Supporting Information

Synthesis of biologically important, fluorescence active 5-hydroxy benzo[*g*]indoles through four-component domino condensations and their fluorescence "Turn-off" sensing of Fe(III) ions

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Photophysical Study

Spectroscopic grade solvents were purchased from Spectrochem, India and used without further distillation. The concentration of the ligands was maintained at 5x10-5 M. Absorption and emission measurements were performed using Hitachi UV-vis U-3501 spectrophotometer and Perkin Elmer LS-55 fluorimeter respectively. The backgrounds of the recorded spectra were appropriately subtracted with a blank solvent in order to eliminate any spectral interference. The experiments have been carried out at room temperature.

Fluorescence quantum yields (ΦF) in various solvents are determined using the following equation

$$\Phi_{sample} = [(A_{std} F_{sample} \eta^2_{sample} / A_{sample} F_{std} \eta^2_{std})] \Phi_{std}$$

In this equation Φ_{sample} and Φ_{std} are the quantum yields of sample and standard, respectively; A_{std} and A_{sample} are the absorbance of the sample and standard, respectively; F_{sample} and F_{std} are integrated emission area across the fluorescence band and η_{sample} and η_{std} are the refractive indexes of the sample and standard solution, respectively.

Table S1. Absorbance (A), fluorescence emission area (F) and refractive index (η) of **9** in different Solvents.

Compounds	Solvents	Absorbance (A)	Emission area (F)	Refractive index (η)
11u	CH_2Cl_2	0.412	33426.0203	1.4242
	CH_3CN	0.329	26286.5744	1.3460
	CH_3OH	0.292	23897.9378	1.3314
11w	CH_2Cl_2	0.470	35860.6285	1.4242
	CH_3CN	0.343	28482.5987	1.3460

	CH_3OH	0.295	26438.4931	1.3314
11v	CH_2Cl_2	0.425	29644.7671	1.4242
	CH_3CN	0.356	28117.1088	1.3460
	CH_3OH	0.296	26468.2118	1.3314

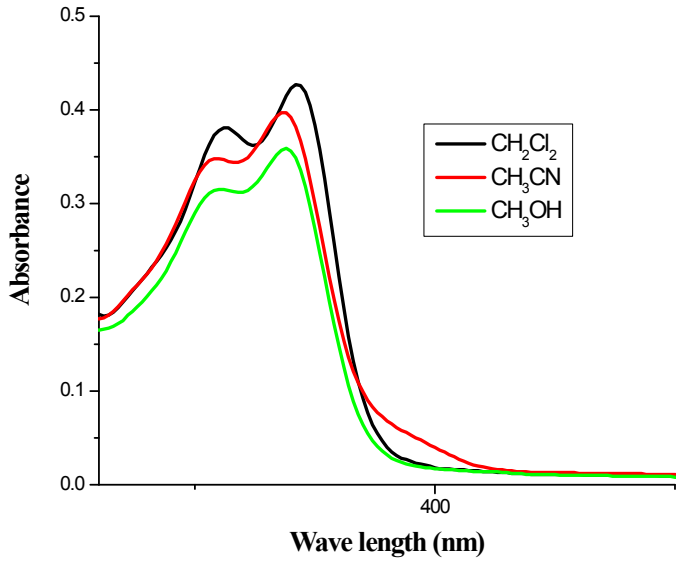


Fig. S1 UV-vis absorption spectra of compound **11v** in different solvents ([**11v**] ~ 5×10^{-5} M).

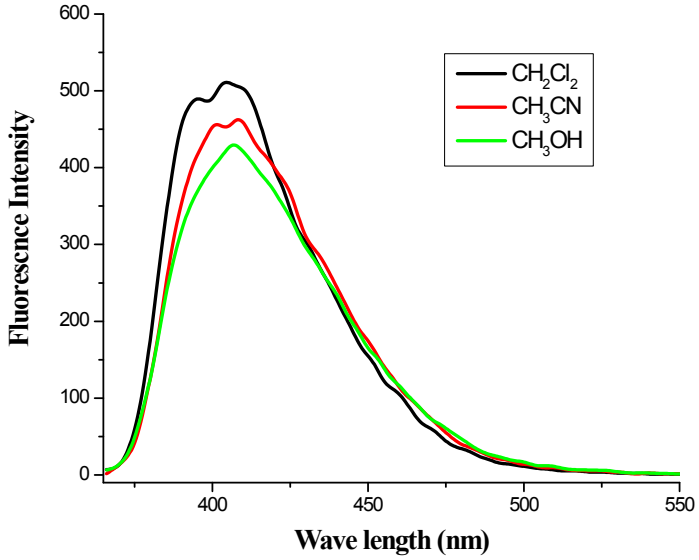


Fig. S2 Fluorescence emission spectra of **11v** in different solvents ([**11v**] ~5×10^{-5} M).

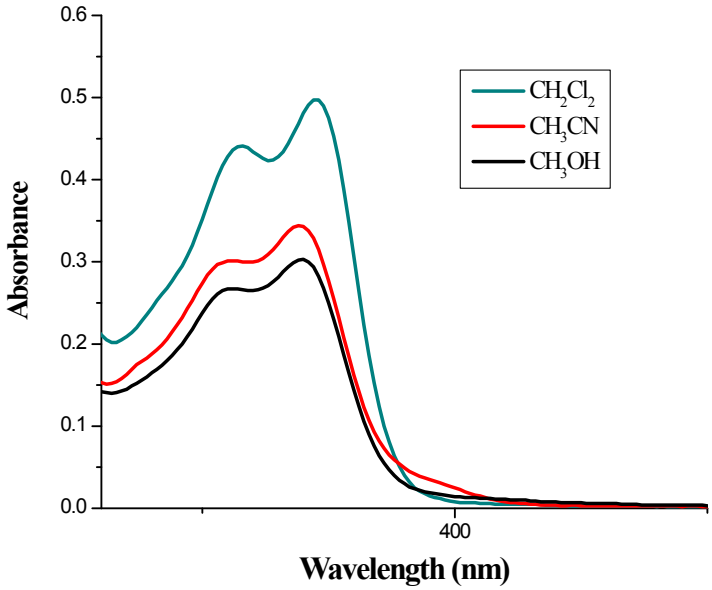


Fig. S3 UV-vis absorption spectra of compound **11w** in different solvents ([**11w**] ~ 5×10^{-5} M).

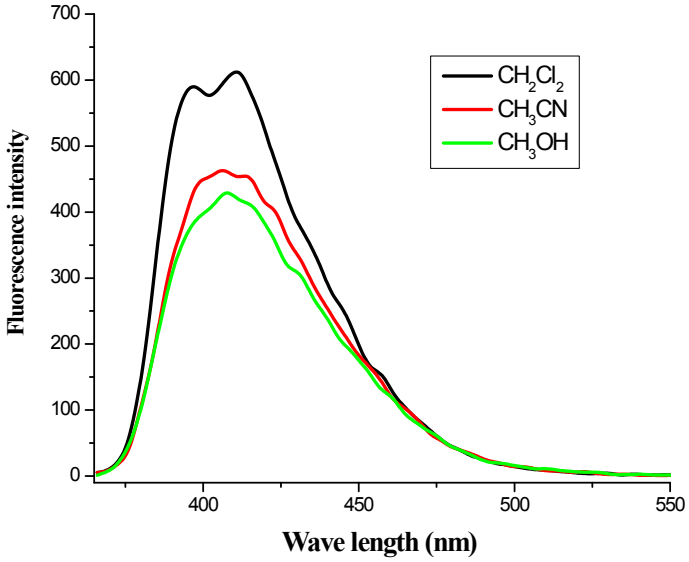


Fig. S4 Fluorescence emission spectra of **11w** in different solvents ([**11w**] ~ 5×10^{-5} M).

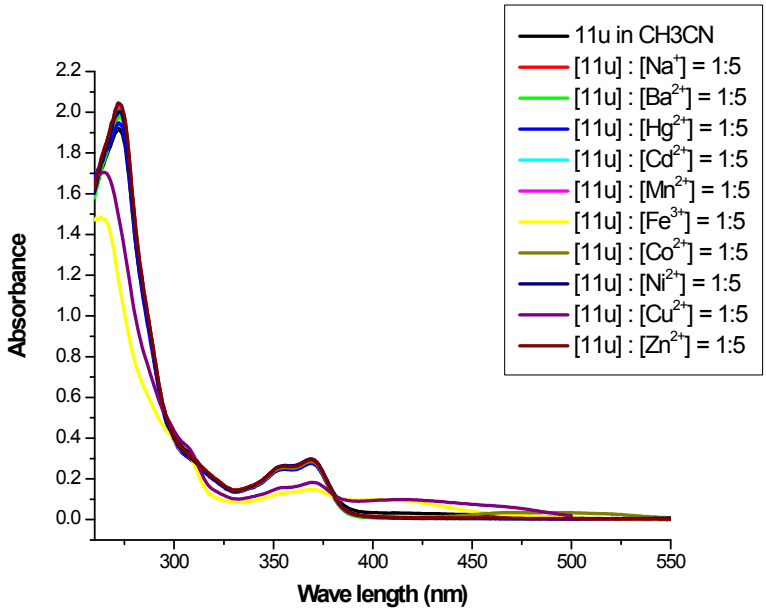


Fig. S5 UV-VIS spectra of **11u** in acetonitrile in presence of various metal ions

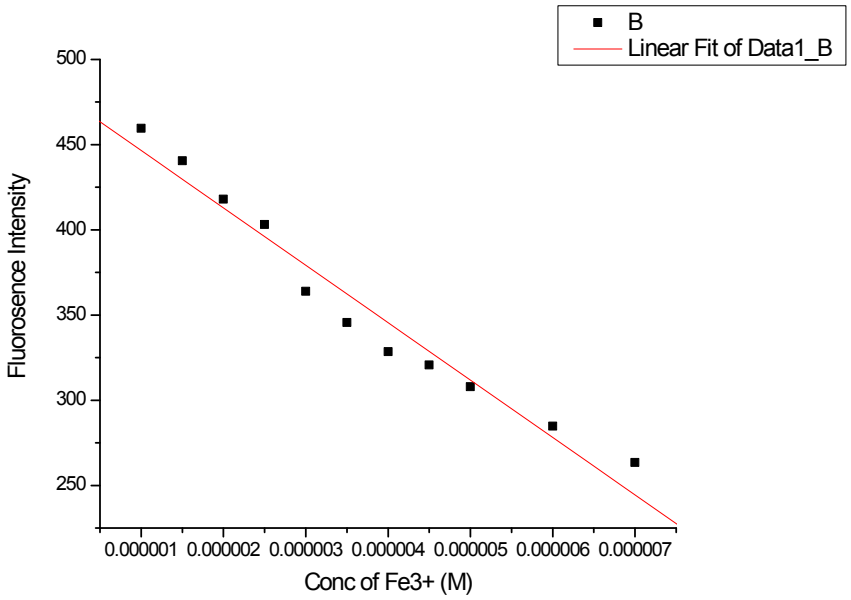


Fig. S6 Change in Fluorescence intensity of **11u** in acetonitrile upon addition of Fe^{3+}

Calculation of limit of detection

The limit of detection of Fe^{3+} has been determined from fluorescence titration curves. 15-20 blank measurements (in absence of metal ion) have been measured over an extended period of time and the standard deviation corresponding to the blank measurements have been calculated. Calibration curve has been obtained by plotting fluorescence intensity against metal (Fe^{3+}) concentration. Finally the limit of detection has been calculated using the following equation

$C_L = k * S_b / S$

C_L is the detection limit

K has been taken as 3

S_b is the standard deviation of the blank measurements

S is the slope of the calibration curve

From Graph, Limiting Concentration (C_L) = 1.2 * 10^{-6} [M]

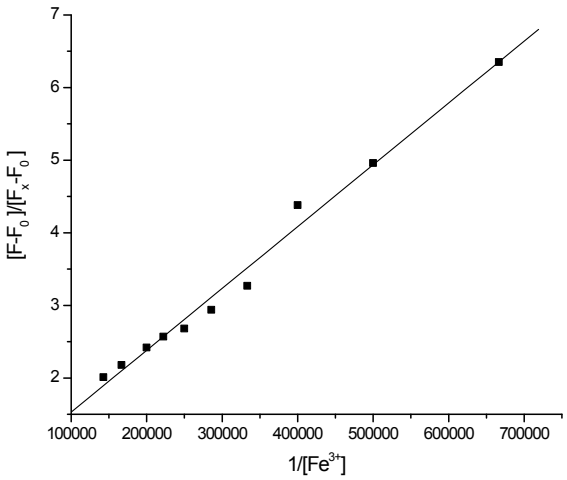


Fig. S7 Plot of $[F-F_0]/[F_x-F_0]$ vs $1/[Fe^{3+}]$ to determine Association constant (Ka) using Benesi–Hildebrand equation.

Where Fo, F, are the fluorescence intensity of Free ligand, full quenching with metal and Fx is the florescence intensity on gradual addition of metal. From slope and intercept we can have the Association constant.

From Graph,

Slope (B) = 8.51548* 10^{-6}

Intercept (A) = 0.67876

The Association constant (Ka) = A/B= 7.97 * 10^3 M^{-1}

Jobs Plot:

Ligand with Metal (Fe^{3+}) binding ratio can be easily determined from JOBS plot.

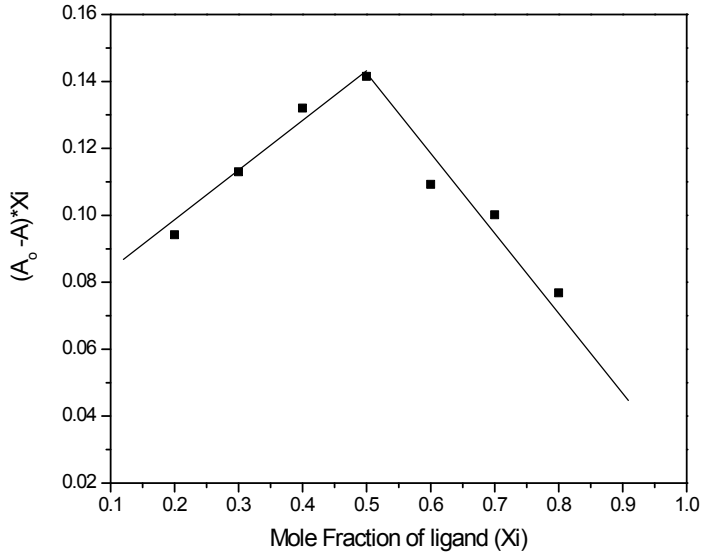


Fig. S8 Plot of $(A_0\text{-}A)^* X_i$ Vs X_i. Where Xi = mole fraction of ligand (**11u**) and A_0 is the Absorbance of pure ligand and A is the absorbance of complex in mixture.

From Graph: Fe^{3+}: 11u= 1:1 (Binding Ratio)

X-ray crystal analyses:

Crystal data for 2-[4-acetyl-5-methyl-1-*p*-tolyl-2-(4-chlorophenyl)-1*H*-3-pyrrolyl]-2-cyanoacetamide (5j): $C_{23}H_{20}ClN_3O_2$, M = 405.87, Orthorhombic, a = 10.0940(18) Å, b = 11.275(2) Å, c = 17.835(3) Å, α = 90, β = 90, γ = 90, V = 2029.7(6) Å^3, T = 296 K, space group P2(1)2(1)2(1), Z = 4, μ(MoKα) = 0.213 mm^{-1}, 9835 reflections measured, 3788 independent reflections (R_{int} = 0.0679). The final R_1 values were 0.0566 (I > 2σ(I)). The final $wR(F^2)$ values were 0.1244 ($I > 2\sigma(I)$). The final R_1 values were 0.1865 (all data). The final $wR(F^2)$ values were 0.1034 (all data). The goodness of fit on F^2 was 0.893. CCDC number 1025342.

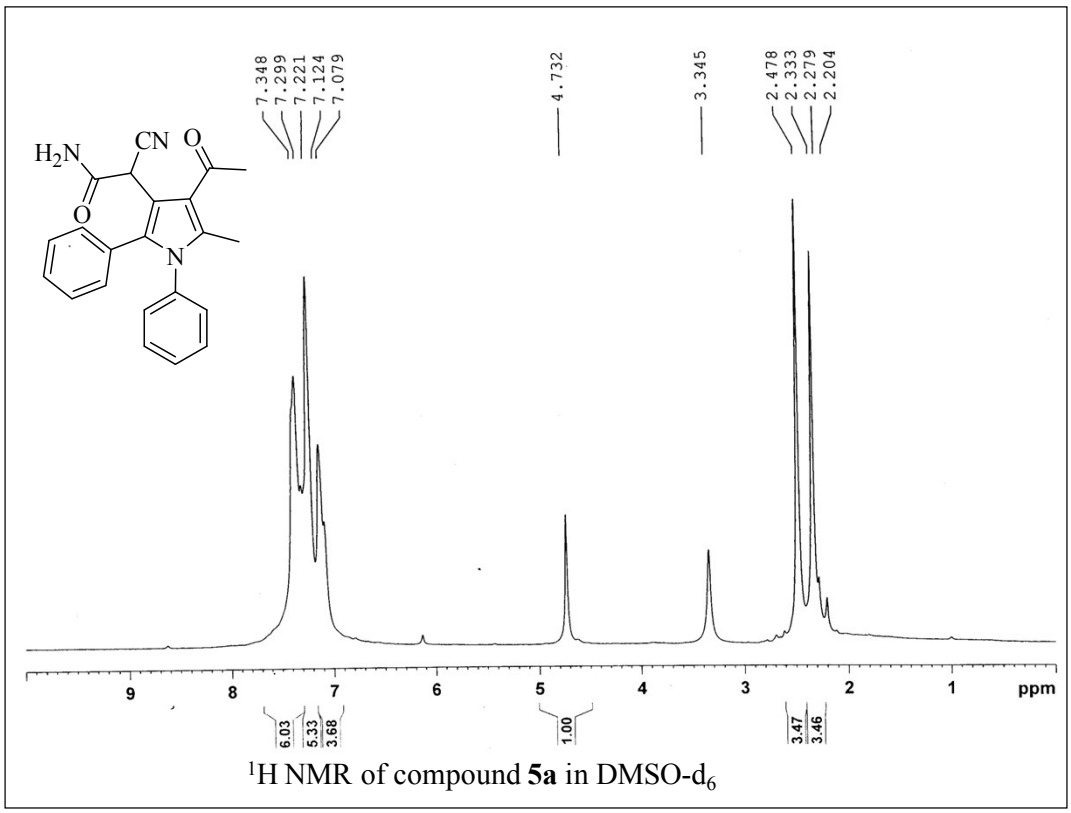
Crystal data for 3-acetyl-5-hydroxy-1-benzyl-2-methyl-1*H*-benzo[*g*]indole-4-carbonitrile (11g): $C_{23}H_{18}N_2O_2$, M = 354.39, Triclinic, a = 8.2226(7) Å, b = 9.7911(7) Å, c = 12.1078(9) Å, α = 85.263(3), β = 72.053(3), γ = 75.796(3), V = 898.97(12) Å^3, T = 296 K, space group P-1, Z = 2, μ(MoKα) = 0.085 mm^{-1}, 13318 reflections measured, 5675 independent reflections (R_{int} = 0.0446). The final R_1 values were 0.0785 (I > 2σ(I)). The final $wR(F^2)$ values were 0.2248 (I > 2σ(I)). The final R_1 values were 0.1938 (all data). The final $wR(F^2)$ values were 0.2844 (all data). The goodness of fit on F^2 was 0.970. CCDC number 1025252.

Crystal data for 3-acetyl-5-hydroxy-1-cyclopropyl-2-methyl-1*H*-benzo[*g*]indole-4-carbonitrile (11h): $C_{19}H_{16}N_2O_2$, M = 304.34, Triclinic, a = 9.4136(7) Å, b = 9.9725(7) Å, c = 10.1281(13) Å, α = 111.742(3), β = 96.696(3), γ = 116.846(2), V = 740.30(12) Å^3, T = 296 K, space group P-1, Z = 2, μ(MoKα) = 0.090 mm^{-1}, 10092 reflections measured, 3771 independent reflections (R_{int} = 0.0285). The final R_1 values were 0.0551 (I > 2σ(I)). The final $wR(F^2)$ values were 0.1347 (I > 2σ(I)). The final R_1 values were 0.0737 (all data). The final $wR(F^2)$ values were 0.1494 (all data). The goodness of fit on F^2 was 1.015. CCDC number 1025253.

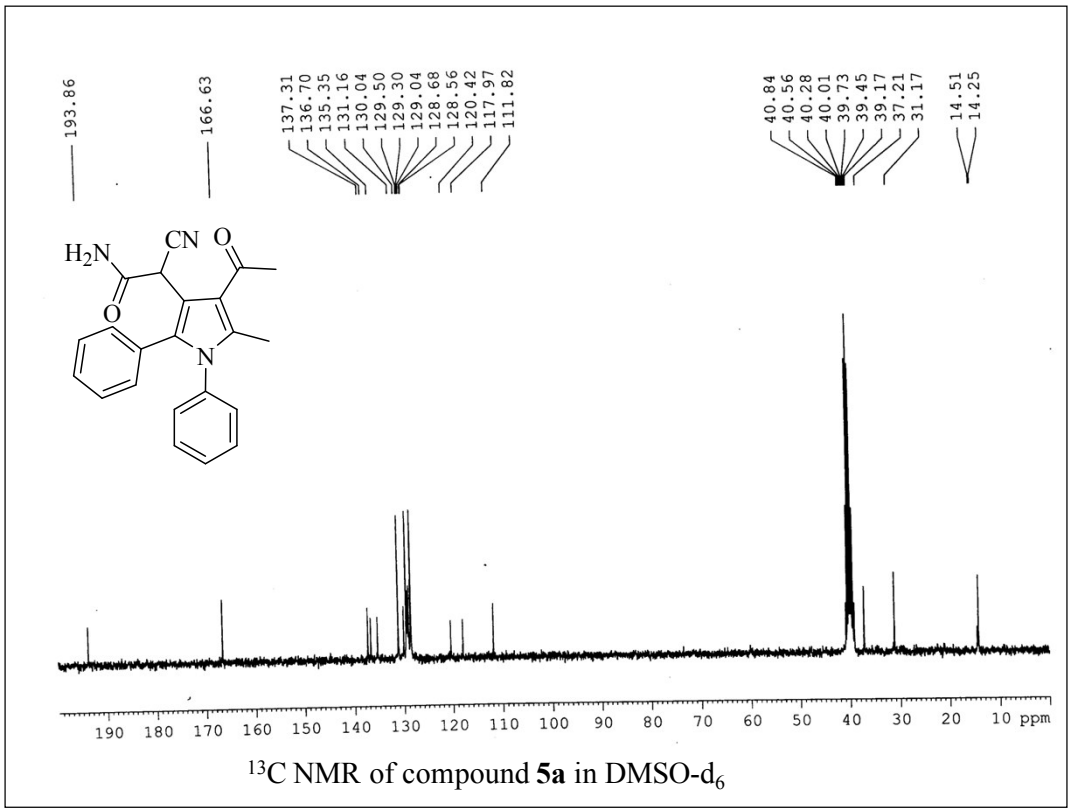
Crystal data for 3-Carboethoxy-5-hydroxy-1-phenyl-2-methyl-1*H*-benzo[*g*]indole-4-carbonitrile (11u): $C_{23}H_{18}N_2O_2$, M = 370.41, Orthorhombic, a = 13.1523(11) Å, b = 14.8790(12) Å, c = 19.1293(15) Å, α = 90, β = 90, γ = 90, V = 3743.5(5) Å^3, T = 296 K, space group Pbca, Z = 8, μ(MoKα) = 0.088 mm^{-1}, 49294 reflections measured, 5650 independent reflections (R_{int} = 0.0948). The final R_1 values were 0.0687 (I > 2σ(I)). The final $wR(F^2)$ values were 0.1693 (I > 2σ(I)). The final R_1 values were 0.1729 (all data). The final $wR(F^2)$ values were 0.2103 (all data). The goodness of fit on F^2 was 0.957. CCDC number 1042549.

General Information:

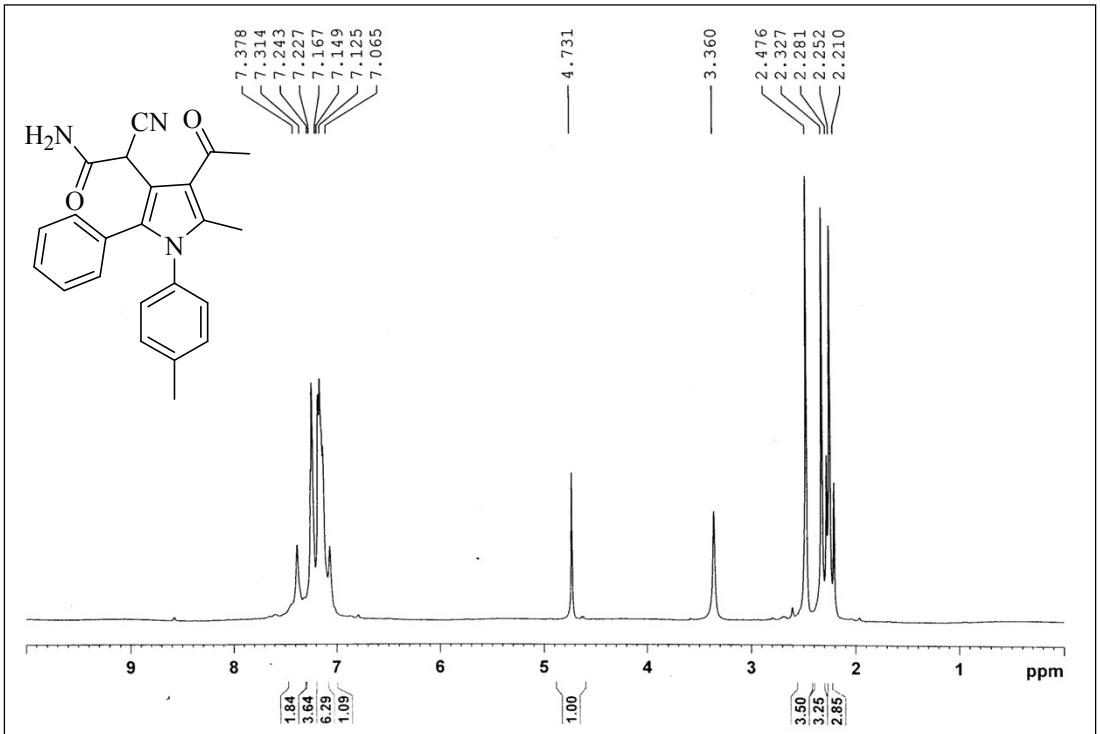
Starting materials and solvents were purchased from commercial suppliers and used without further purification. Melting points were determined in open capillary tubes and were uncorrected. IR spectra were recorded on a Perkin-Elmer 782 spectrophotometer. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on Bruker 300 MHz instrument in [D_6]DMSO. Elemental analyses (C, H and N) were performed using Perkin-Elmer 240C elemental analyzer. . The Xray diffraction data for crystallized compounds were collected with MoKα radiation at 296Kusing the Bruker APEX-II CCD System. The crystals were positioned at 50 mm from the CCD. Frames were measured with a counting time of 5s. Data analyses were carried out with the Bruker APEX2 and Bruker SAINT program. The structures were solved using direct methods with the Shelxs97 program (Sheldrick, 2008).



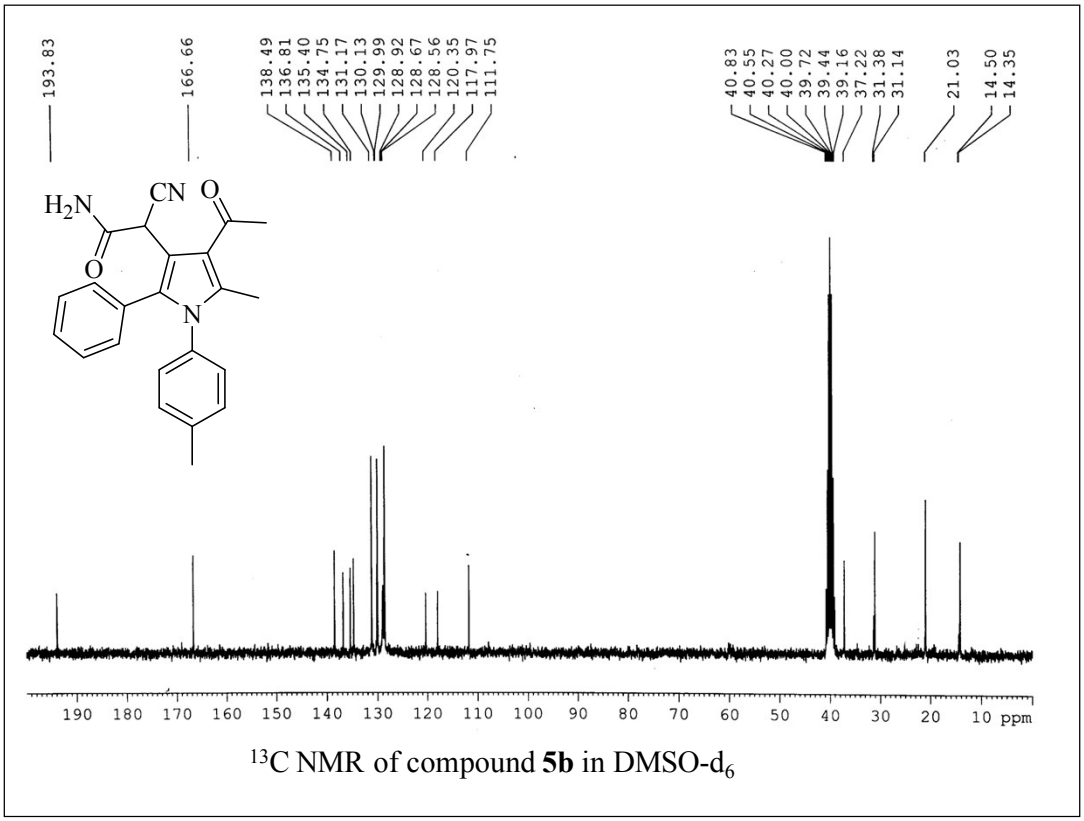
^{1}H NMR of compound **5a** in DMSO-d_6



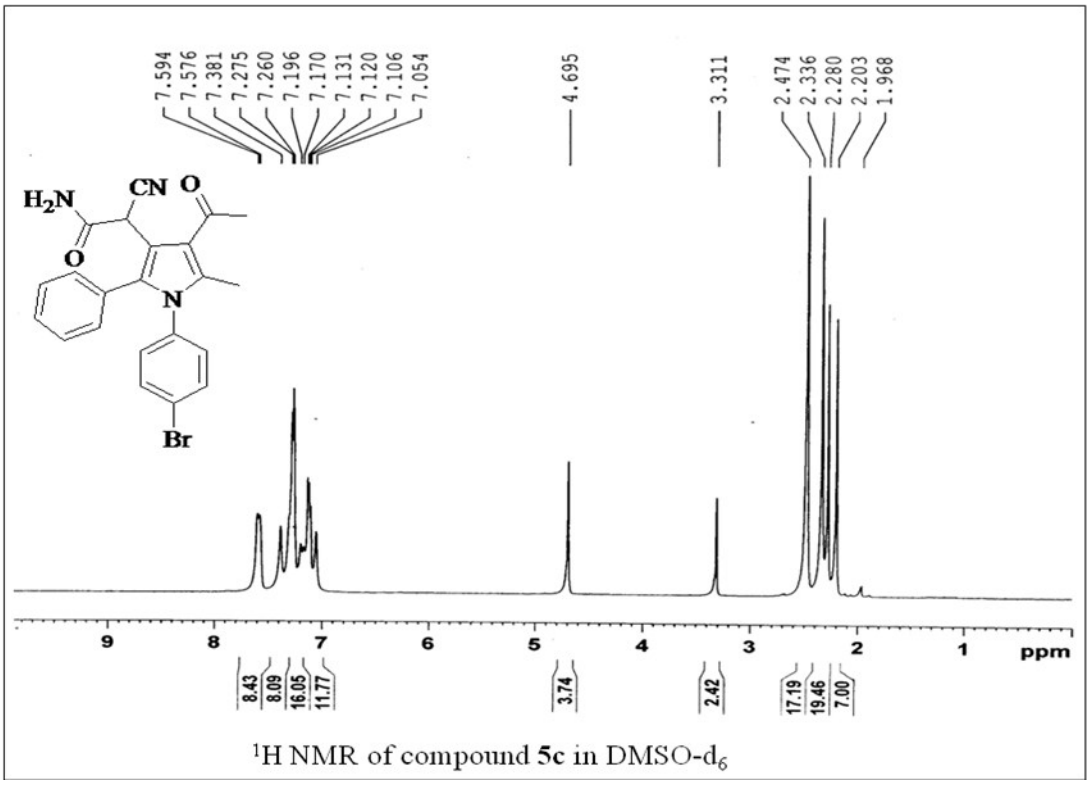
^{13}C NMR of compound **5a** in DMSO-d_6



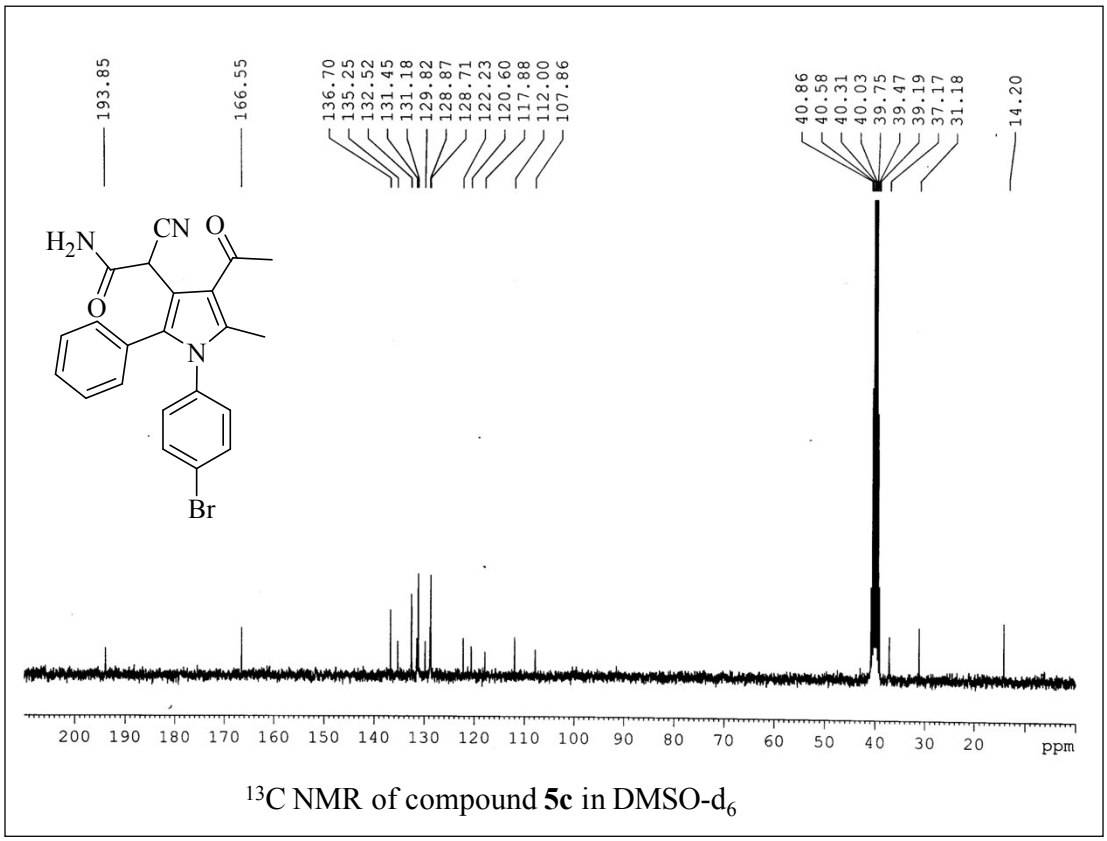
^{1}H NMR of compound **5b** in DMSO-d_6



