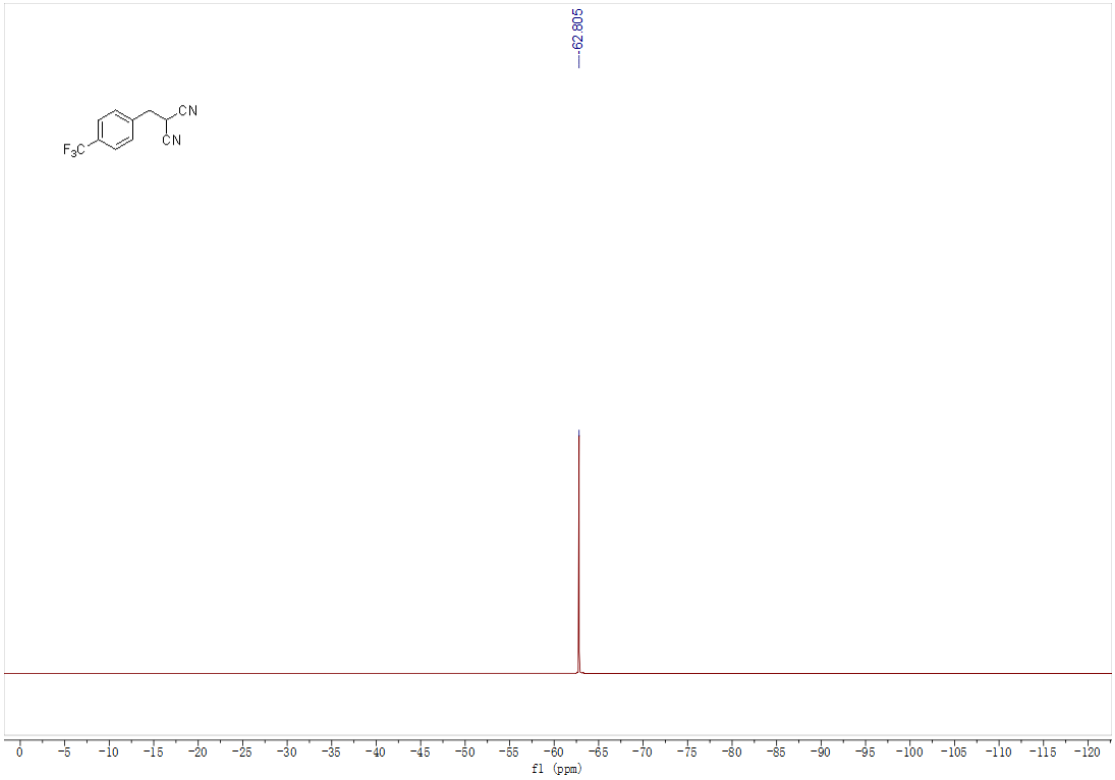
^{1}H NMR Spectrum of **4e**



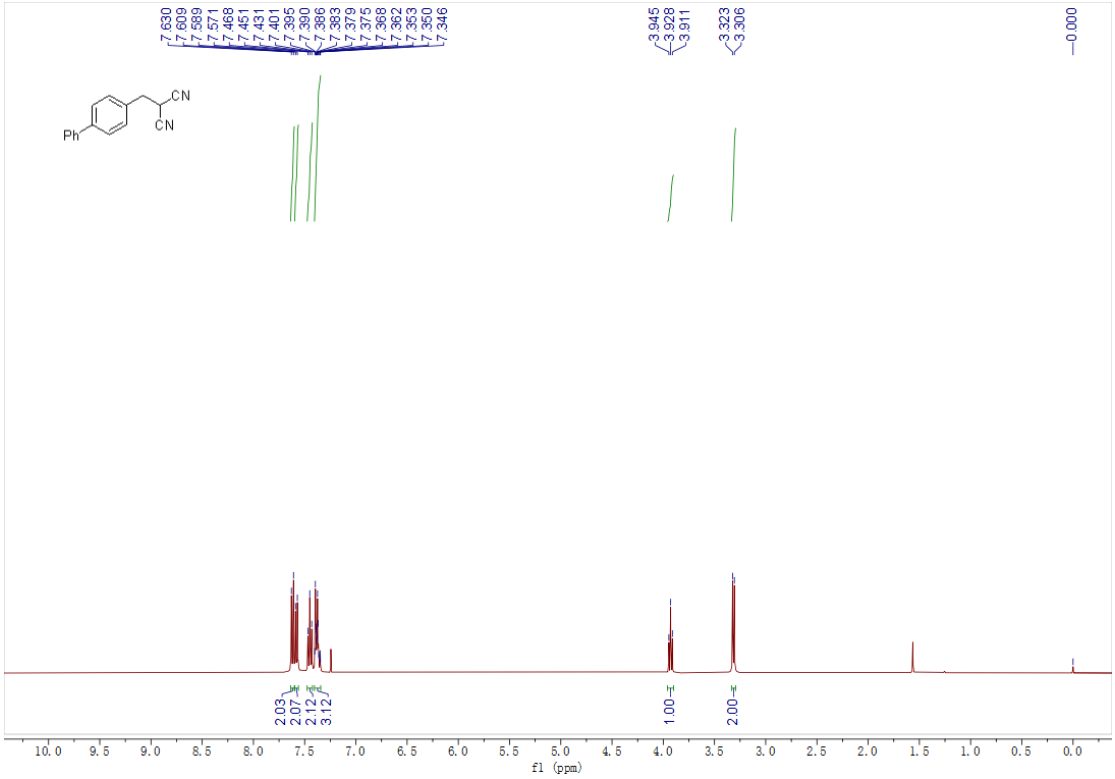
^{13}C NMR Spectrum of **4e**



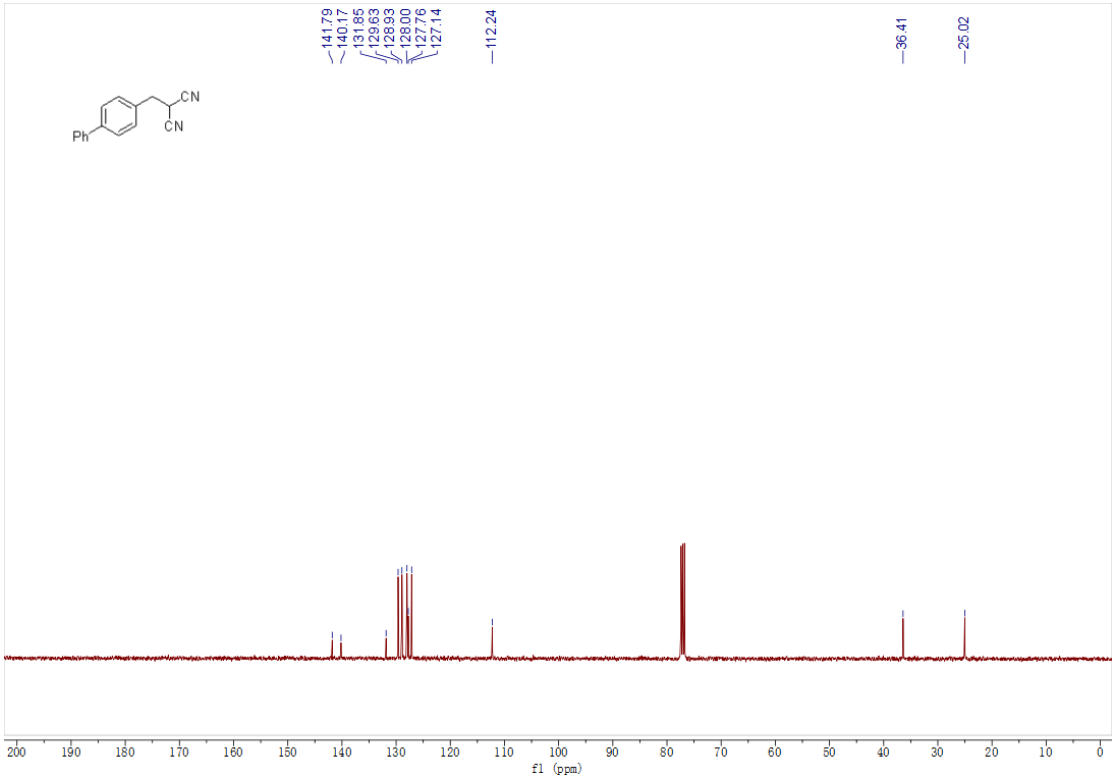
^{19}F NMR Spectrum of **4e**



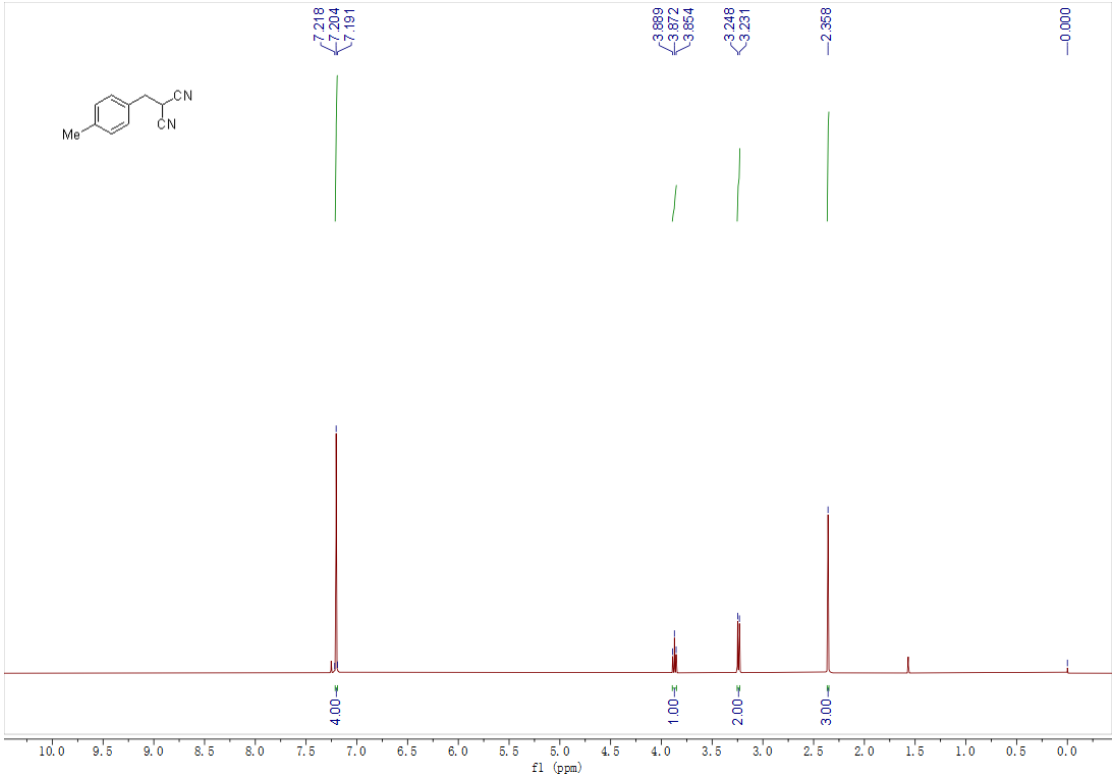
^{1}H NMR Spectrum of **4f**



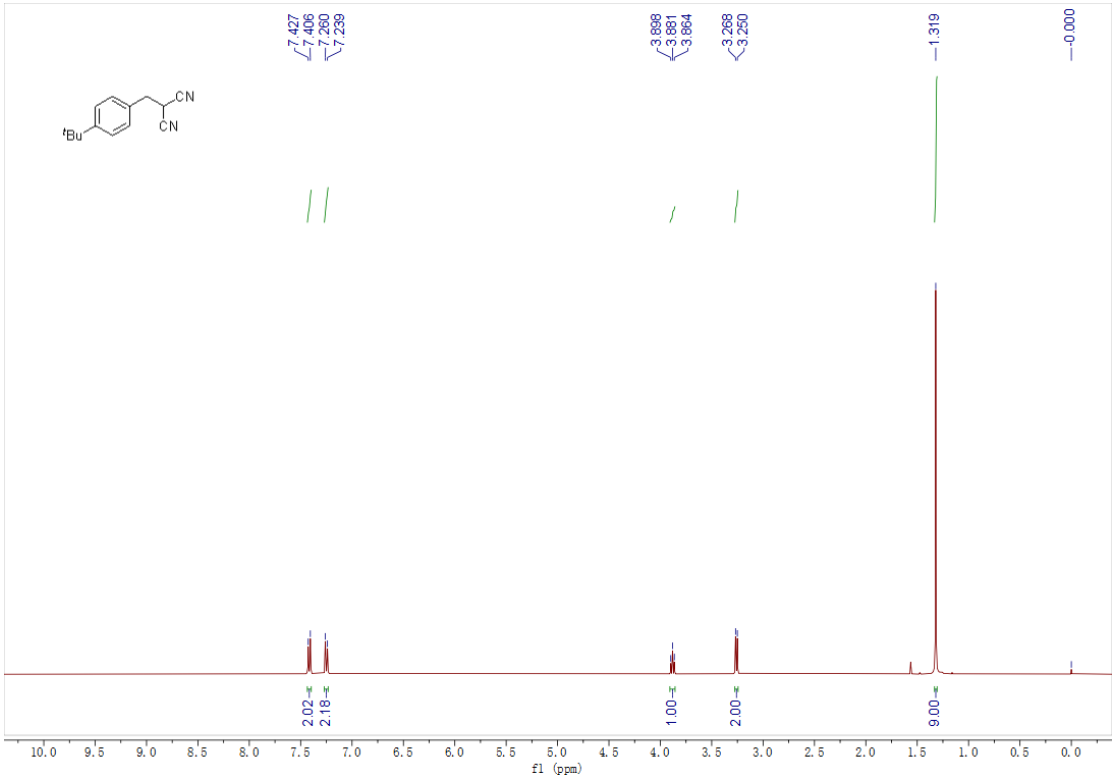
^{13}C NMR Spectrum of **4f**



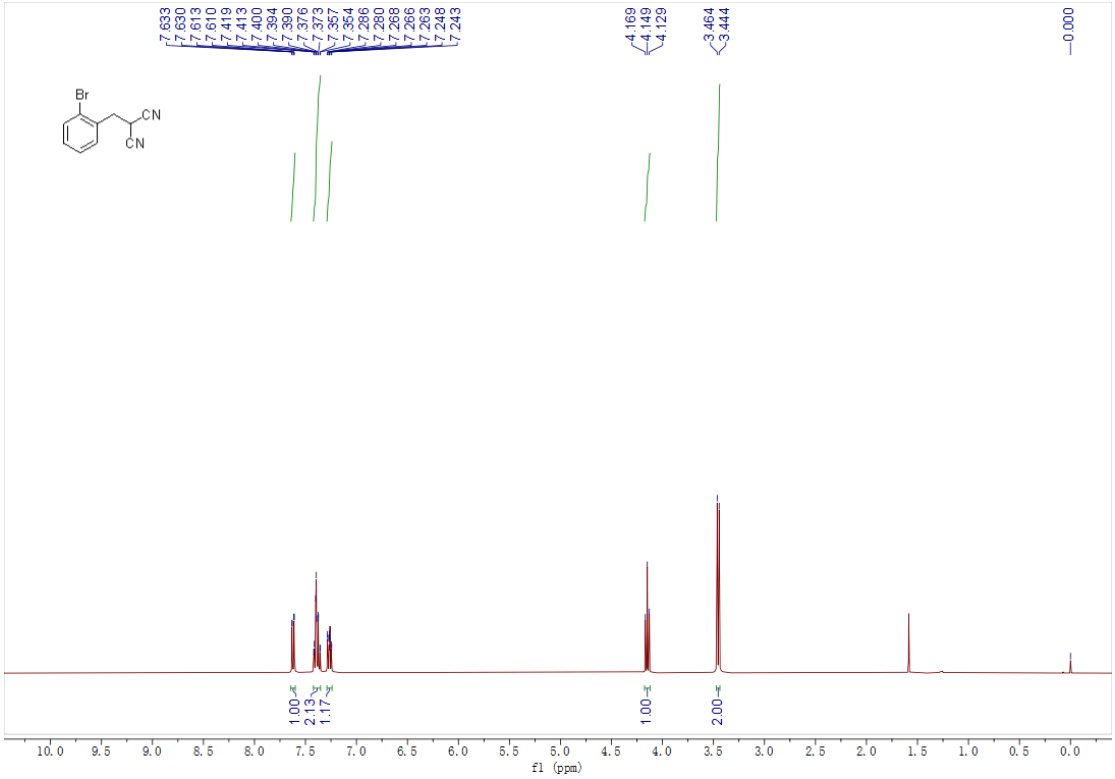
^{1}H NMR Spectrum of **4g**



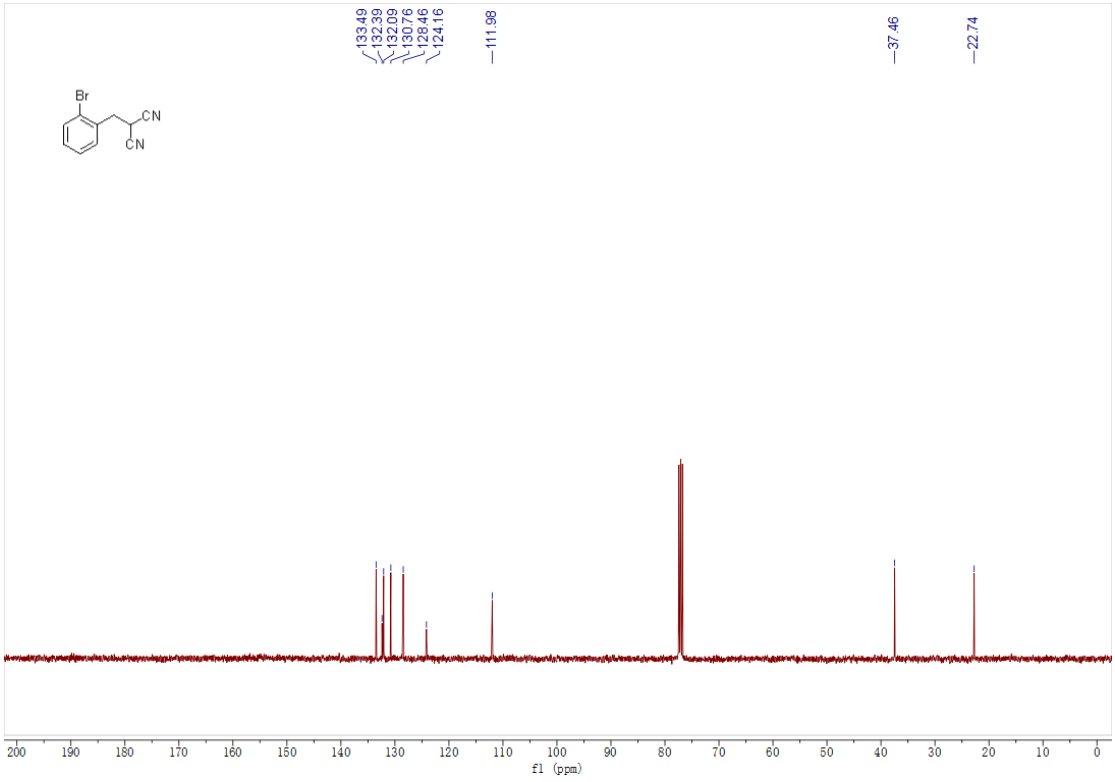
^{1}H NMR Spectrum of **4h**



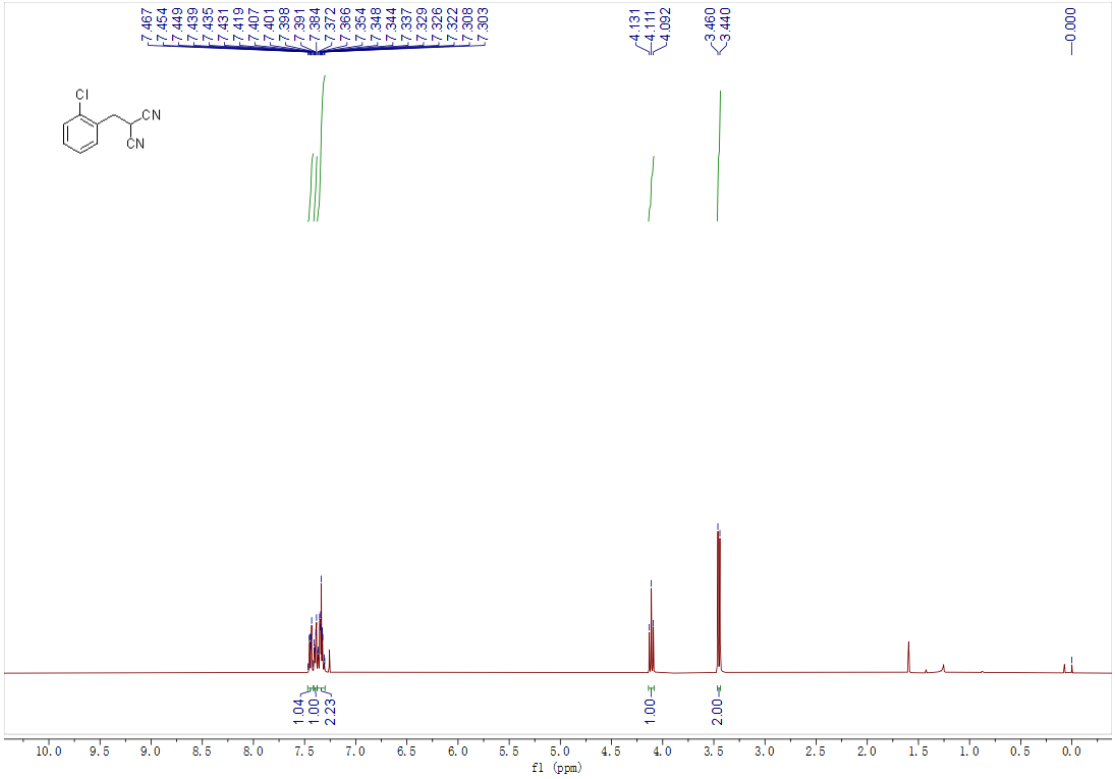
^{1}H NMR Spectrum of **4i**



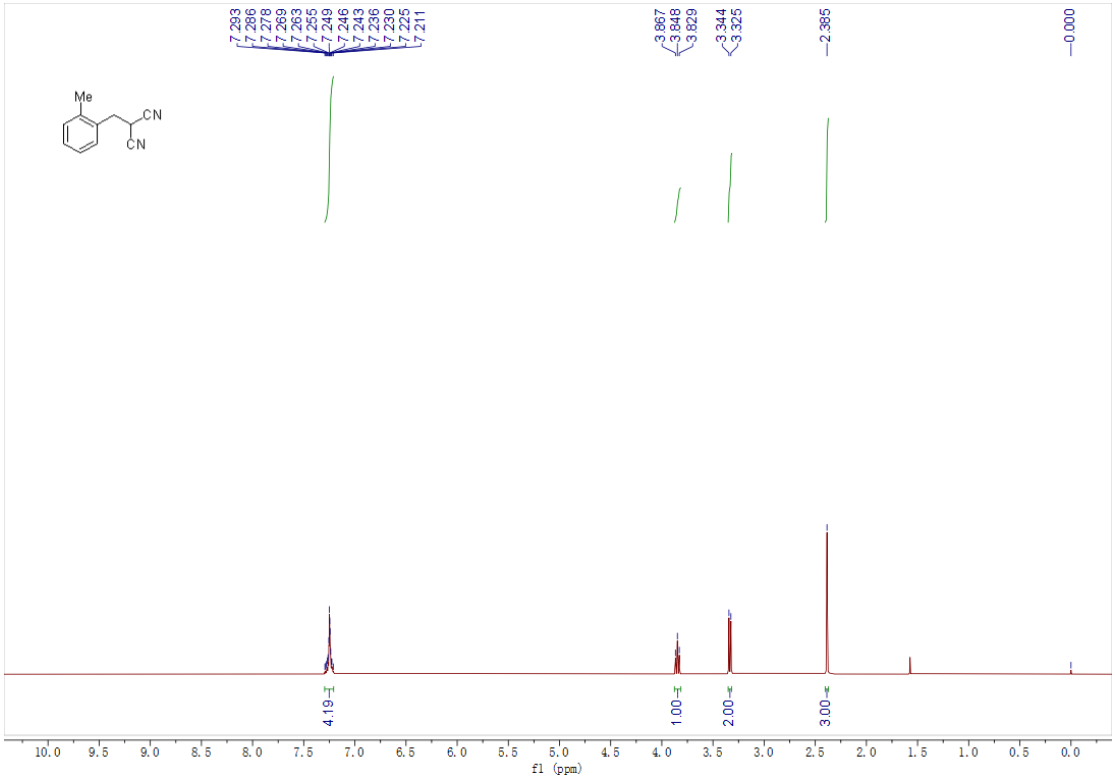
^{13}C NMR Spectrum of **4i**



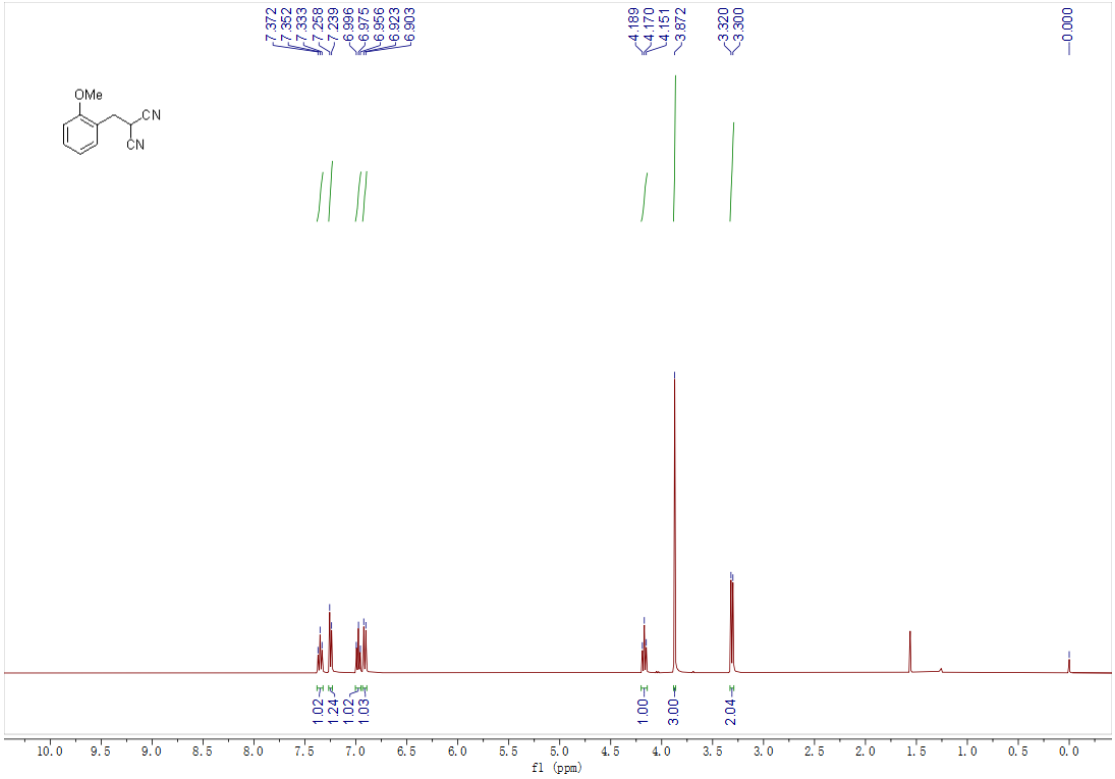
^{1}H NMR Spectrum of **4j**



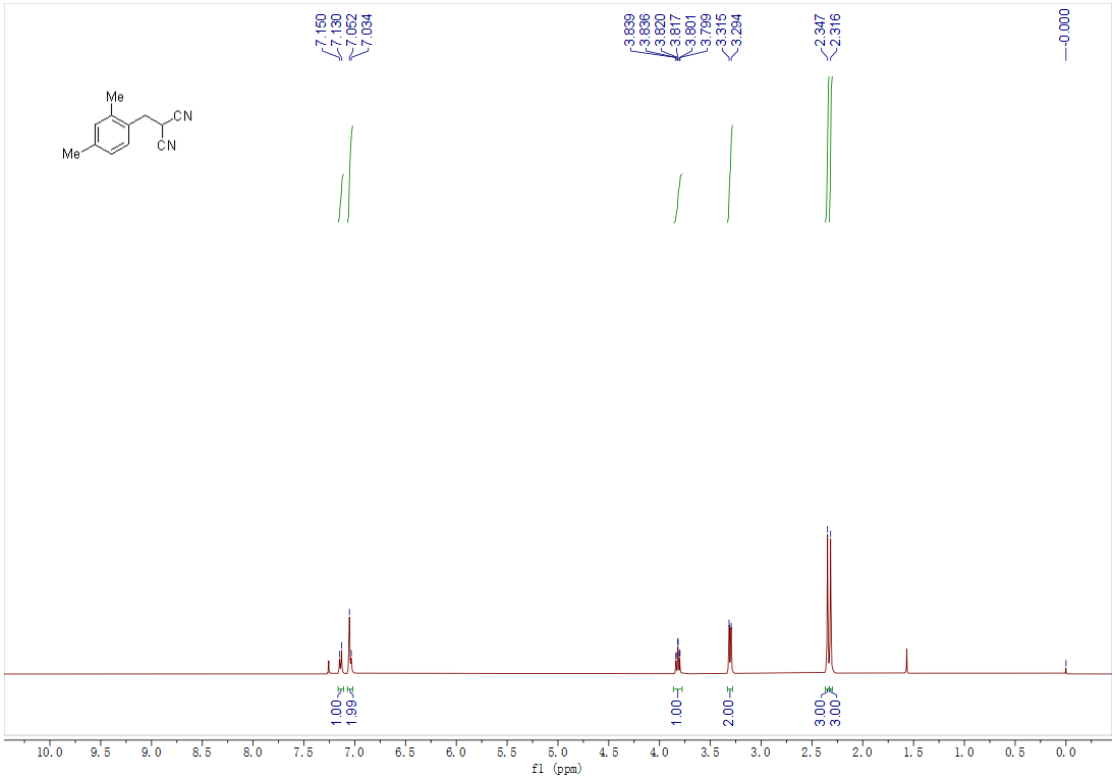
^{1}H NMR Spectrum of **4k**



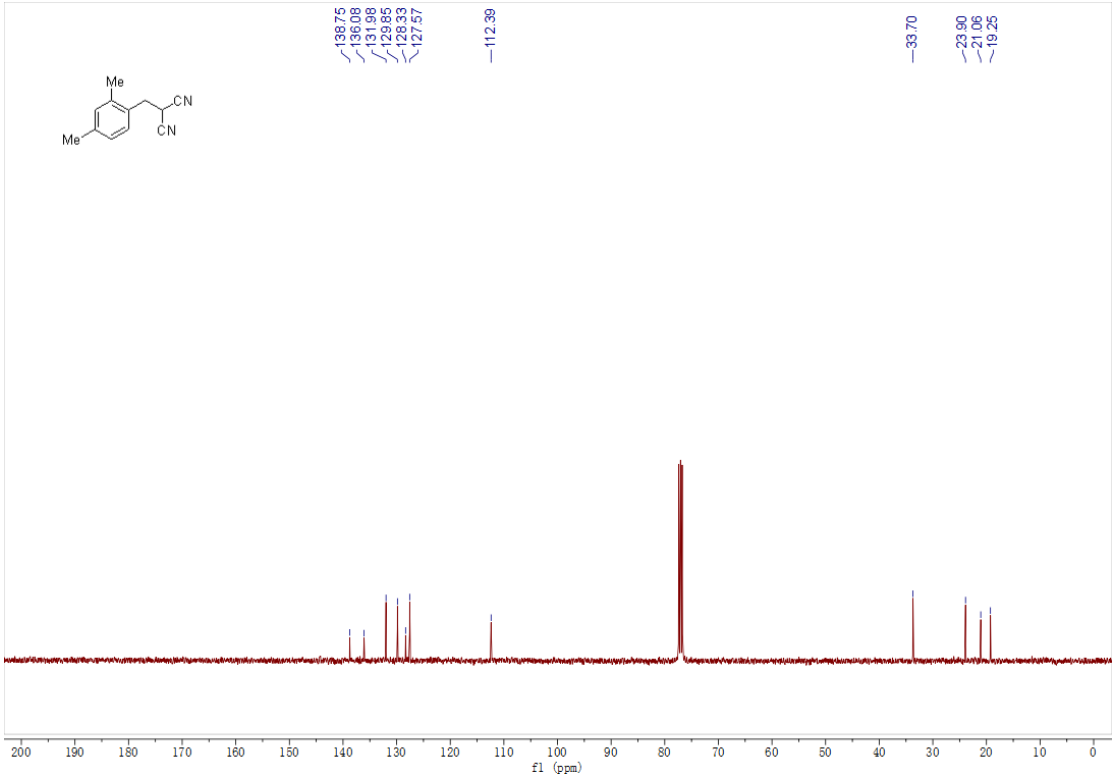
^{1}H NMR Spectrum of **4l**



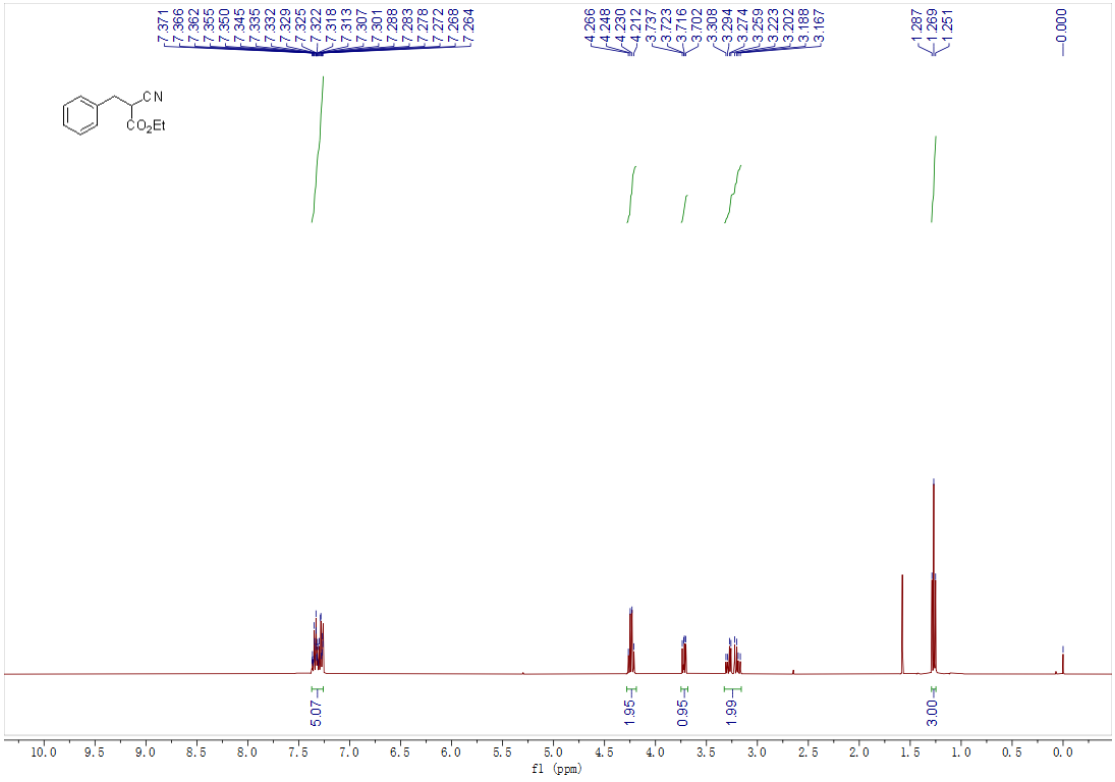
^{1}H NMR Spectrum of **4m**



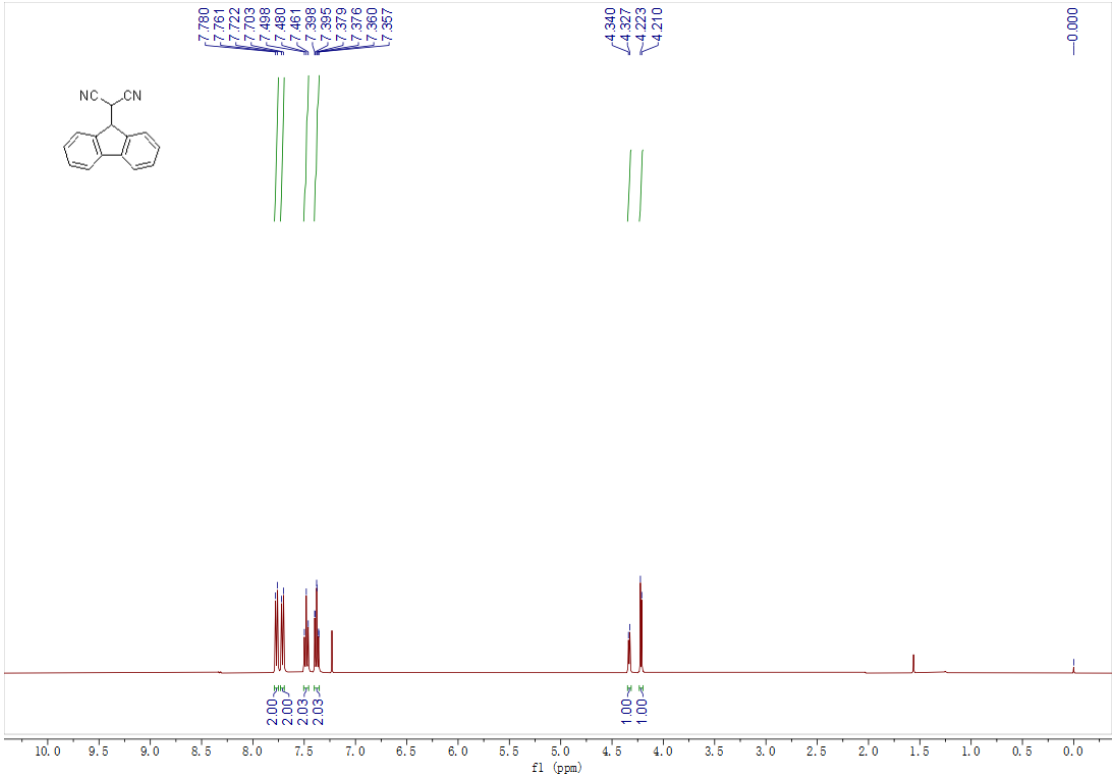
^{13}C NMR Spectrum of **4m**



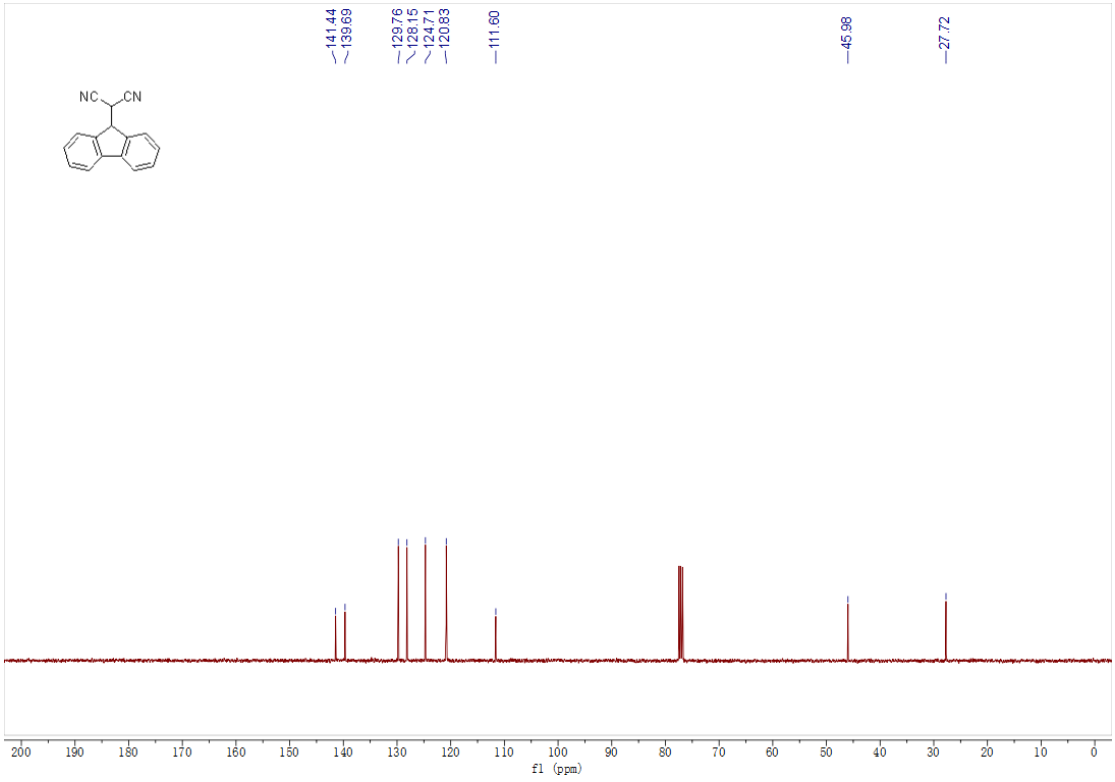
^{1}H NMR Spectrum of **4n**