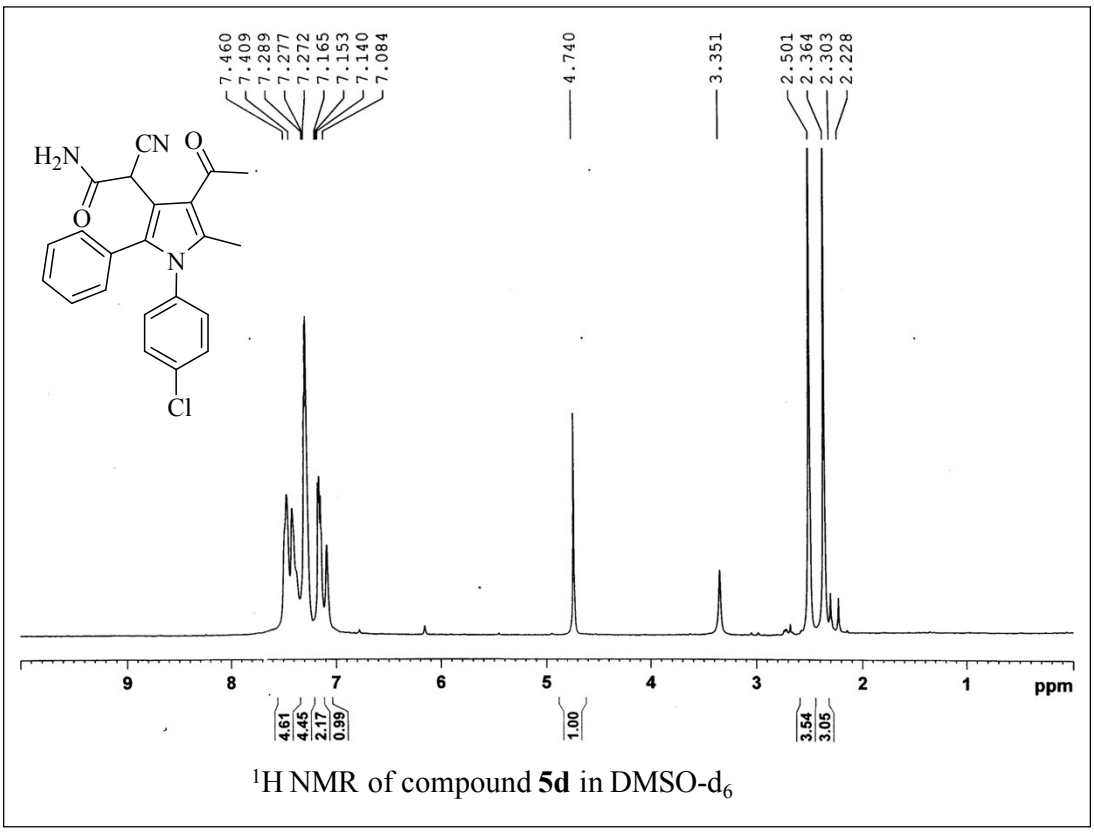
^{13}C NMR of compound **5b** in DMSO-d_6



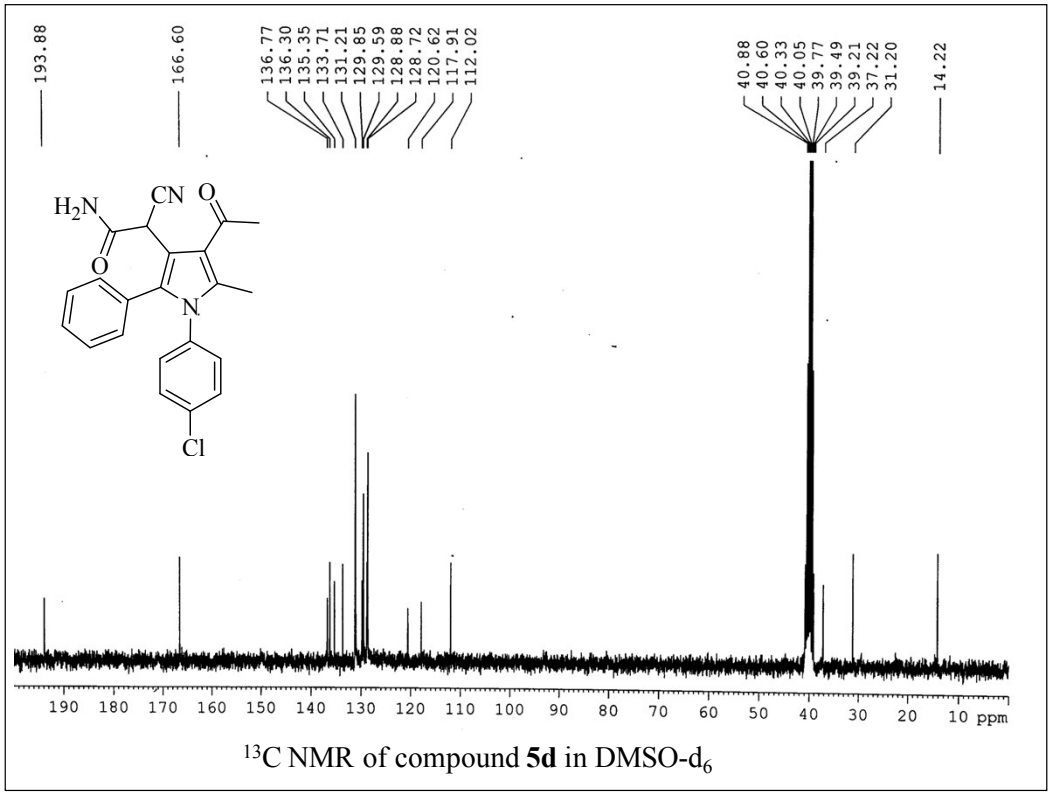
^{1}H NMR of compound **5c** in DMSO-d_6



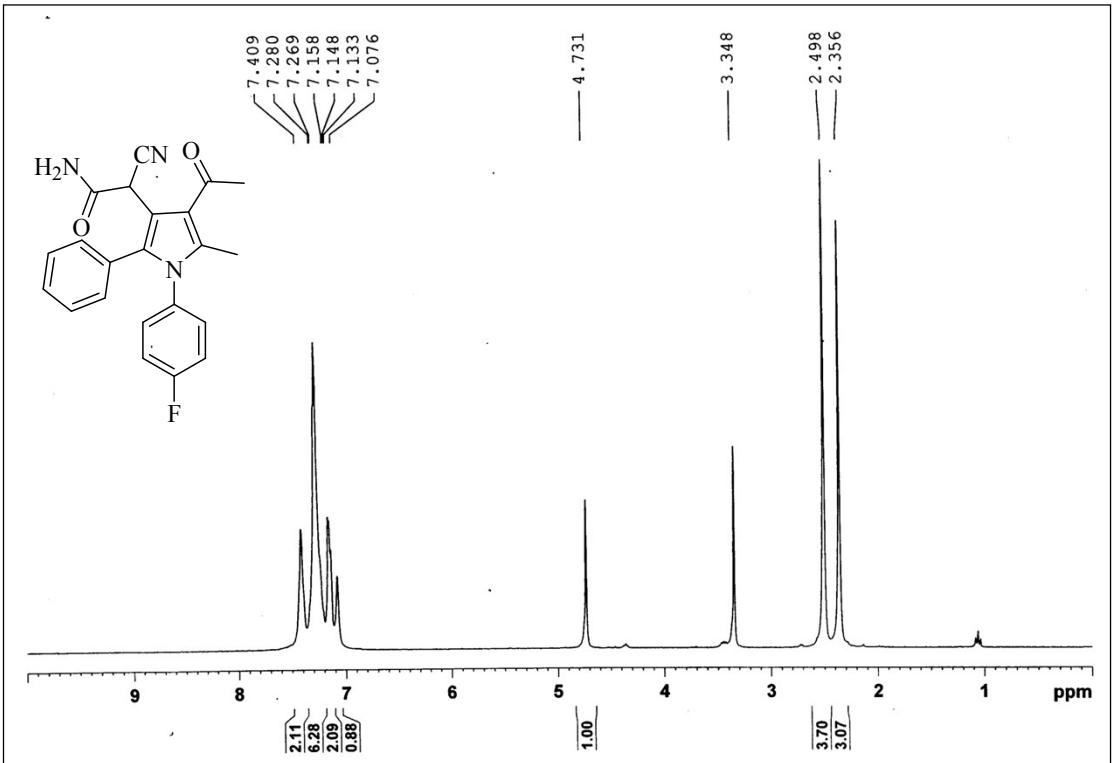
^{13}C NMR of compound **5c** in DMSO-d_6



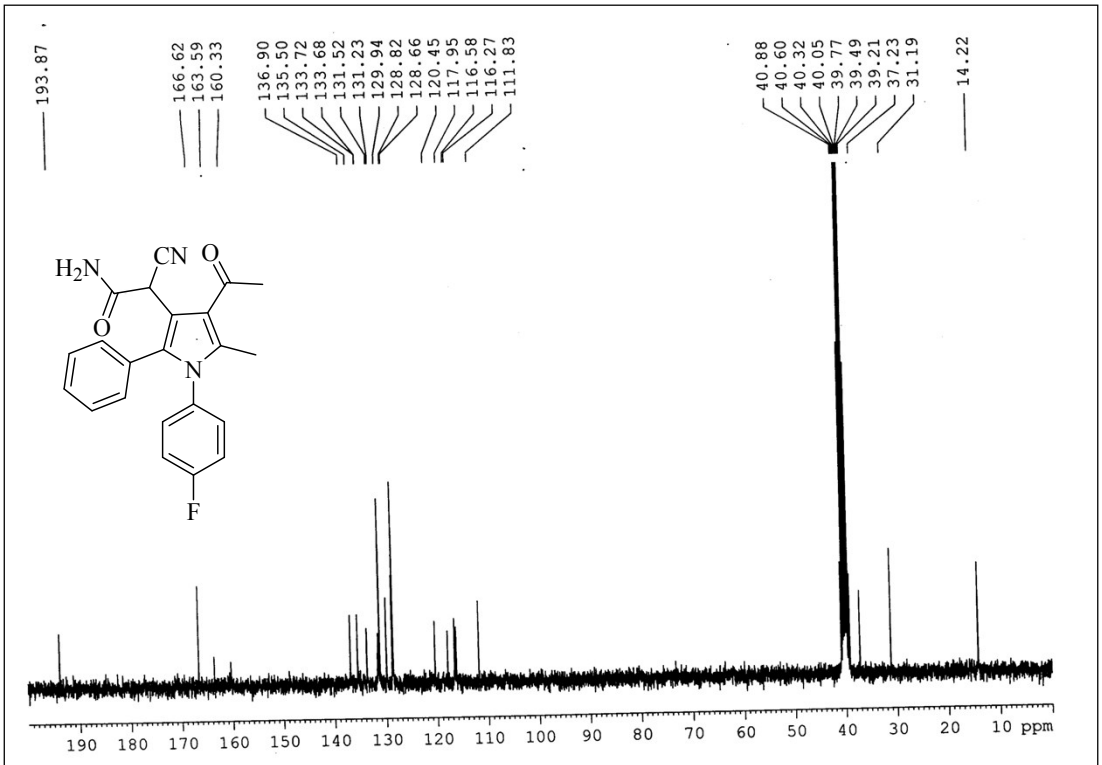
^{1}H NMR of compound **5d** in DMSO-d_6



^{13}C NMR of compound **5d** in DMSO-d_6



^{1}H NMR of compound **5e** in DMSO-d_6



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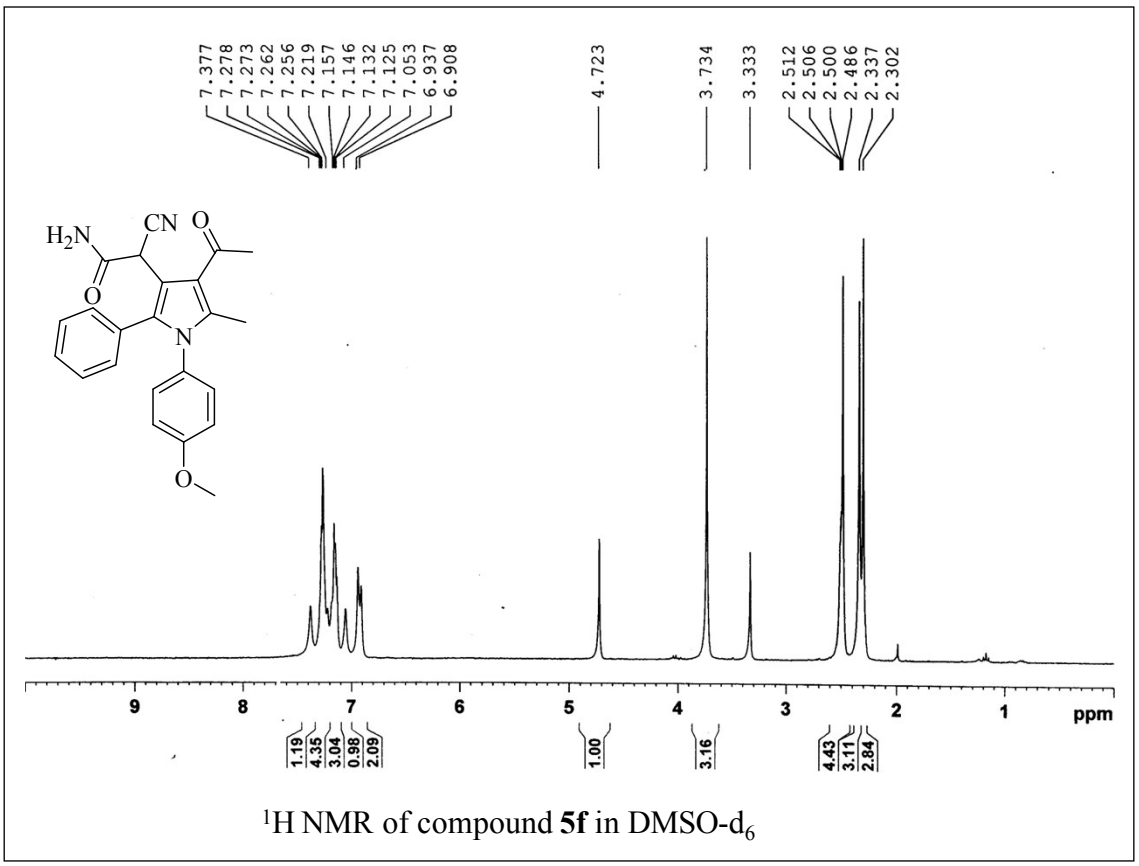
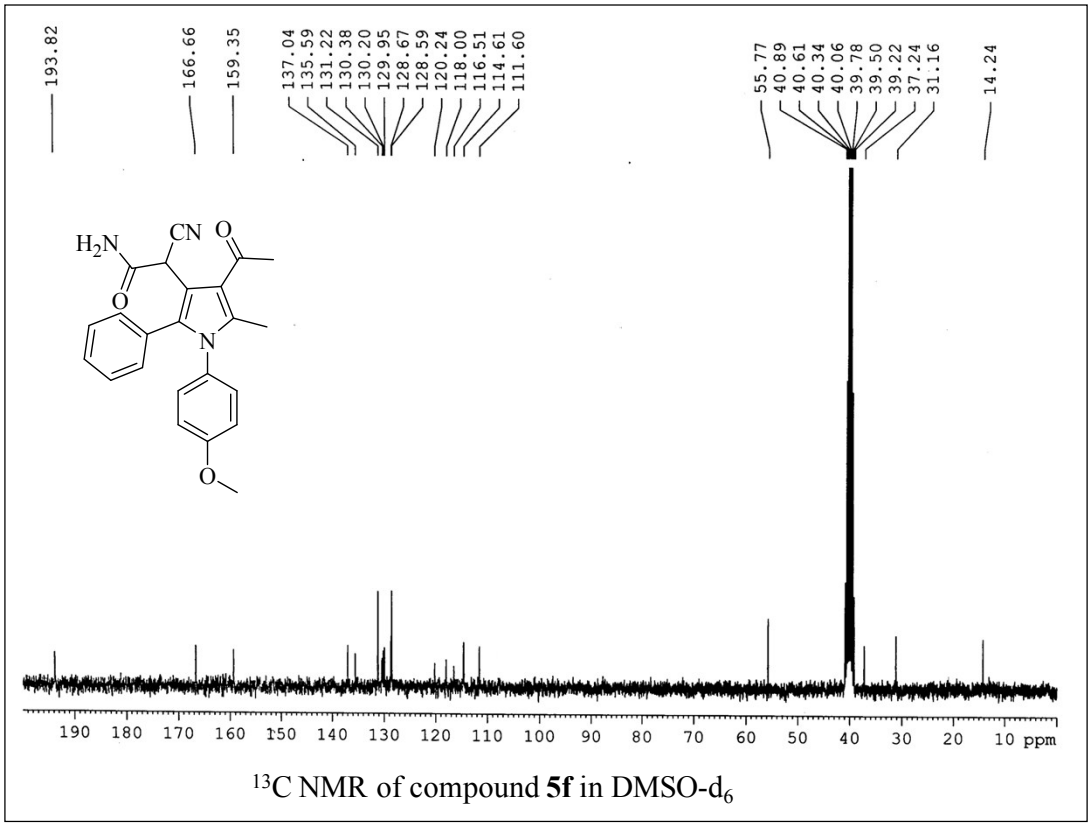
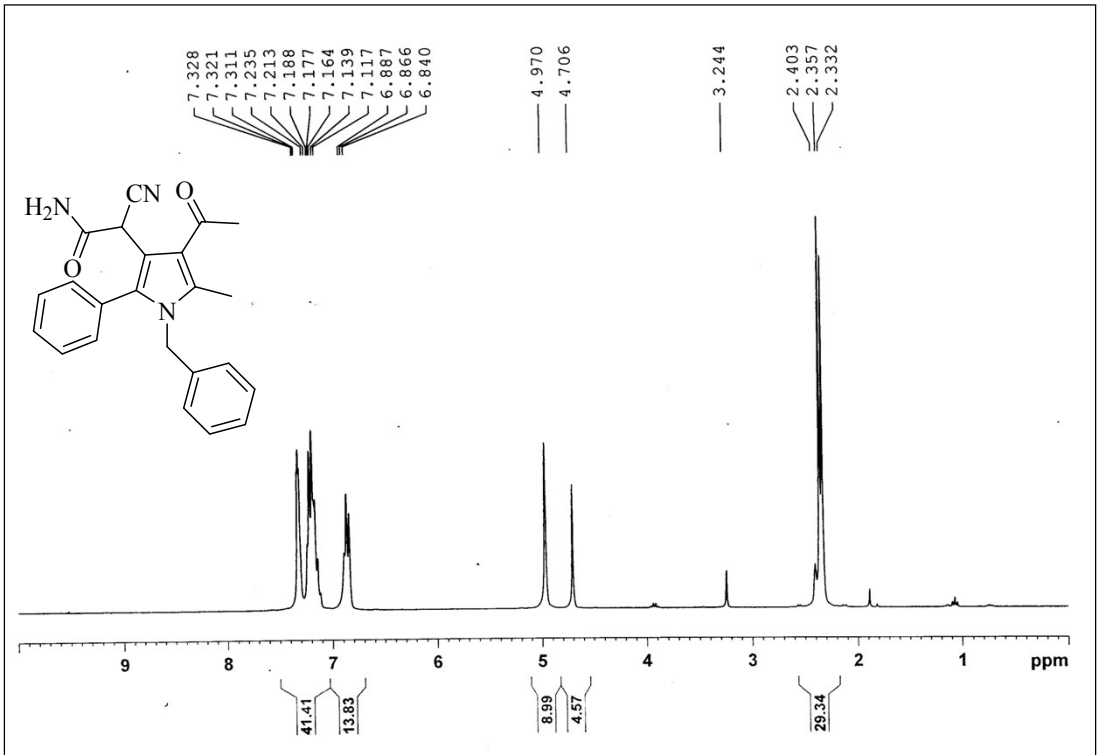


^{1}H NMR of compound **5f** in DMSO-d_6



^{13}C NMR of compound **5f** in DMSO-d_6



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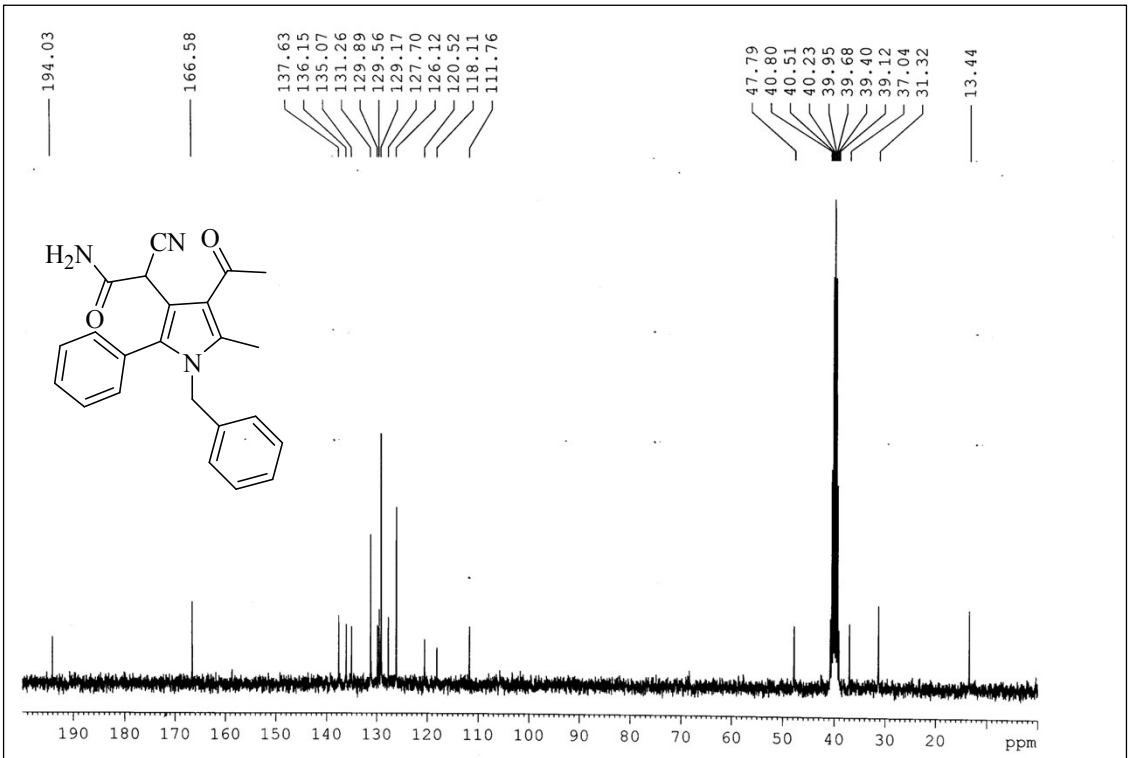

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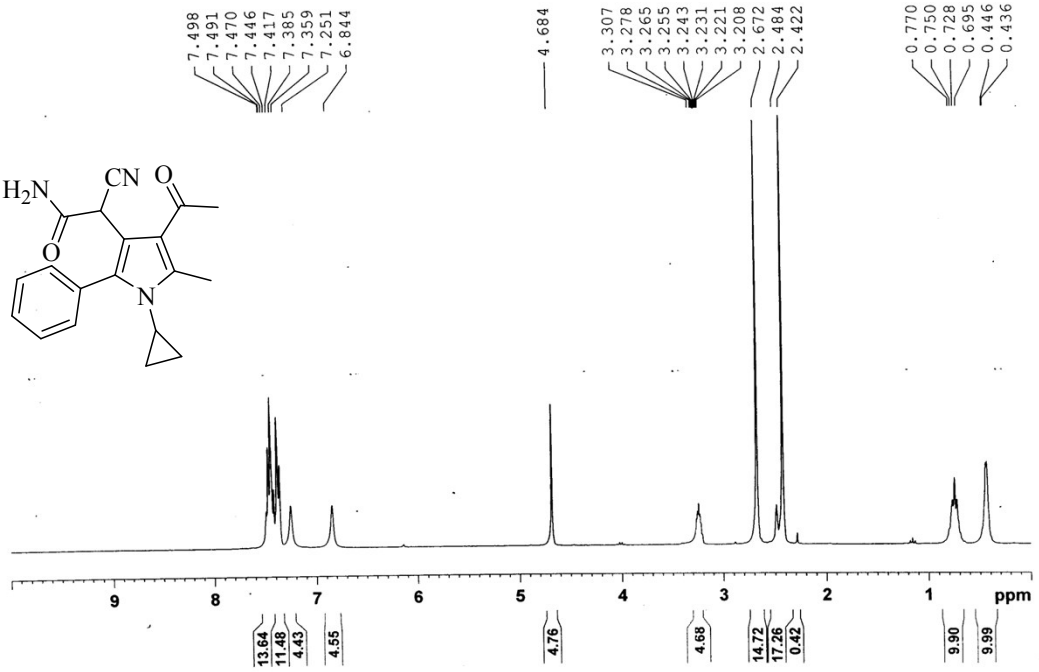

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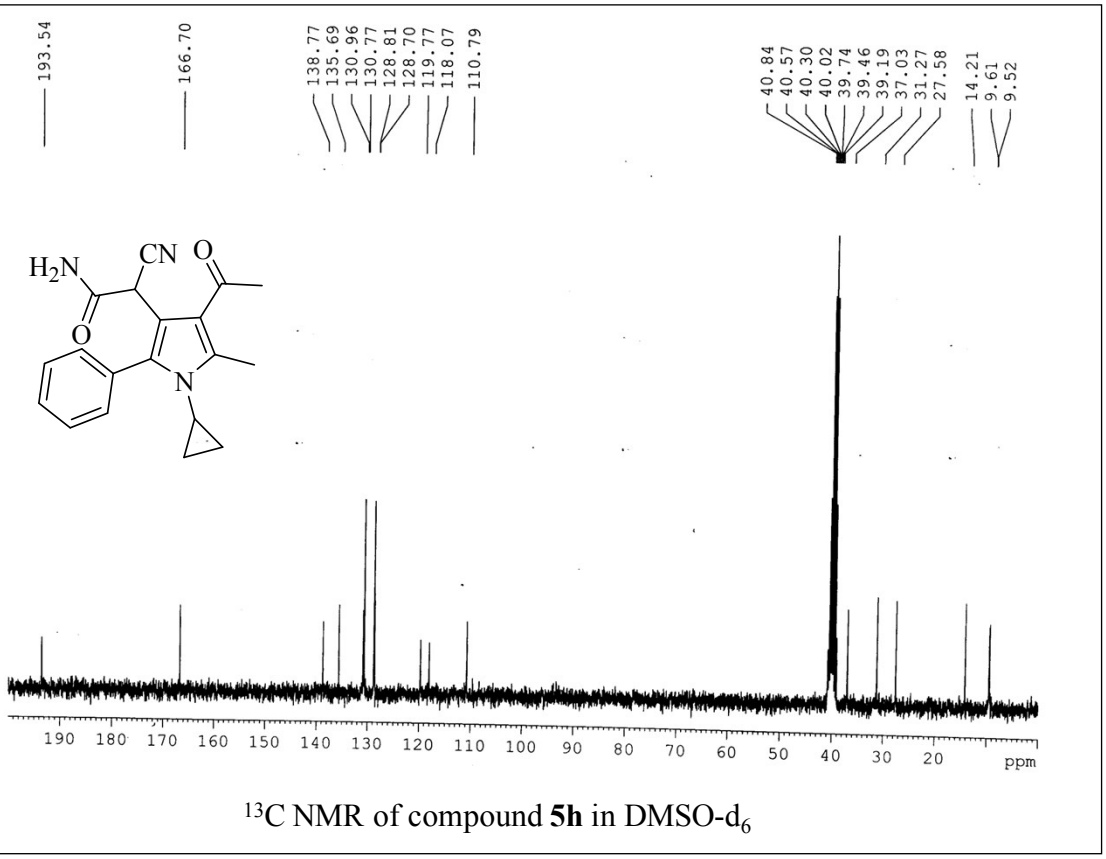

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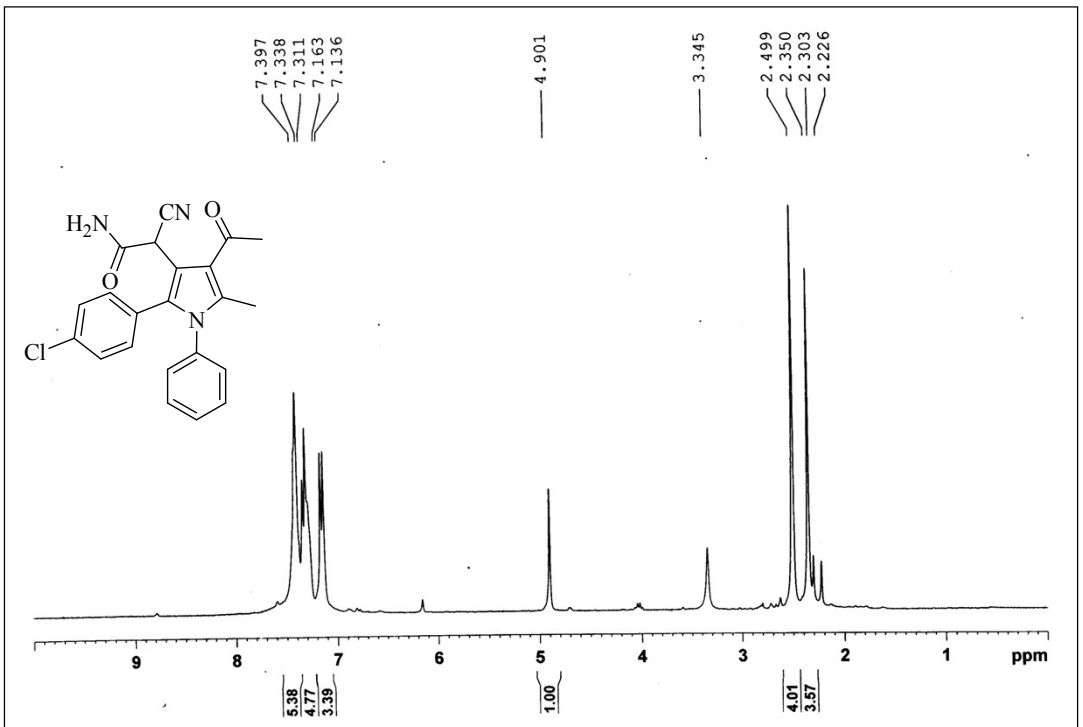

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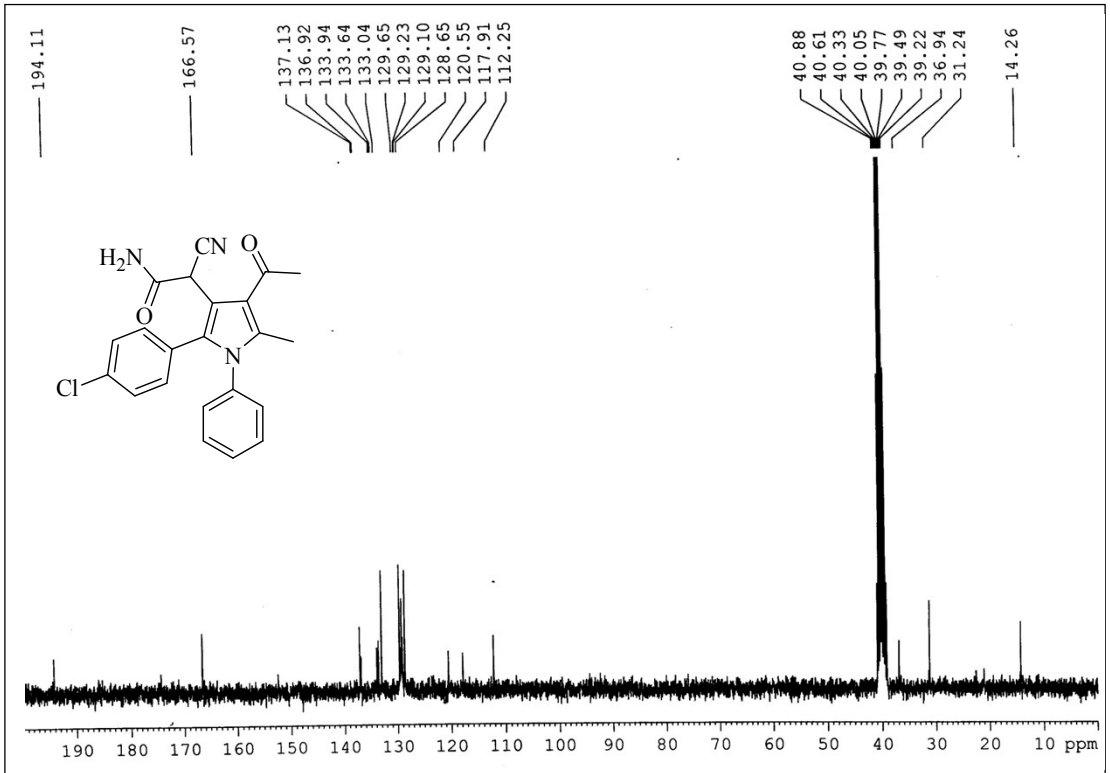