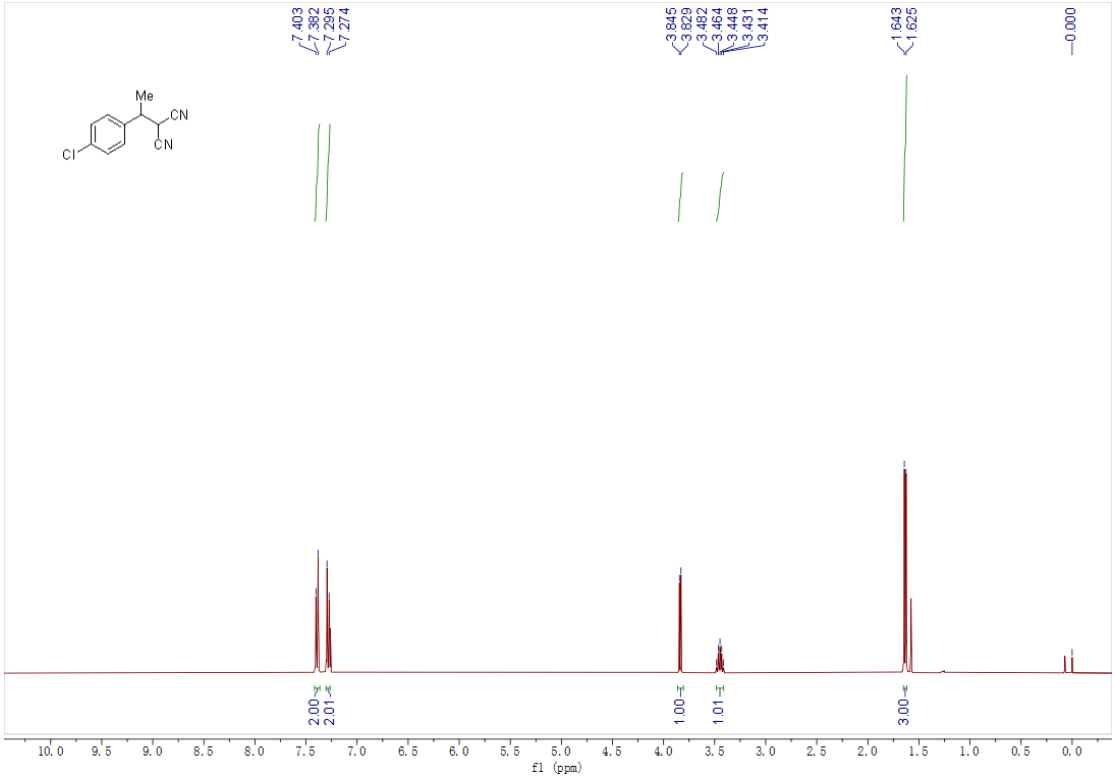
^{1}H NMR Spectrum of **4o**



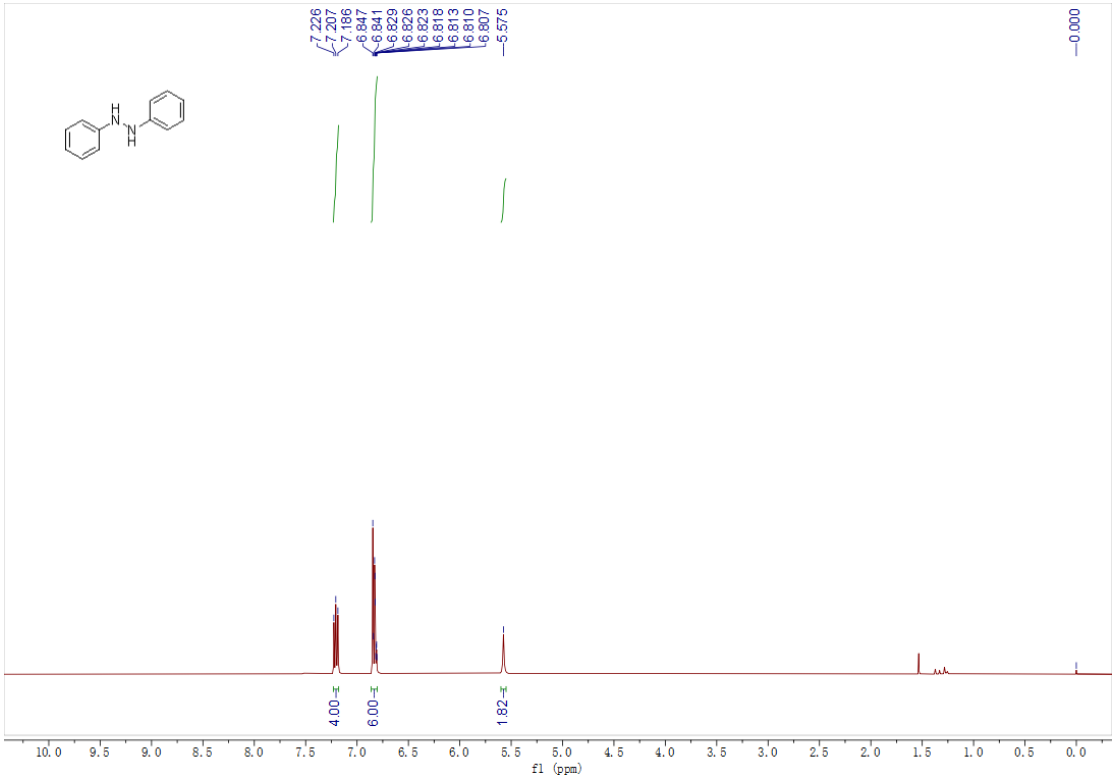
^{13}C NMR Spectrum of **4o**



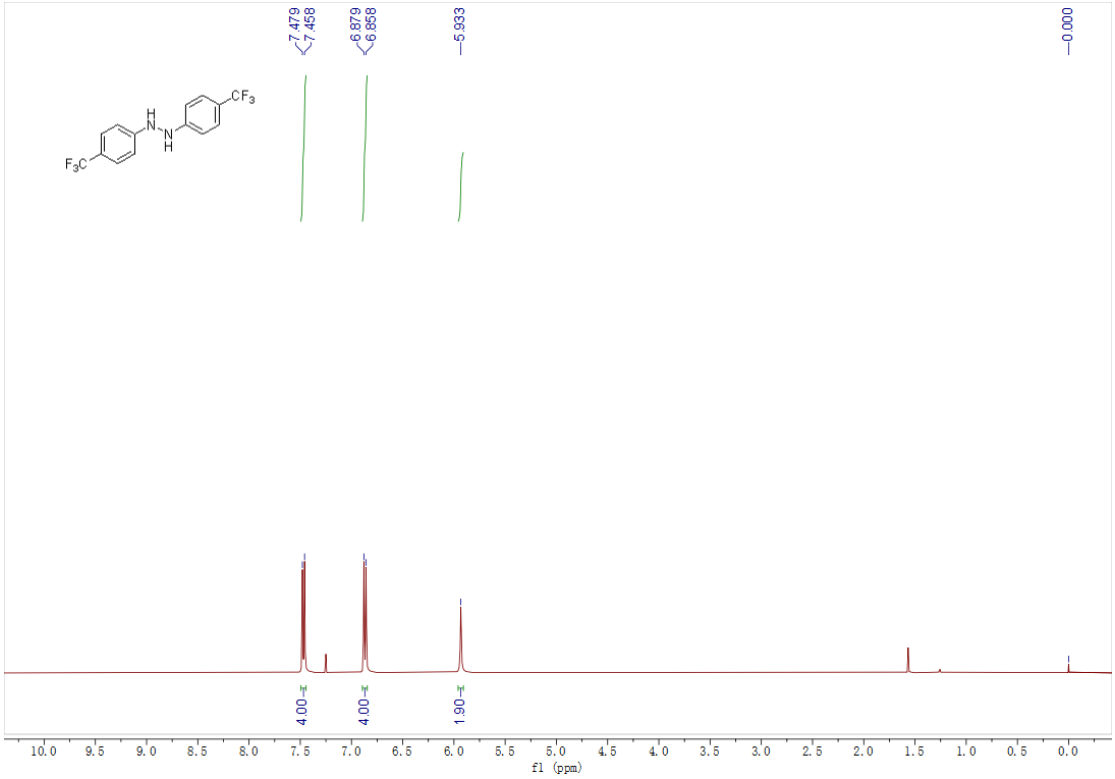
^{1}H NMR Spectrum of **4p**



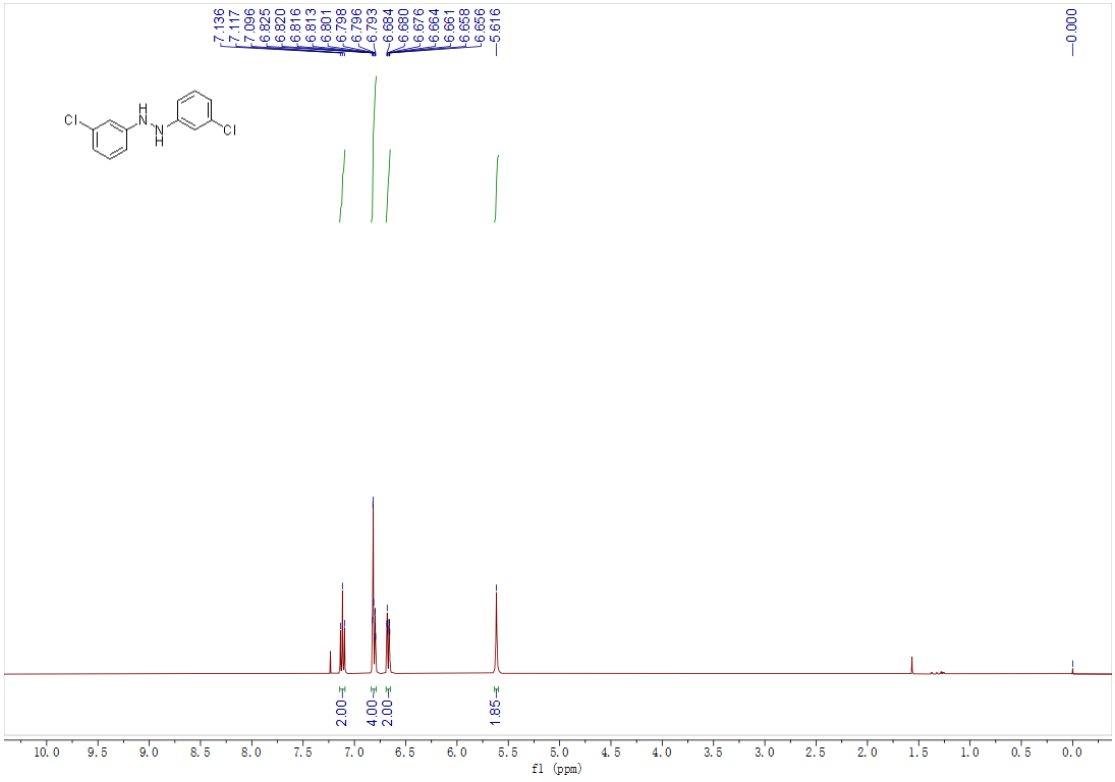
^{1}H NMR Spectrum of **6a**



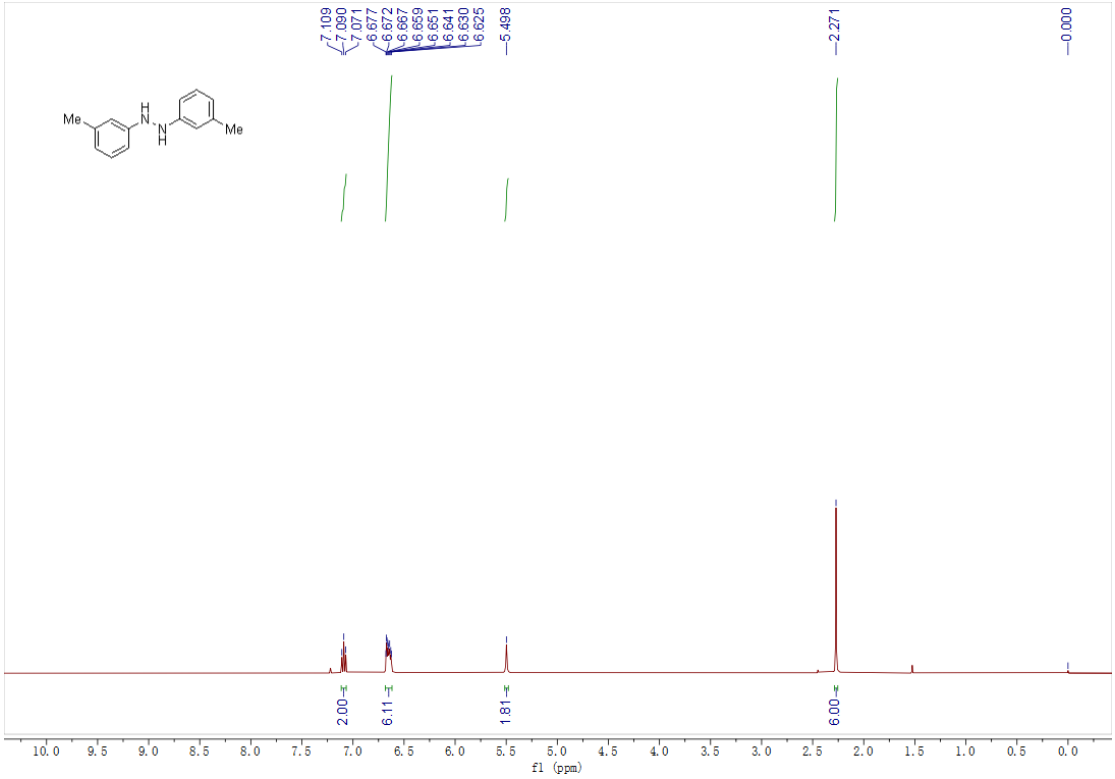
^{1}H NMR Spectrum of **6b**



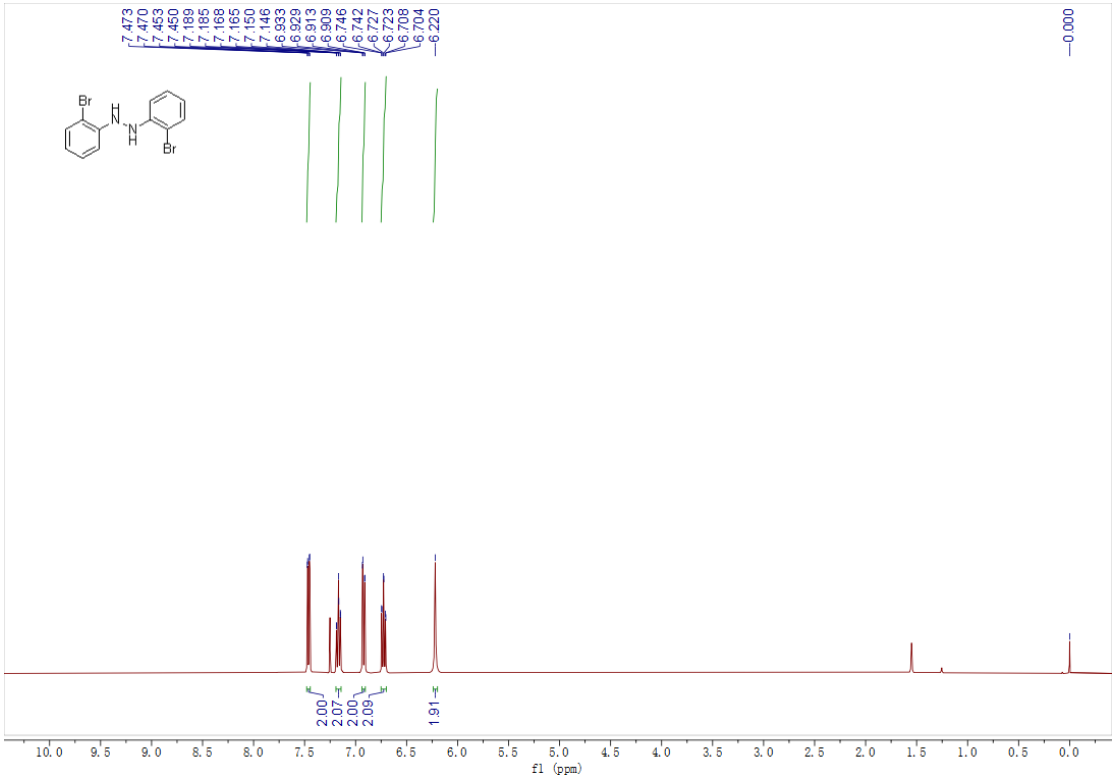
^{1}H NMR Spectrum of **6c**



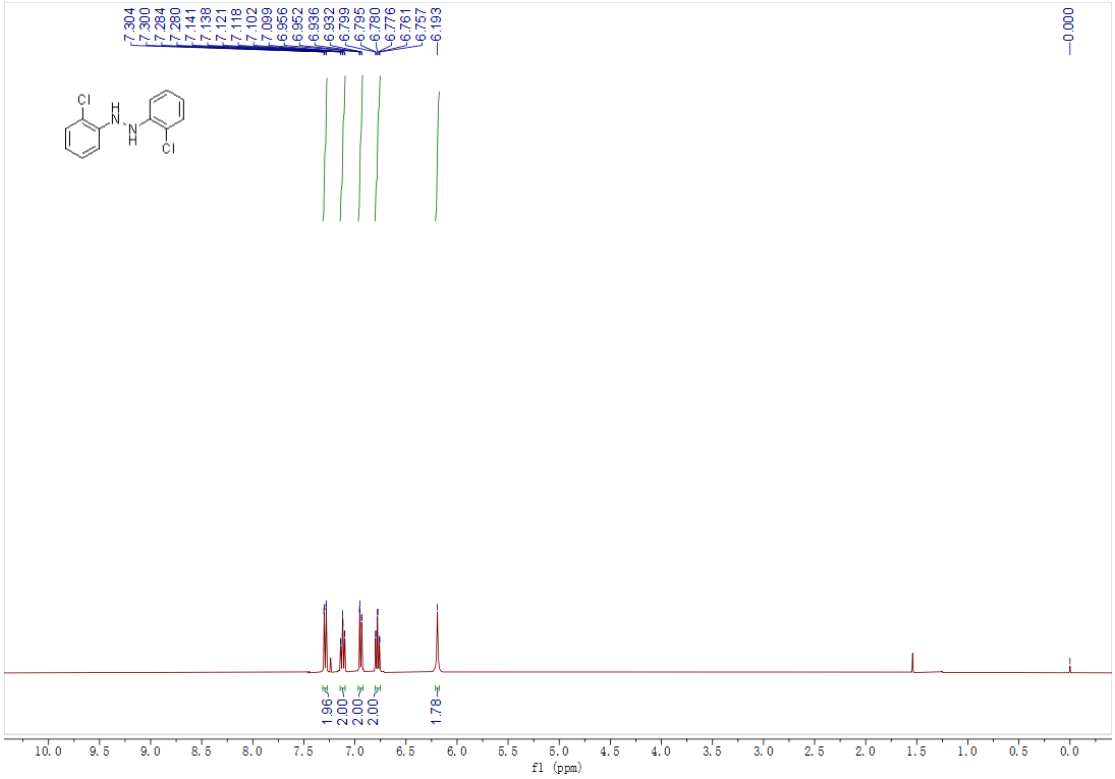
^{1}H NMR Spectrum of **6d**