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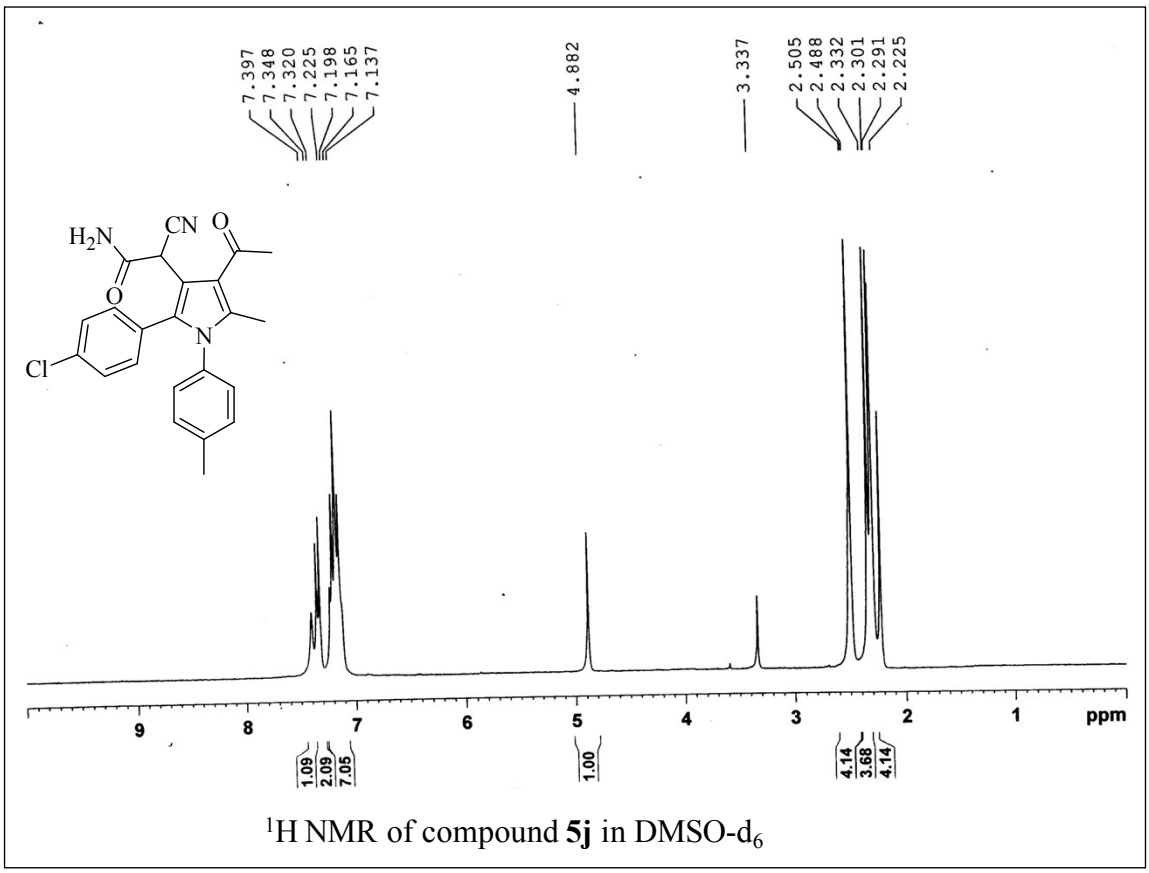

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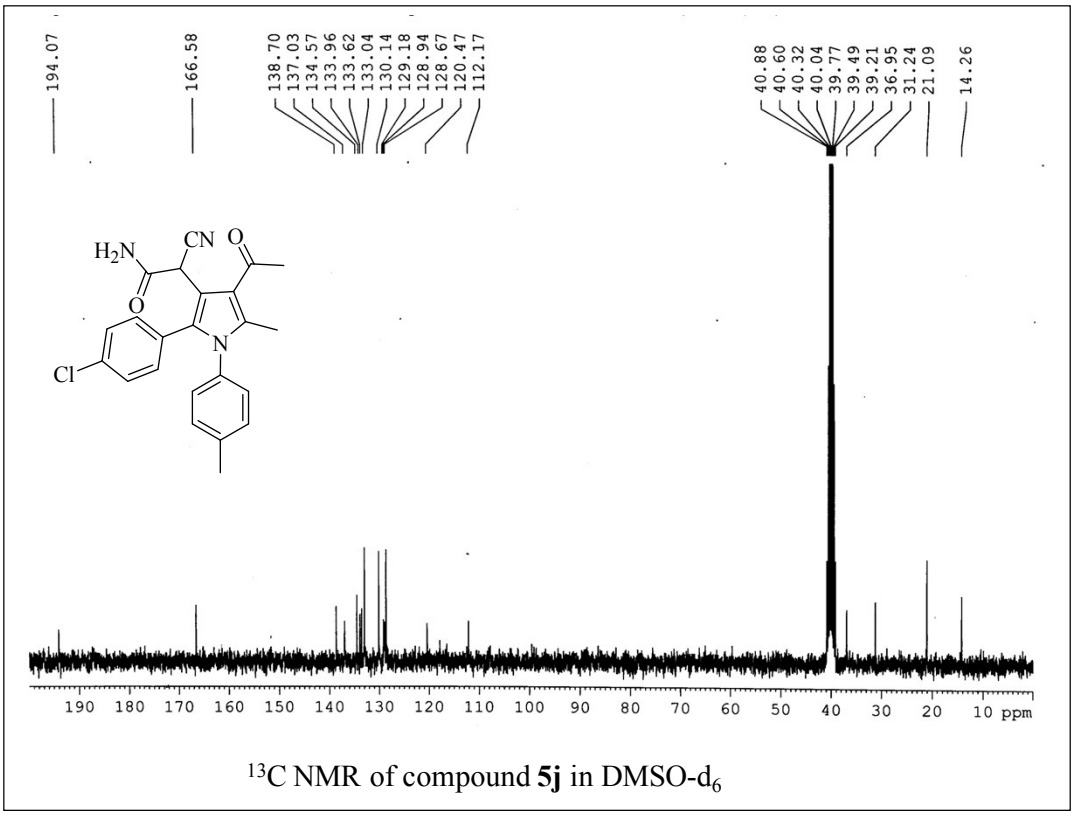

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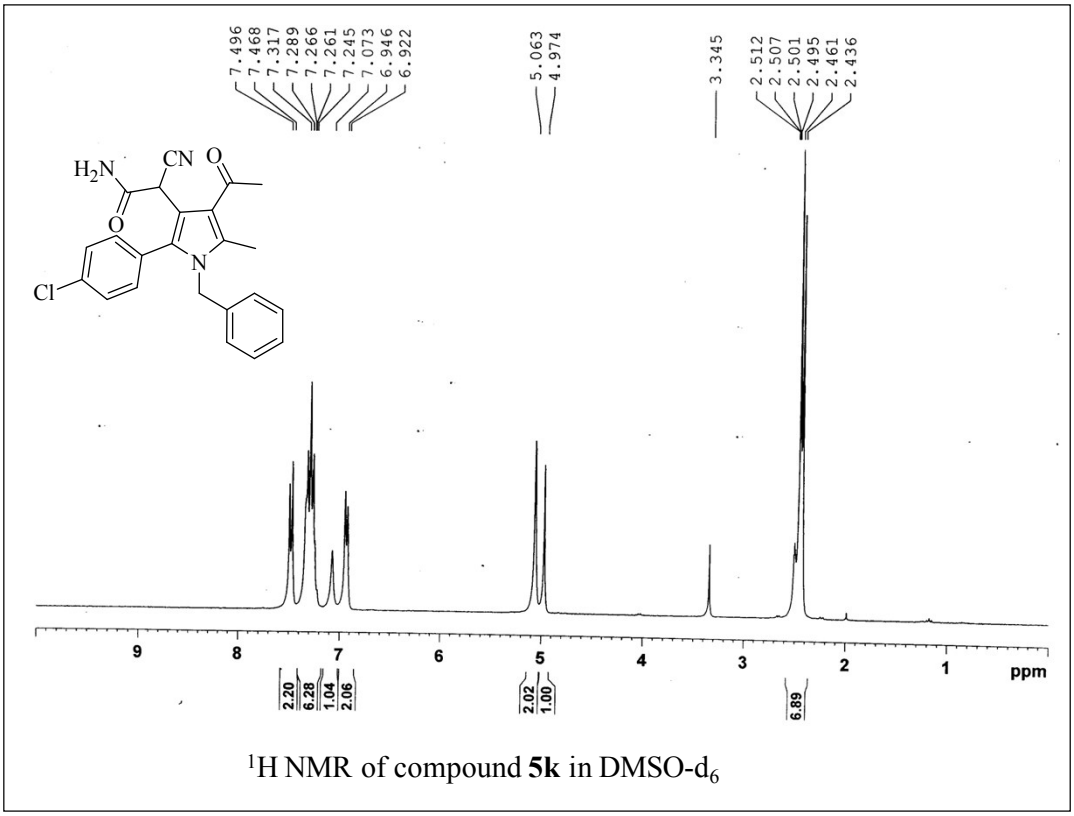

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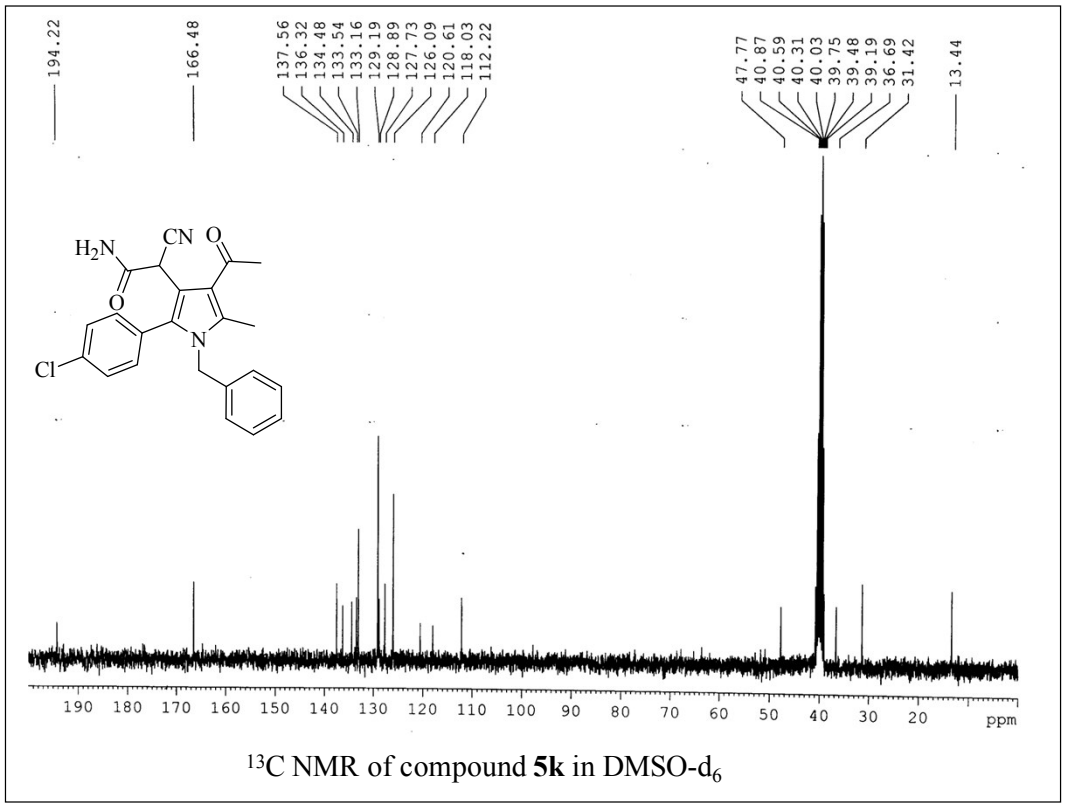

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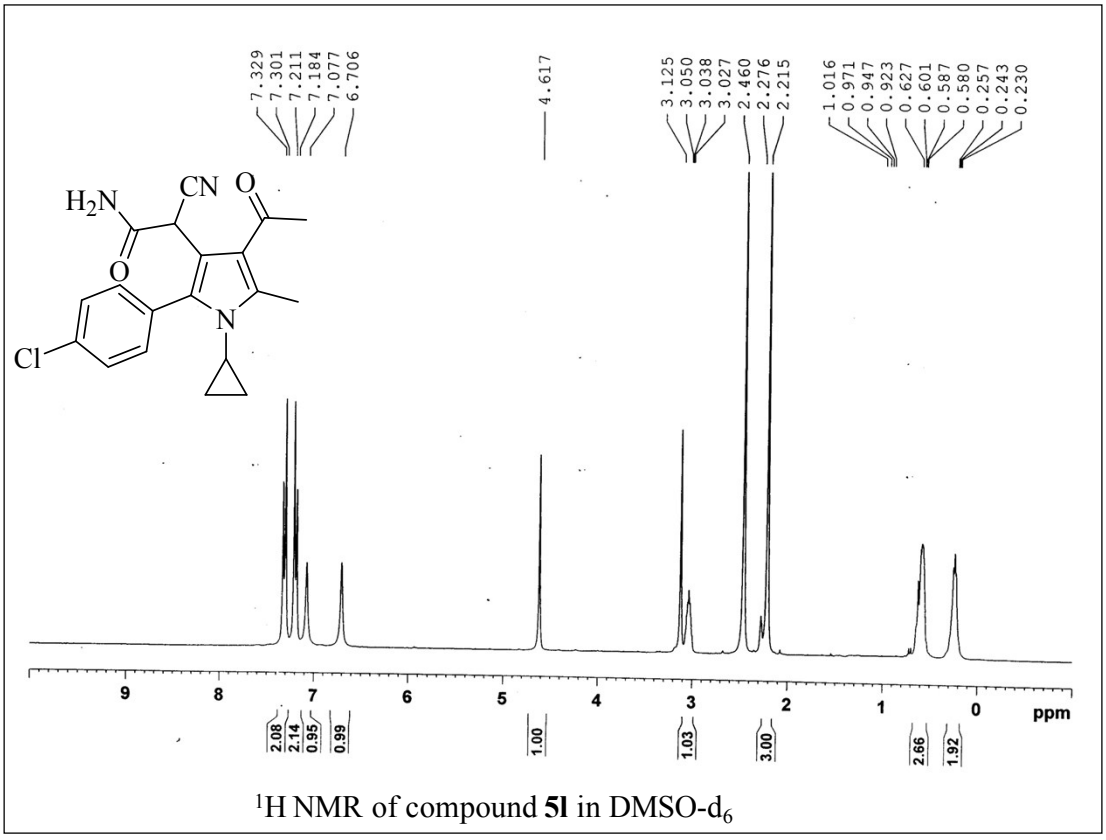
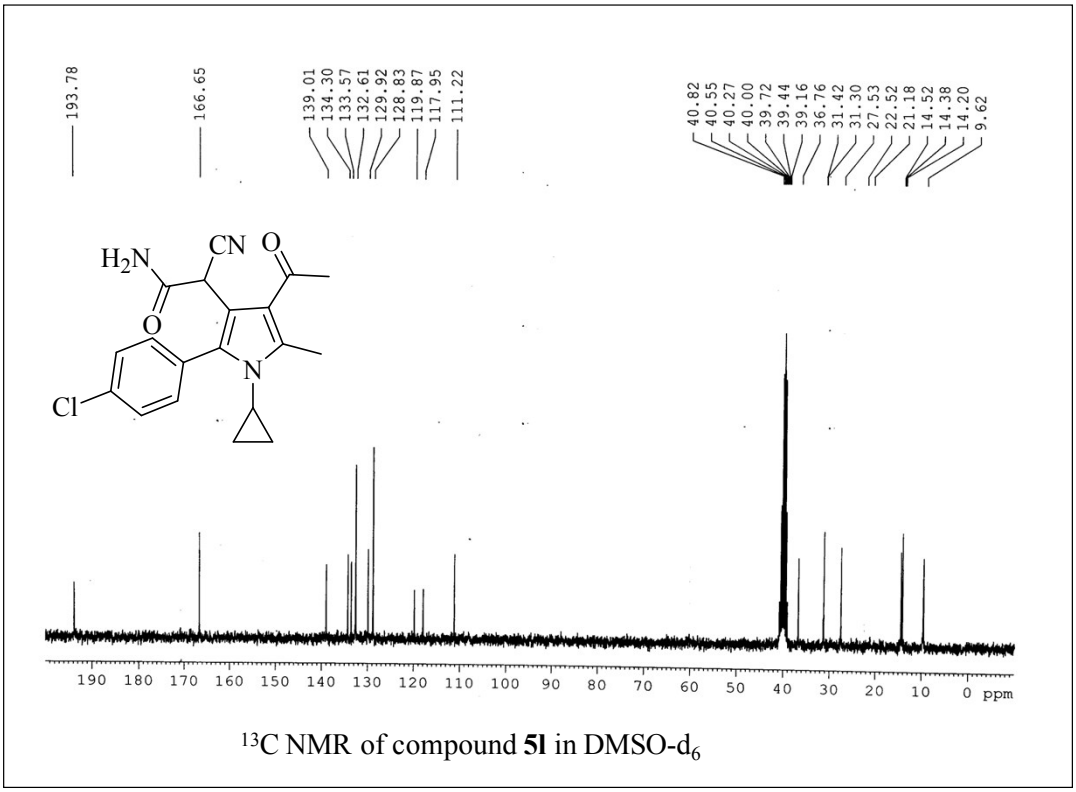


^{1}H NMR of compound **5l** in DMSO-d_6



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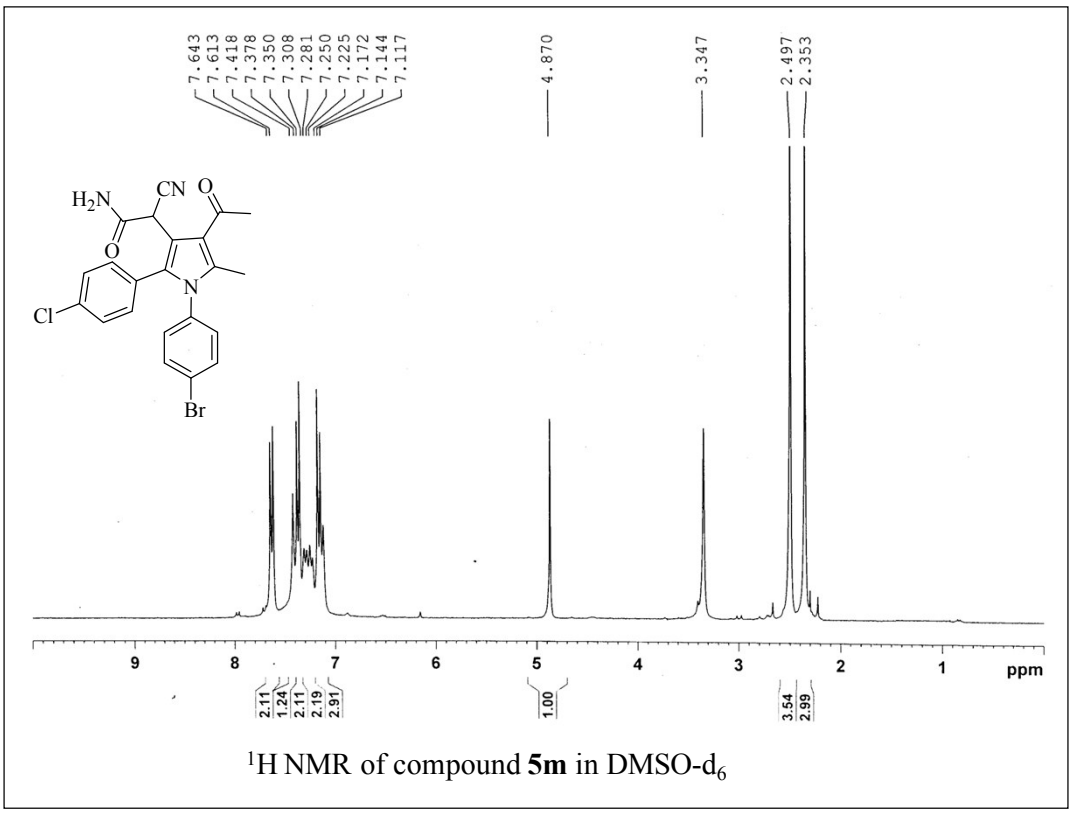
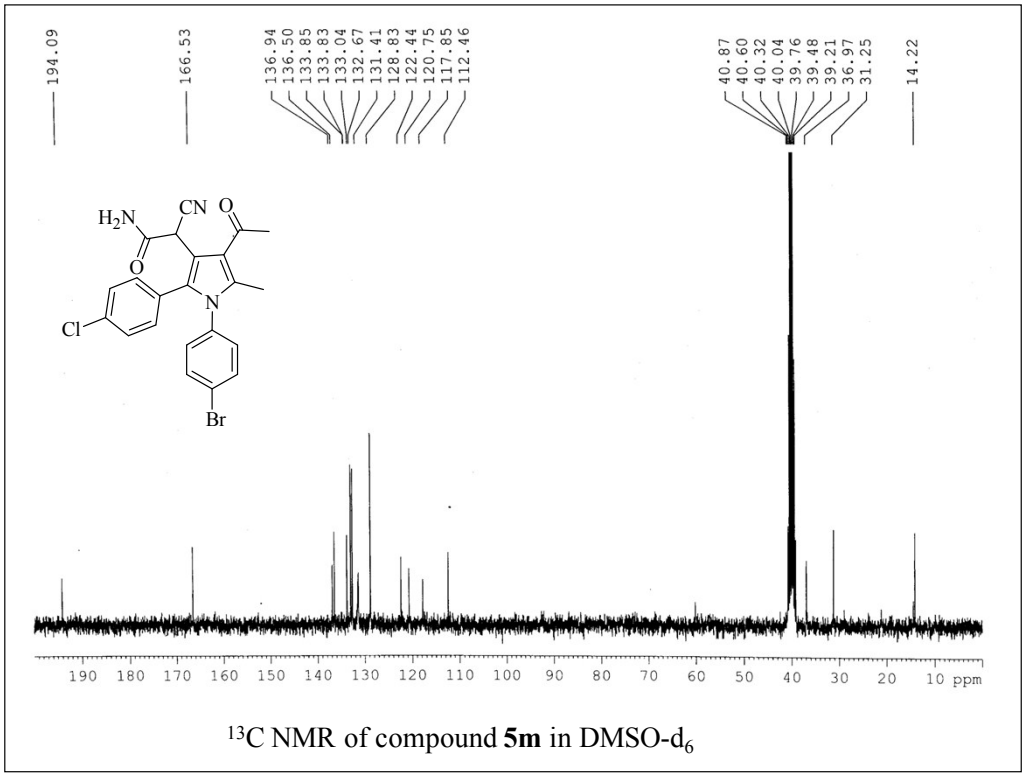
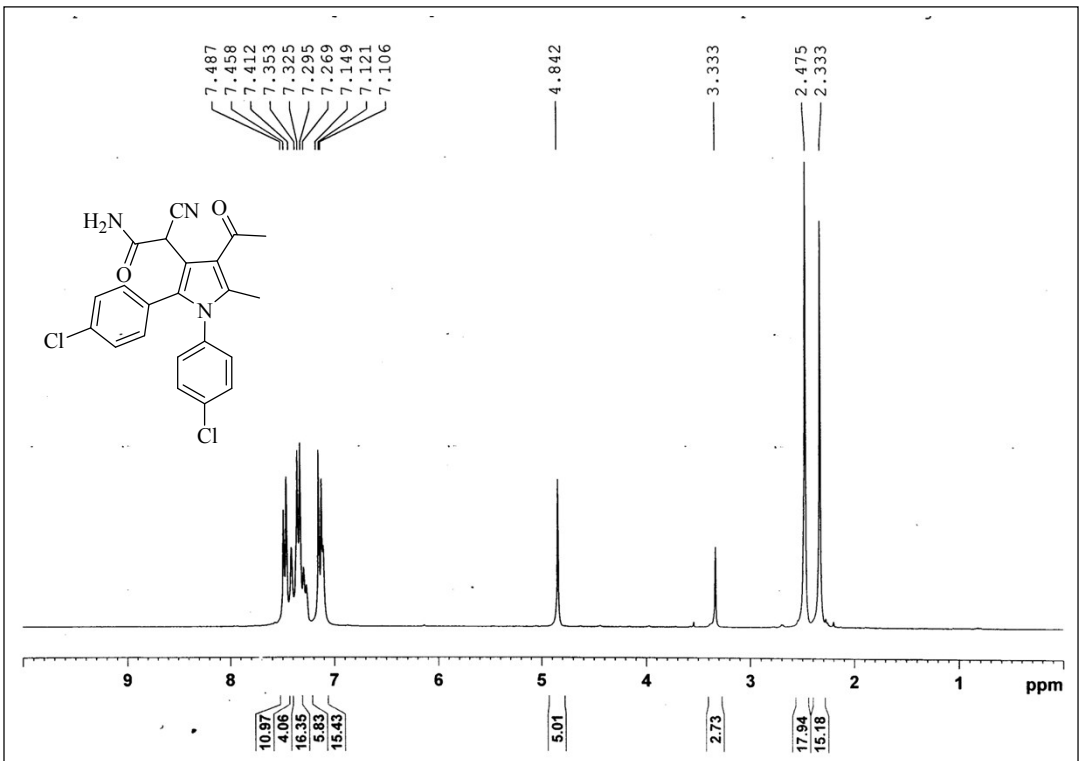


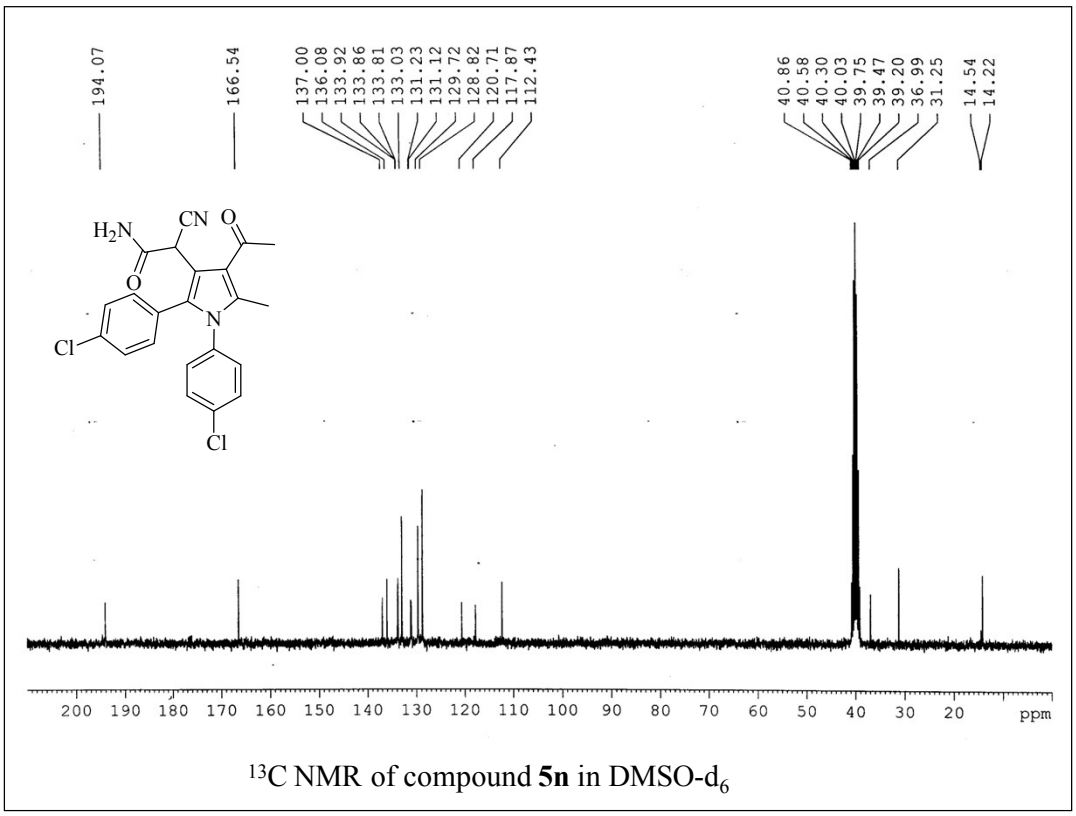
^{1}H NMR of compound **5m** in DMSO-d_6



^{13}C NMR of compound **5m** in DMSO-d_6



^{1}H NMR of compound **5n** in DMSO-d_6



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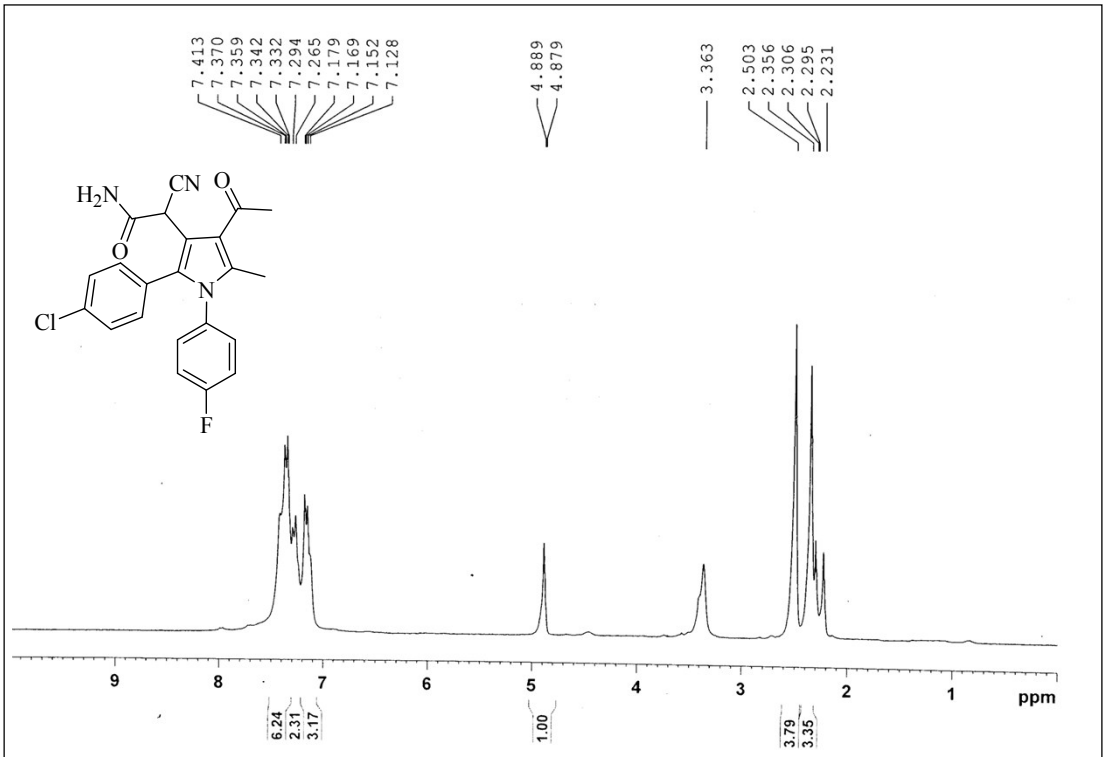
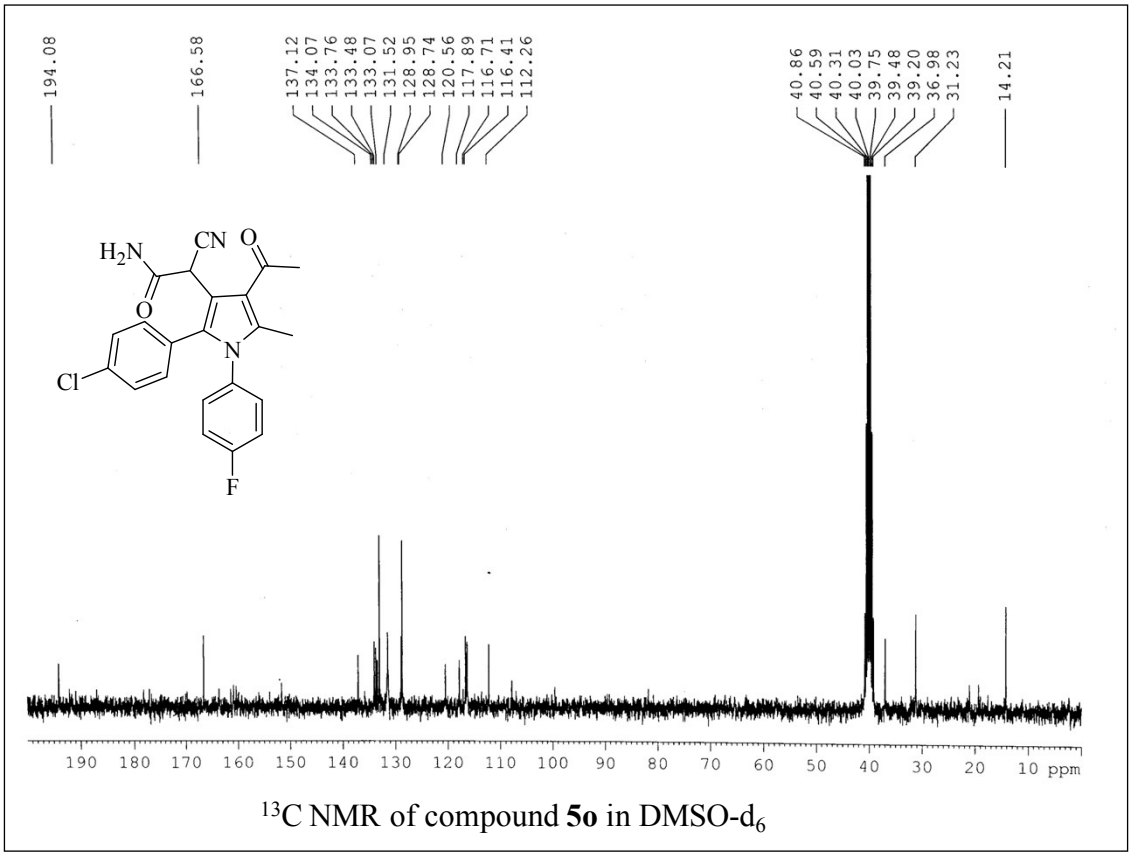
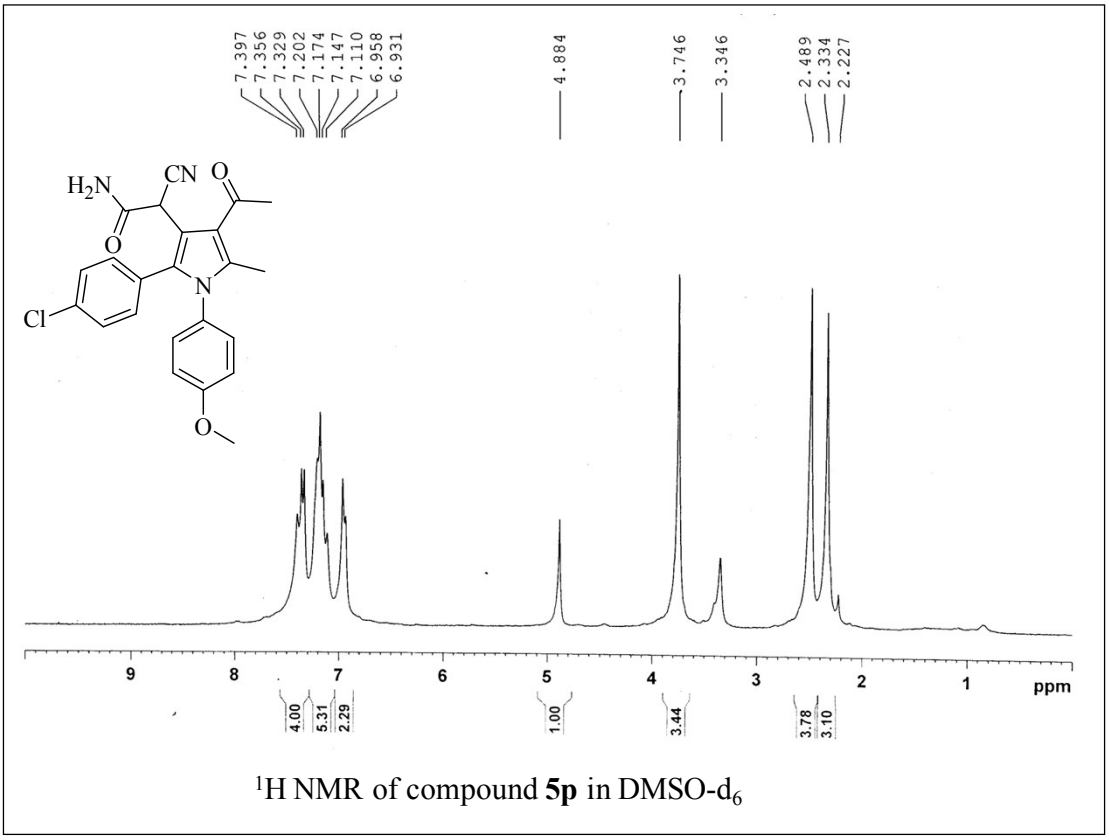