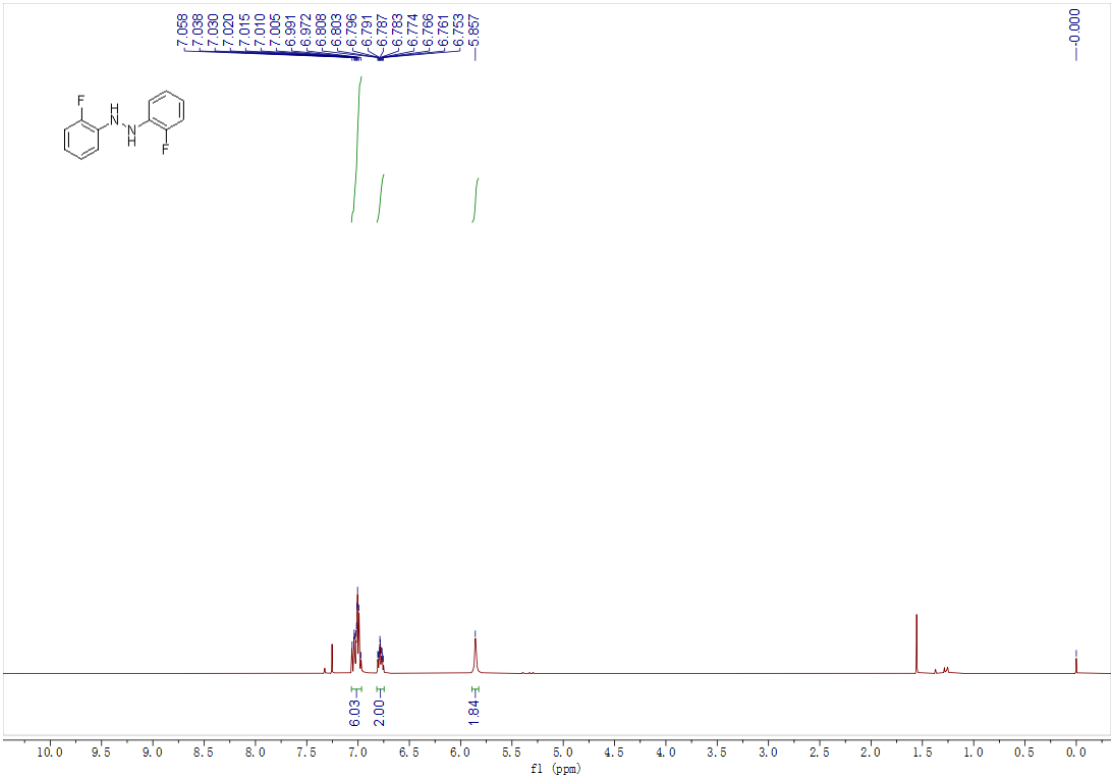
^{1}H NMR Spectrum of **6e**



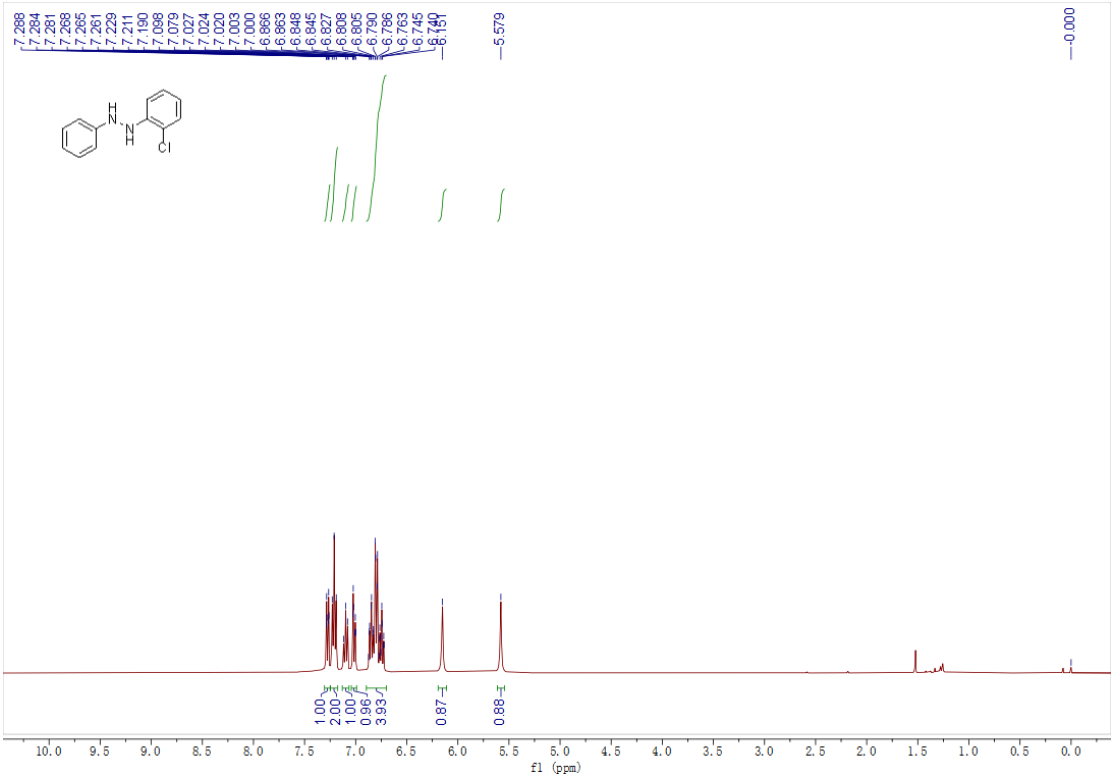
^{1}H NMR Spectrum of **6f**



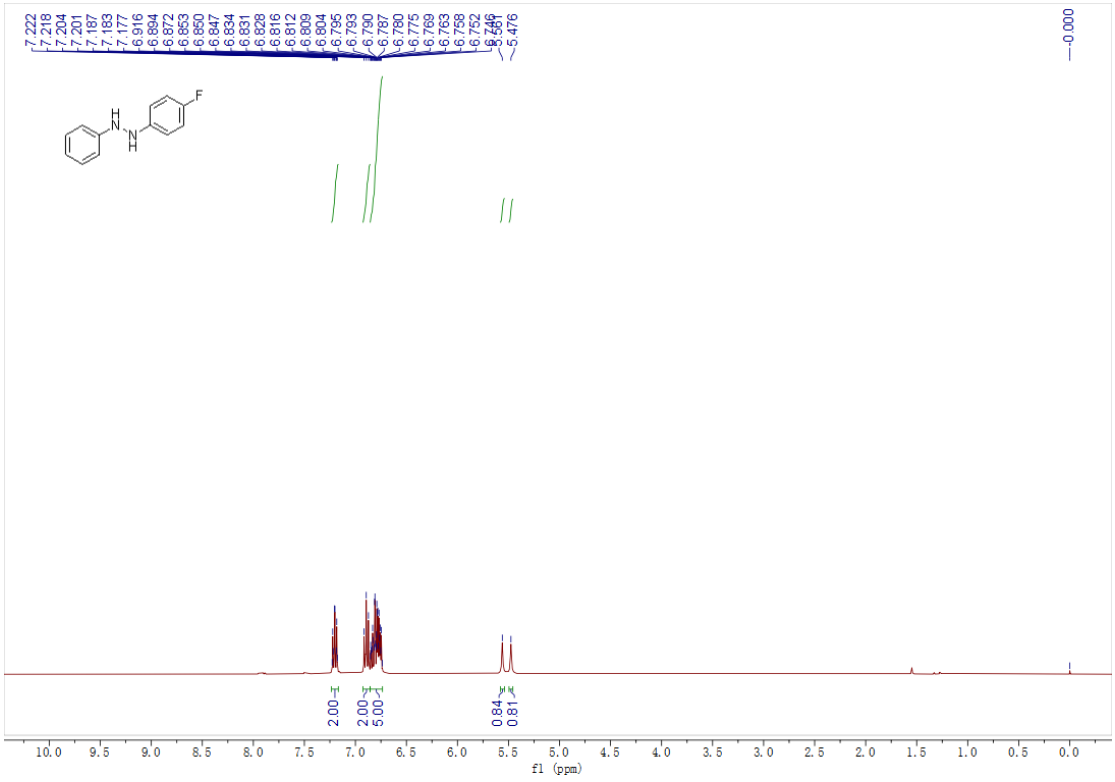
^{1}H NMR Spectrum of **6g**



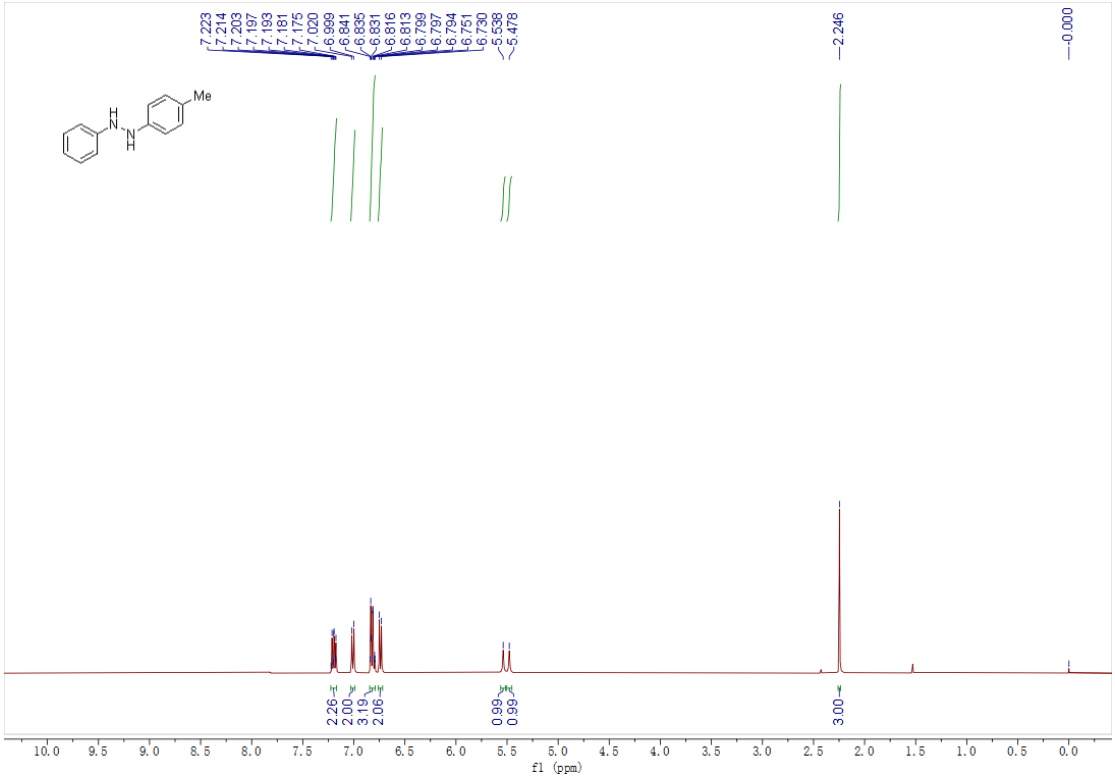
^{1}H NMR Spectrum of **6h**



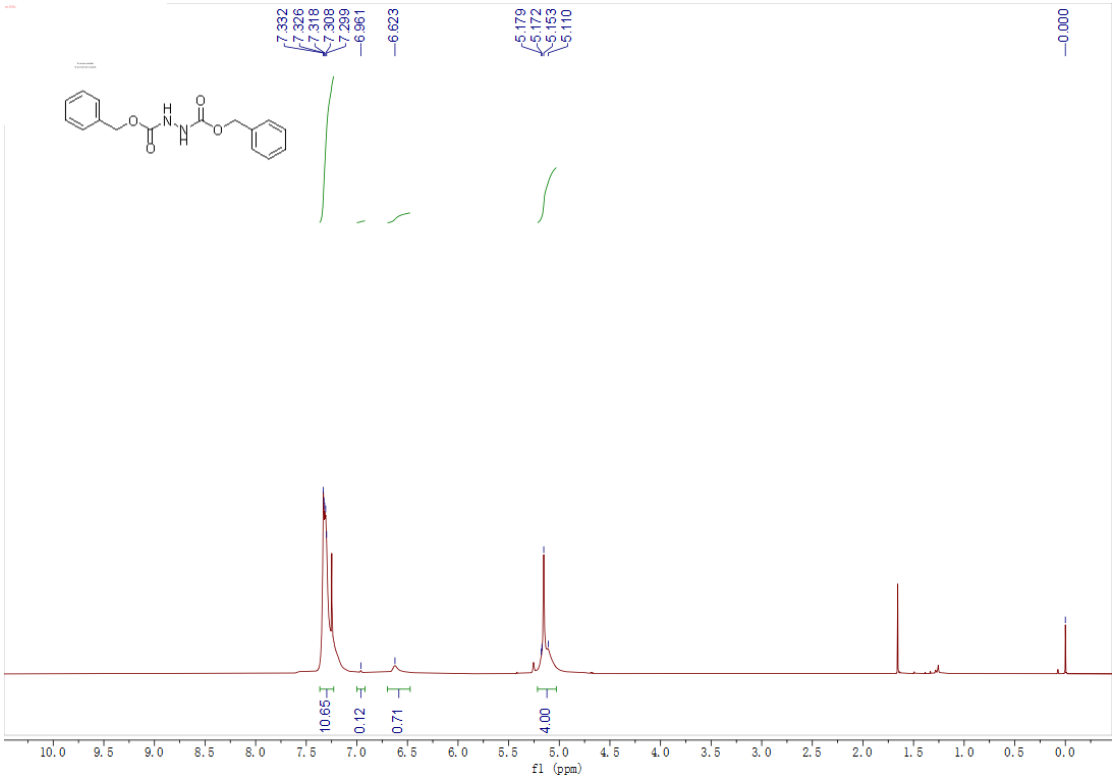
^{1}H NMR Spectrum of **6i**



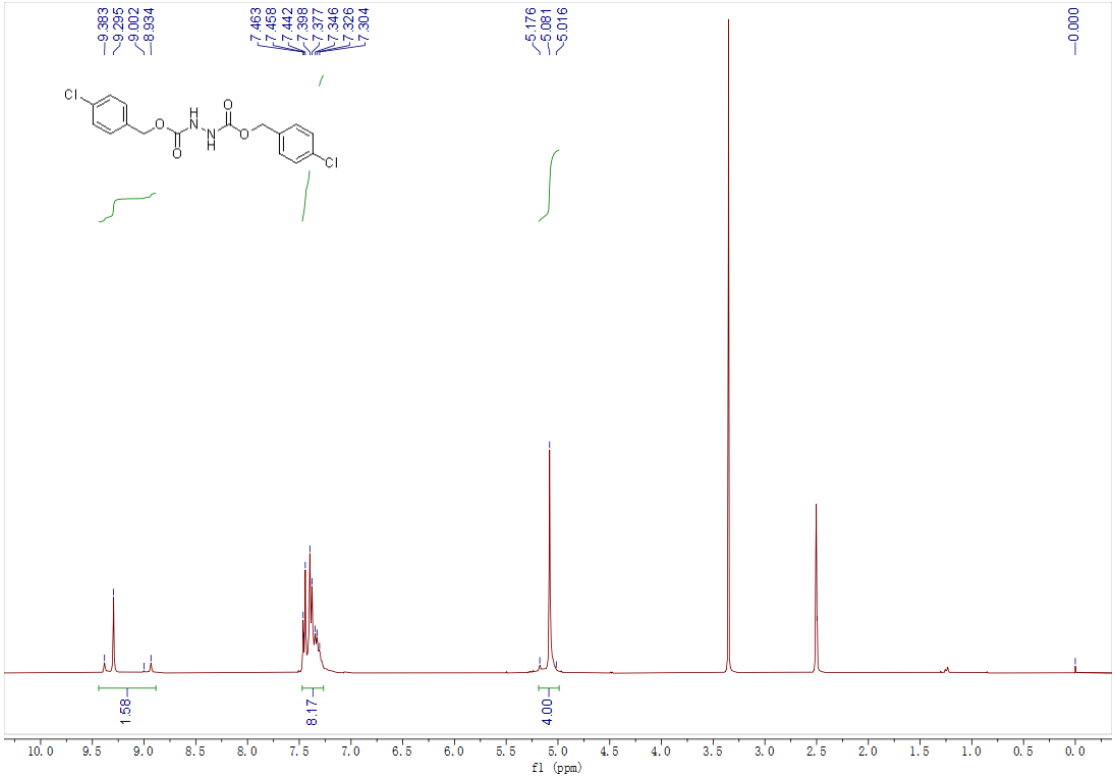
^{1}H NMR Spectrum of **6j**



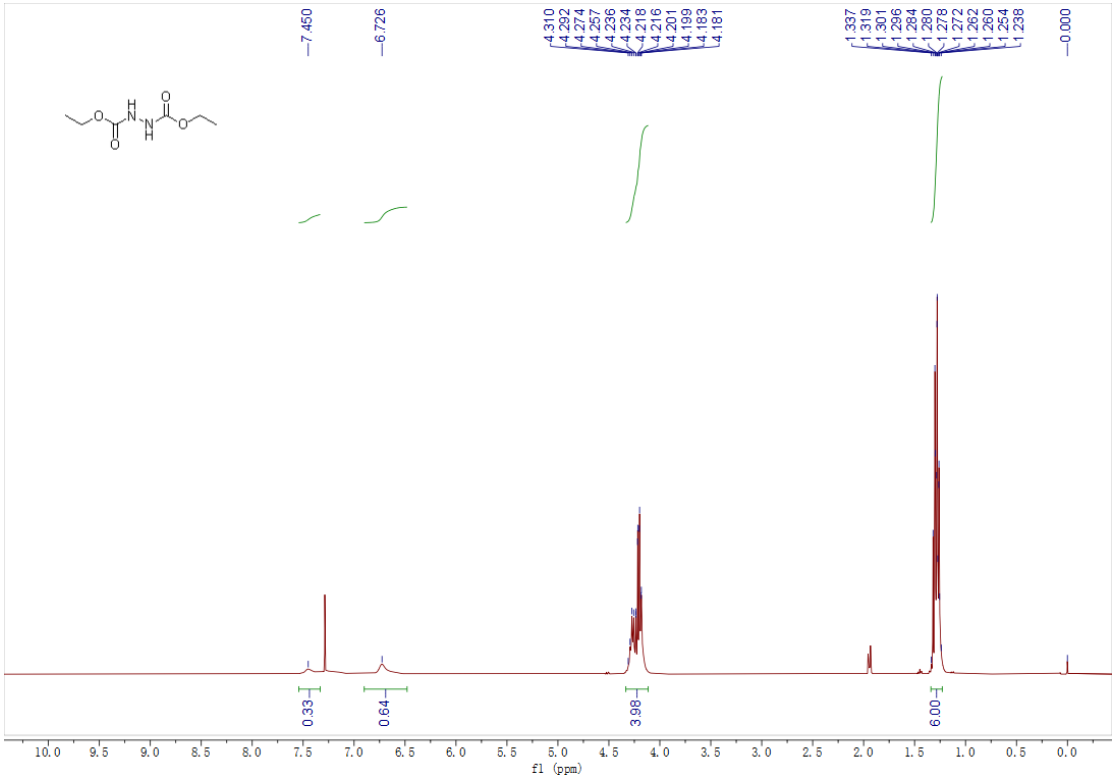
^{1}H NMR Spectrum of **6k**



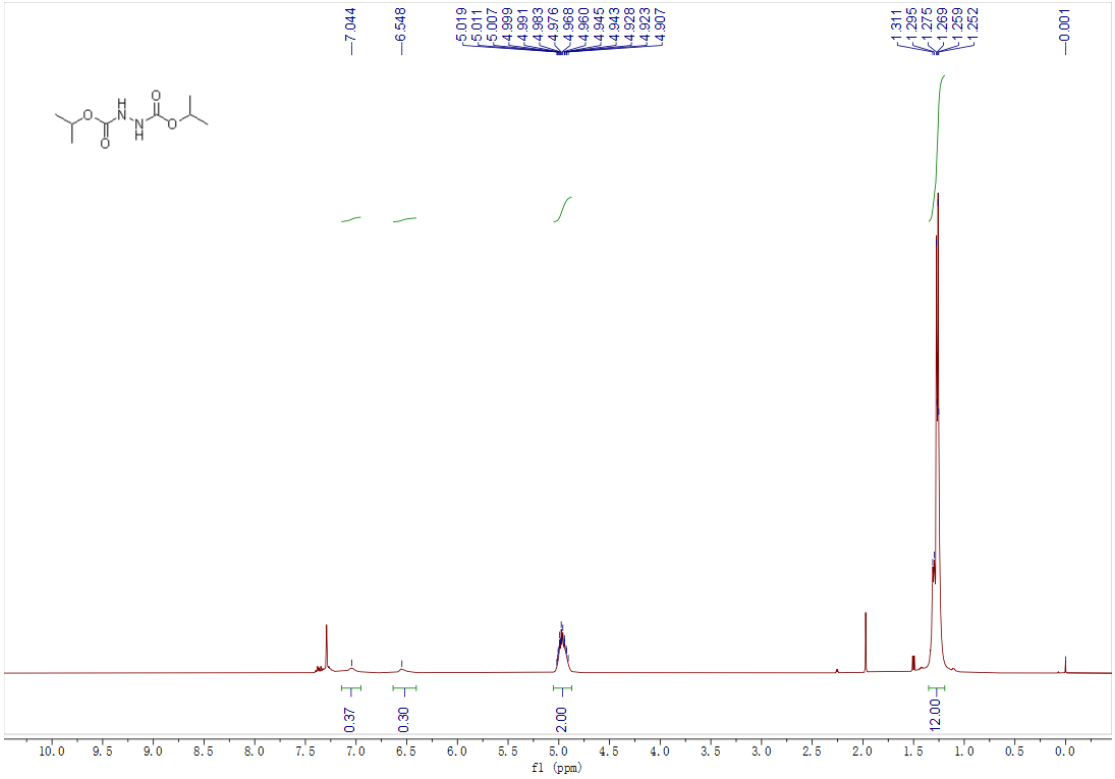
^{1}H NMR Spectrum of **6l**



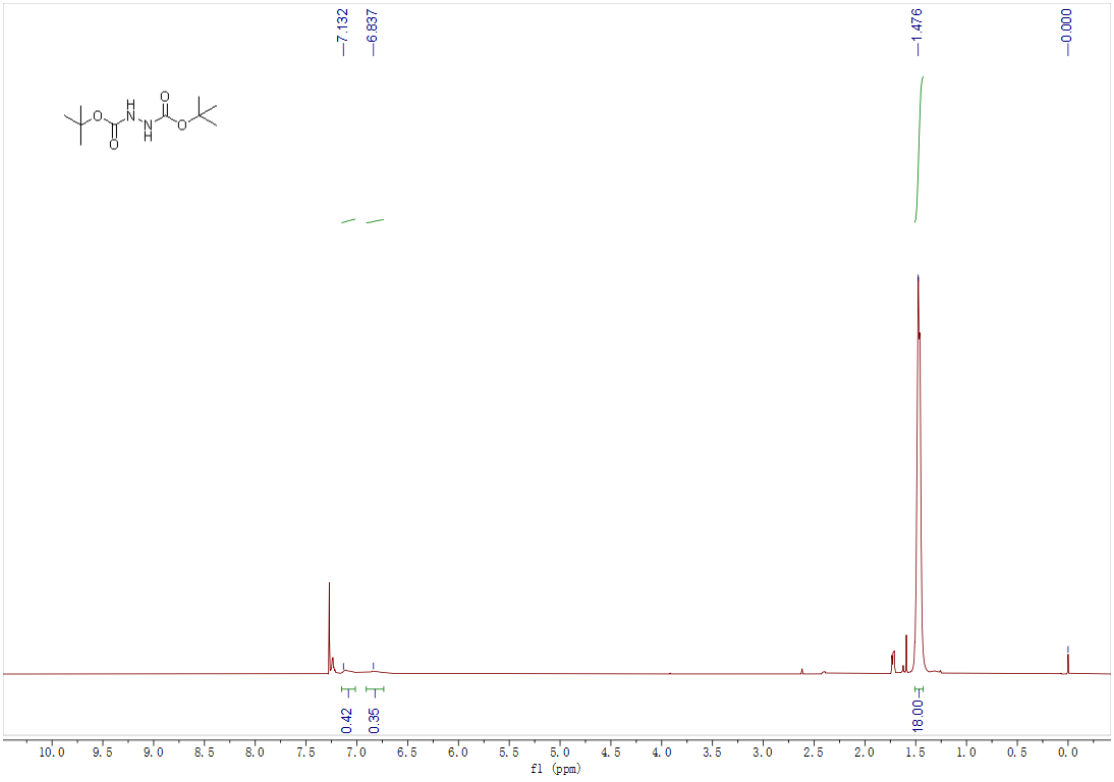
^{1}H NMR Spectrum of **6m**



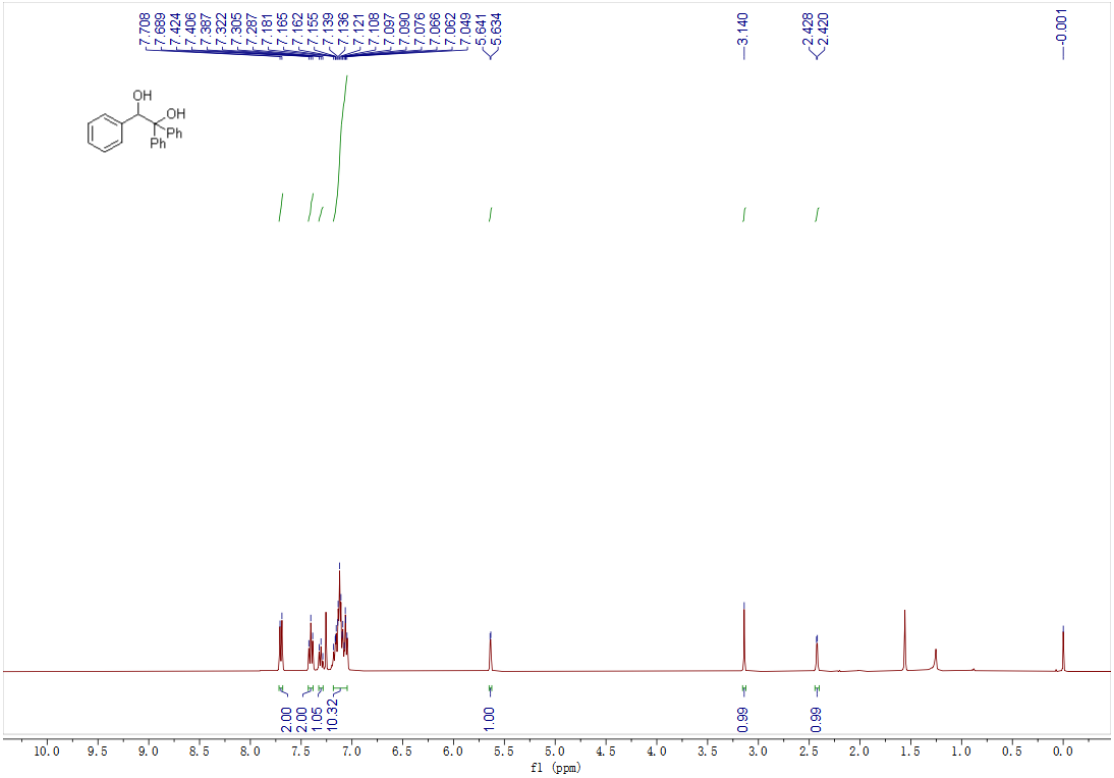
^{1}H NMR Spectrum of **6n**



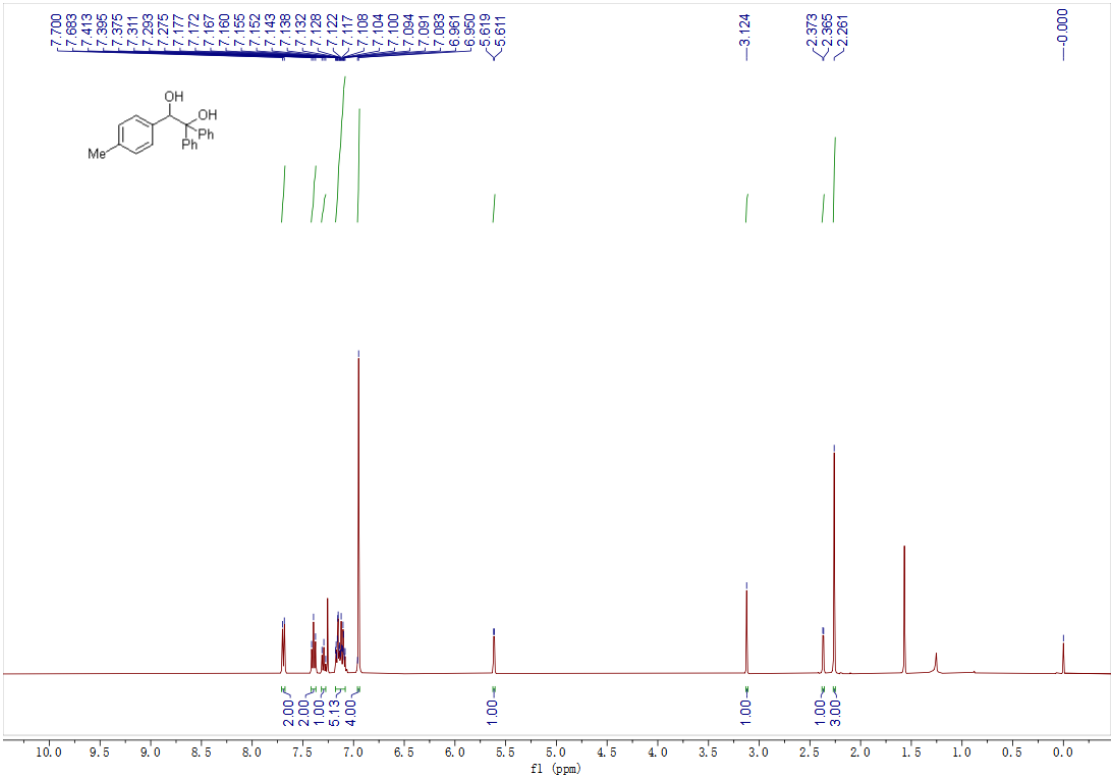
^{1}H NMR Spectrum of **6o**



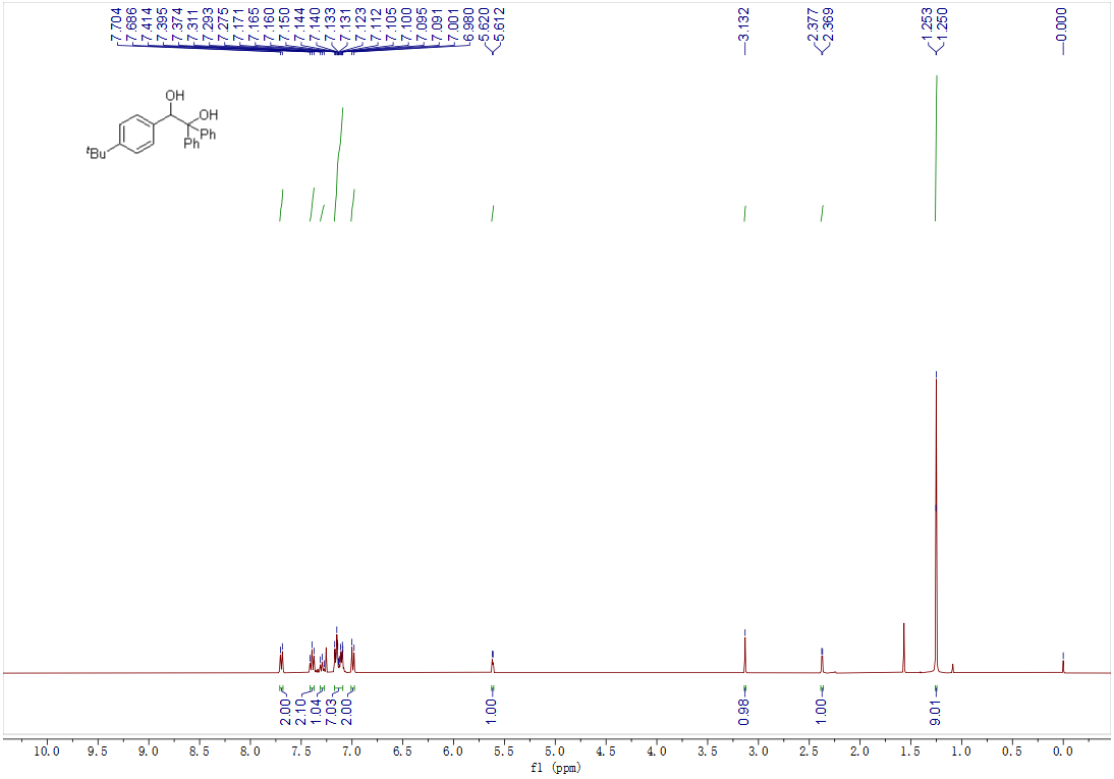
^{1}H NMR Spectrum of **8a**



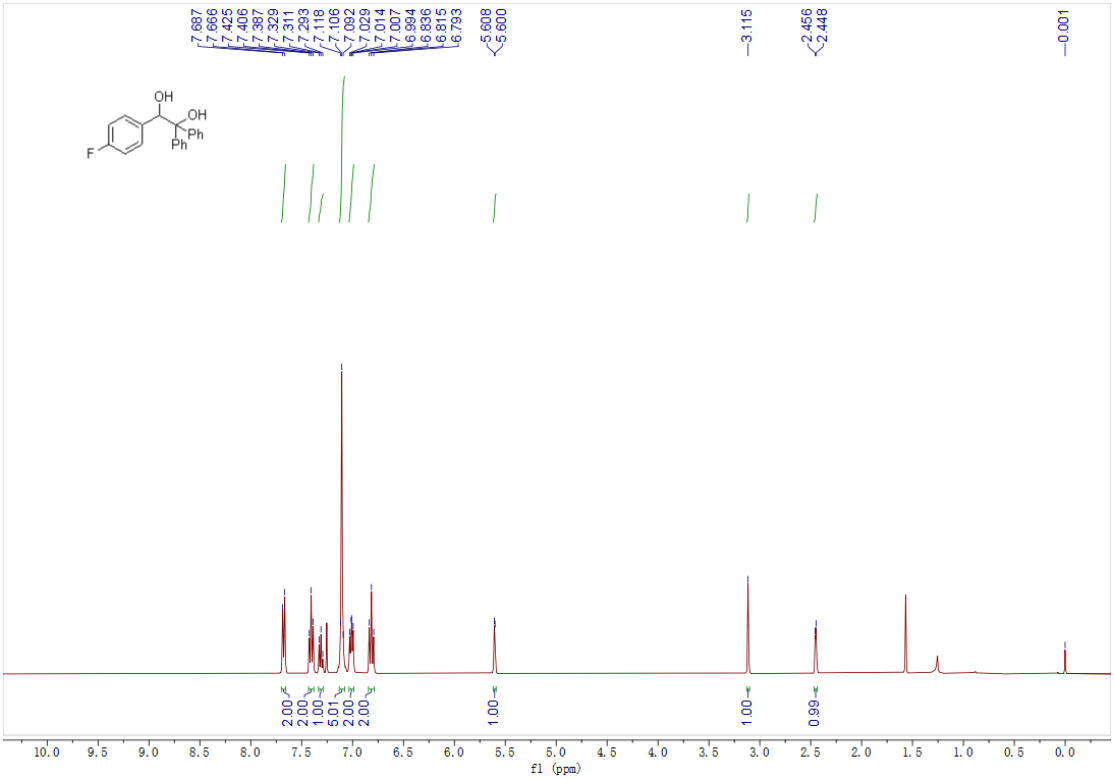
^{1}H NMR Spectrum of **8b**



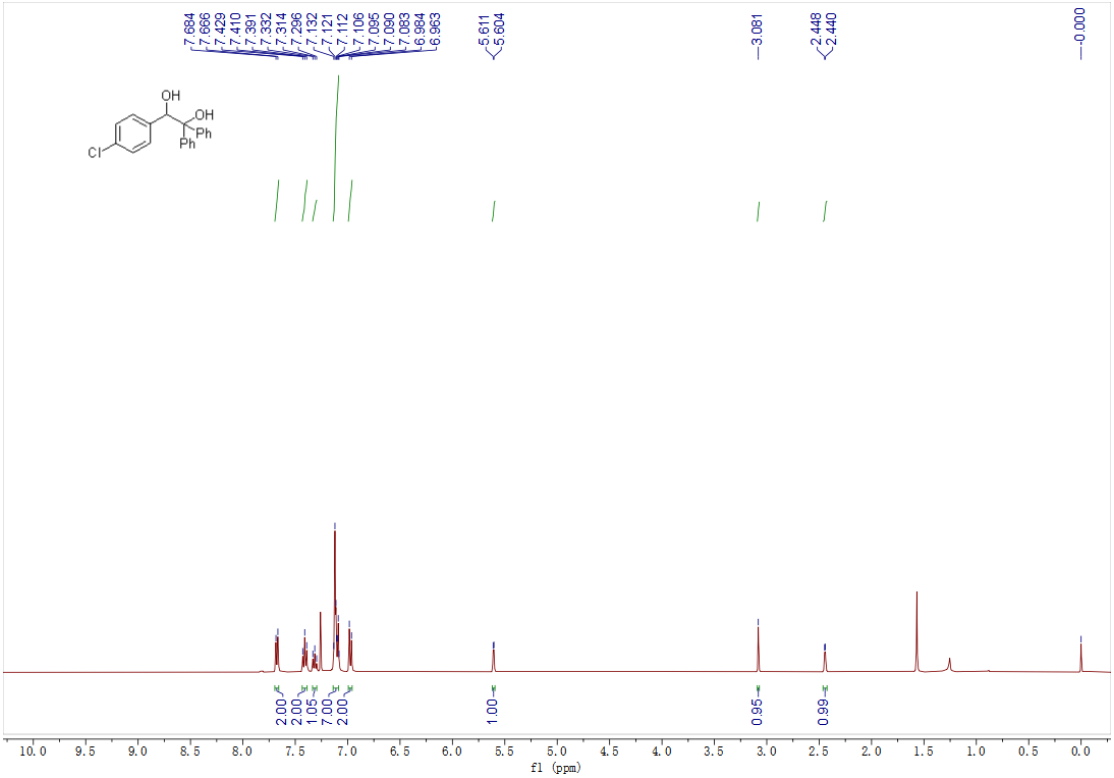
^{1}H NMR Spectrum of **8c**



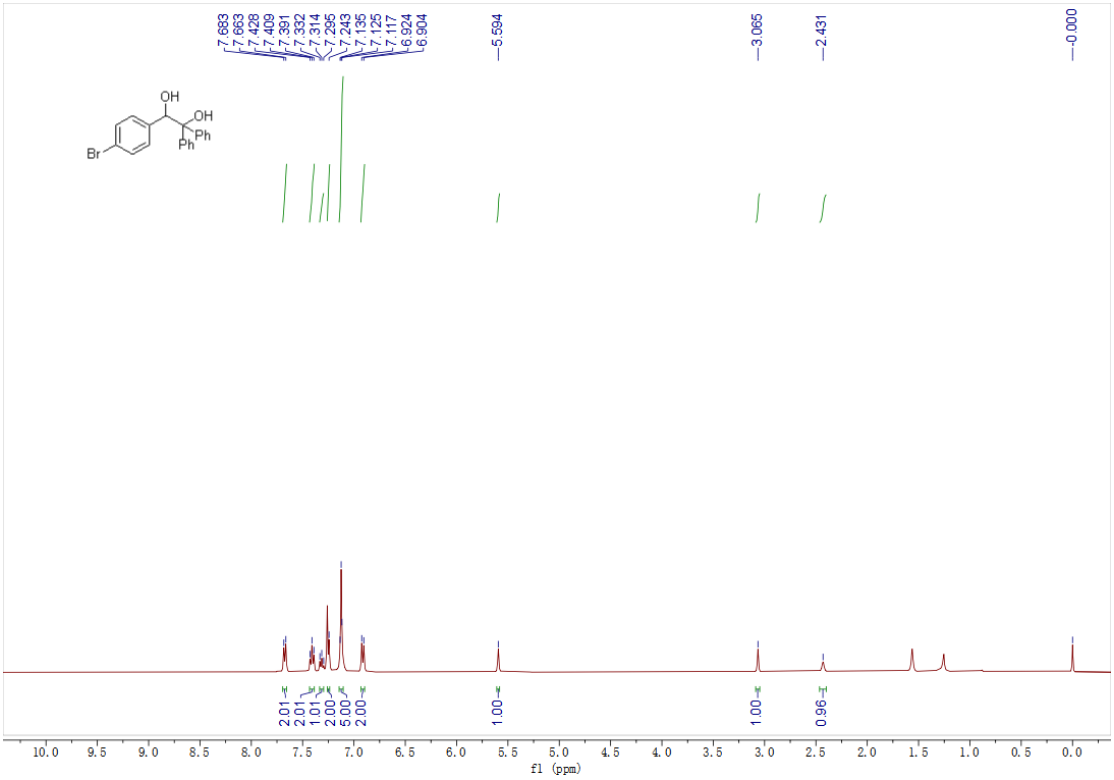
^{1}H NMR Spectrum of **8d**