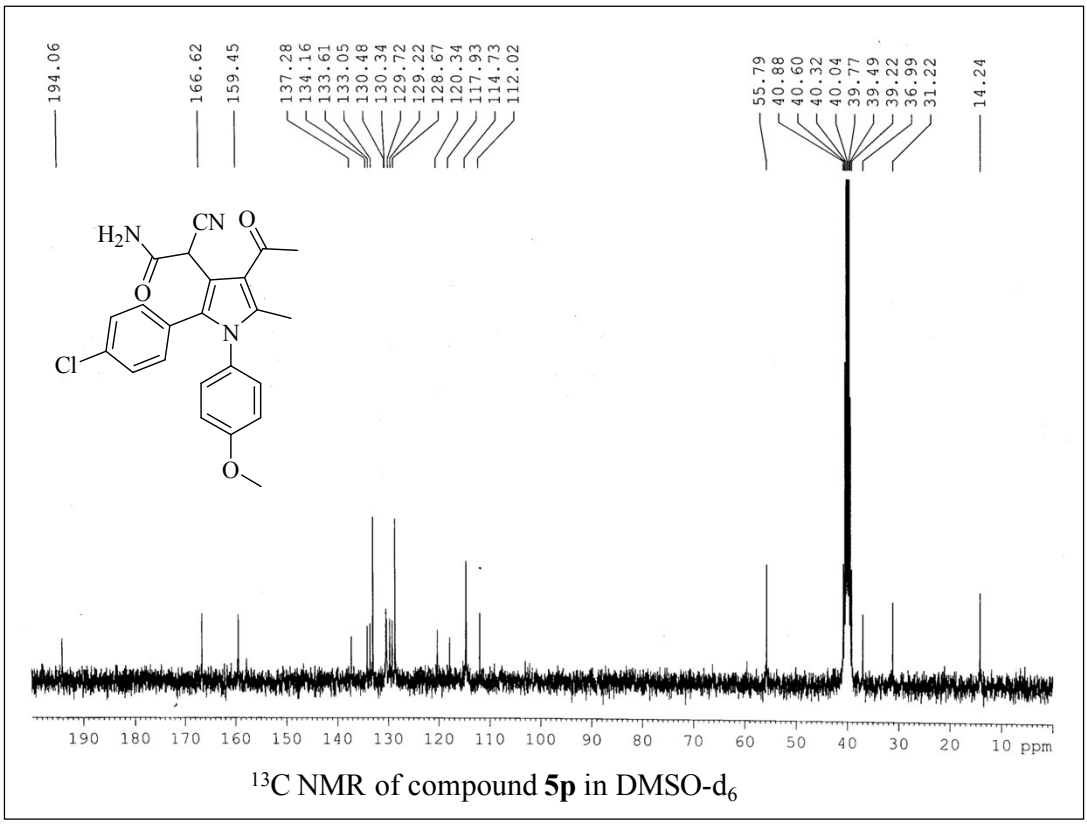
^{1}H NMR of compound **5o** in DMSO-d_6



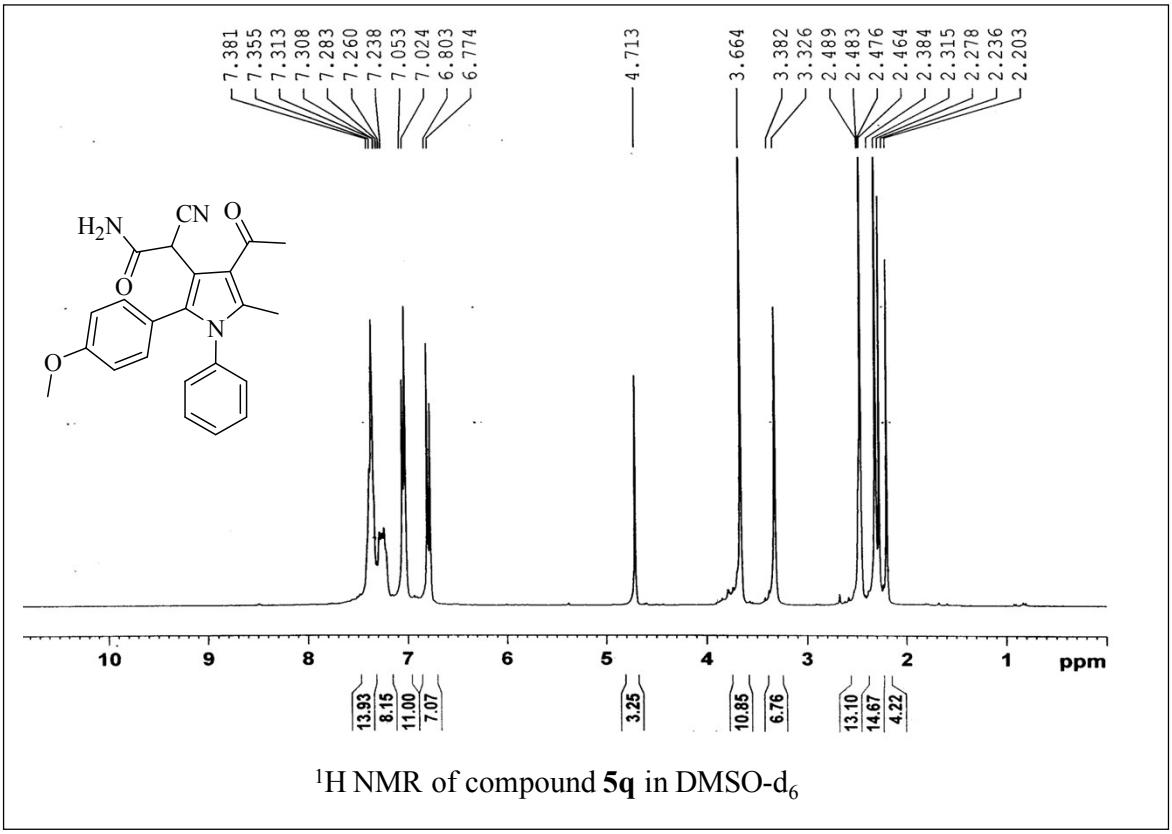
^{13}C NMR of compound **5o** in DMSO-d_6



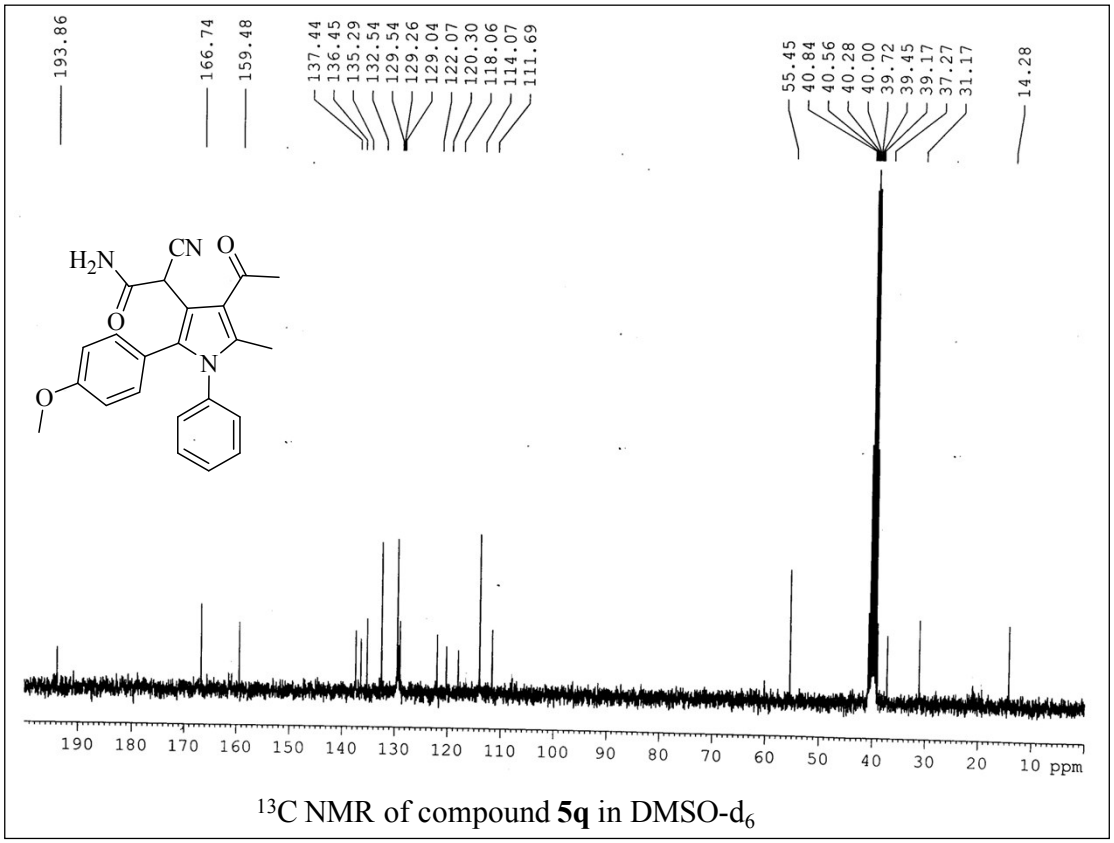
^{1}H NMR of compound **5p** in DMSO-d_6



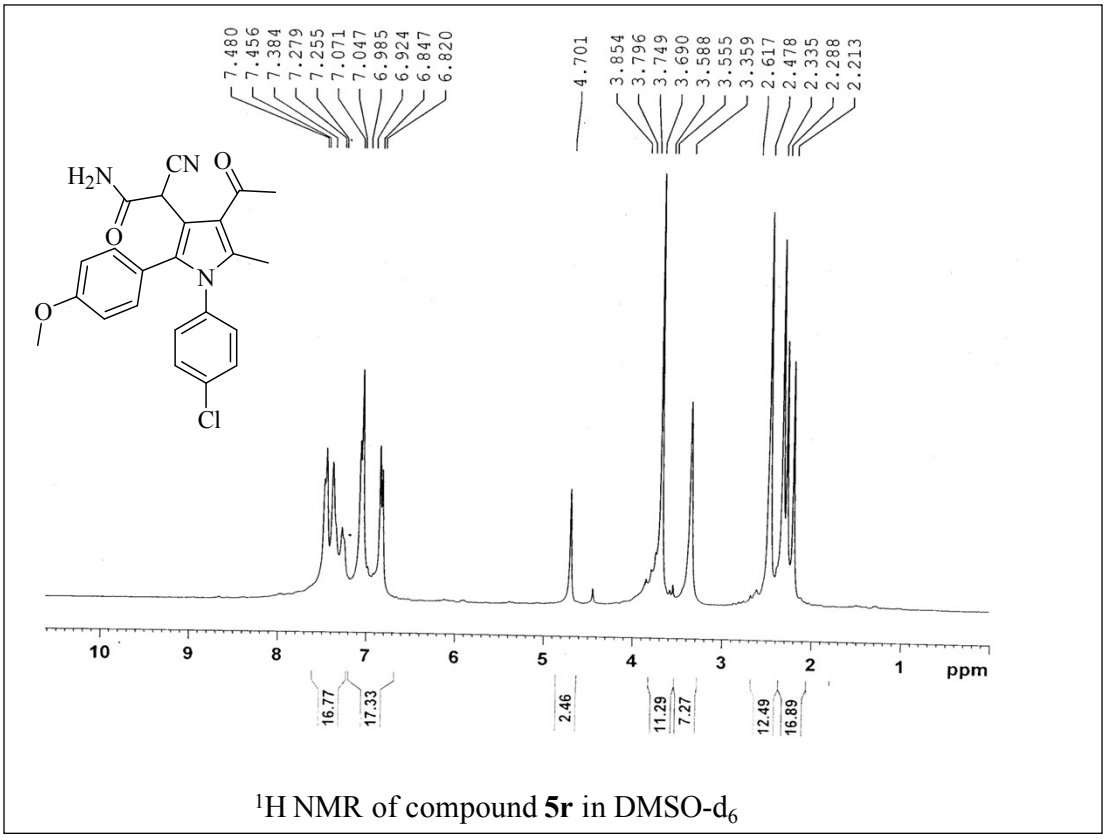
^{13}C NMR of compound **5p** in DMSO-d_6



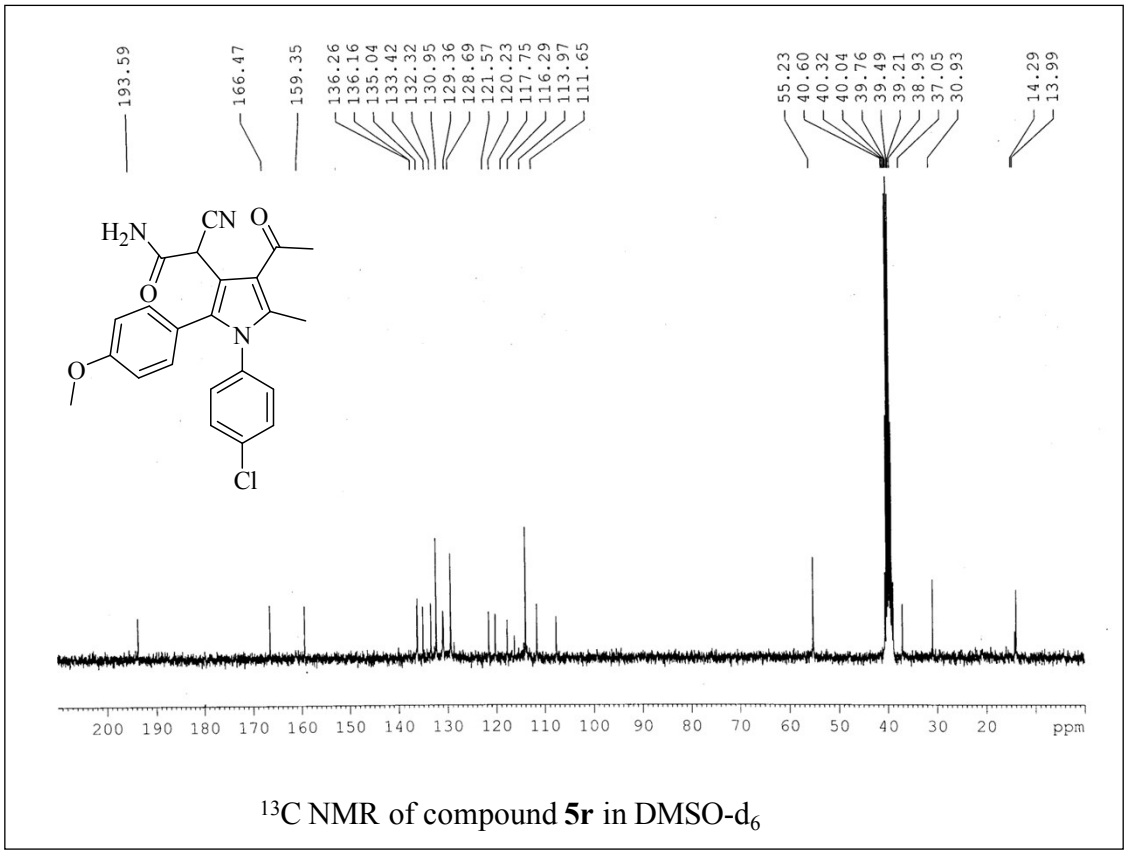
^{1}H NMR of compound **5q** in DMSO-d_6



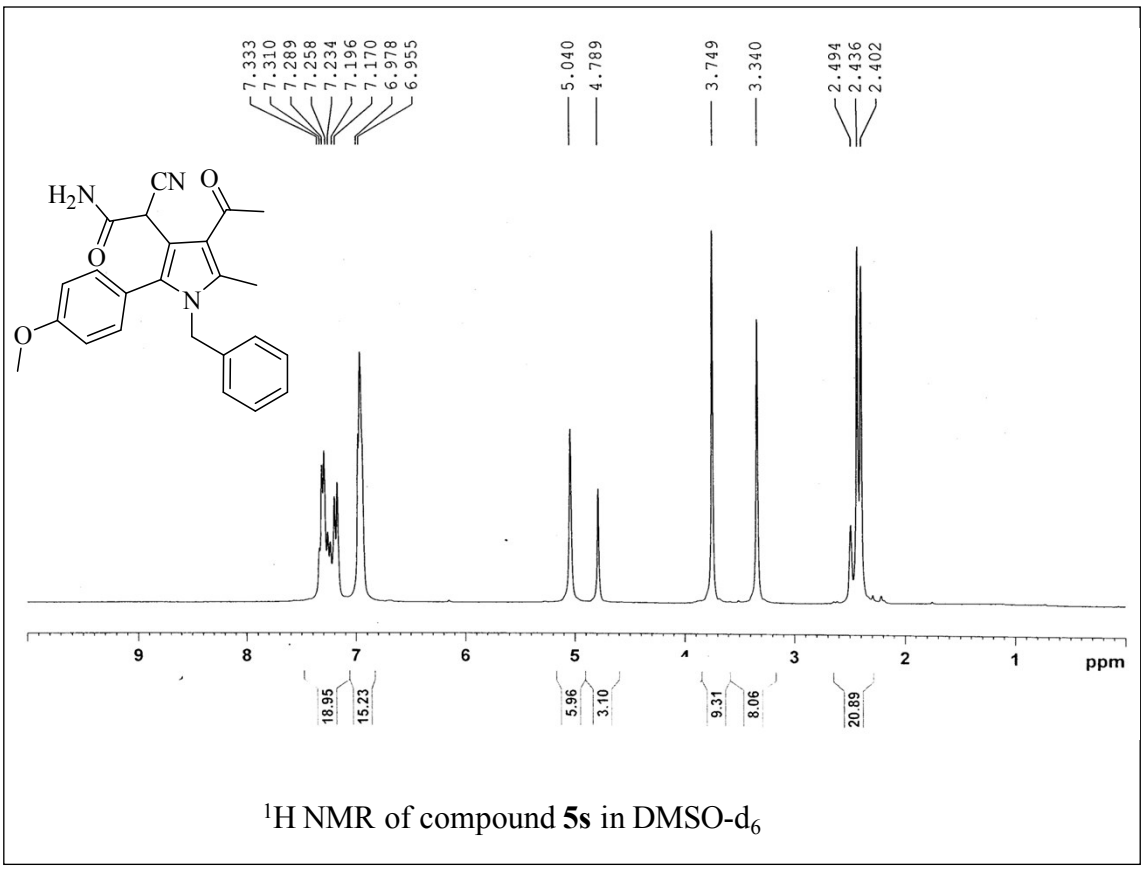
^{13}C NMR of compound **5q** in DMSO-d_6



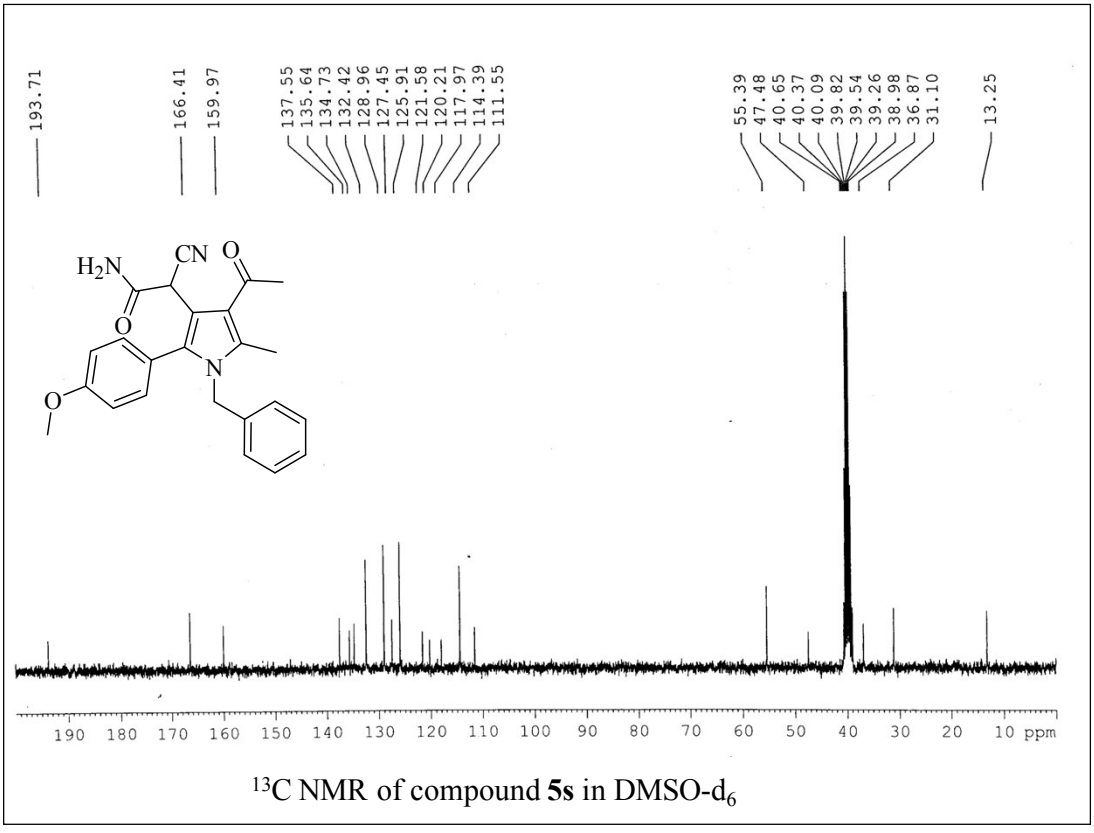
^{1}H NMR of compound **5r** in DMSO-d_6



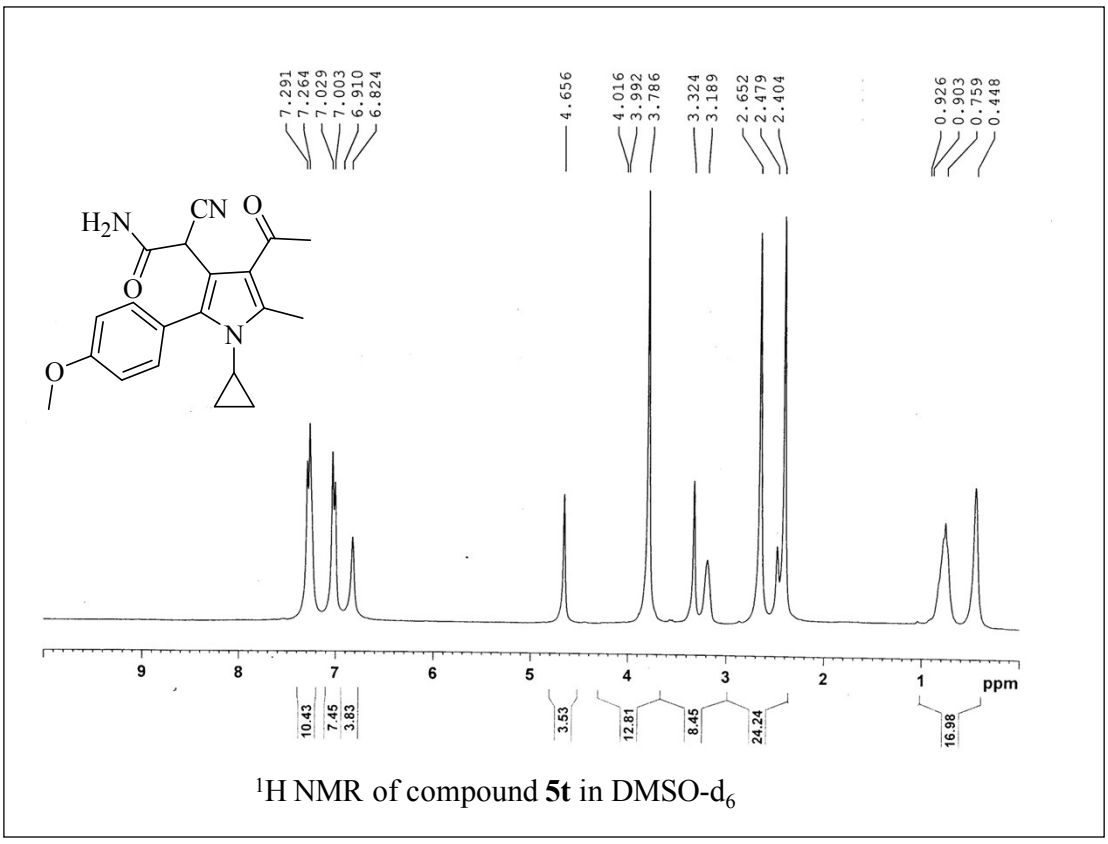
^{13}C NMR of compound **5r** in DMSO-d_6



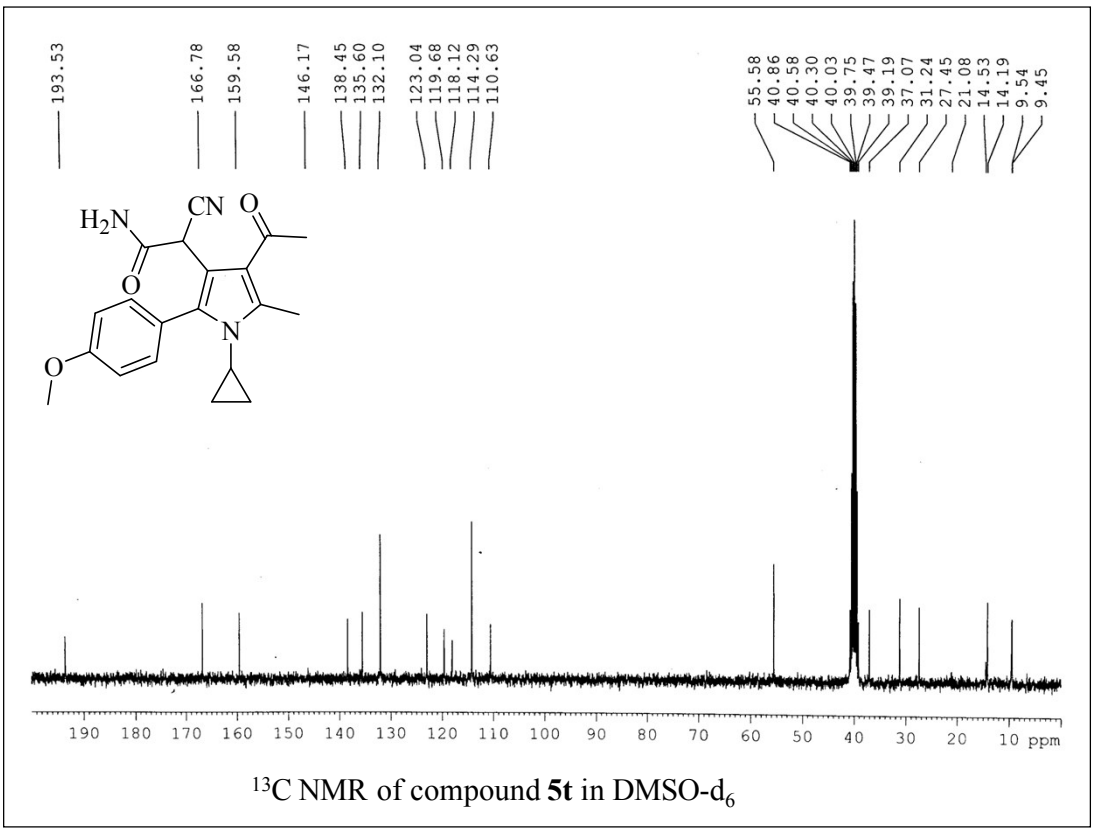
^{1}H NMR of compound **5s** in DMSO-d_6



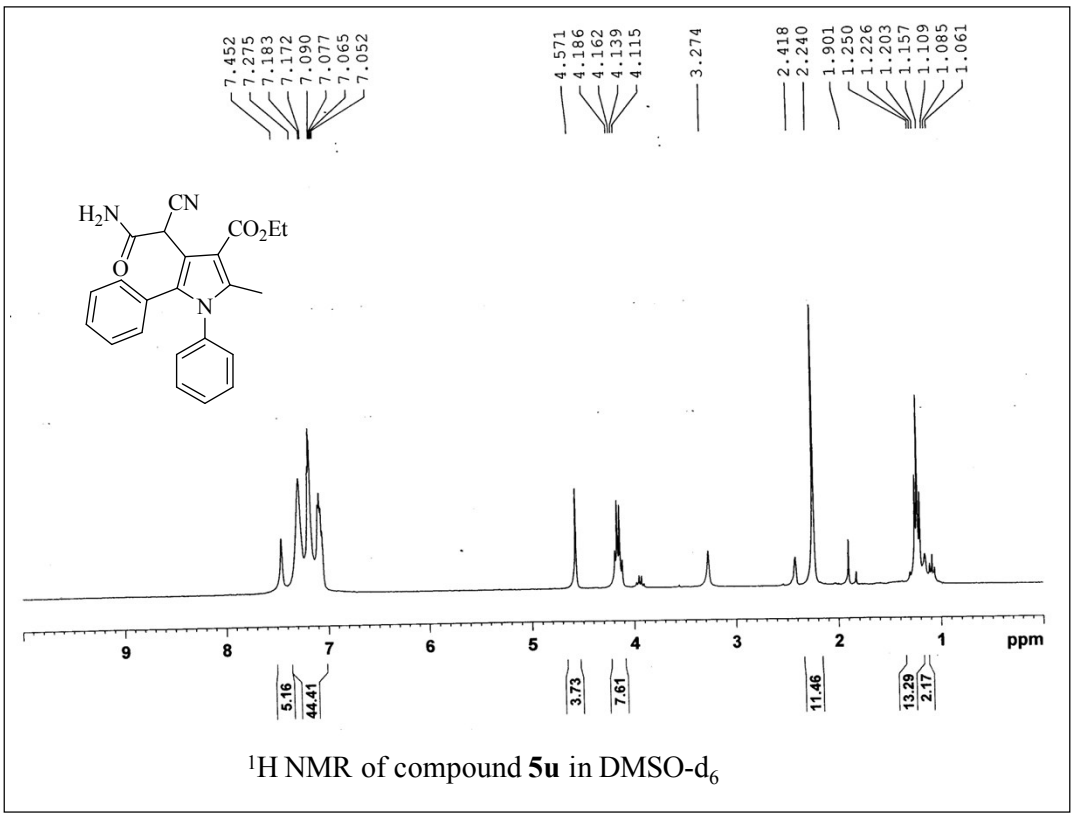
^{13}C NMR of compound **5s** in DMSO-d_6



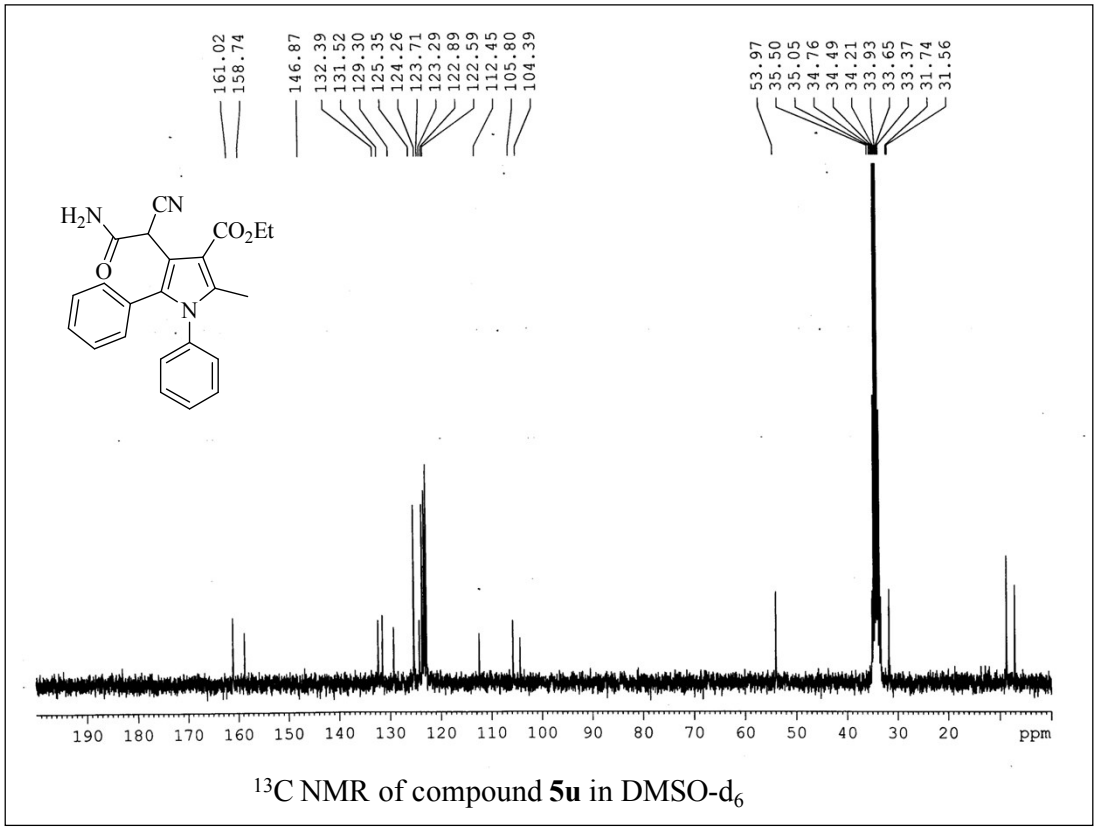
^{1}H NMR of compound **5t** in DMSO-d_6



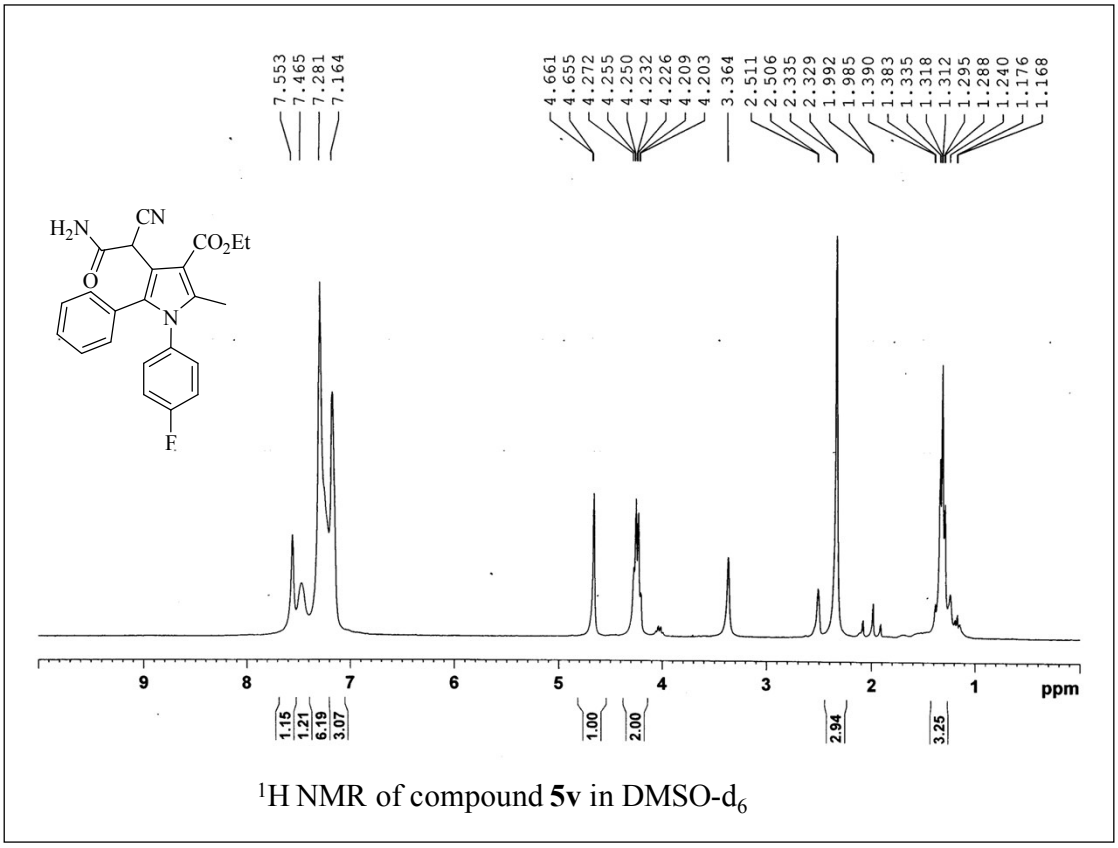
^{13}C NMR of compound **5t** in DMSO-d_6