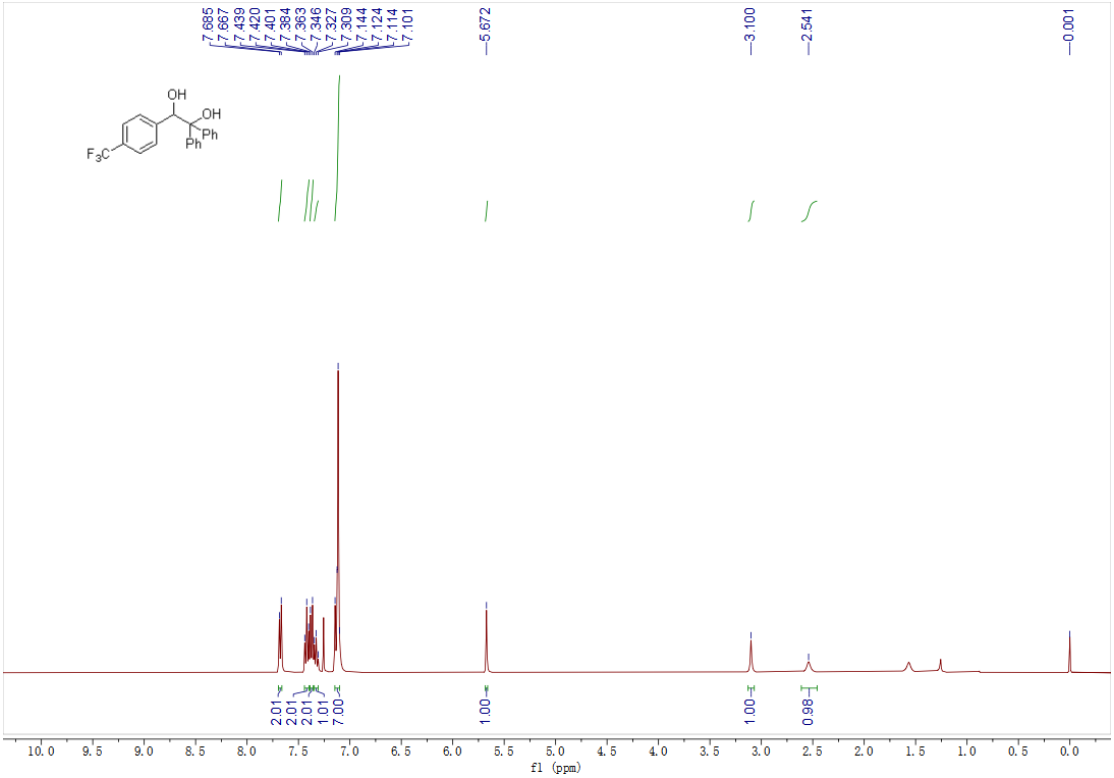
^{1}H NMR Spectrum of **8e**



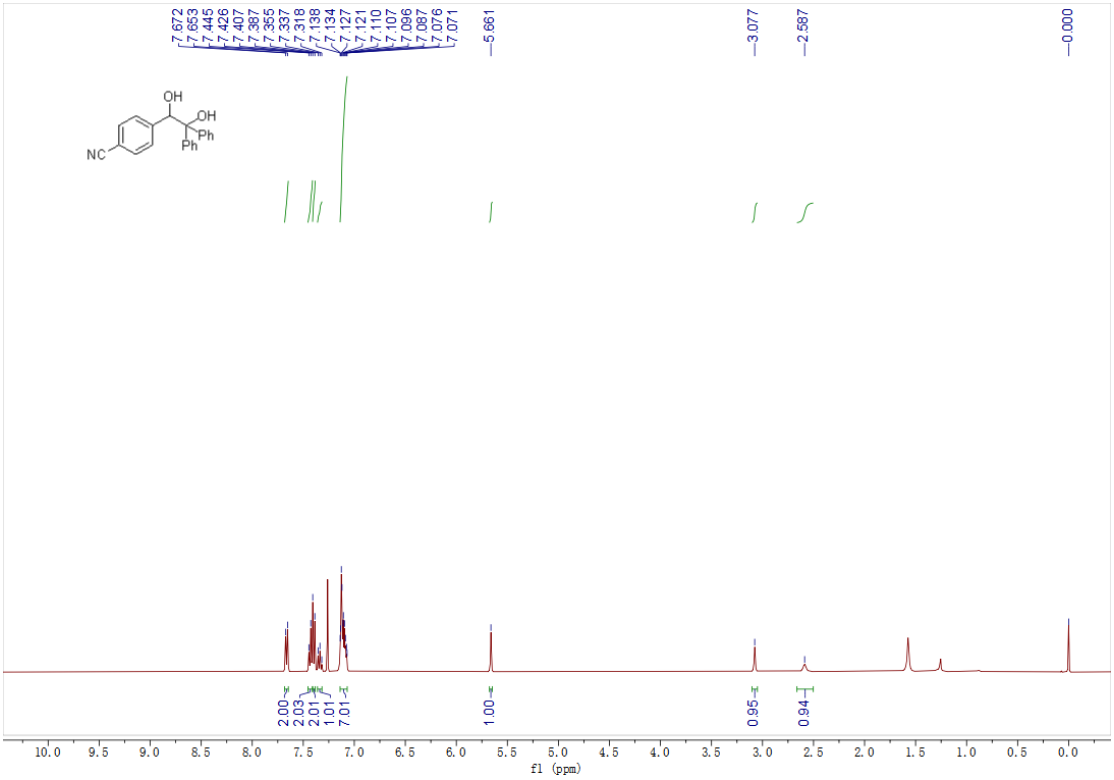
^{1}H NMR Spectrum of **8f**



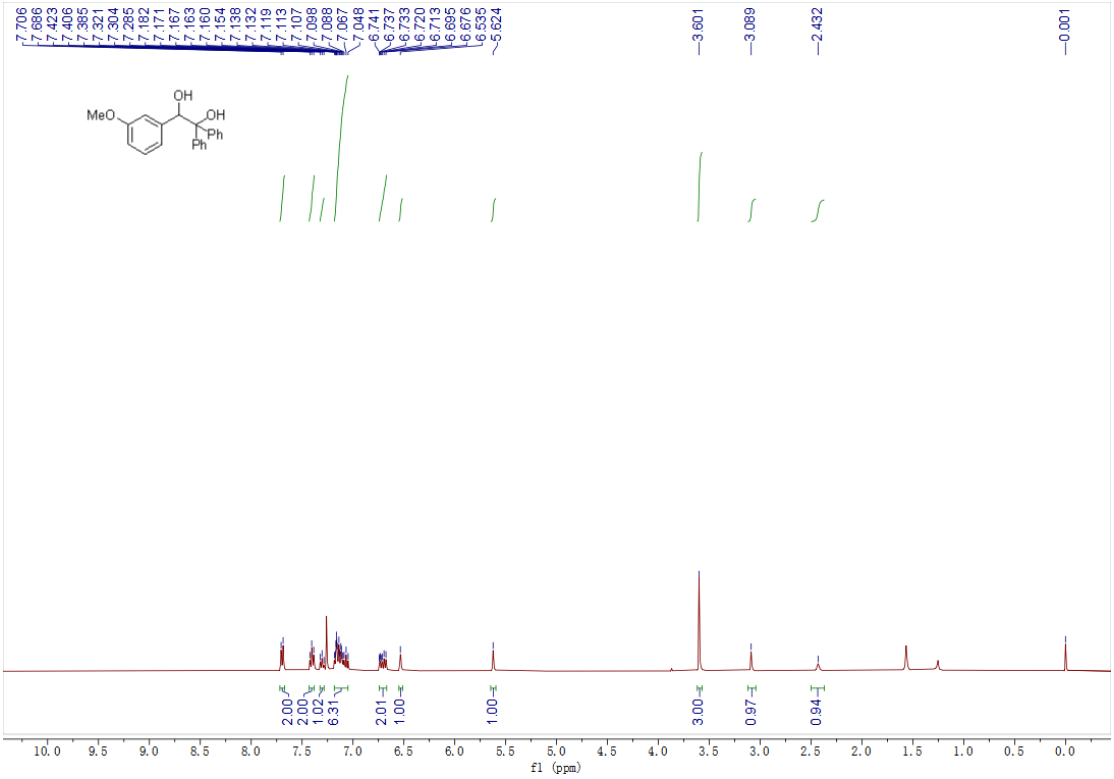
^{1}H NMR Spectrum of **8g**



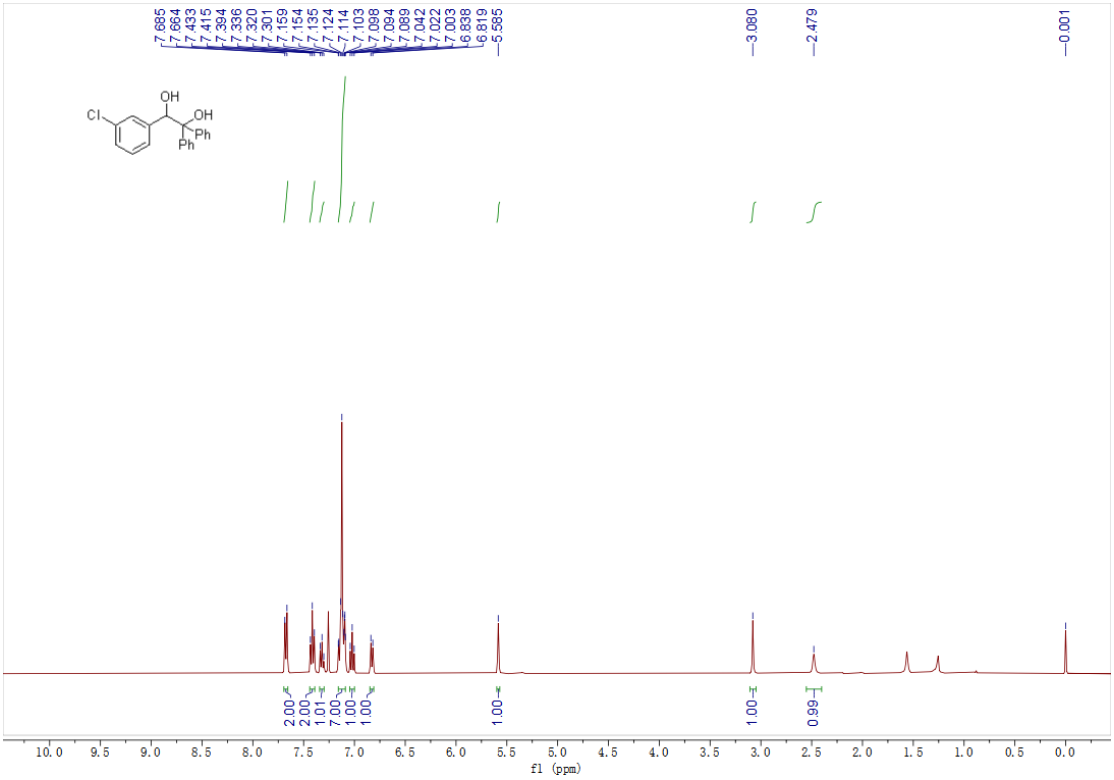
^{1}H NMR Spectrum of **8h**



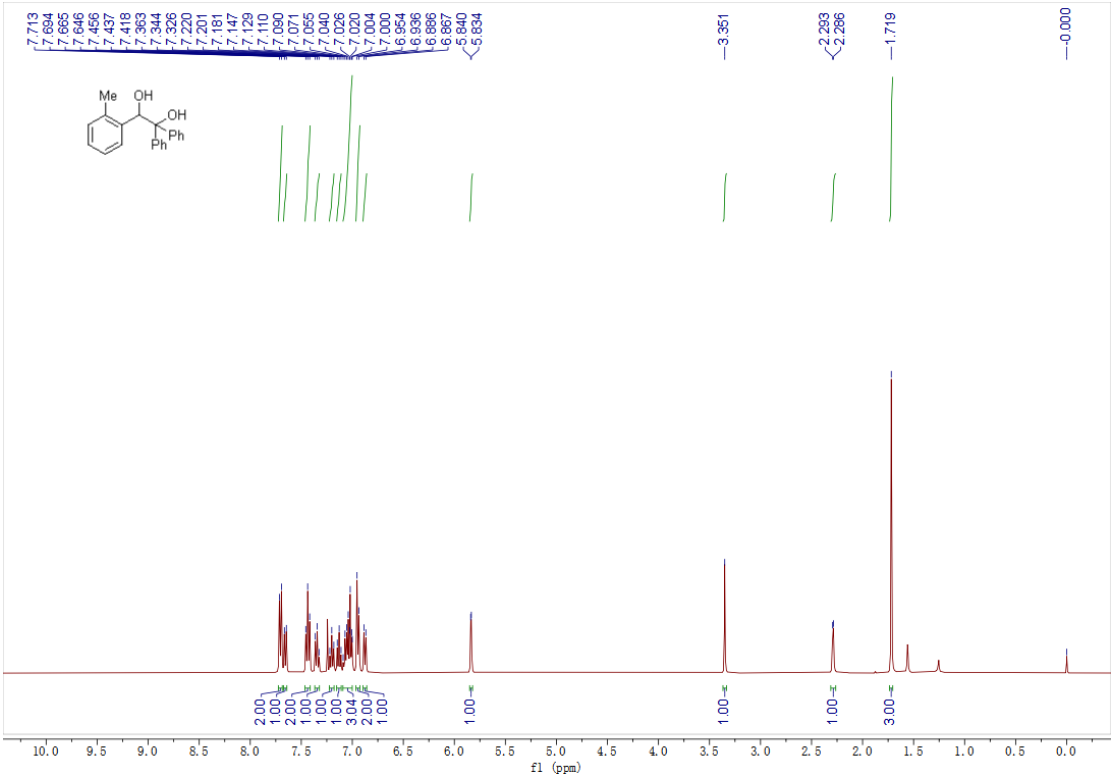
^{1}H NMR Spectrum of **8i**



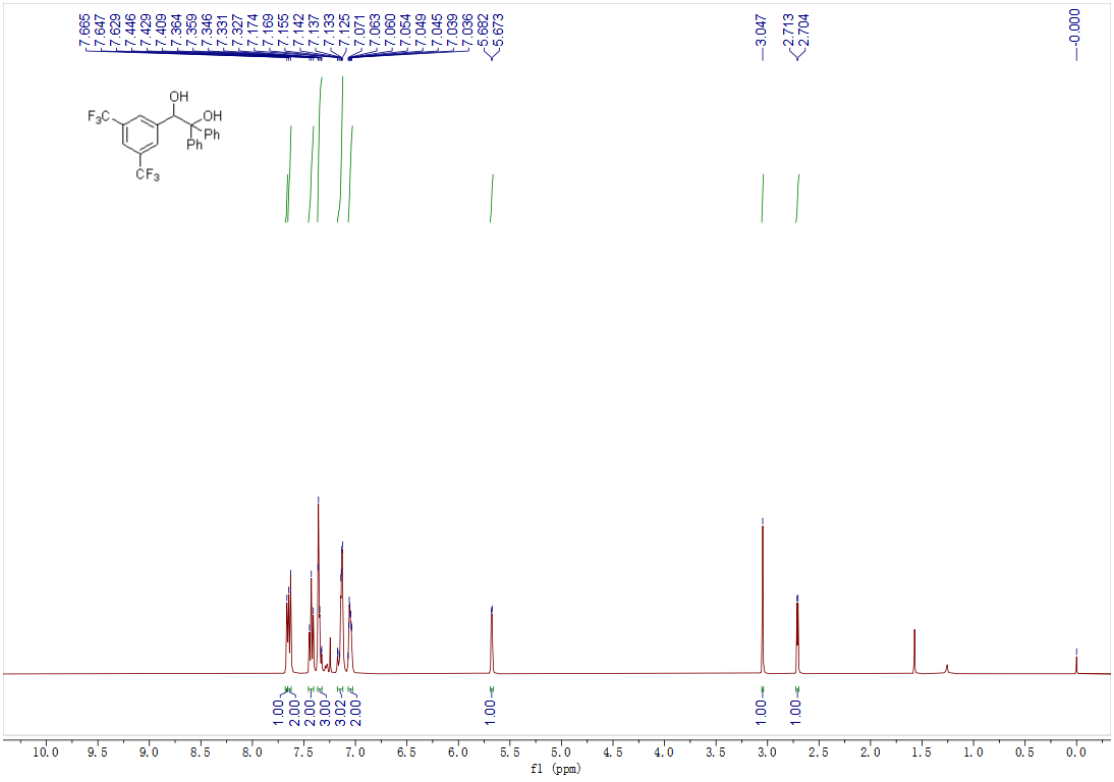
^{1}H NMR Spectrum of **8j**



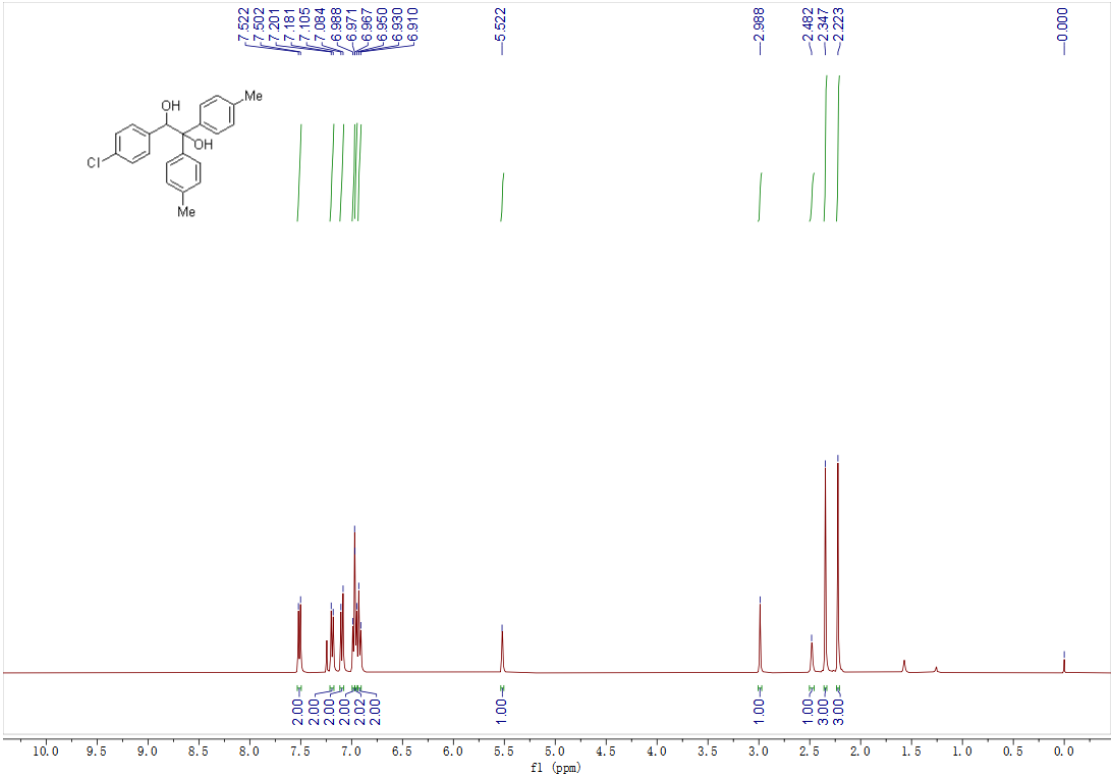
^{1}H NMR Spectrum of **8k**



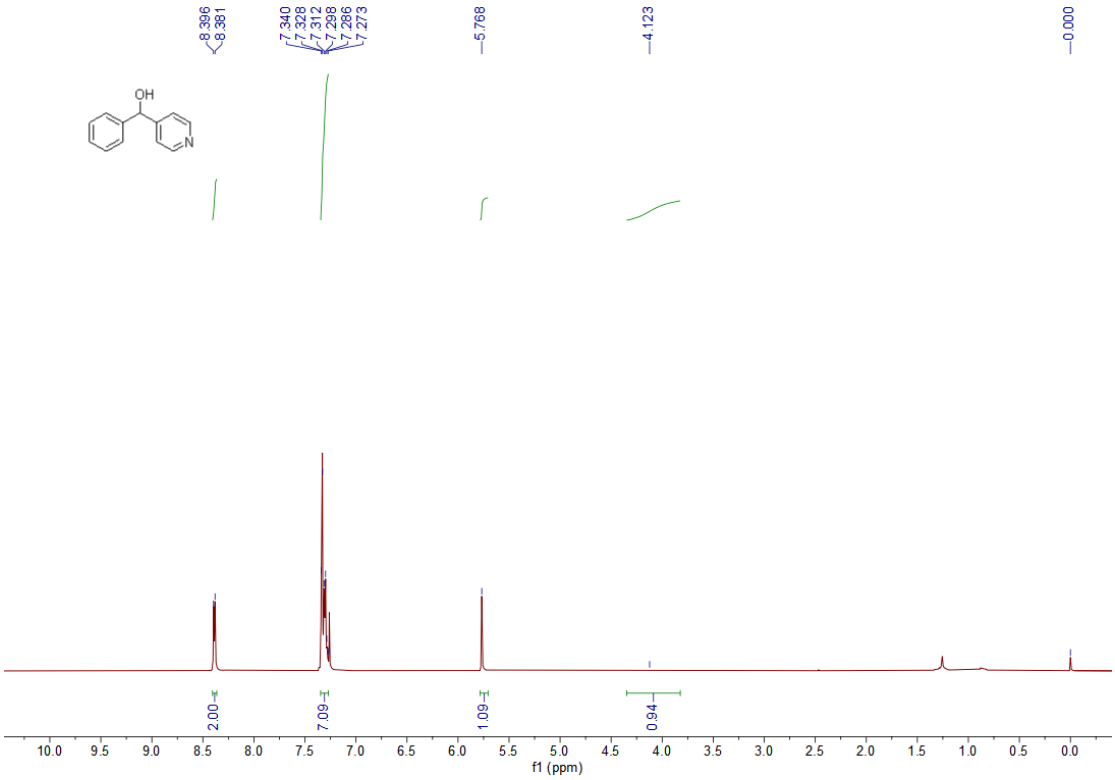
^{1}H NMR Spectrum of **8l**



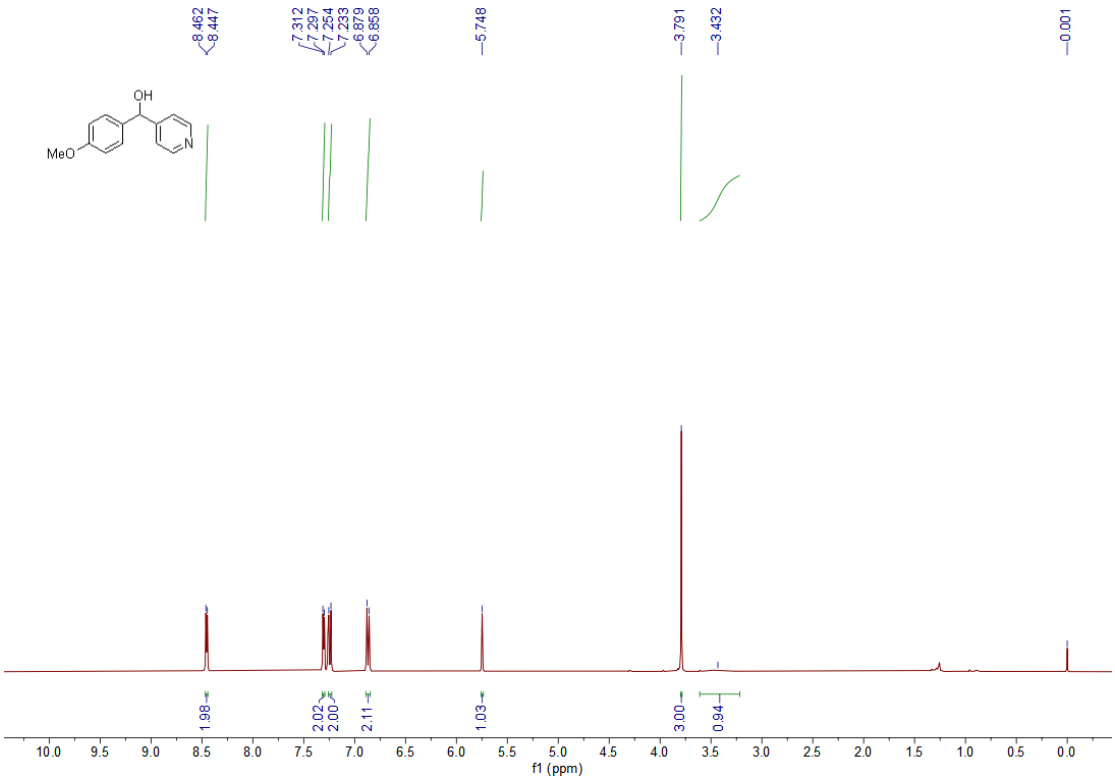
^{1}H NMR Spectrum of **8m**



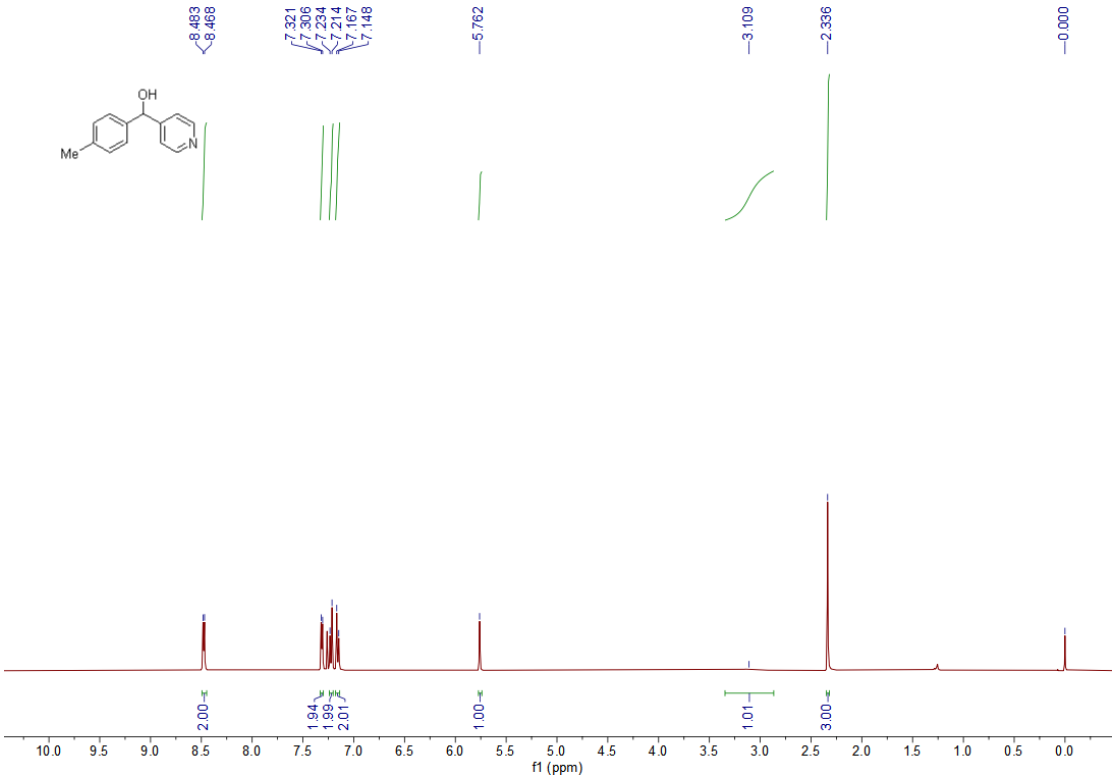
^{1}H NMR Spectrum of **10a**



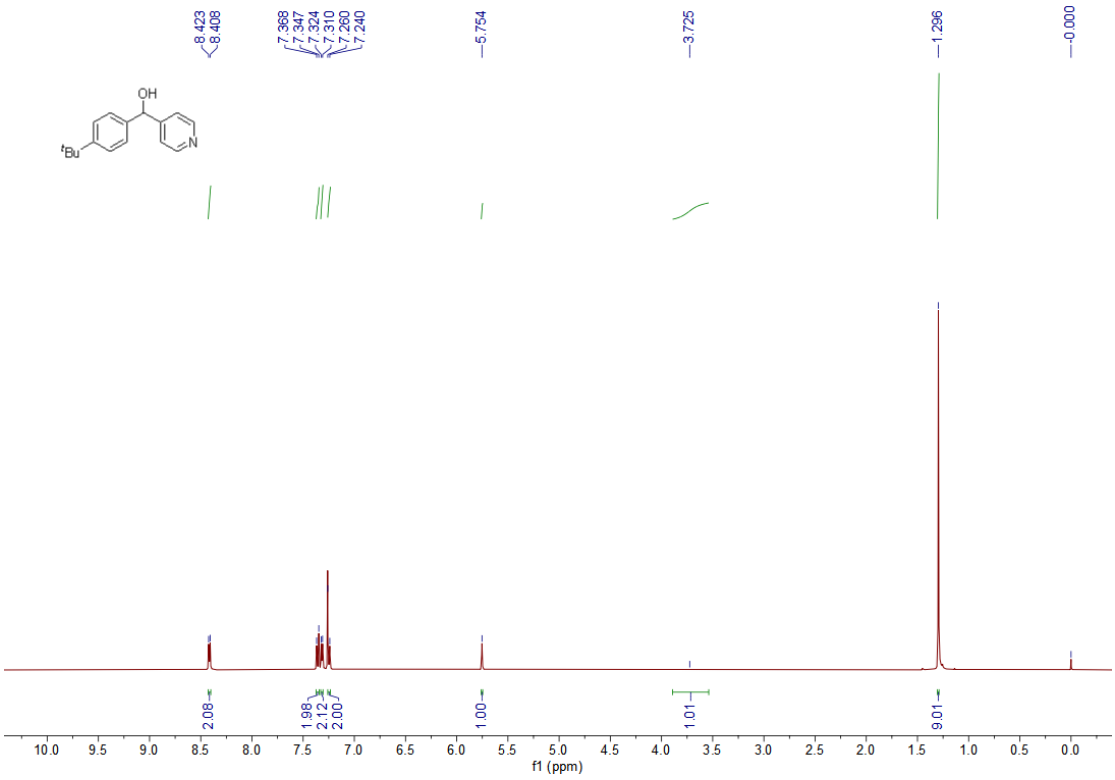
^{1}H NMR Spectrum of **10b**



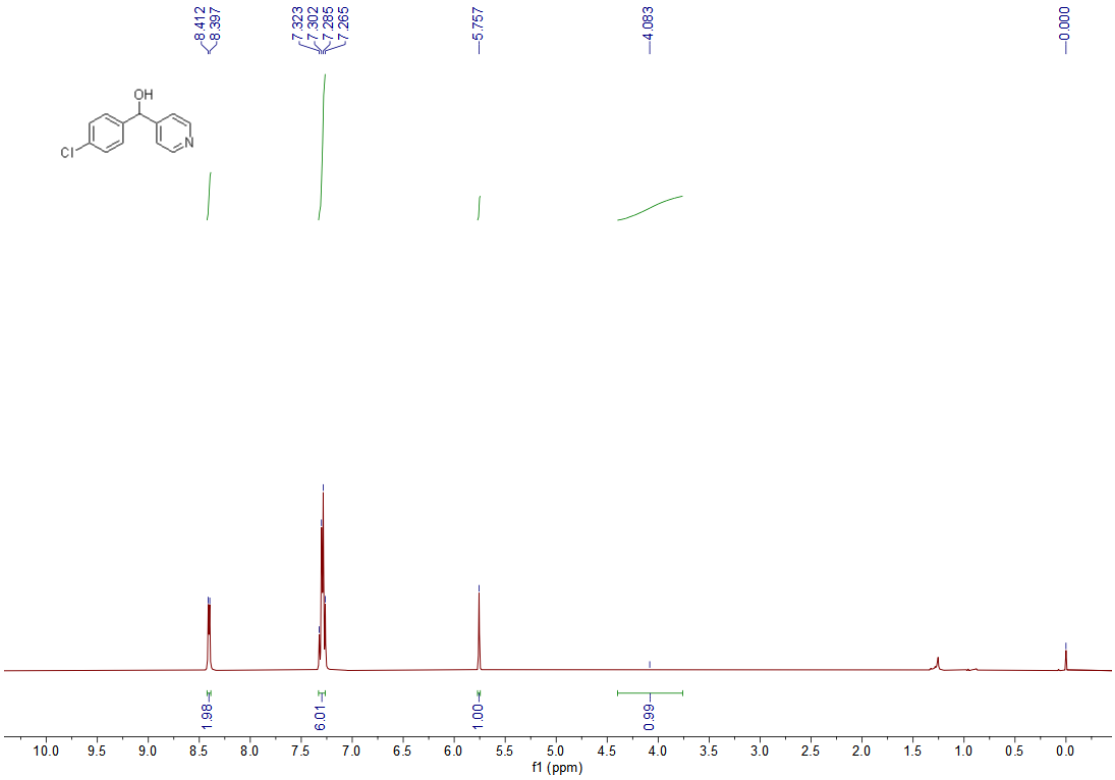
^{1}H NMR Spectrum of **10c**



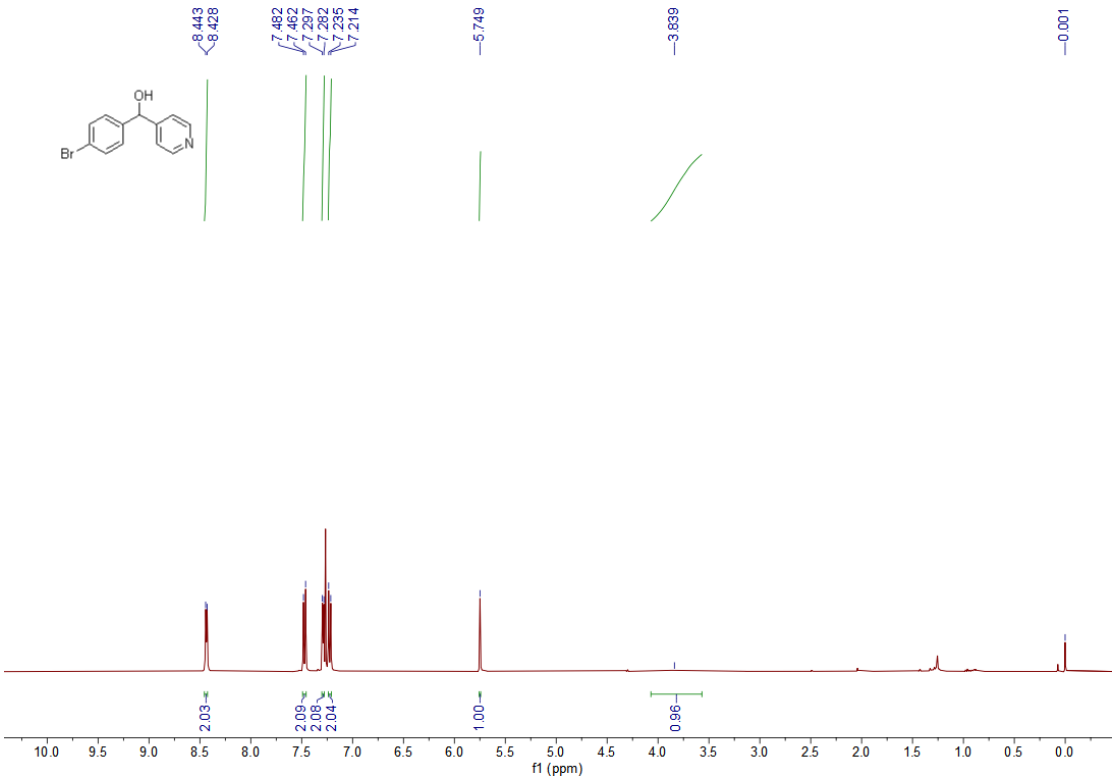
^{1}H NMR Spectrum of **10d**



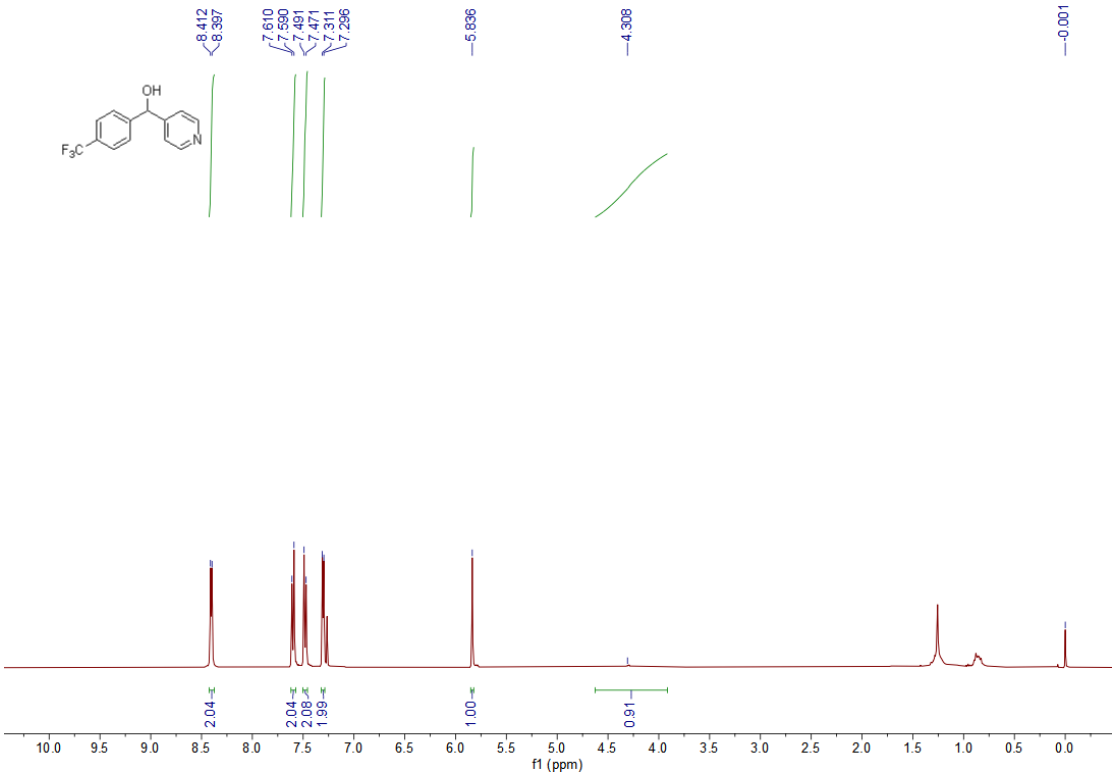
^{1}H NMR Spectrum of **10e**



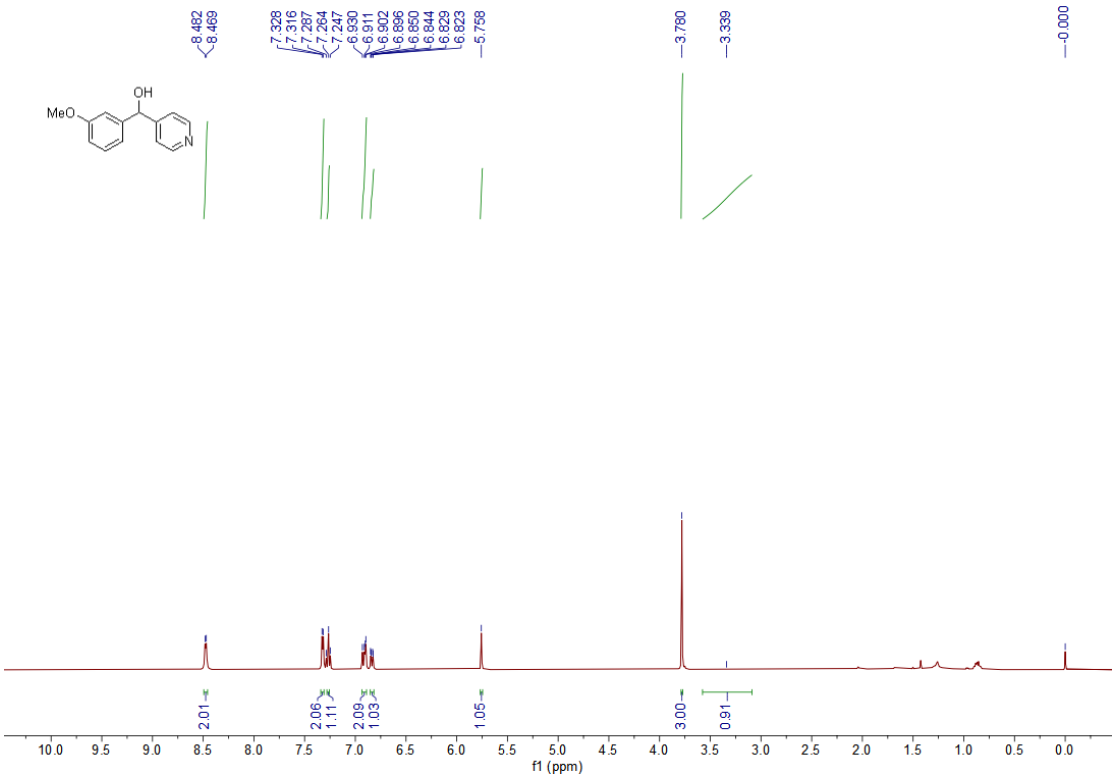
^{1}H NMR Spectrum of **10f**