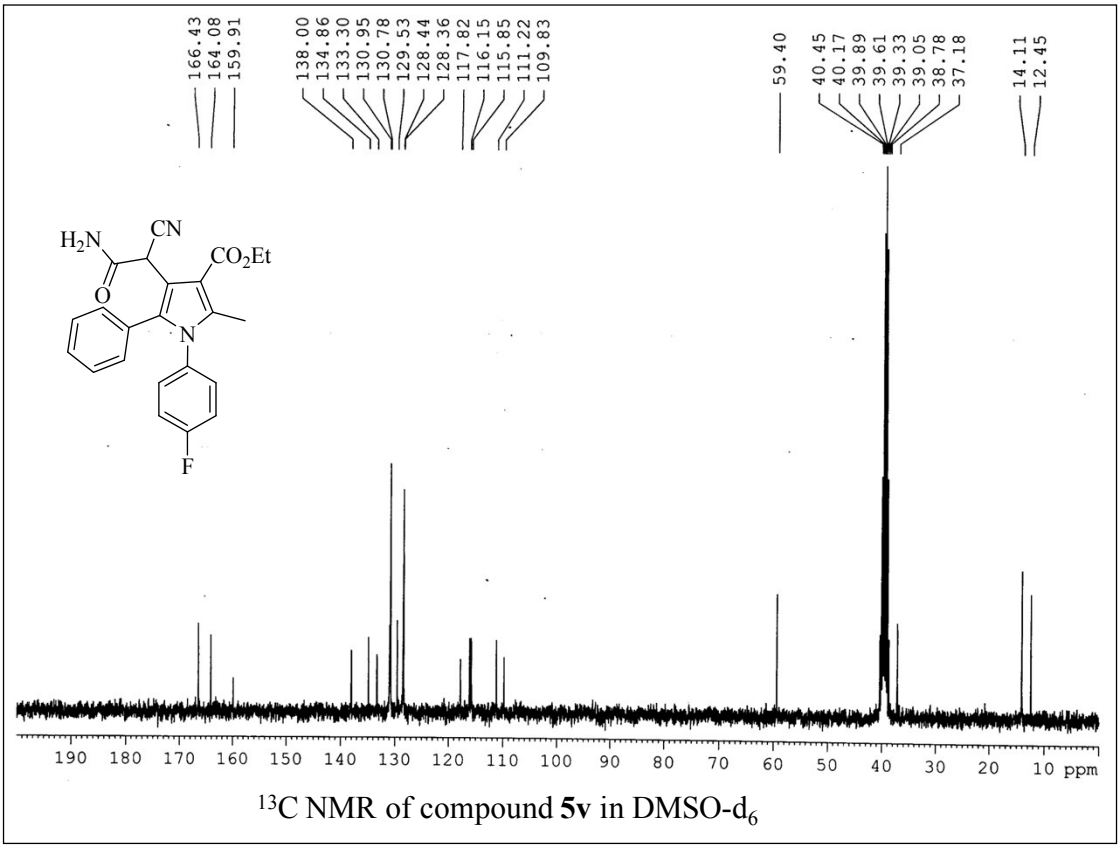
^{1}H NMR of compound **5u** in DMSO-d_6



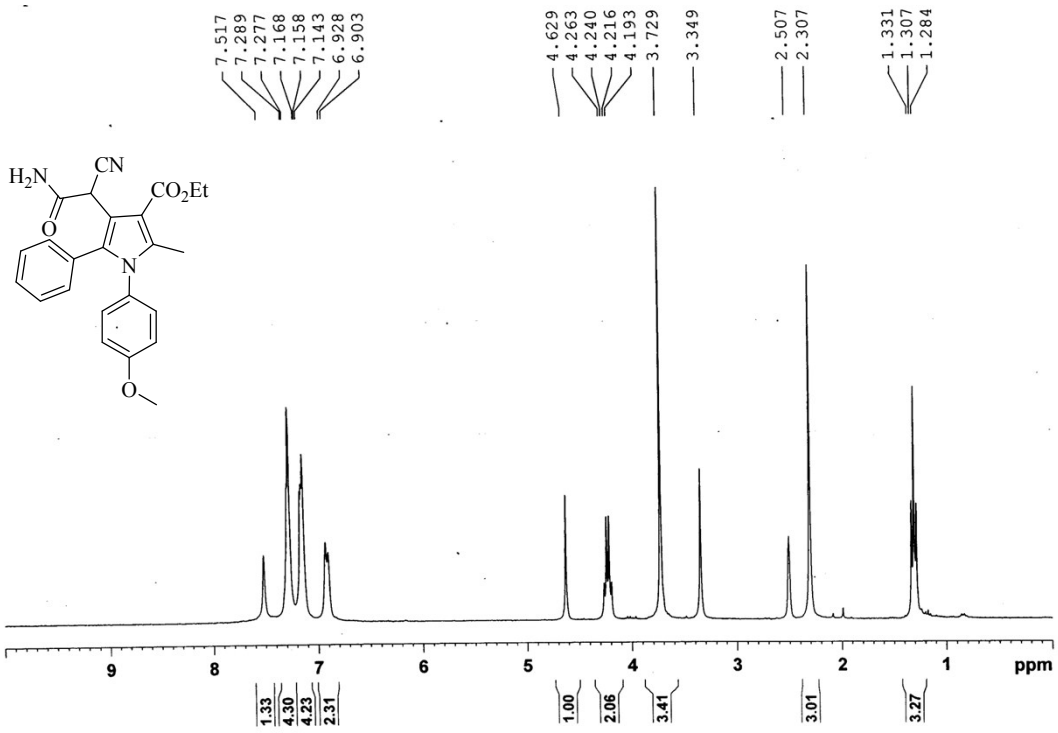
^{13}C NMR of compound **5u** in DMSO-d_6



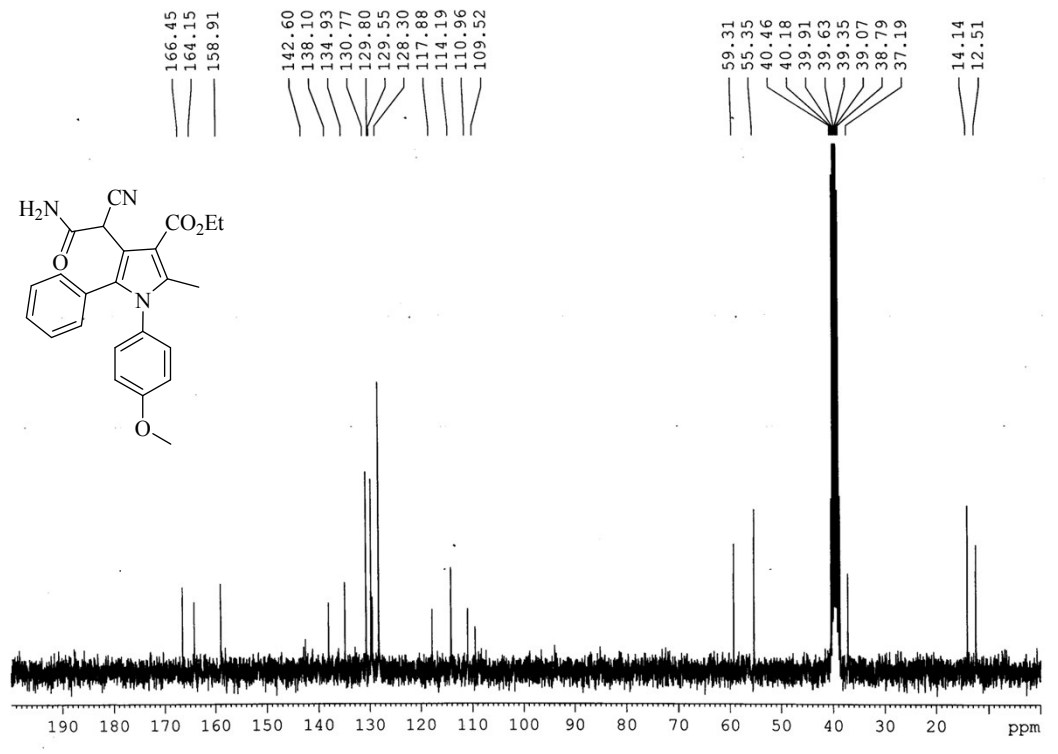
^{1}H NMR of compound **5v** in DMSO-d_6



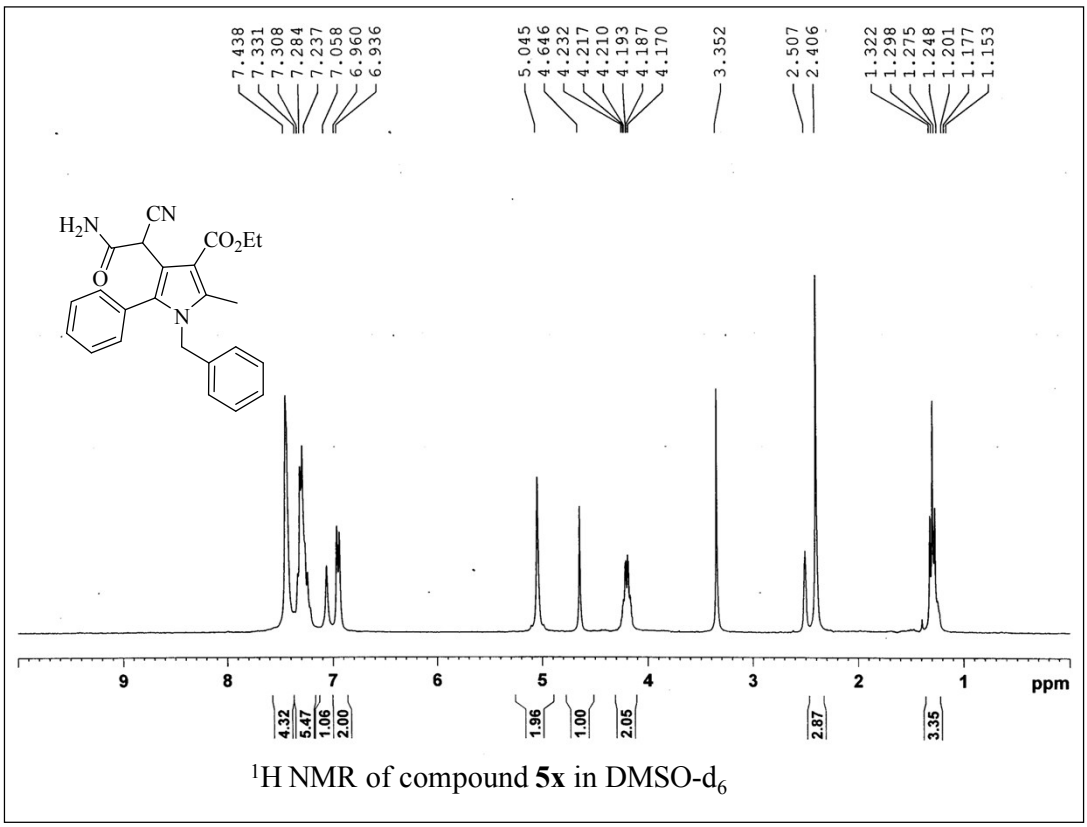
^{13}C NMR of compound **5v** in DMSO-d_6



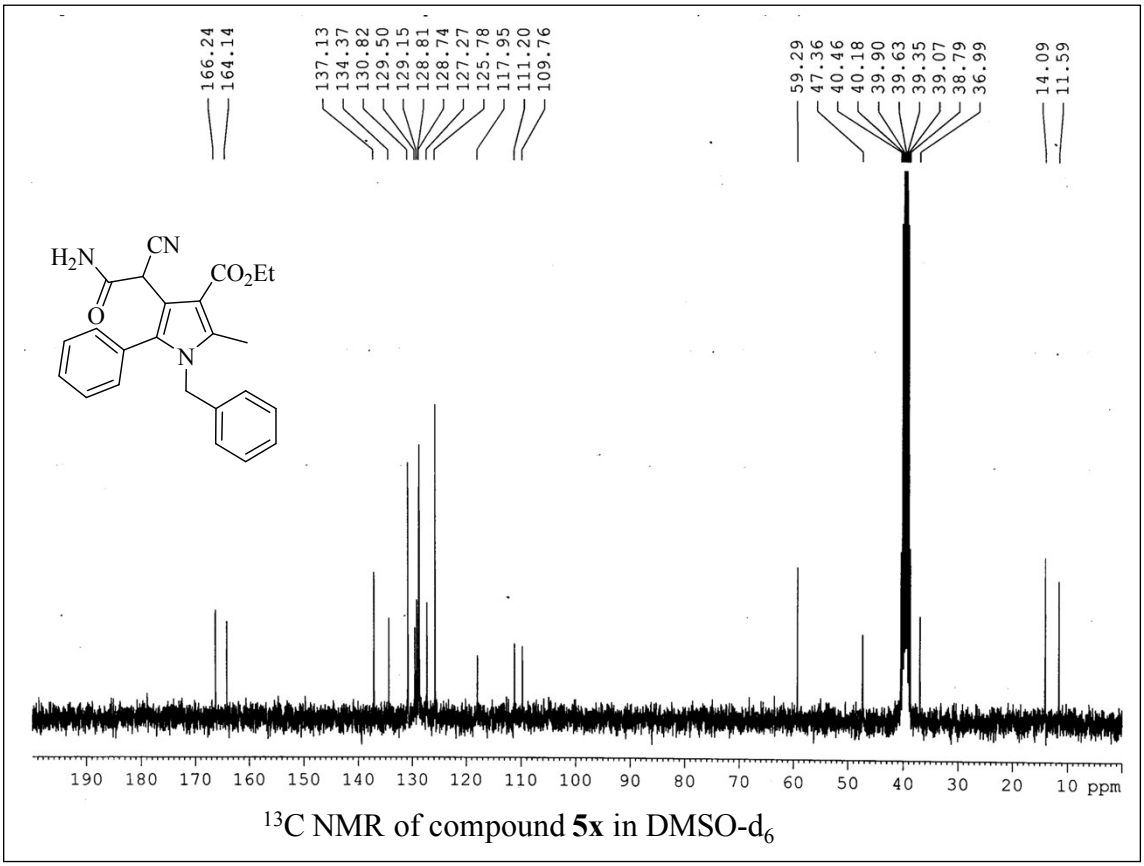
^{1}H NMR of compound **5w** in DMSO-d_6



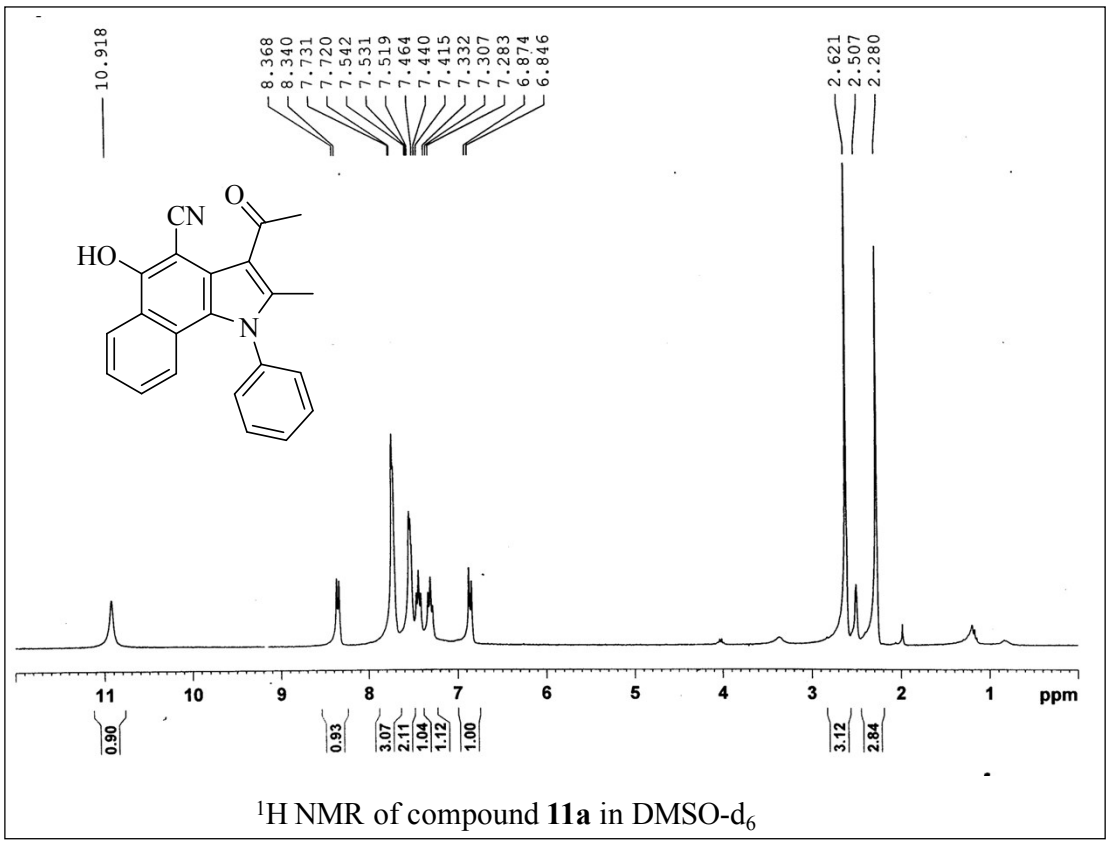
^{13}C NMR of compound **5w** in DMSO-d_6



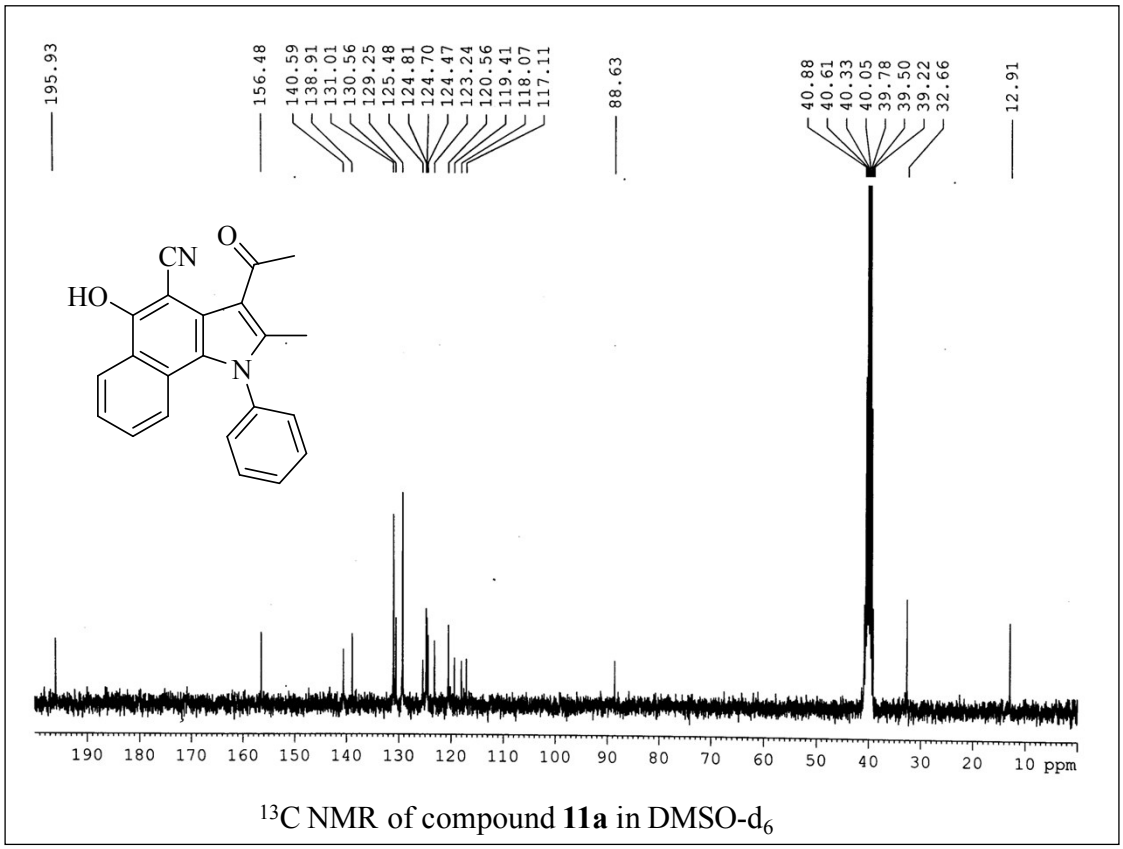
^{1}H NMR of compound **5x** in DMSO-d_6



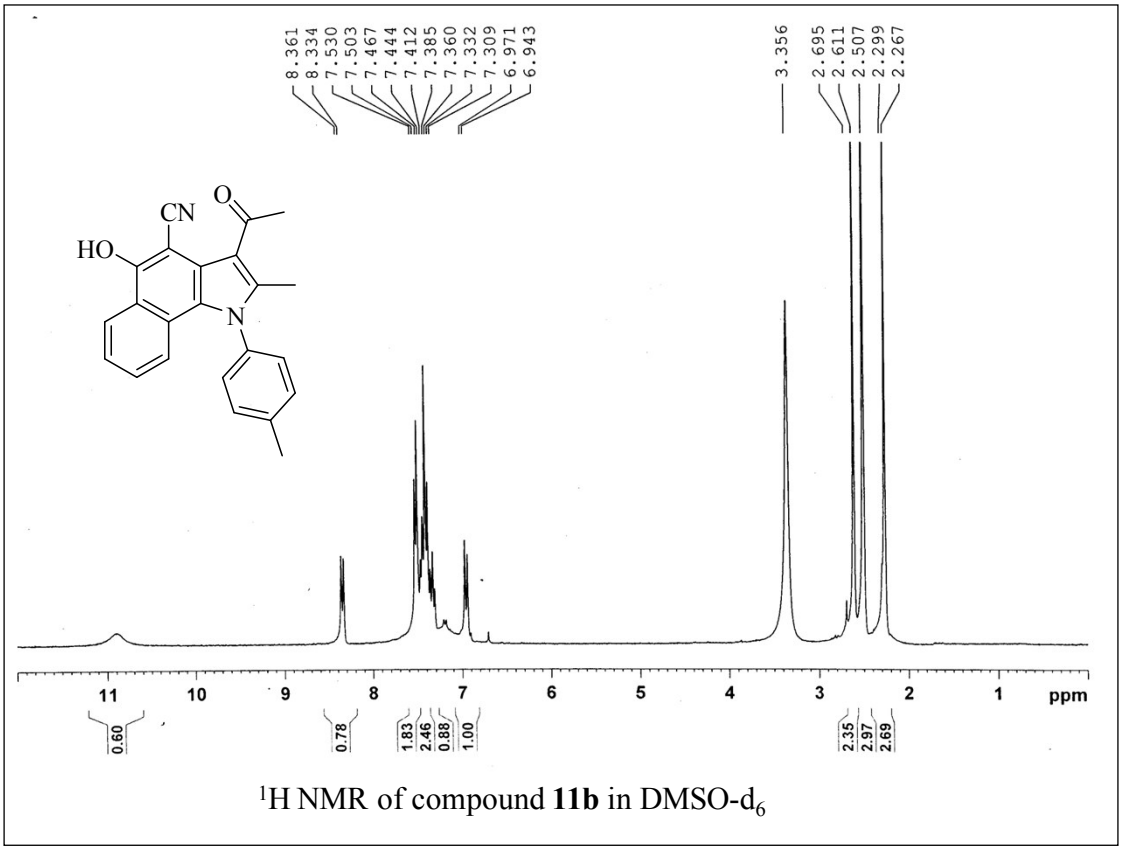
^{13}C NMR of compound **5x** in DMSO-d_6



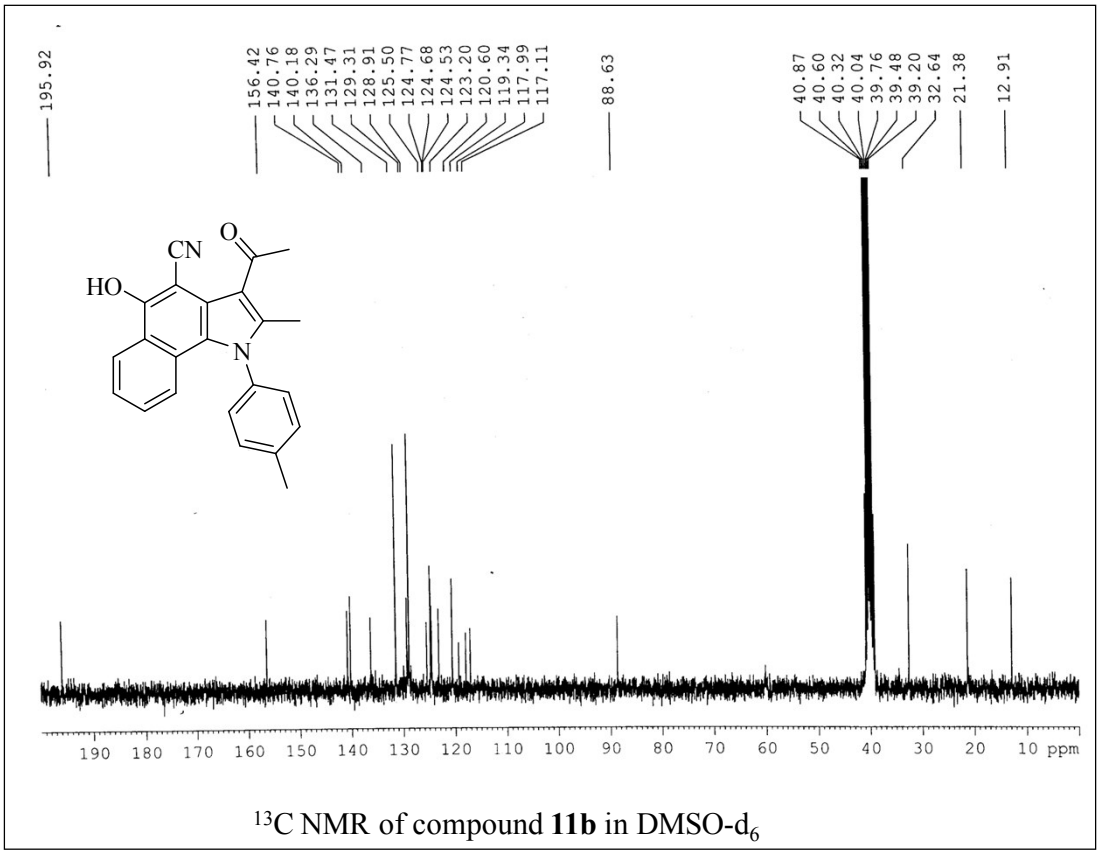
^{1}H NMR of compound **11a** in DMSO-d_6



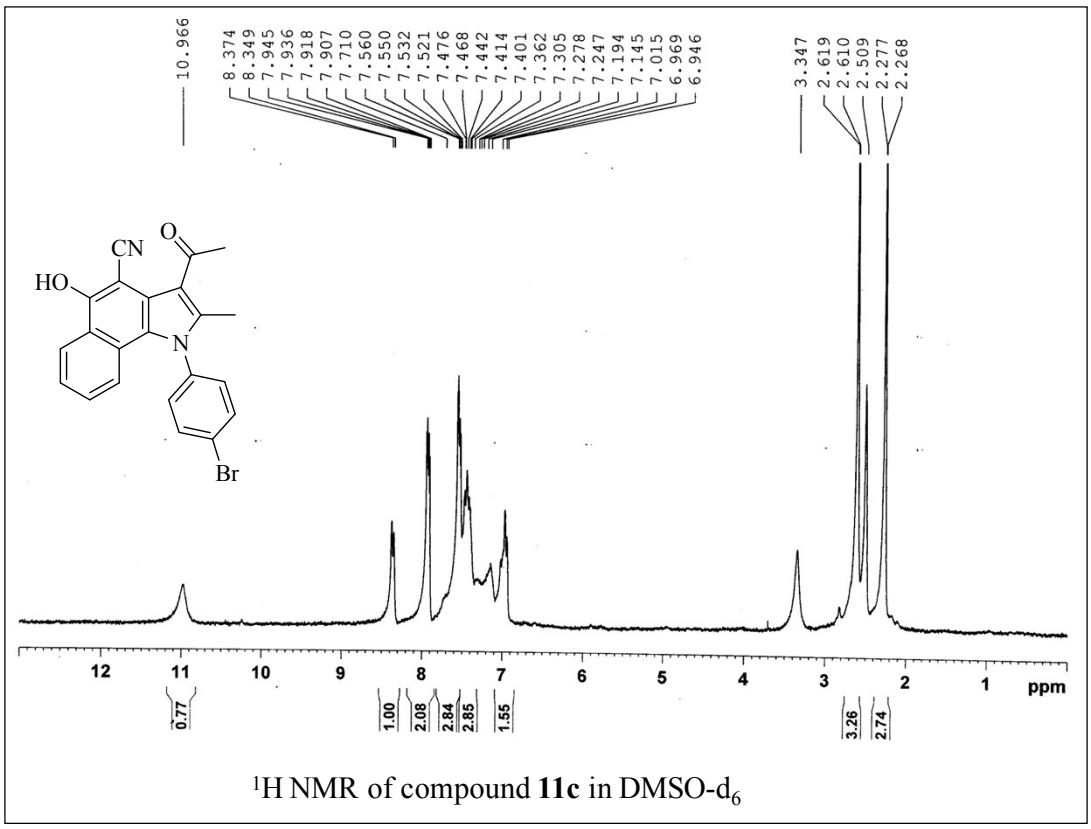
^{13}C NMR of compound **11a** in DMSO-d_6



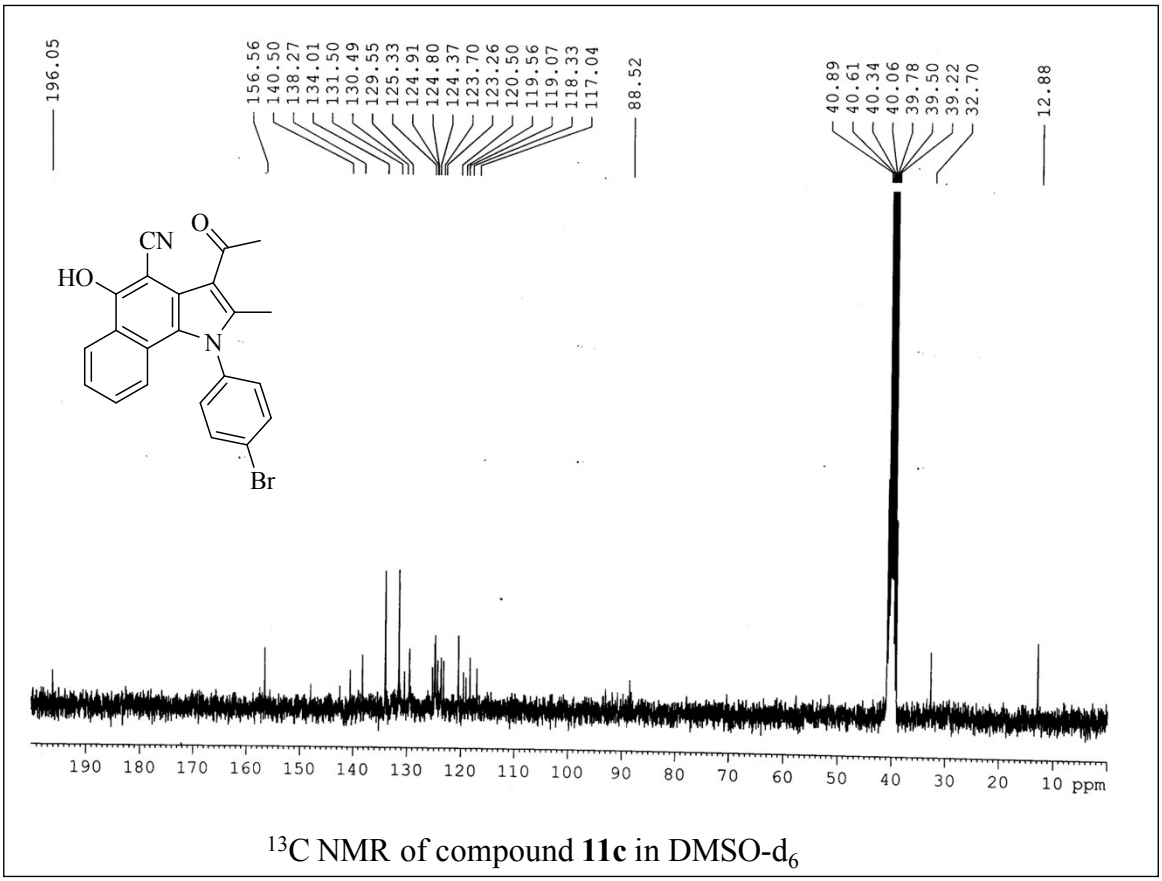
^{1}H NMR of compound **11b** in DMSO-d_6



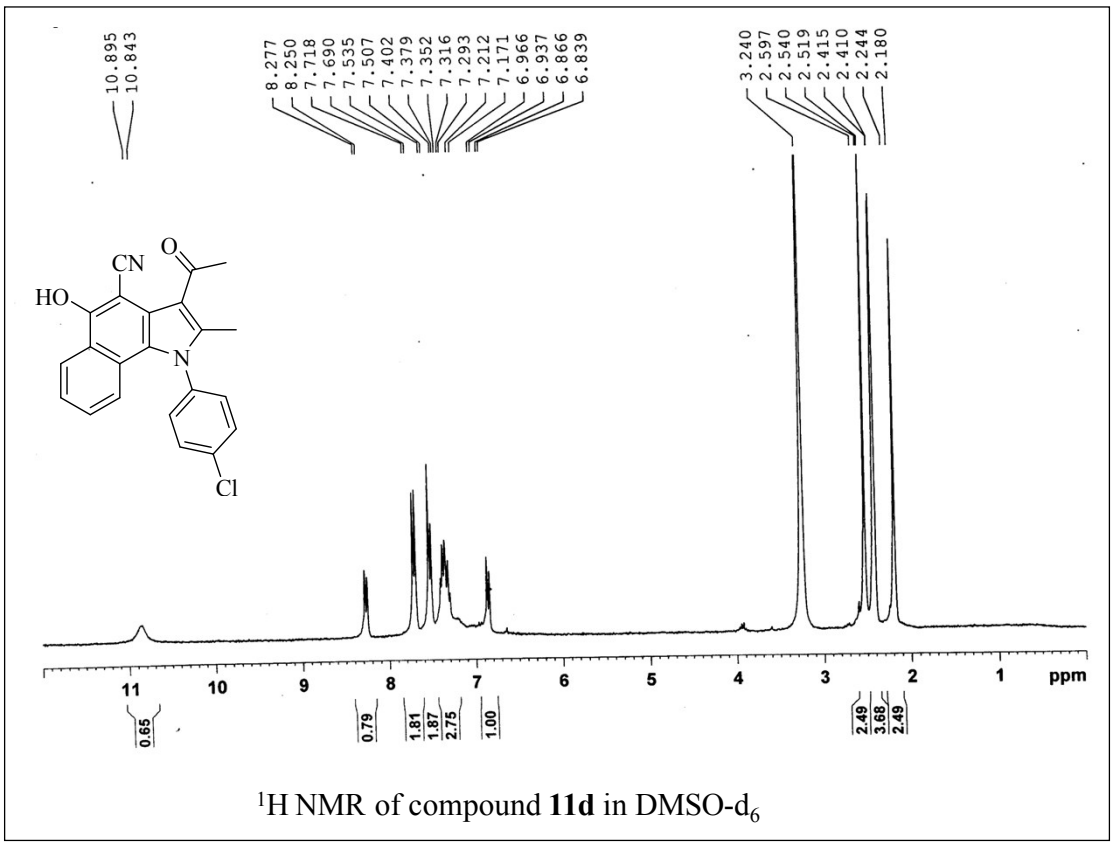
^{13}C NMR of compound **11b** in DMSO-d_6



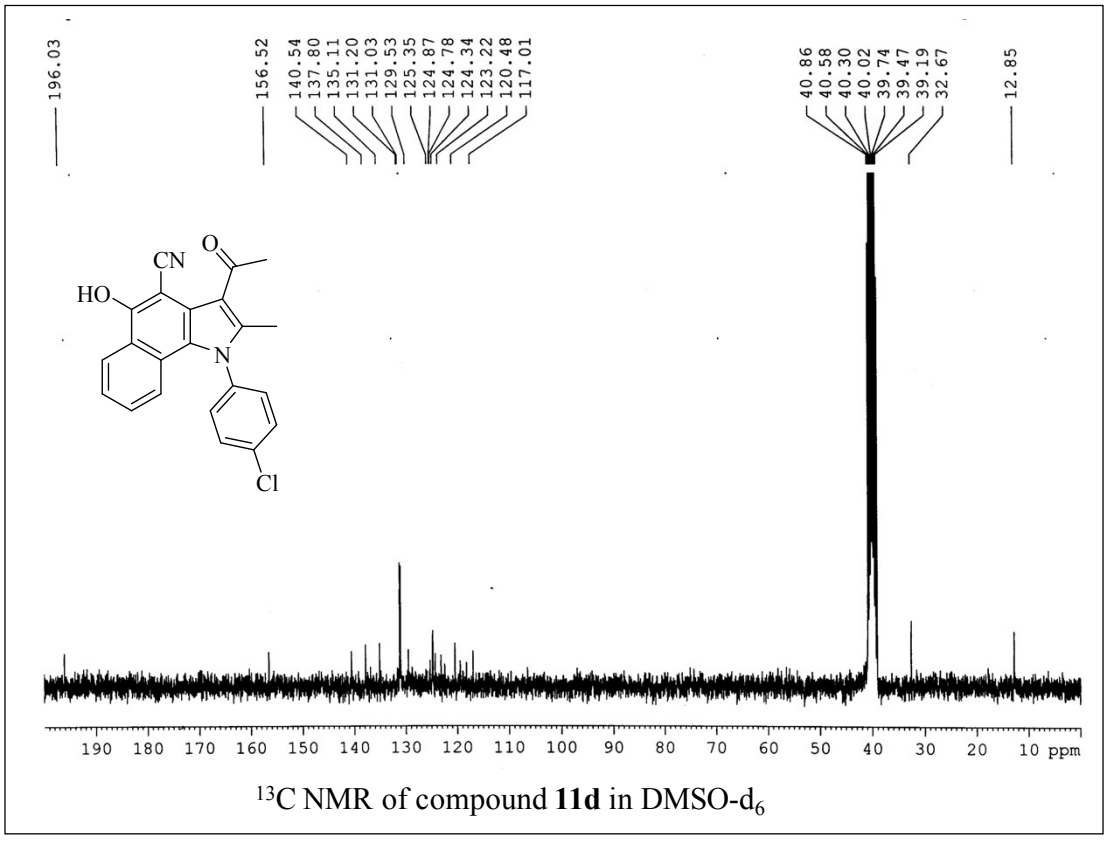
^{1}H NMR of compound **11c** in DMSO-d_6



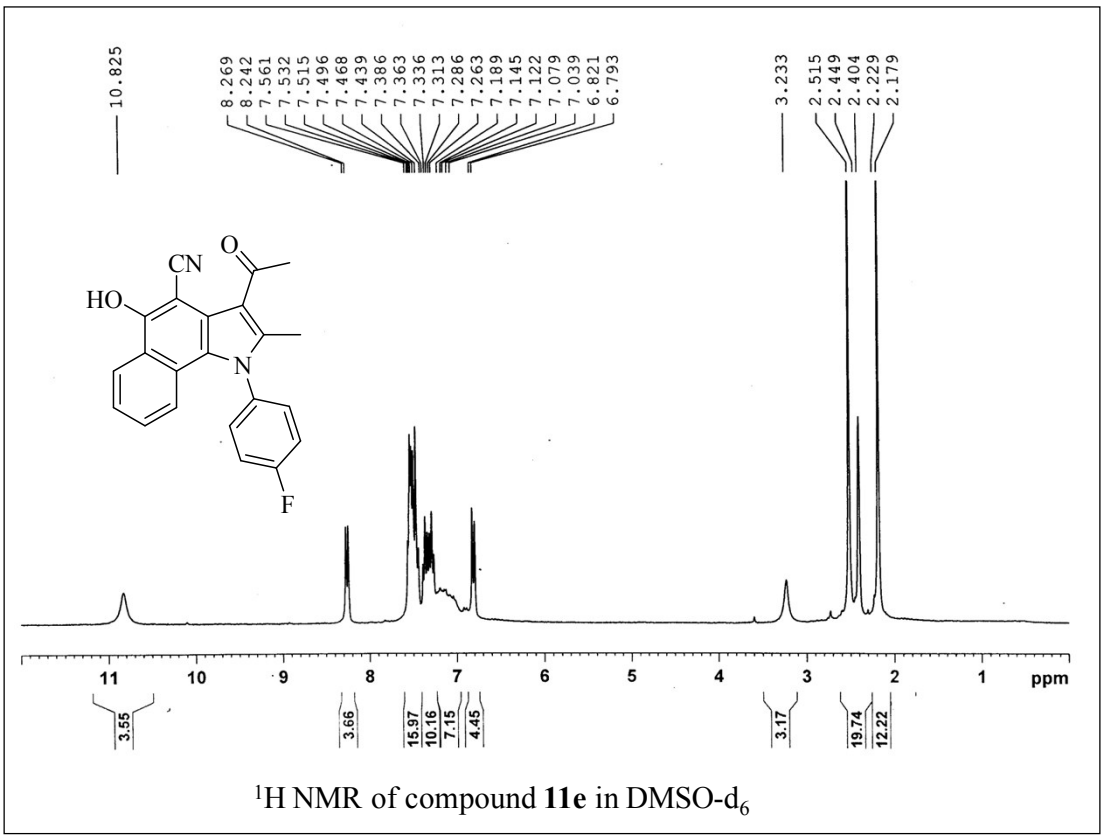
^{13}C NMR of compound **11c** in DMSO-d_6



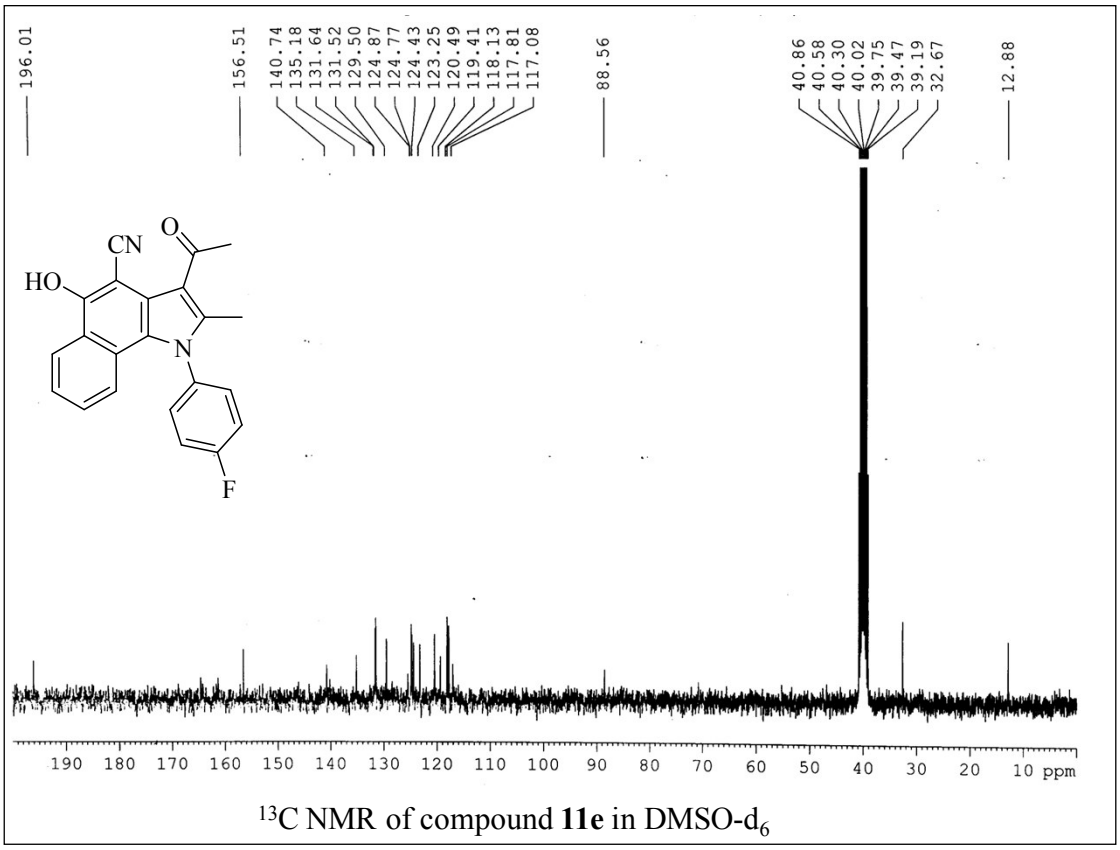
^{1}H NMR of compound **11d** in DMSO-d_6



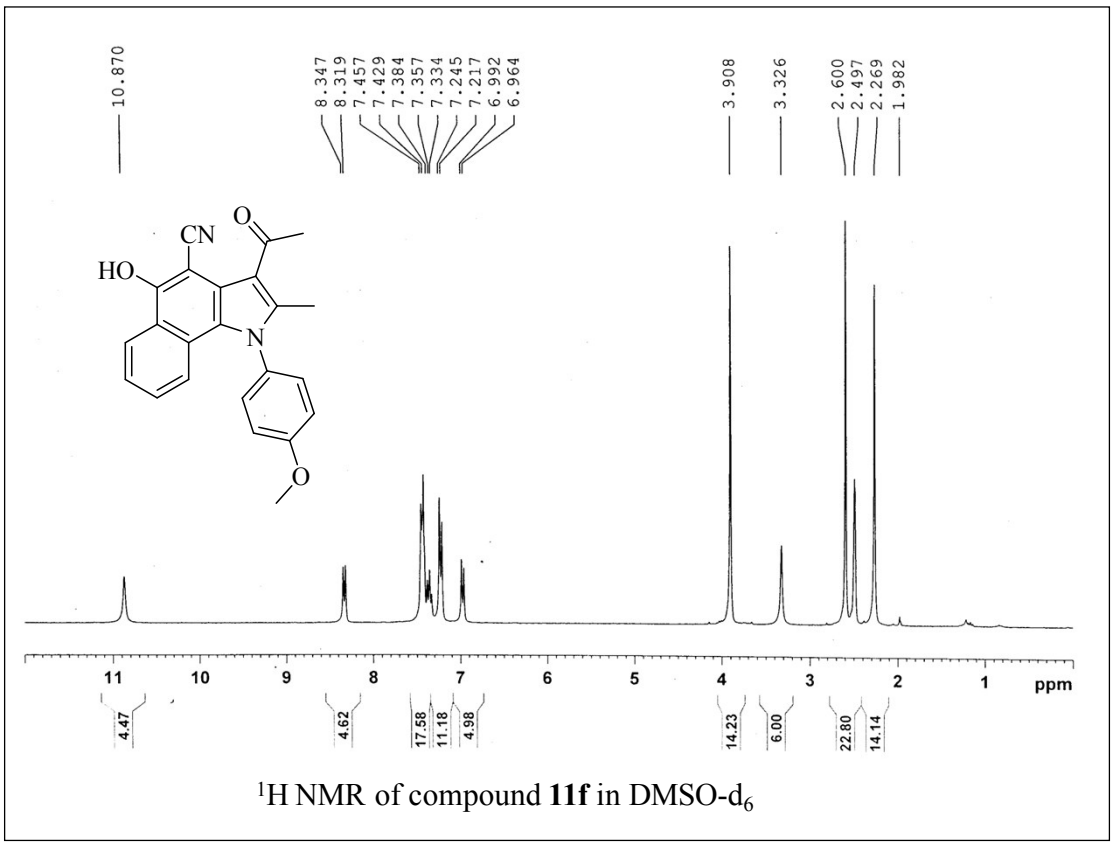
^{13}C NMR of compound **11d** in DMSO-d_6



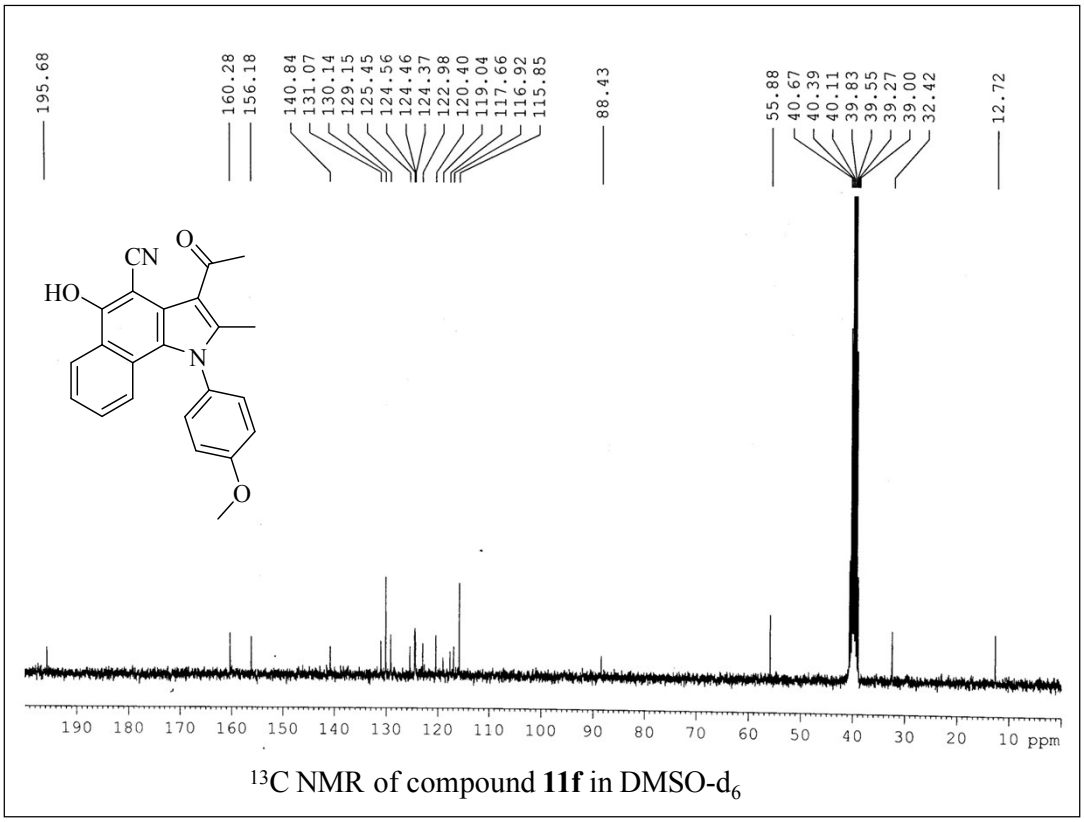
^{1}H NMR of compound **11e** in DMSO-d_6



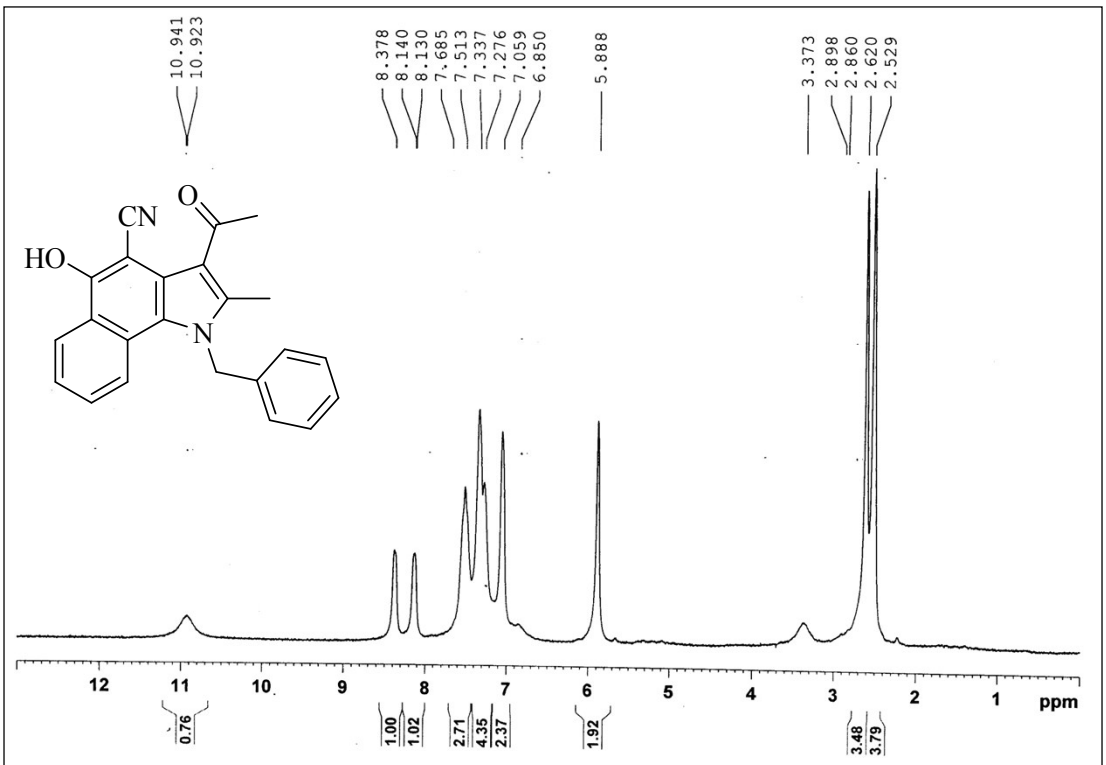
^{13}C NMR of compound **11e** in DMSO-d_6



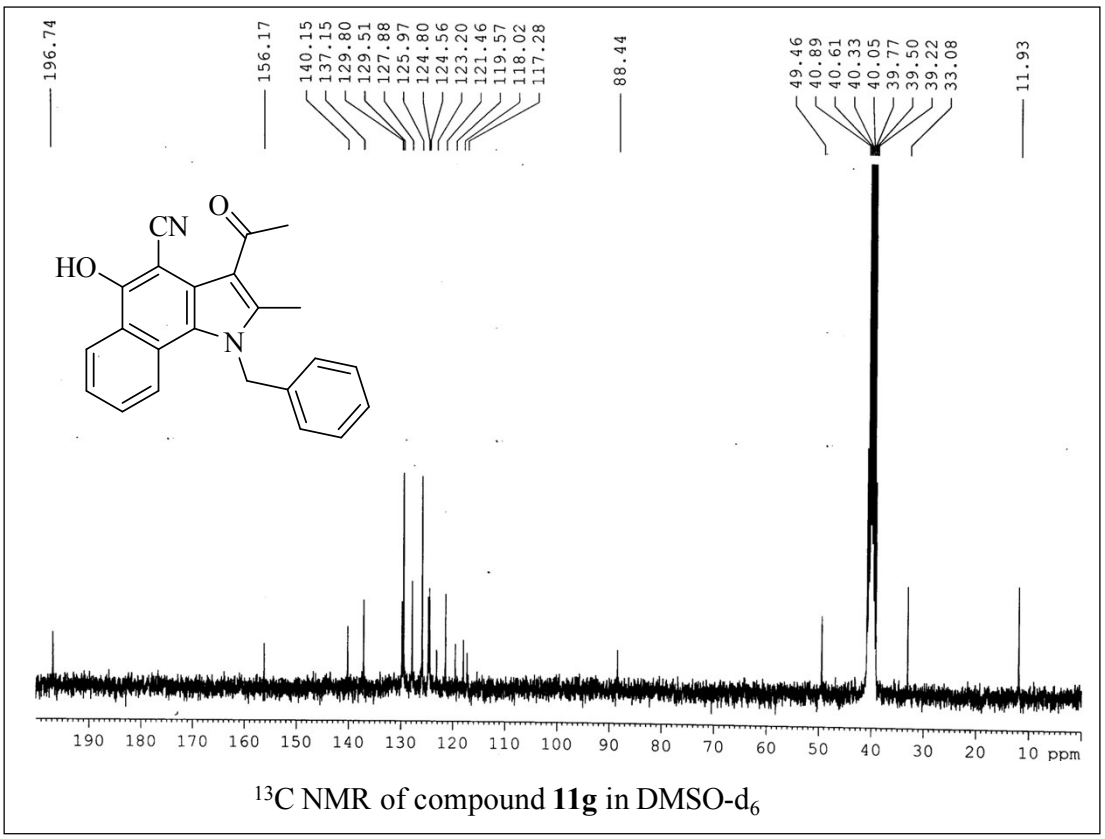
^{1}H NMR of compound **11f** in DMSO-d_6



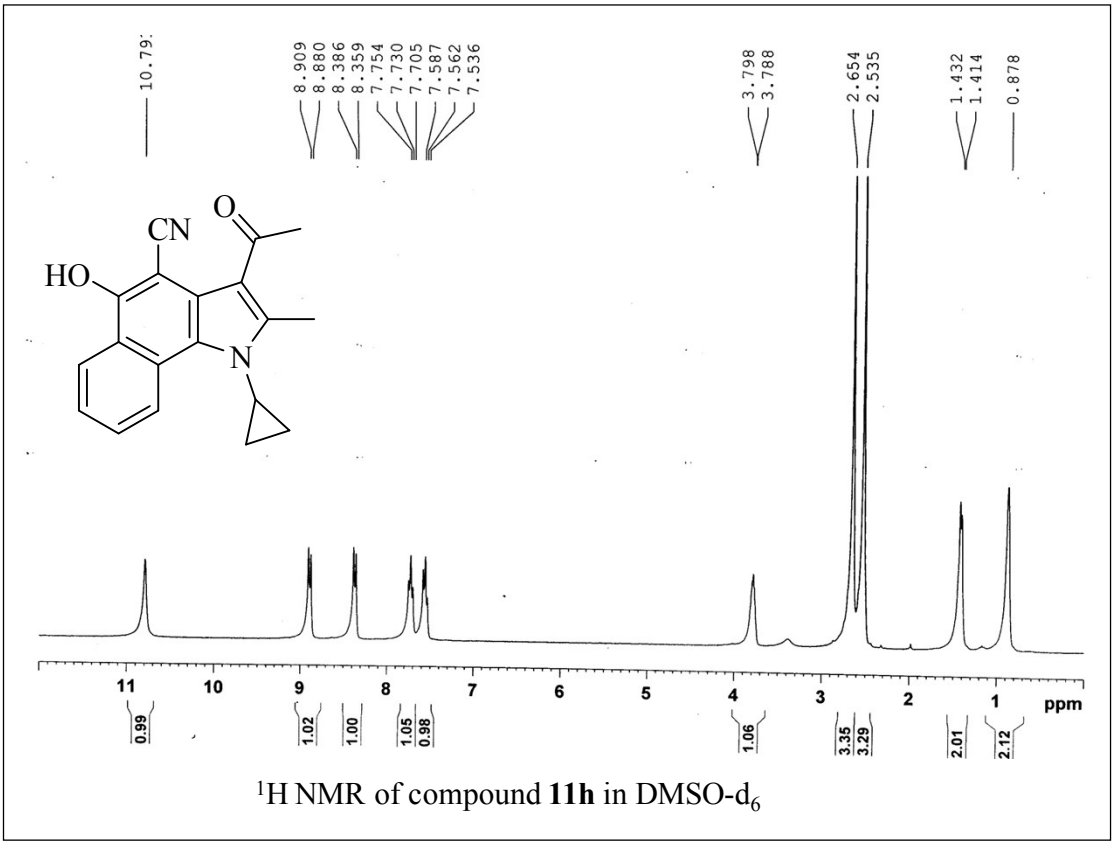
^{13}C NMR of compound **11f** in DMSO-d_6



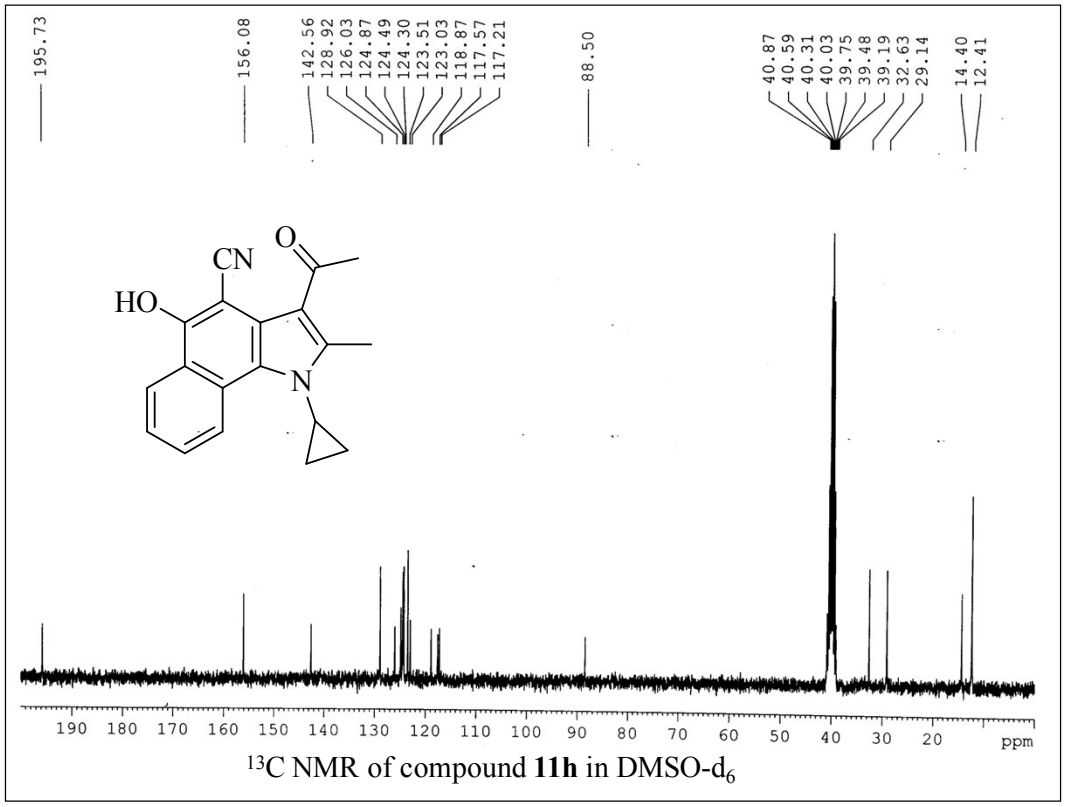
^{1}H NMR of compound **11g** in DMSO-d_6



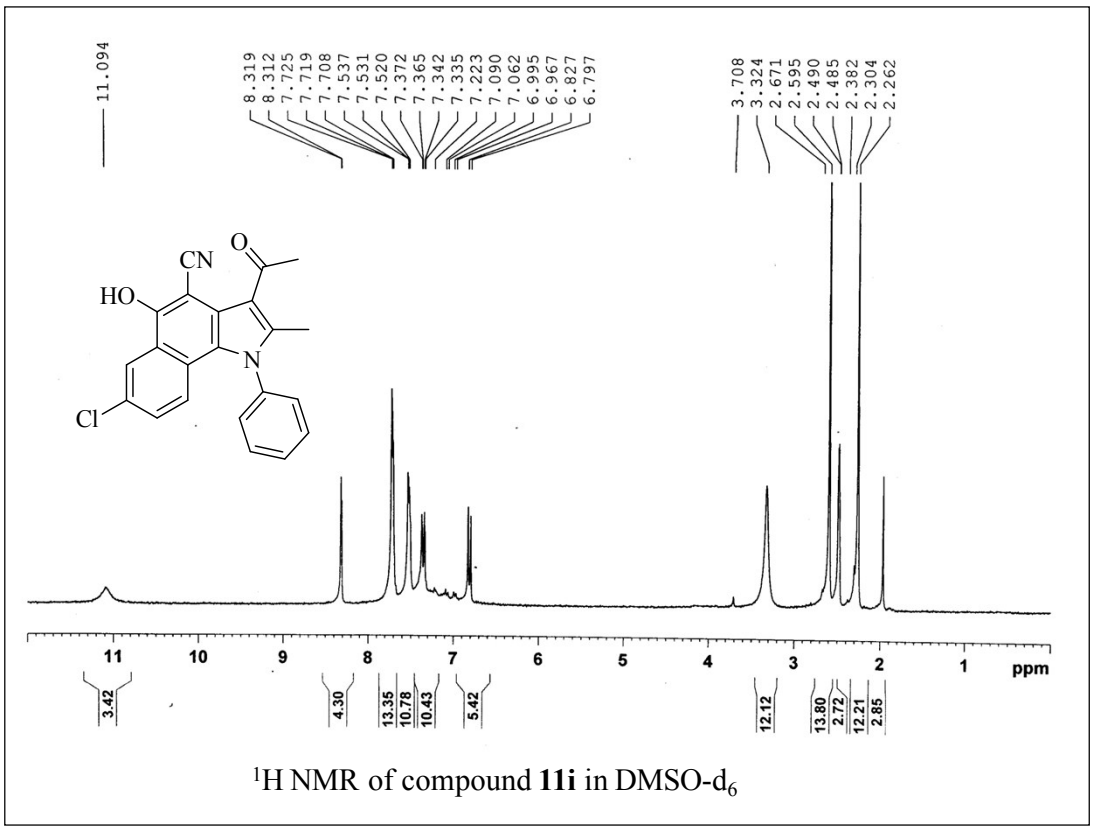
^{13}C NMR of compound **11g** in DMSO-d_6



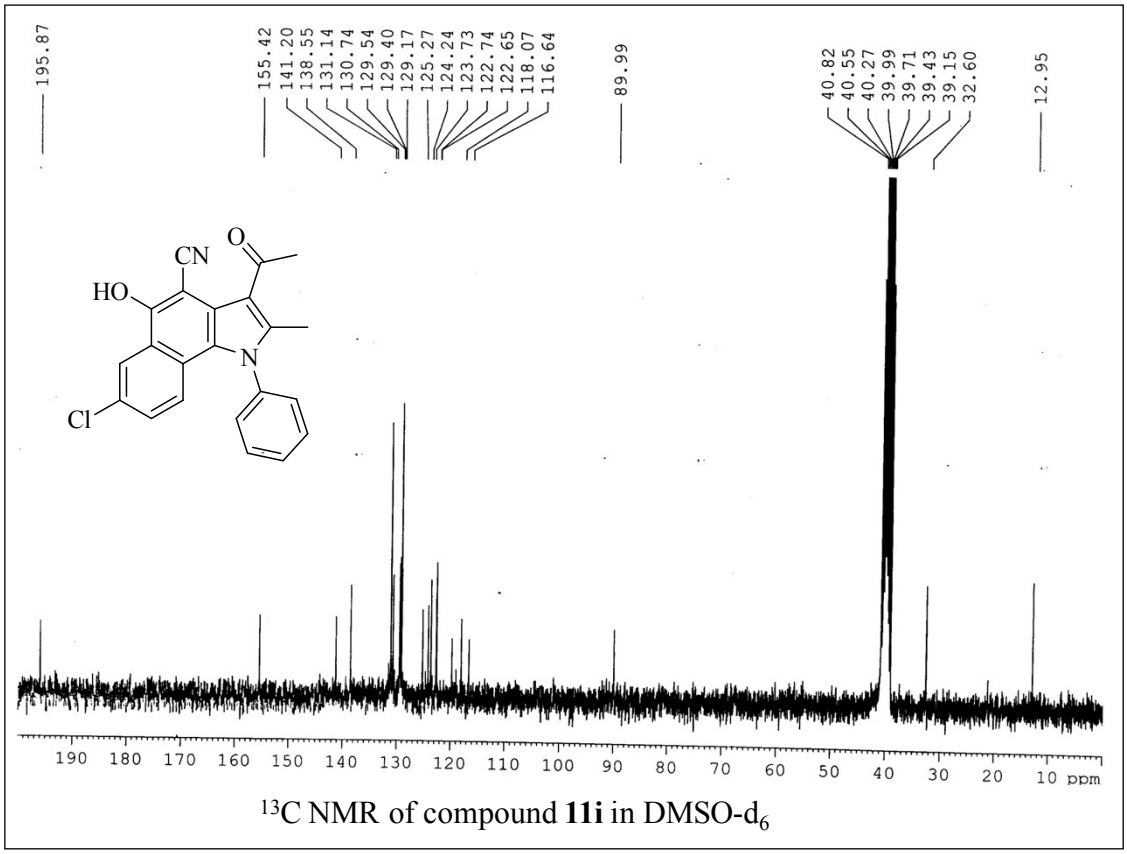
^{1}H NMR of compound **11h** in DMSO-d_6