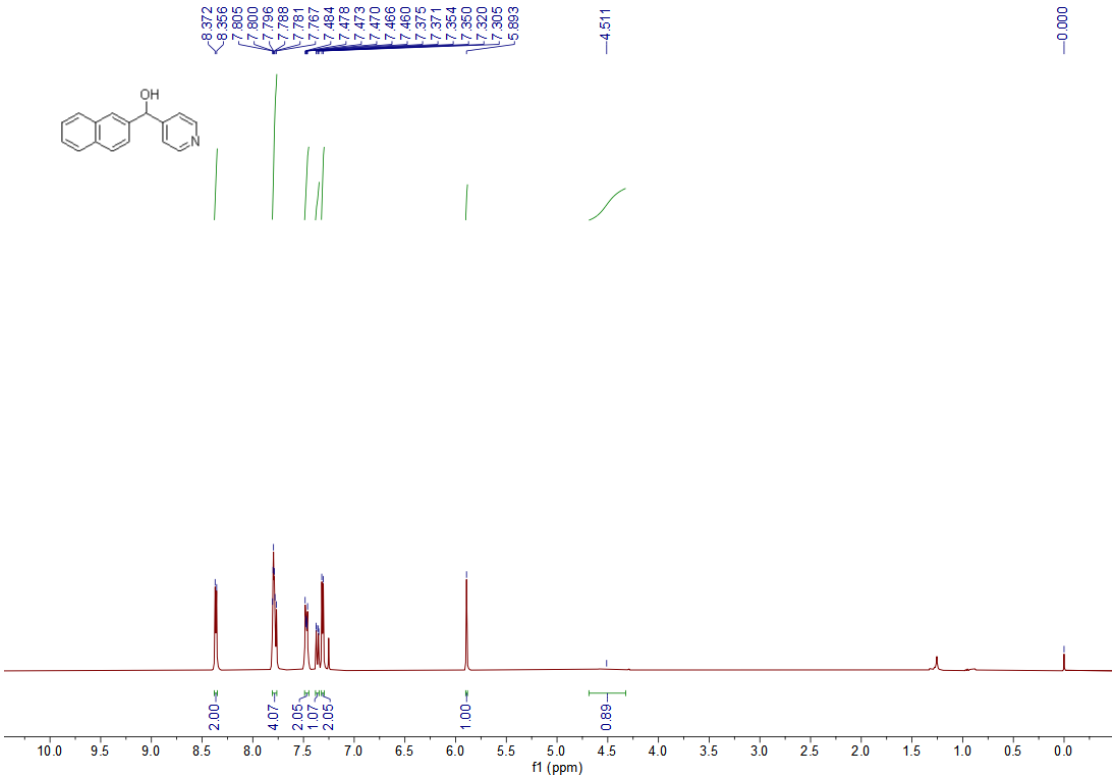
^{1}H NMR Spectrum of **10g**



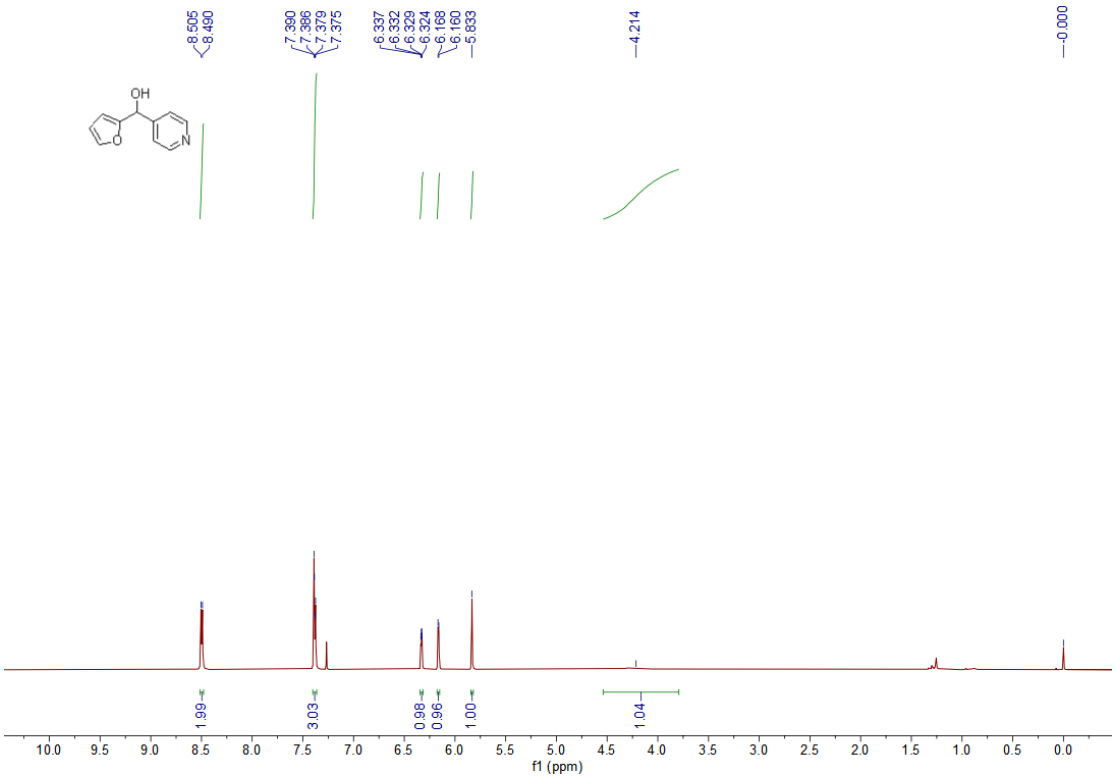
^{1}H NMR Spectrum of **10h**



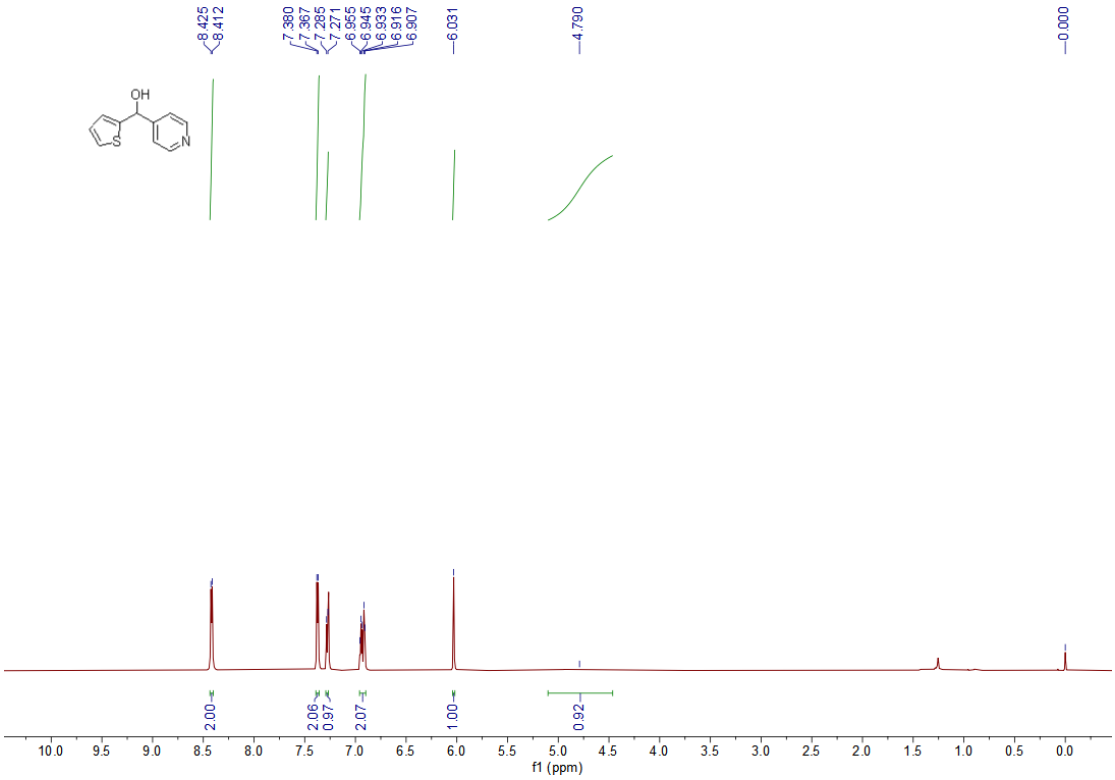
^{1}H NMR Spectrum of **10i**



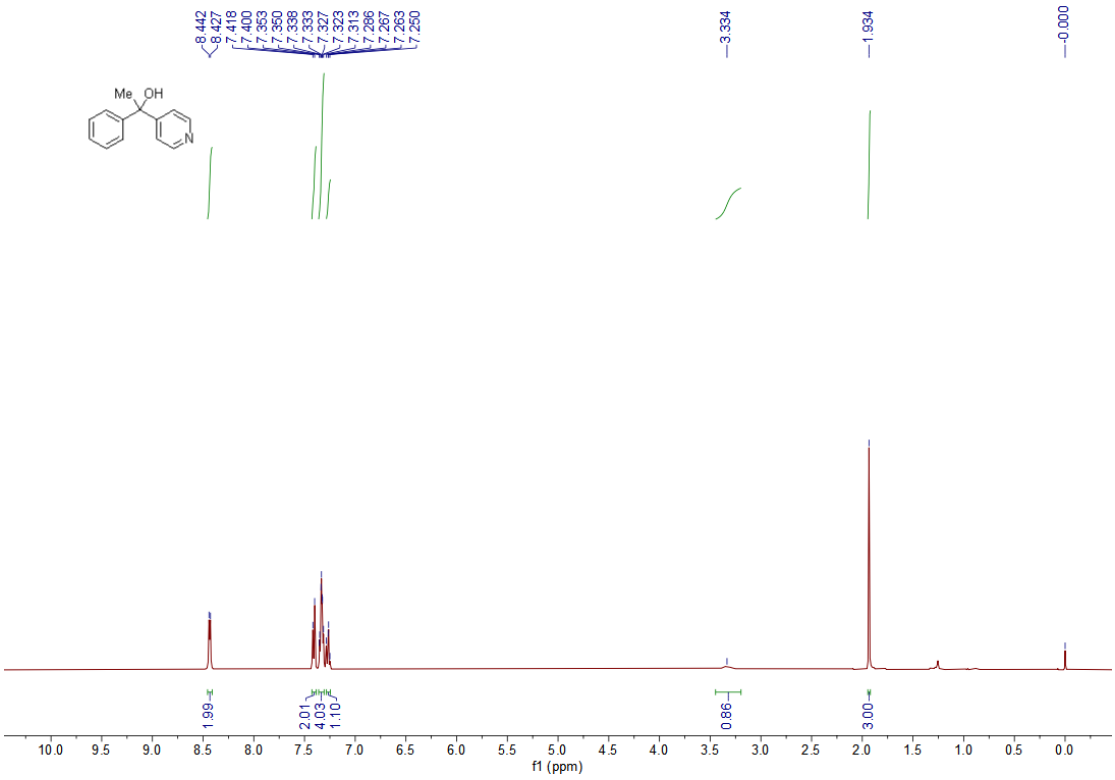
^{1}H NMR Spectrum of **10j**



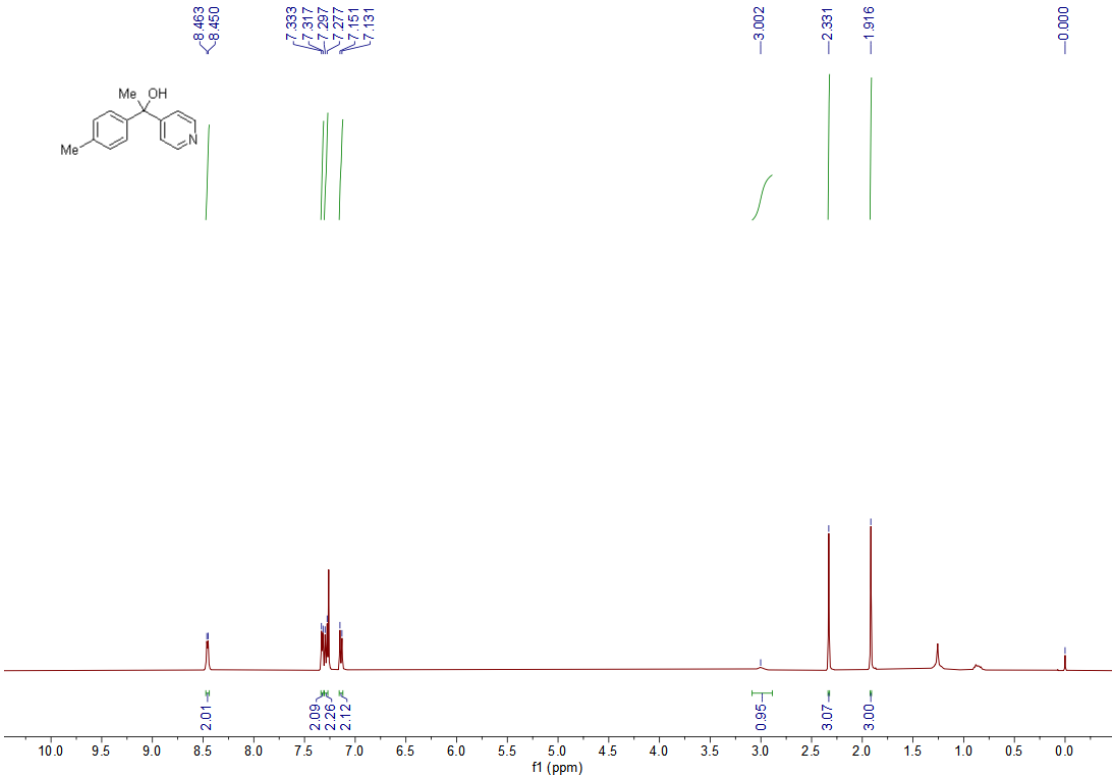
^{1}H NMR Spectrum of **10k**



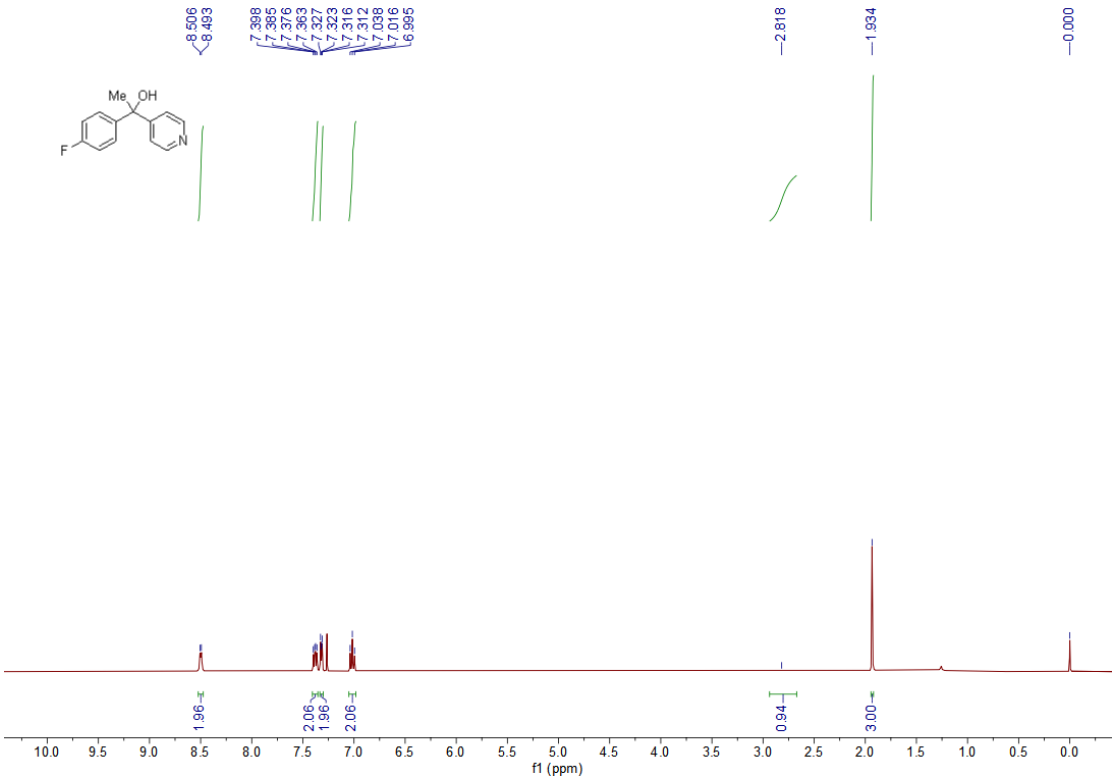
^{1}H NMR Spectrum of **10l**



^{1}H NMR Spectrum of **10m**



^{1}H NMR Spectrum of **10n**



^{1}H NMR Spectrum of **10o**