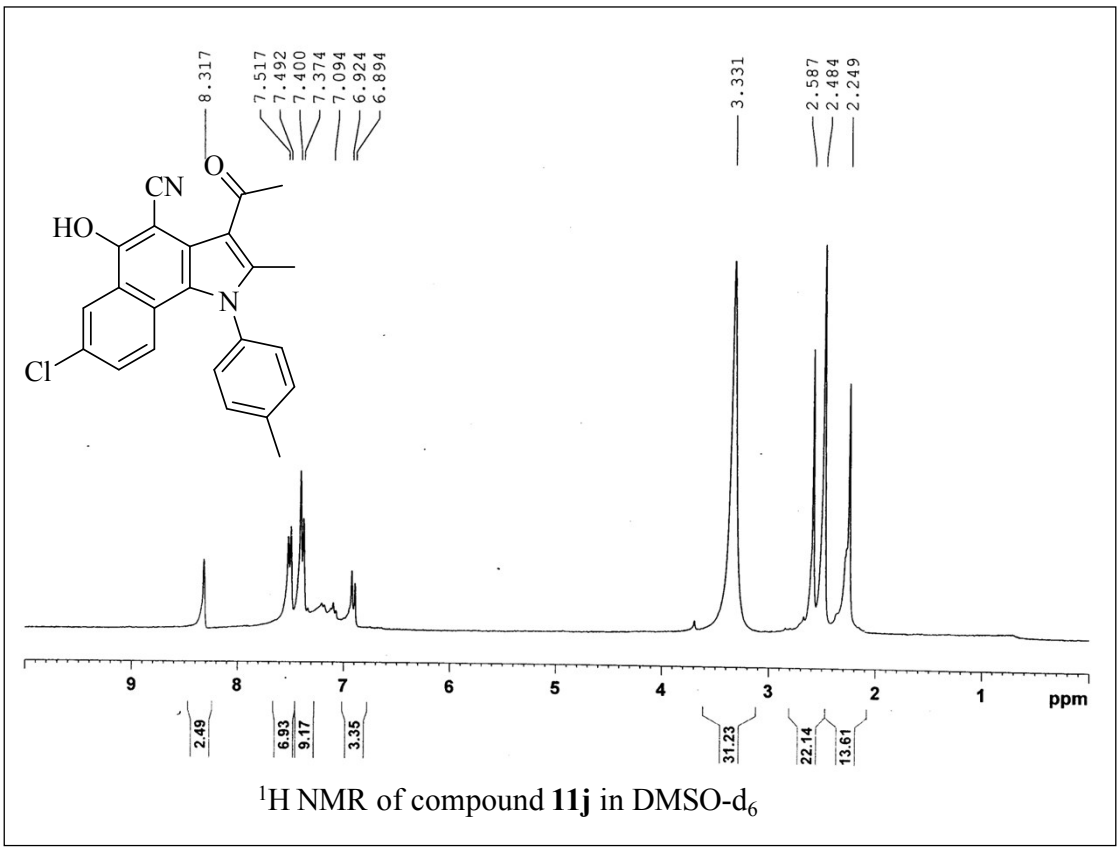
^{13}C NMR of compound **11h** in DMSO-d_6



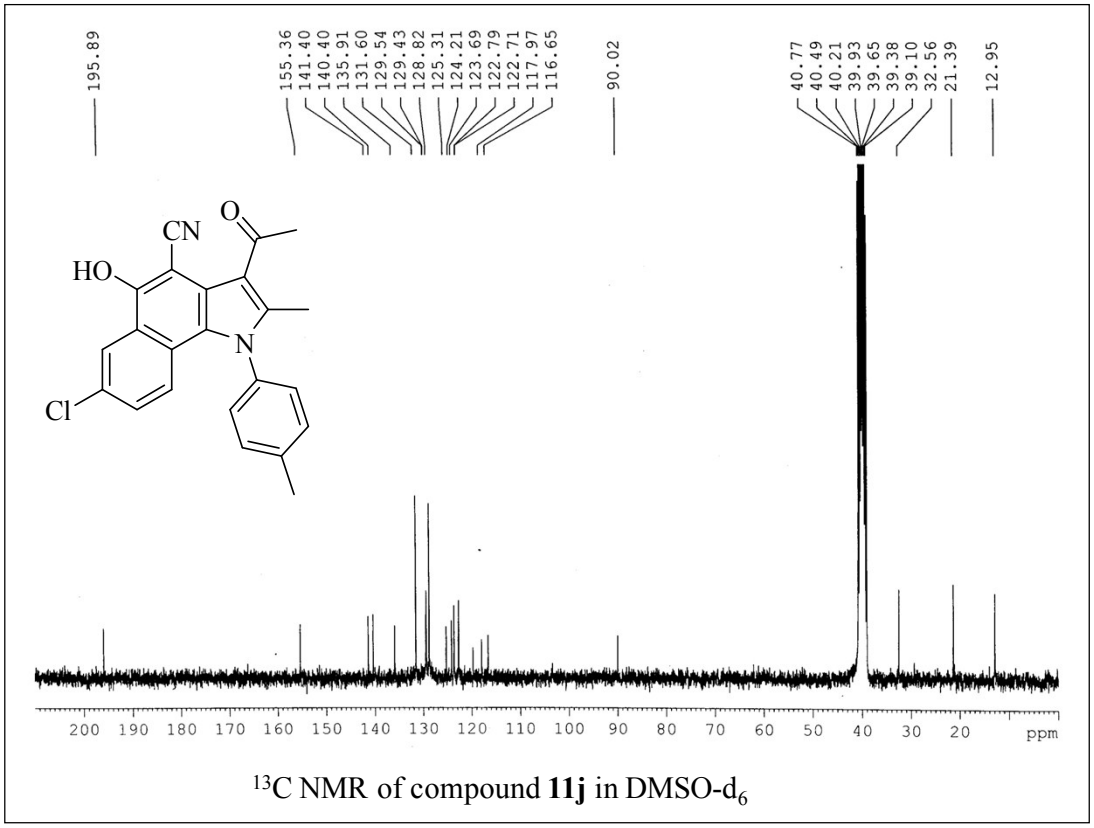
^{1}H NMR of compound **11i** in DMSO-d_6



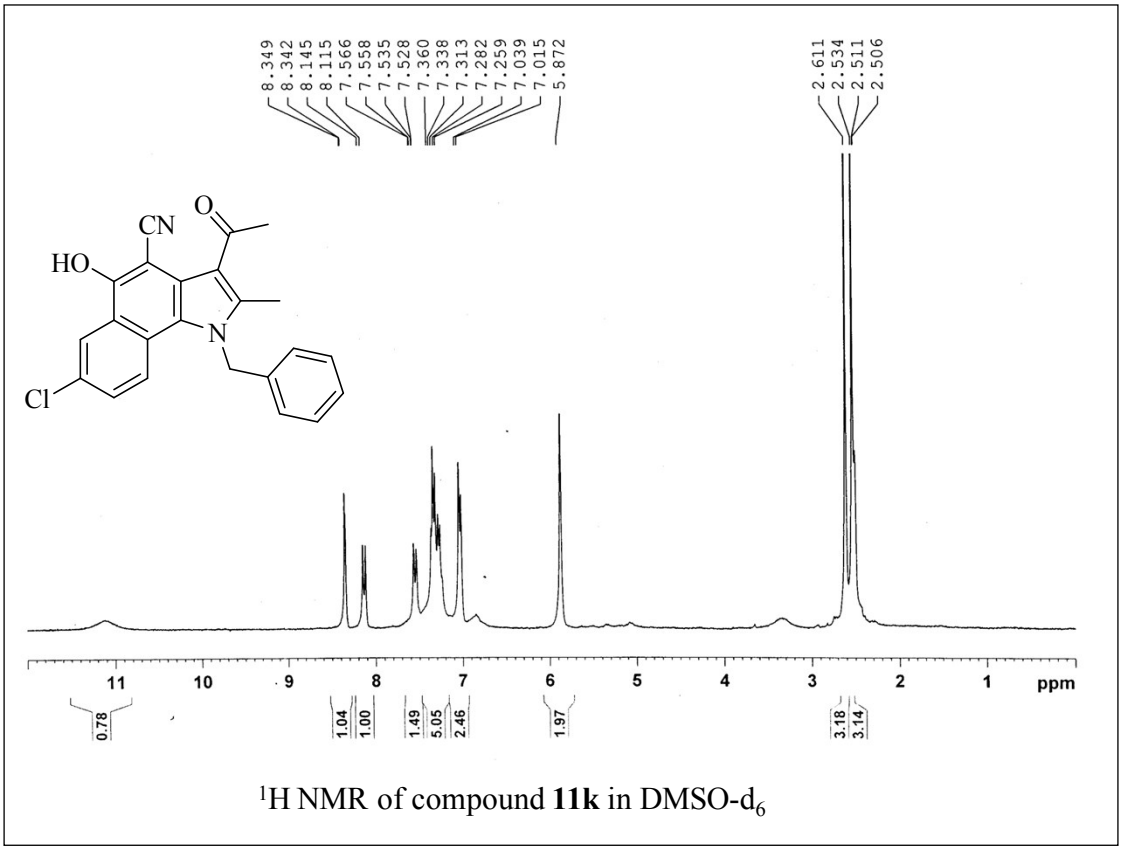
^{13}C NMR of compound **11i** in DMSO-d_6



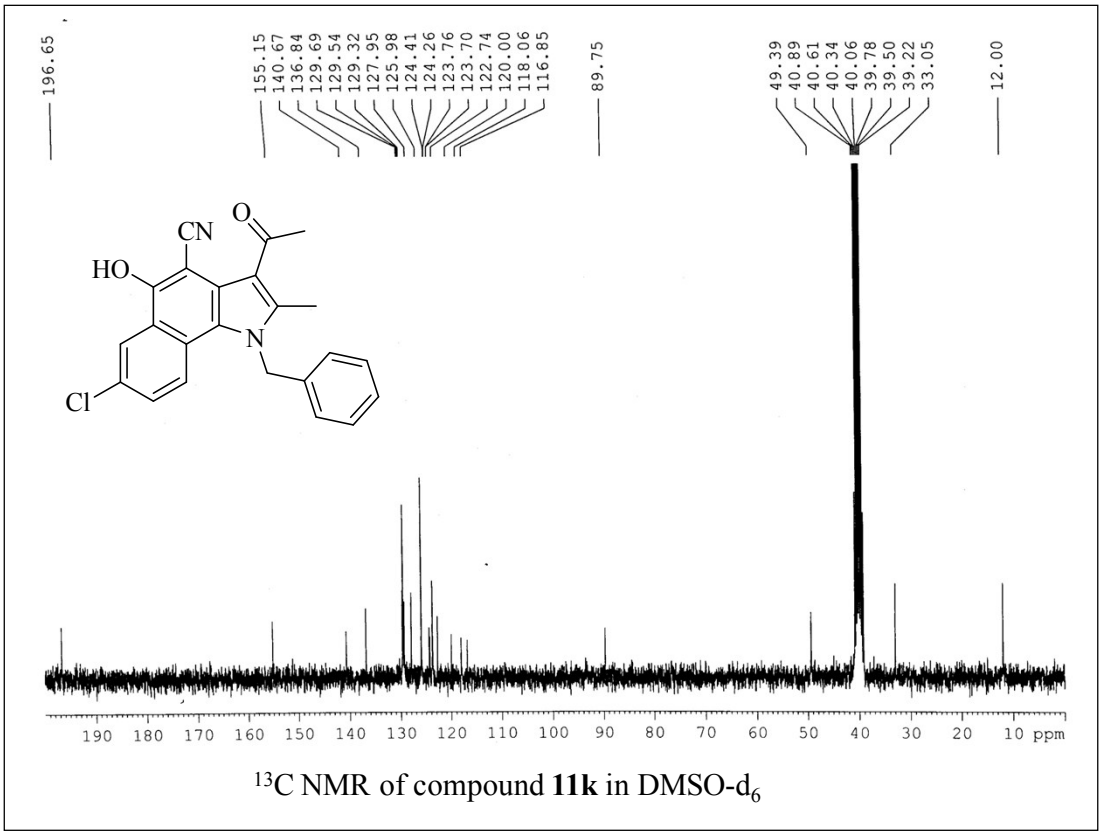
^{1}H NMR of compound **11j** in DMSO-d_6



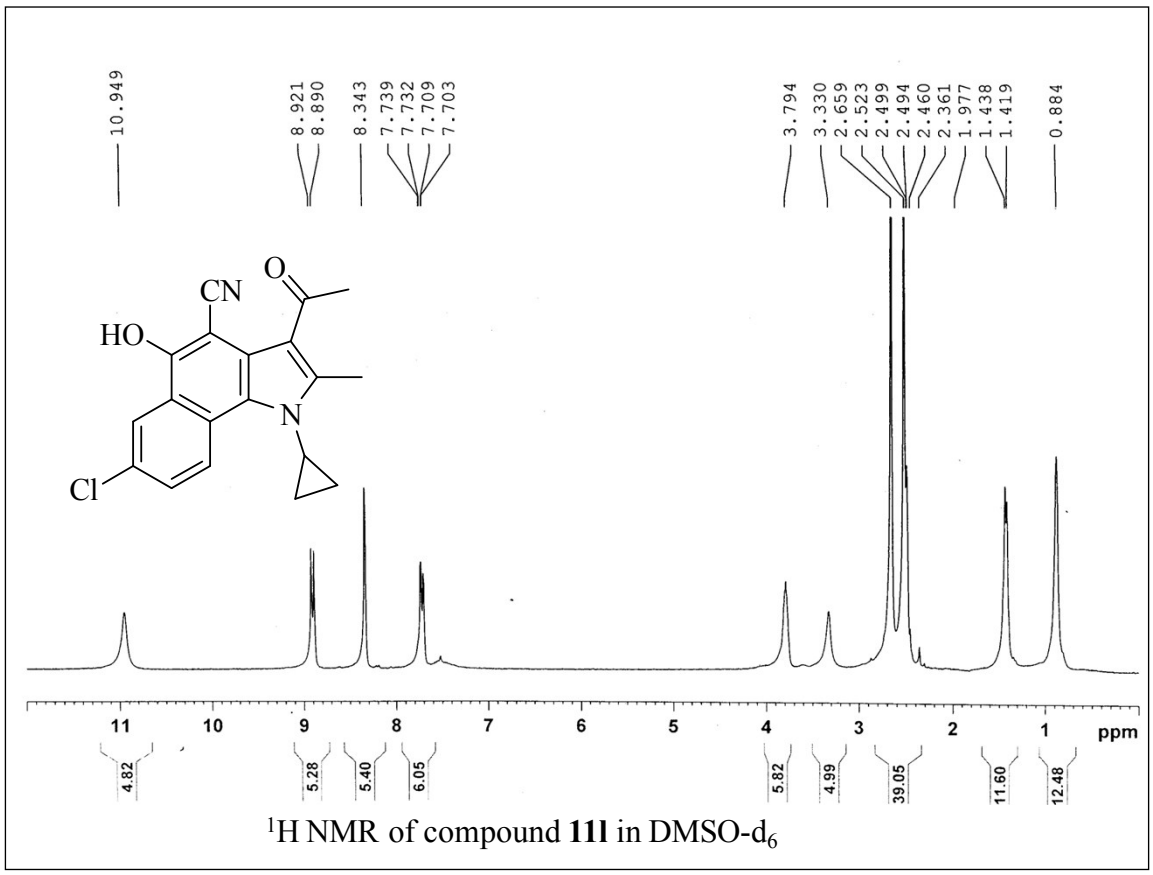
^{13}C NMR of compound **11j** in DMSO-d_6



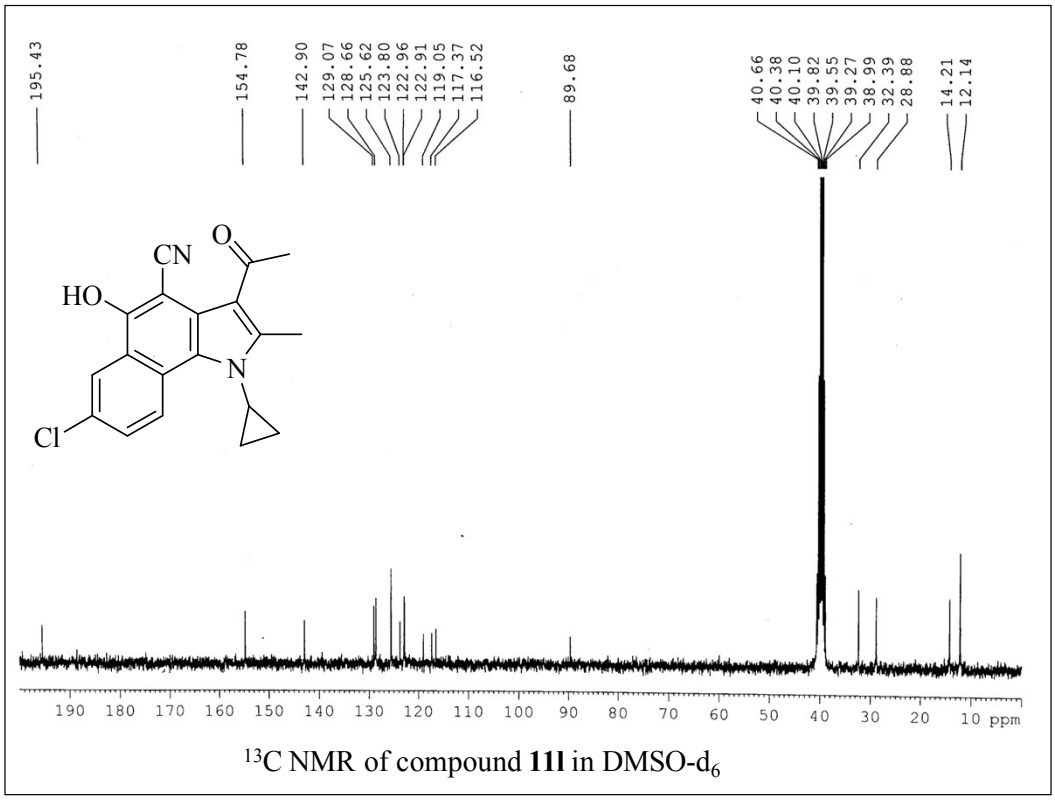
^{1}H NMR of compound **11k** in DMSO-d_6



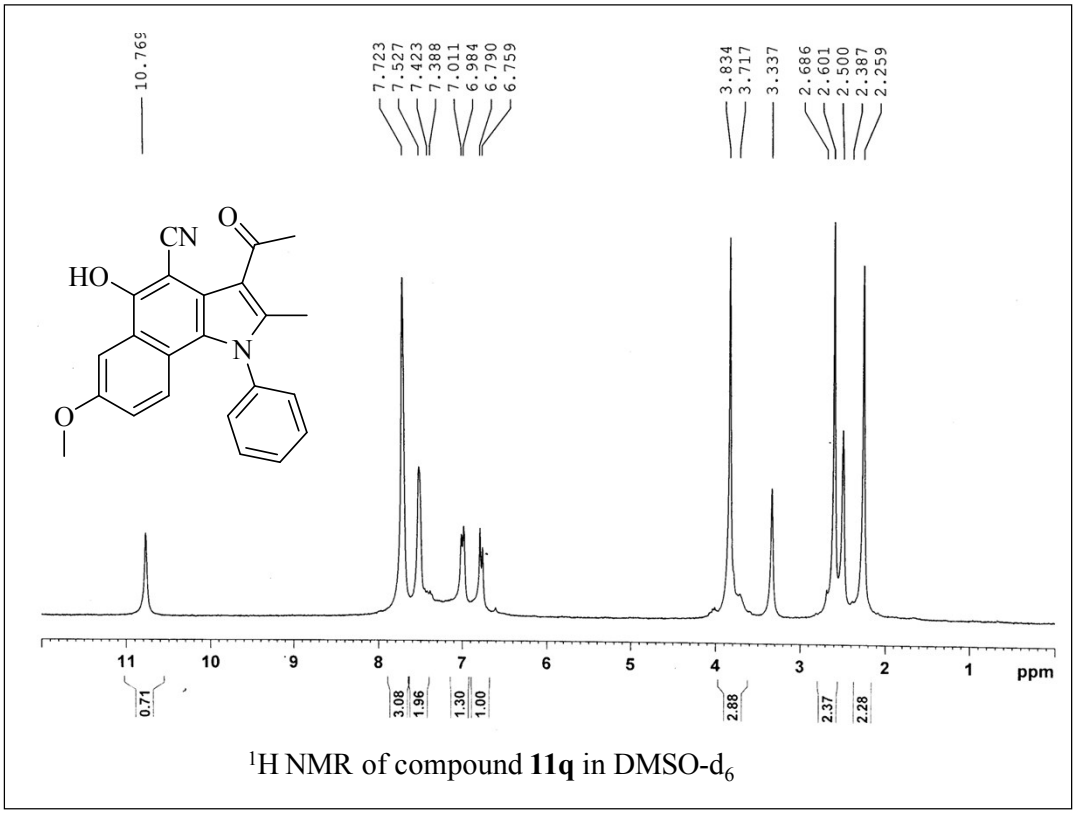
^{13}C NMR of compound **11k** in DMSO-d_6



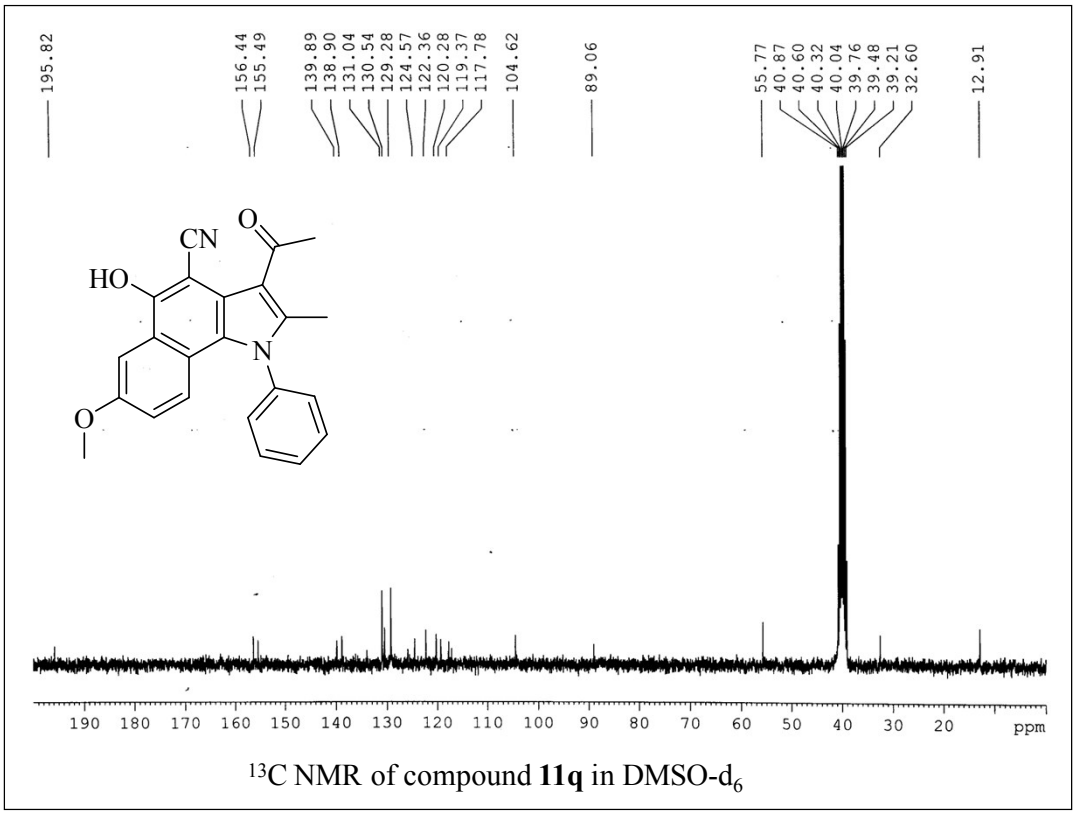
^{1}H NMR of compound **11l** in DMSO-d_6



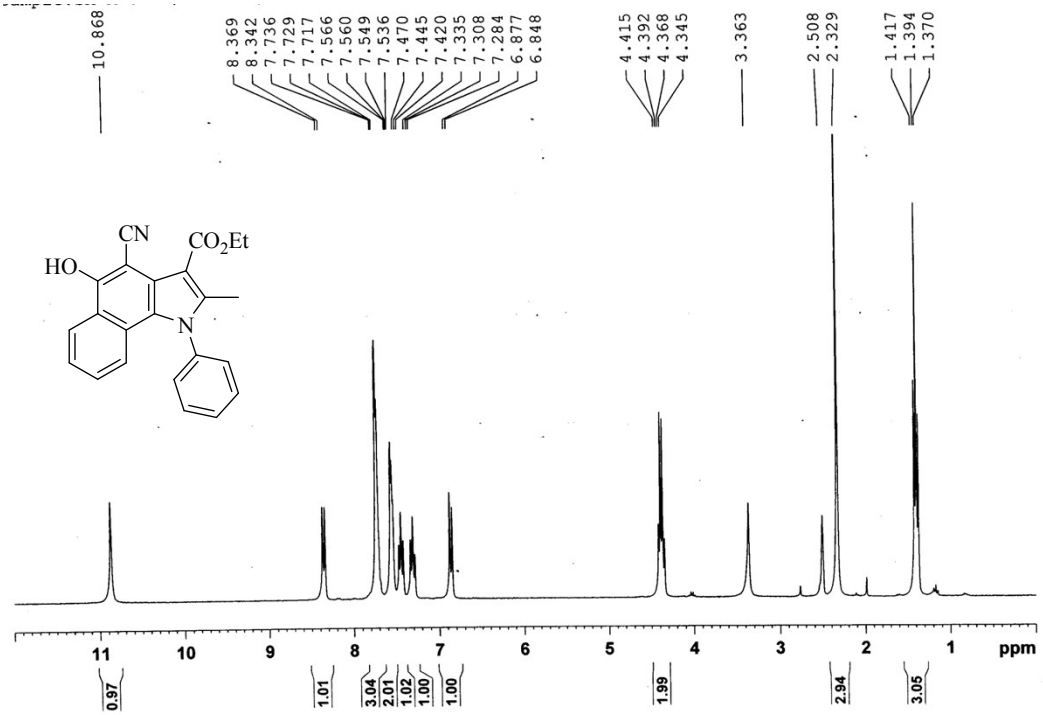
^{13}C NMR of compound **11l** in DMSO-d_6



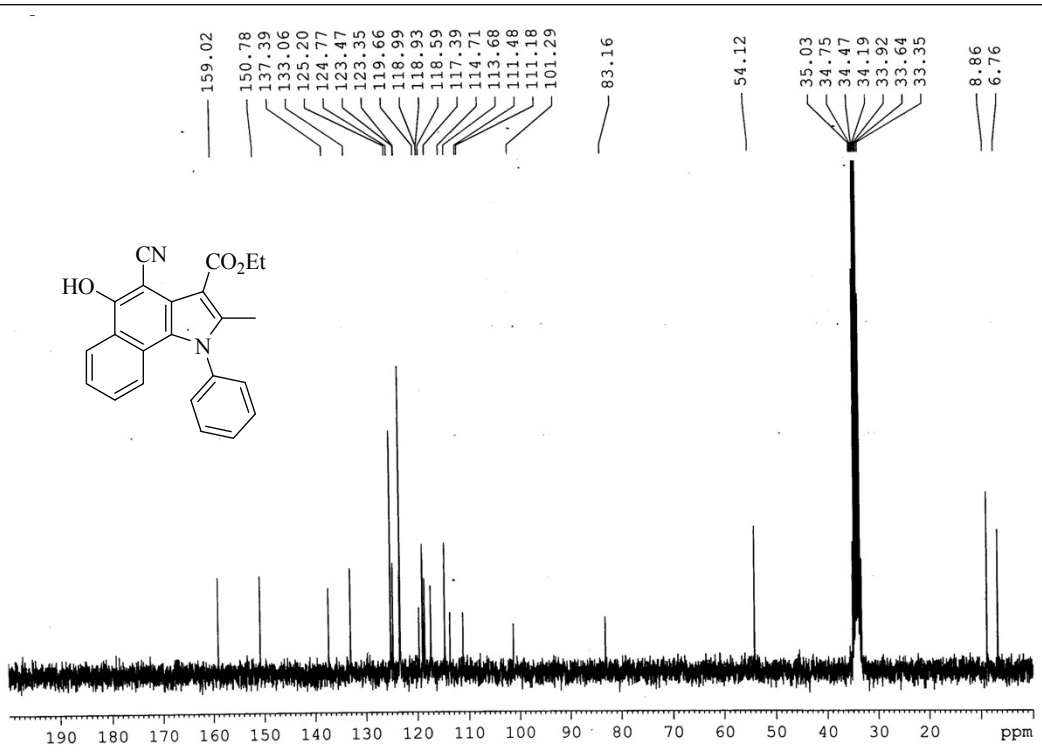
^{1}H NMR of compound **11q** in DMSO-d_6



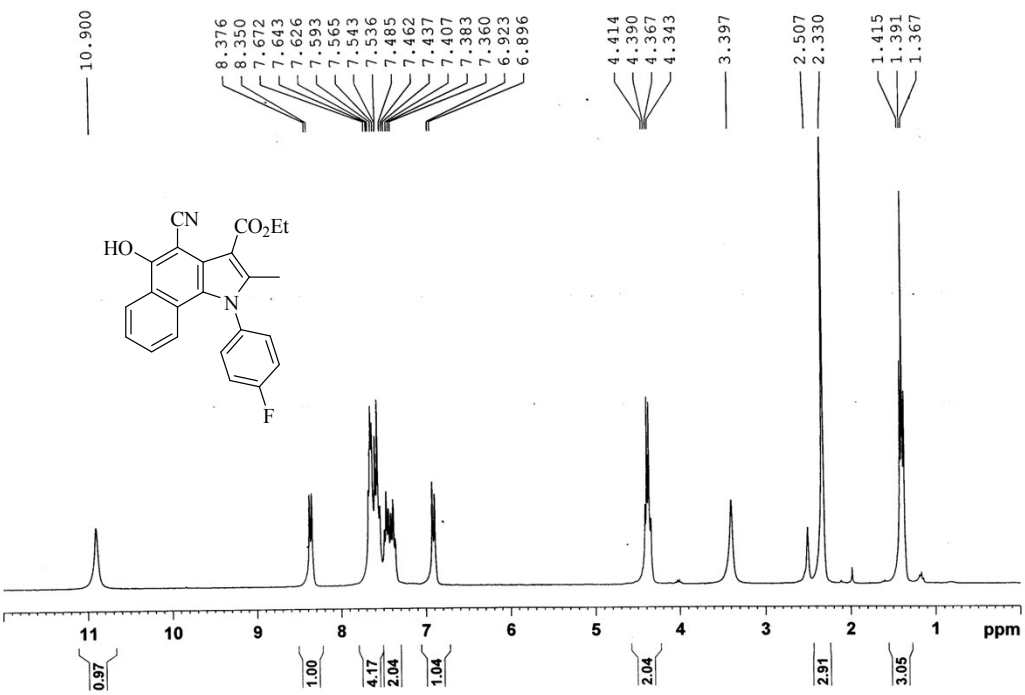
^{13}C NMR of compound **11q** in DMSO-d_6



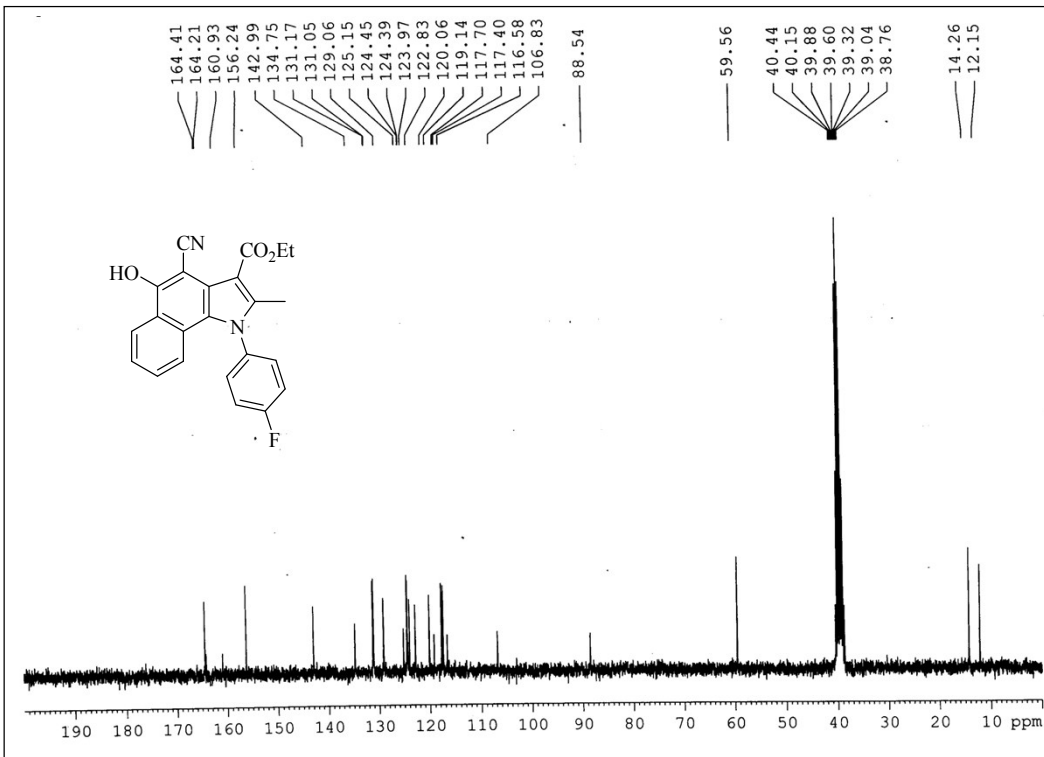
^{1}H NMR of compound **11u** in DMSO-d_6



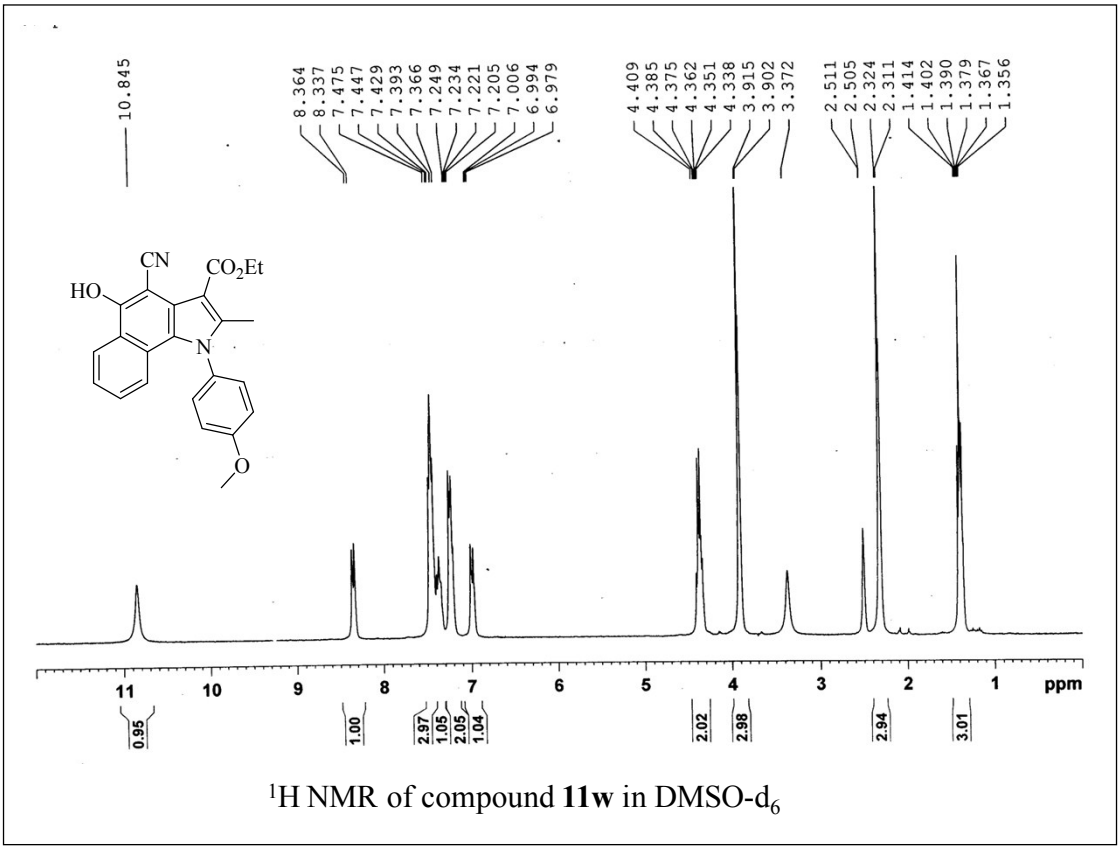
^{13}C NMR of compound **11u** in DMSO-d_6



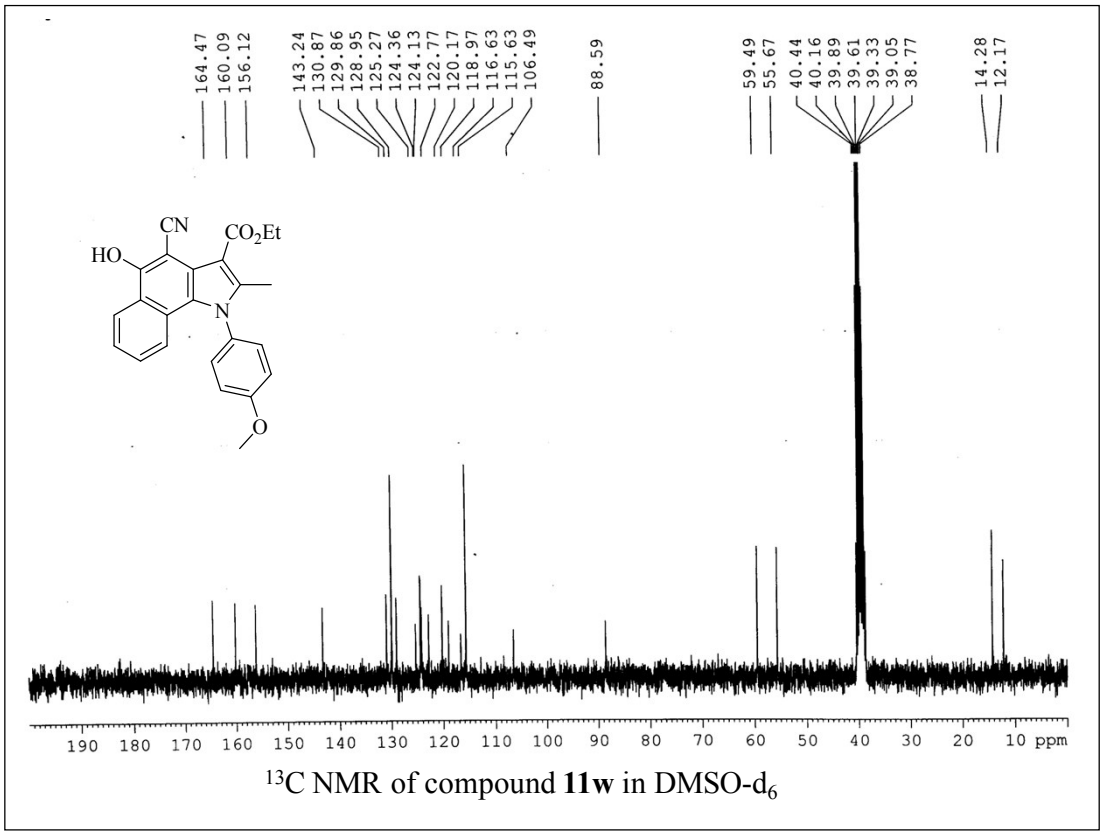
^{1}H NMR of compound **11v** in DMSO-d_6



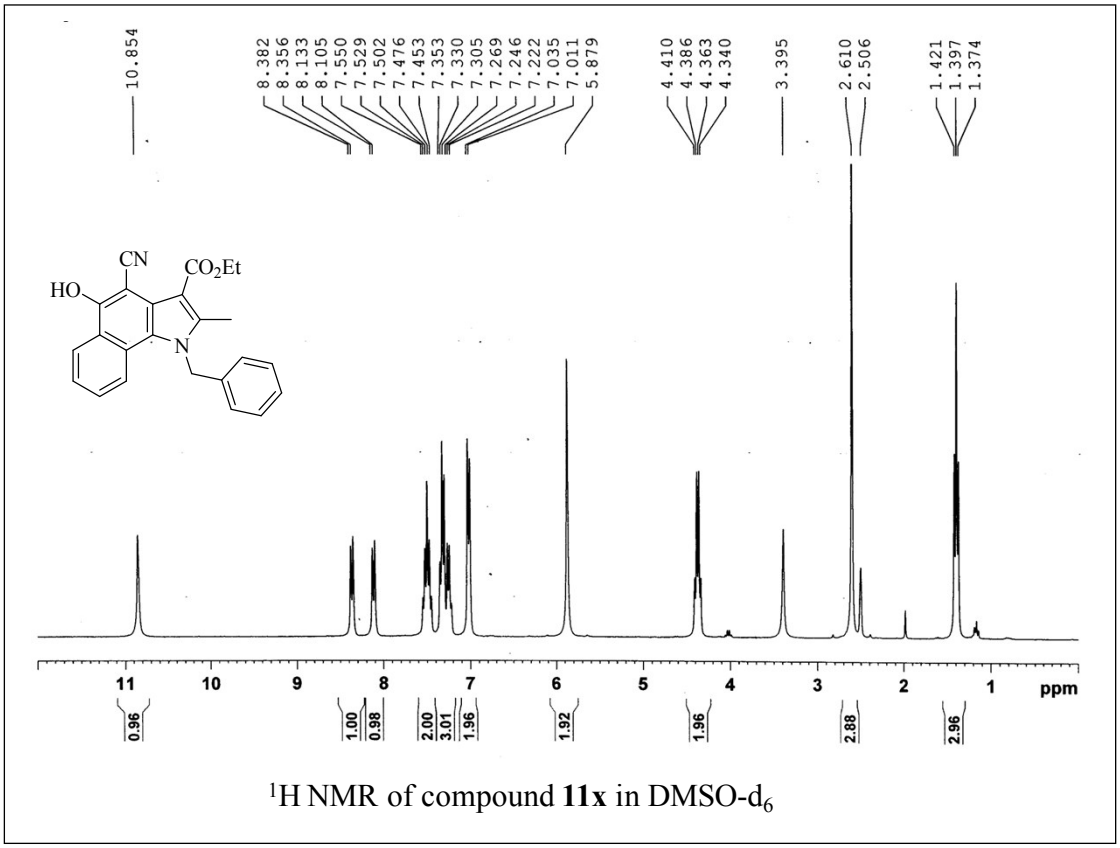
^{13}C NMR of compound **11v** in DMSO-d_6



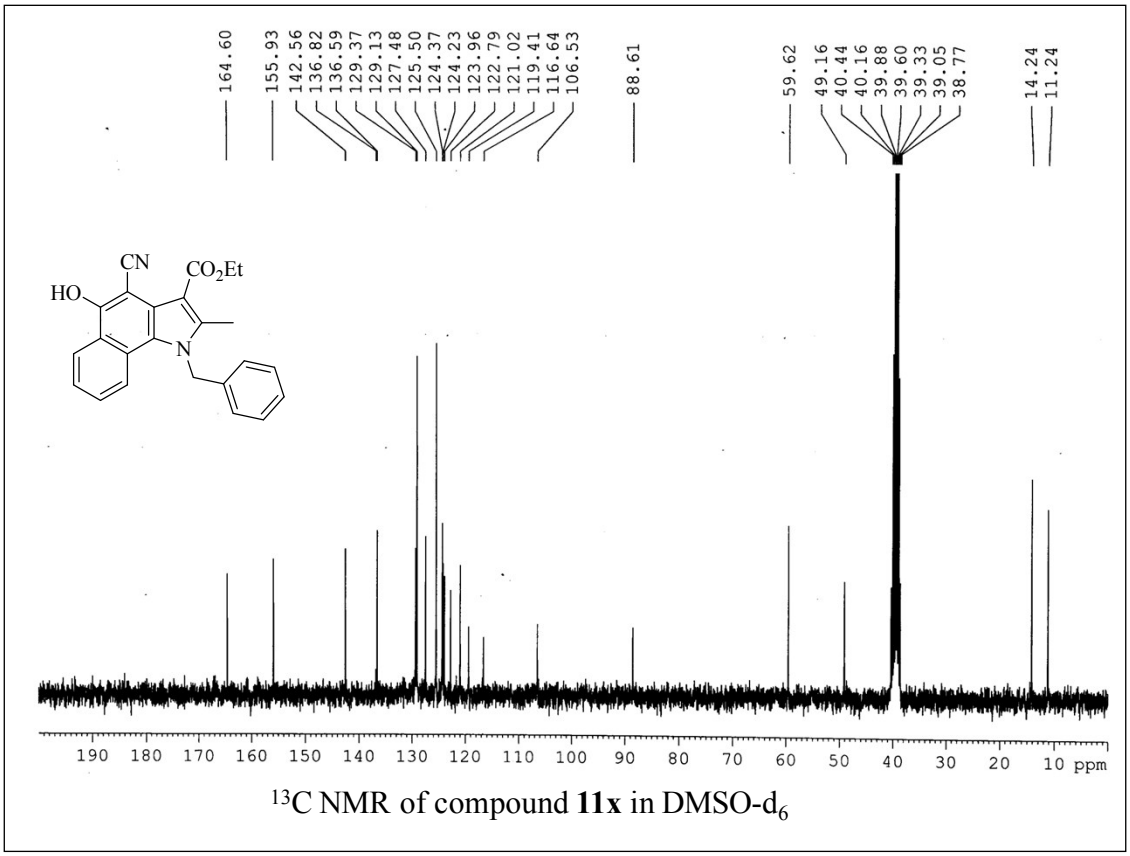
^{1}H NMR of compound **11w** in DMSO-d_6



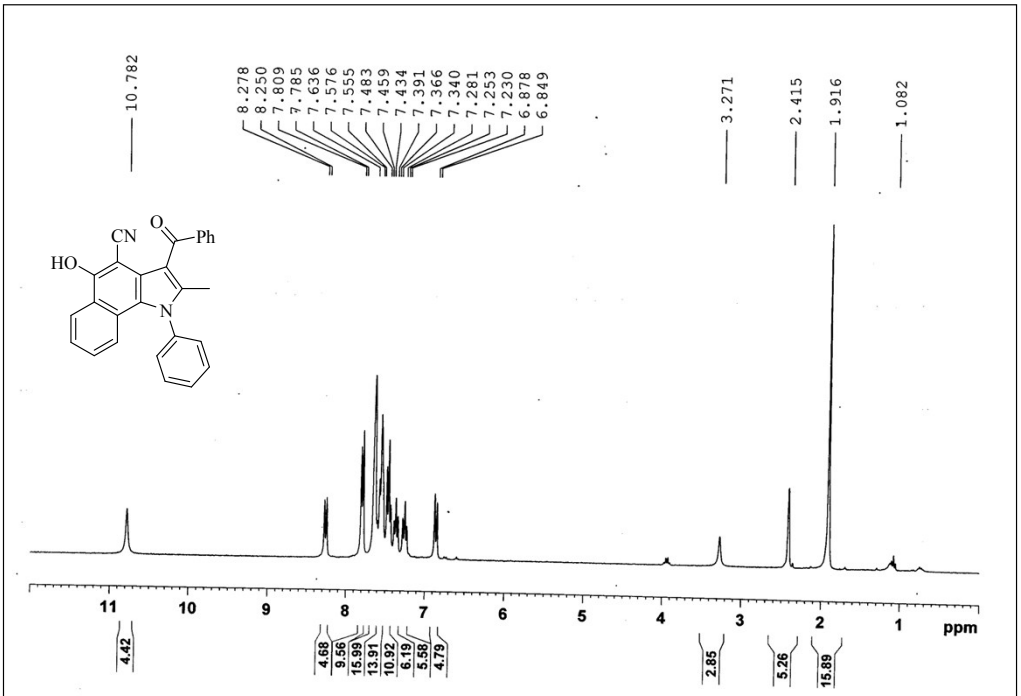
^{13}C NMR of compound **11w** in DMSO-d_6



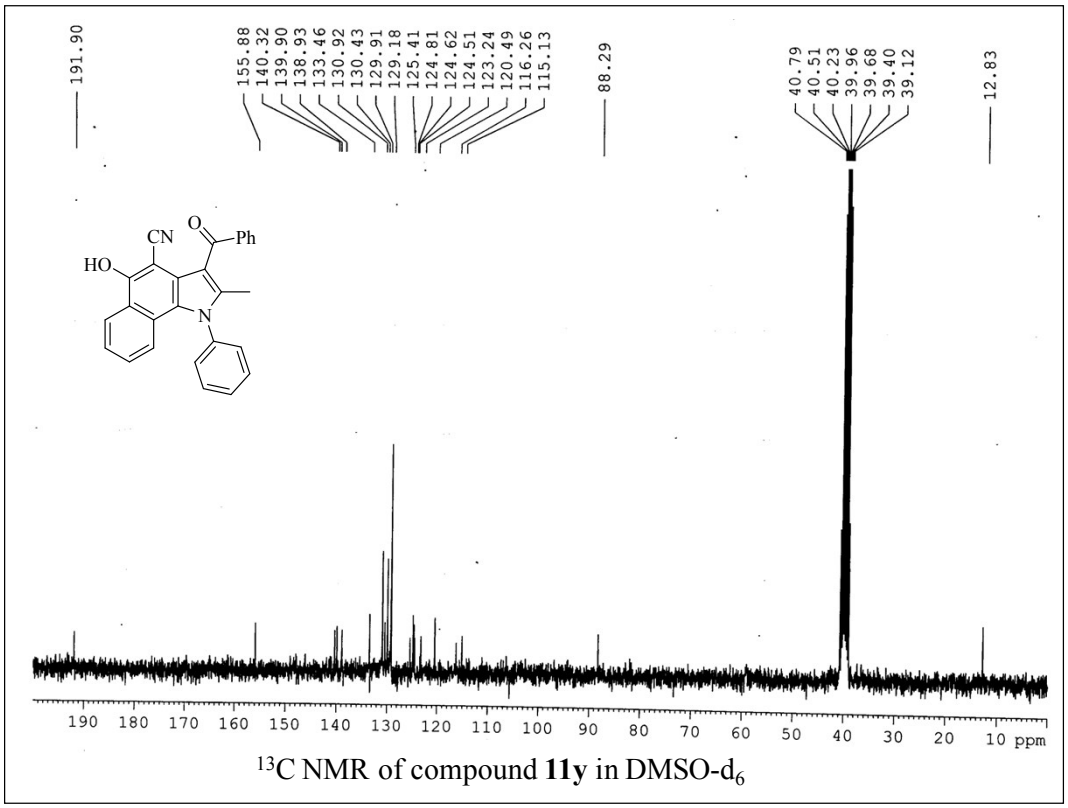
^{1}H NMR of compound **11x** in DMSO-d_6



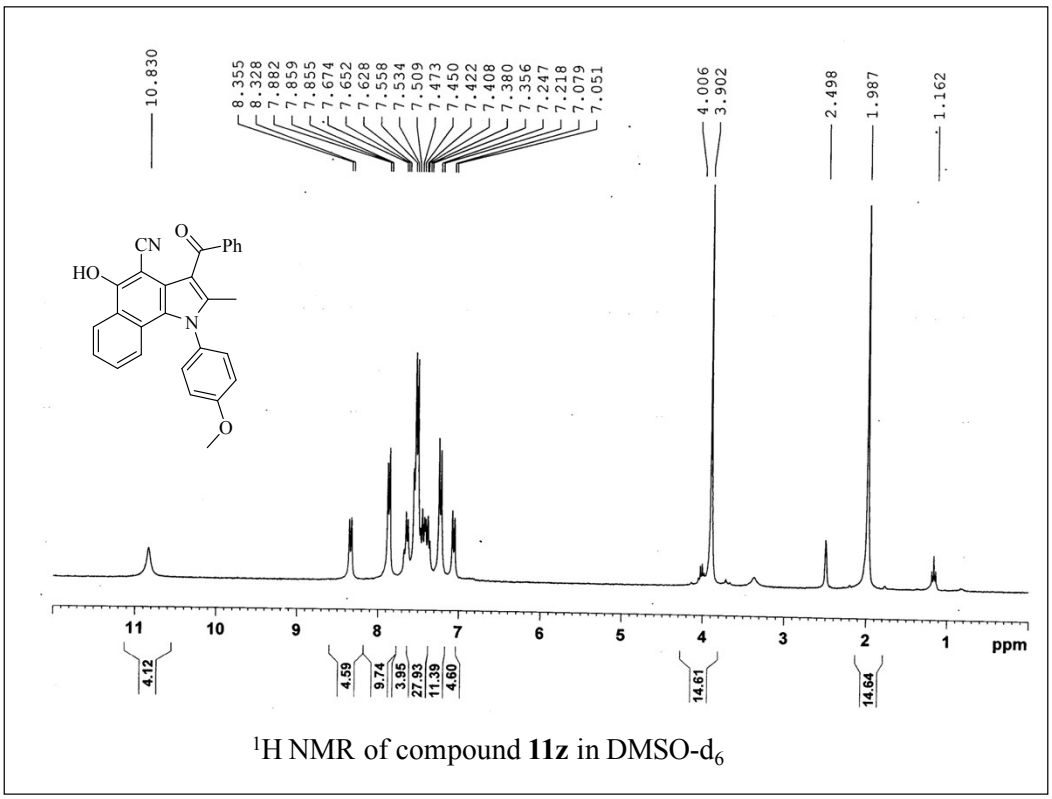
^{13}C NMR of compound **11x** in DMSO-d_6



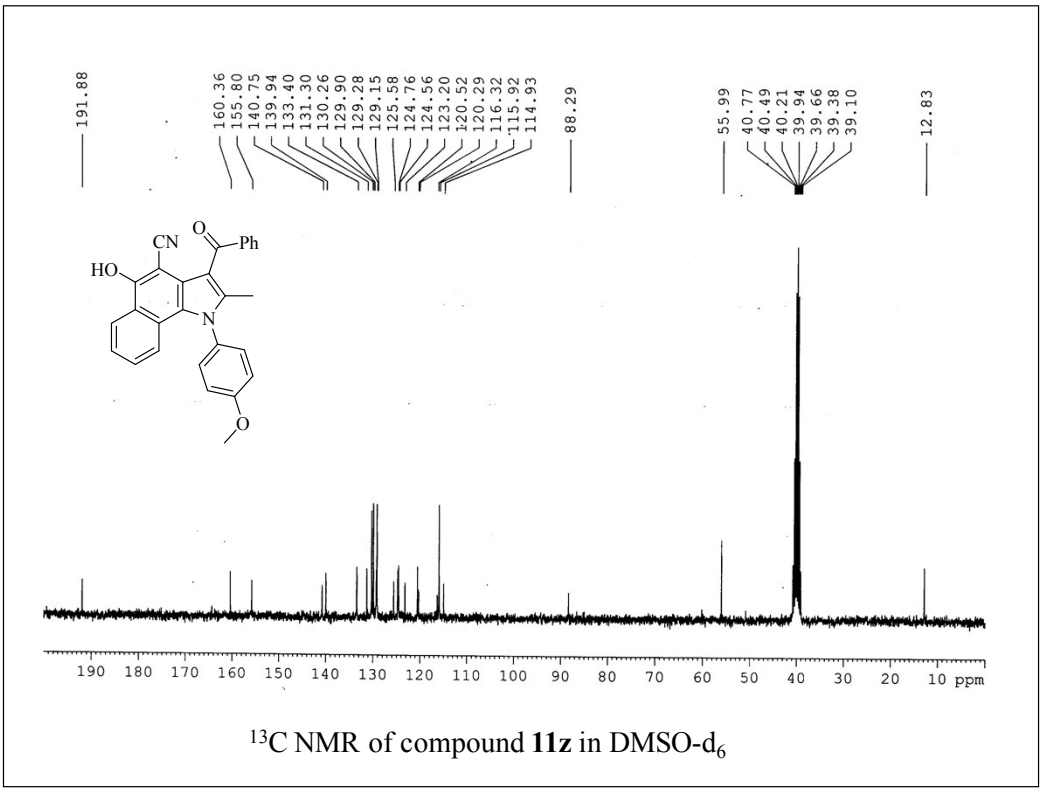
^{1}H NMR of compound **11y** in DMSO-d_6



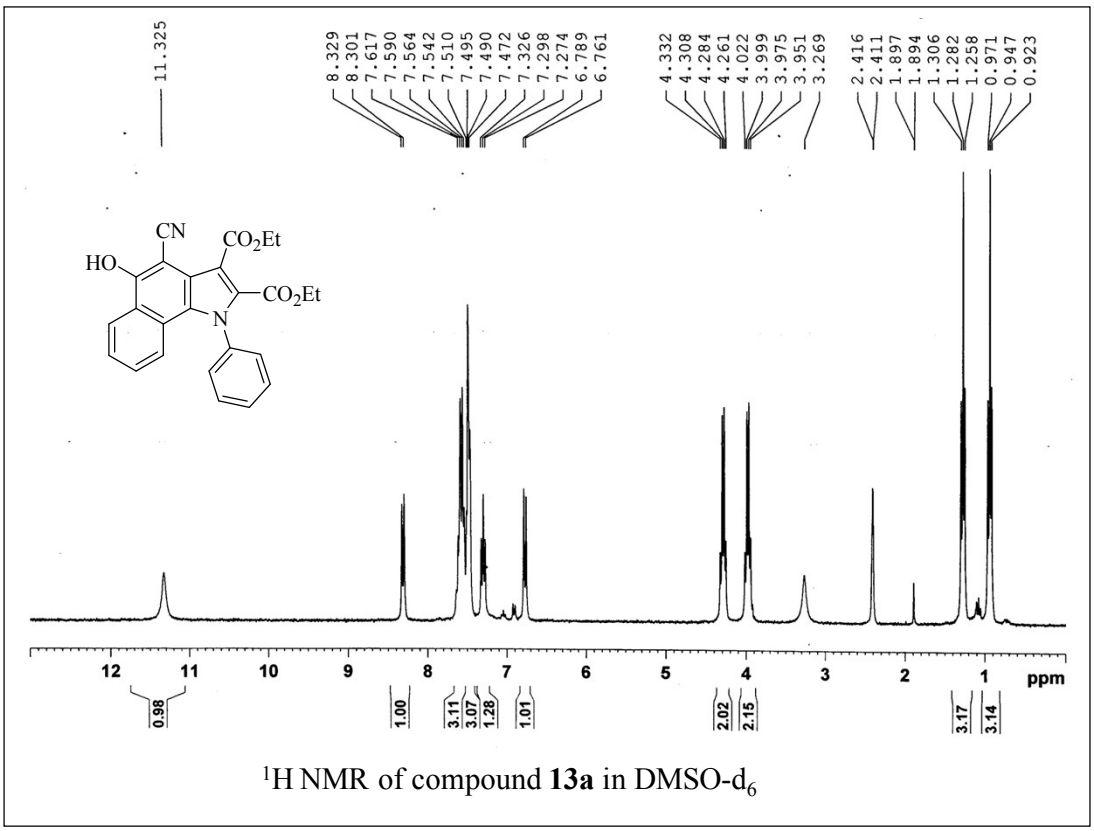
^{13}C NMR of compound **11y** in DMSO-d_6



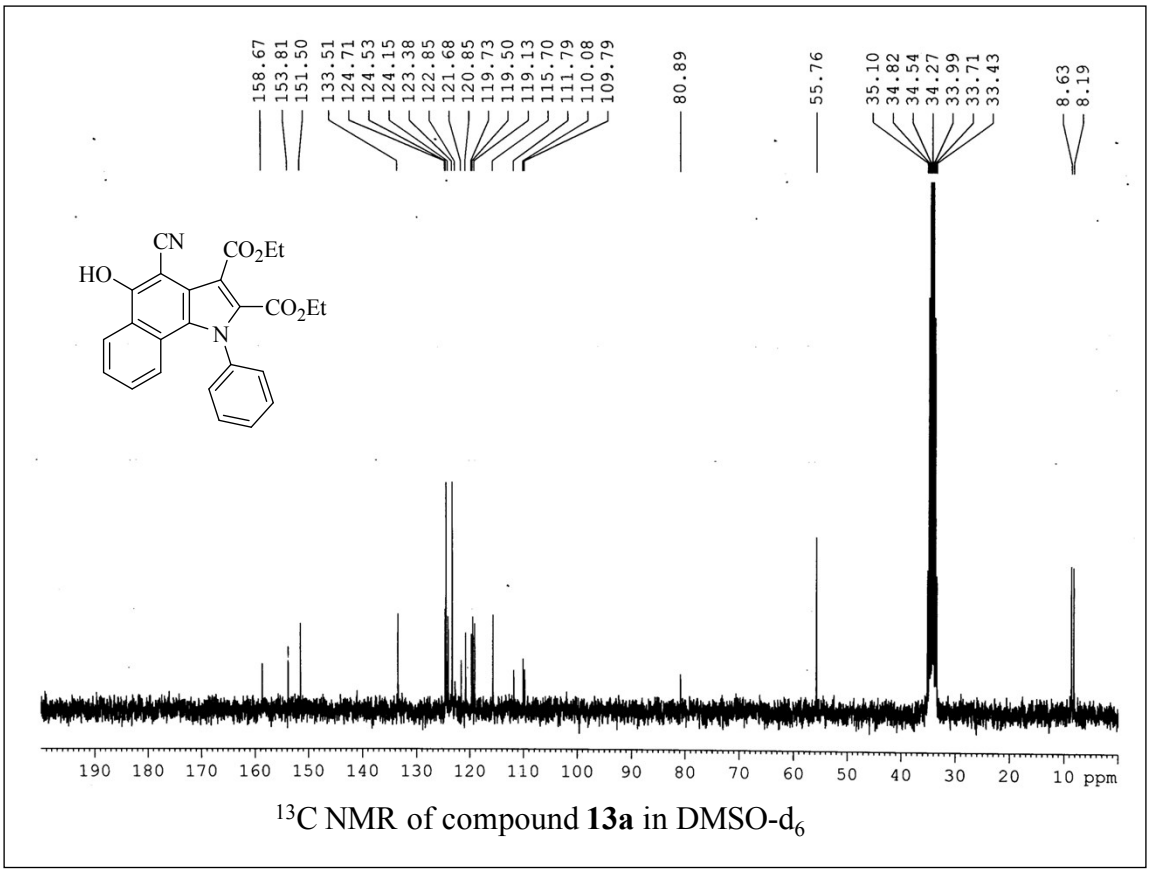
^{1}H NMR of compound **11z** in DMSO-d_6



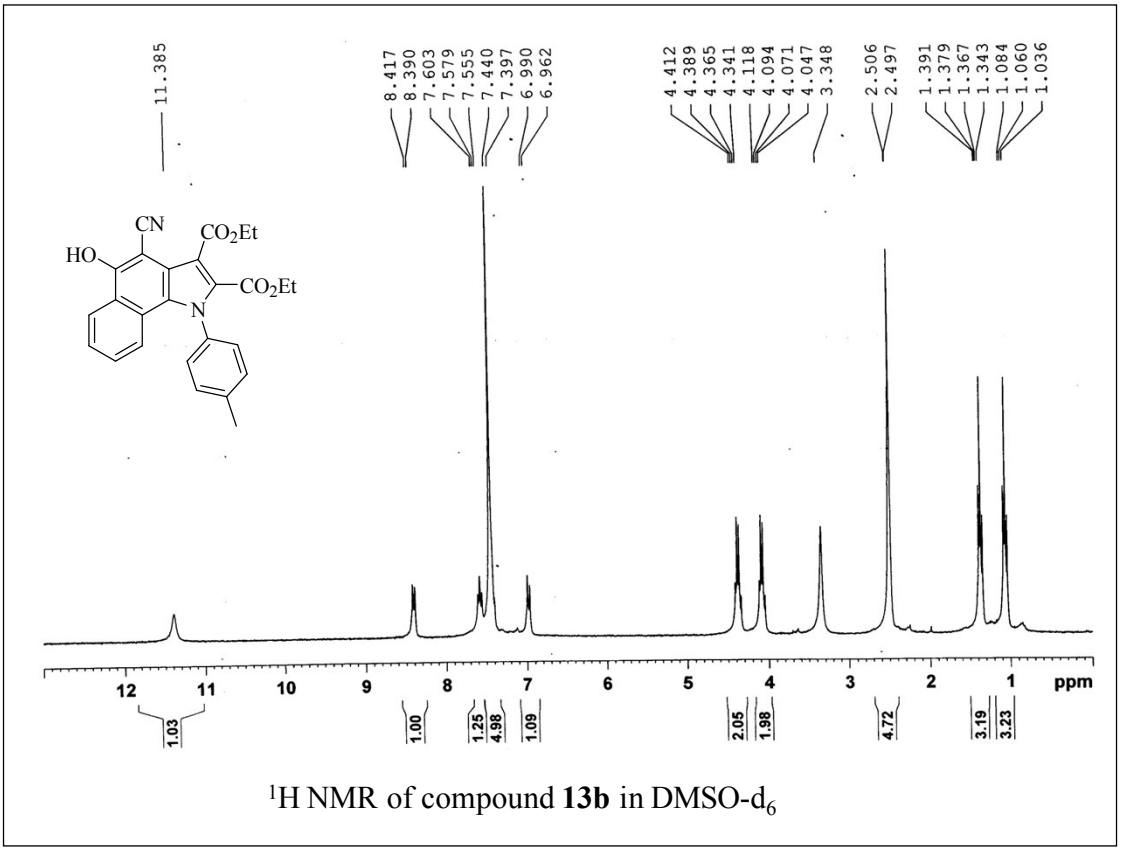
^{13}C NMR of compound **11z** in DMSO-d_6



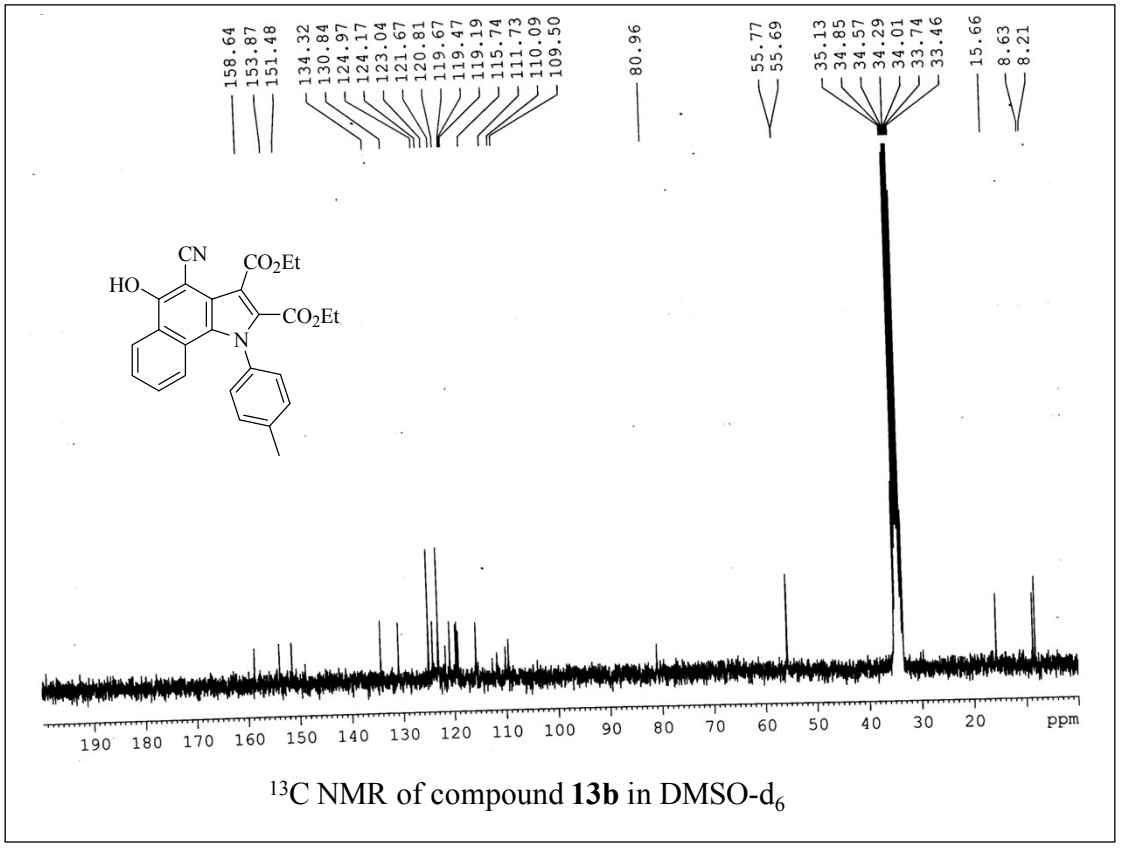
^{1}H NMR of compound **13a** in DMSO-d_6



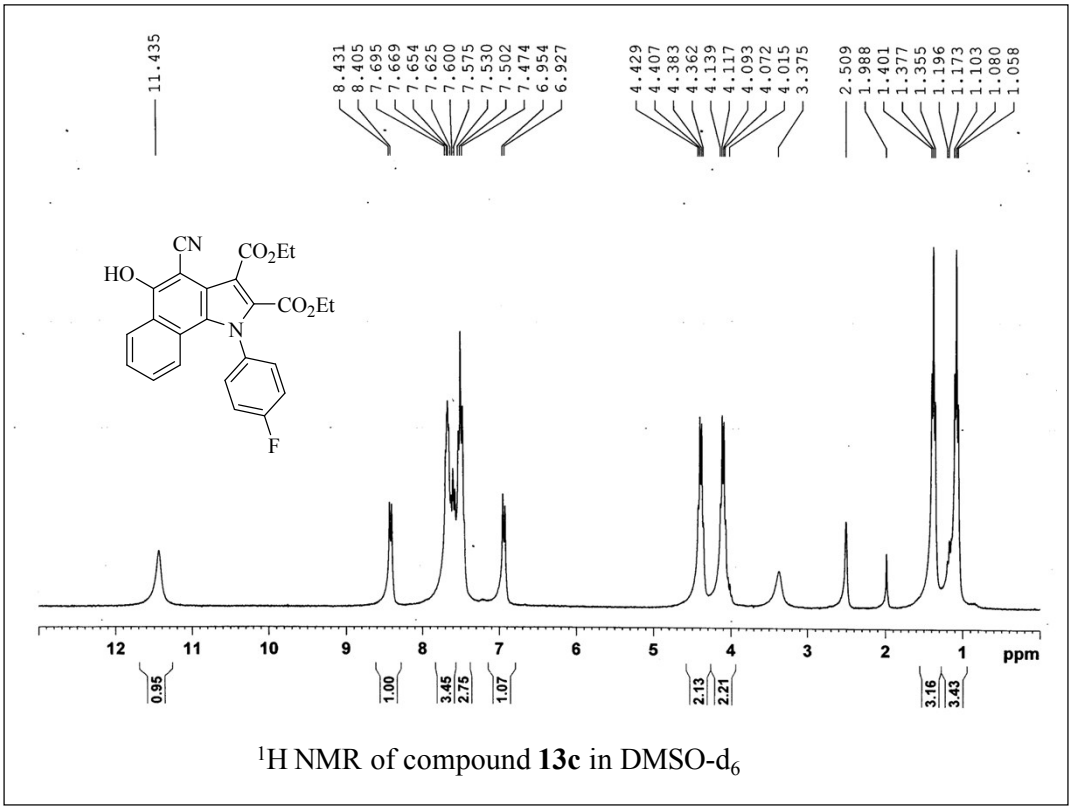
^{13}C NMR of compound **13a** in DMSO-d_6



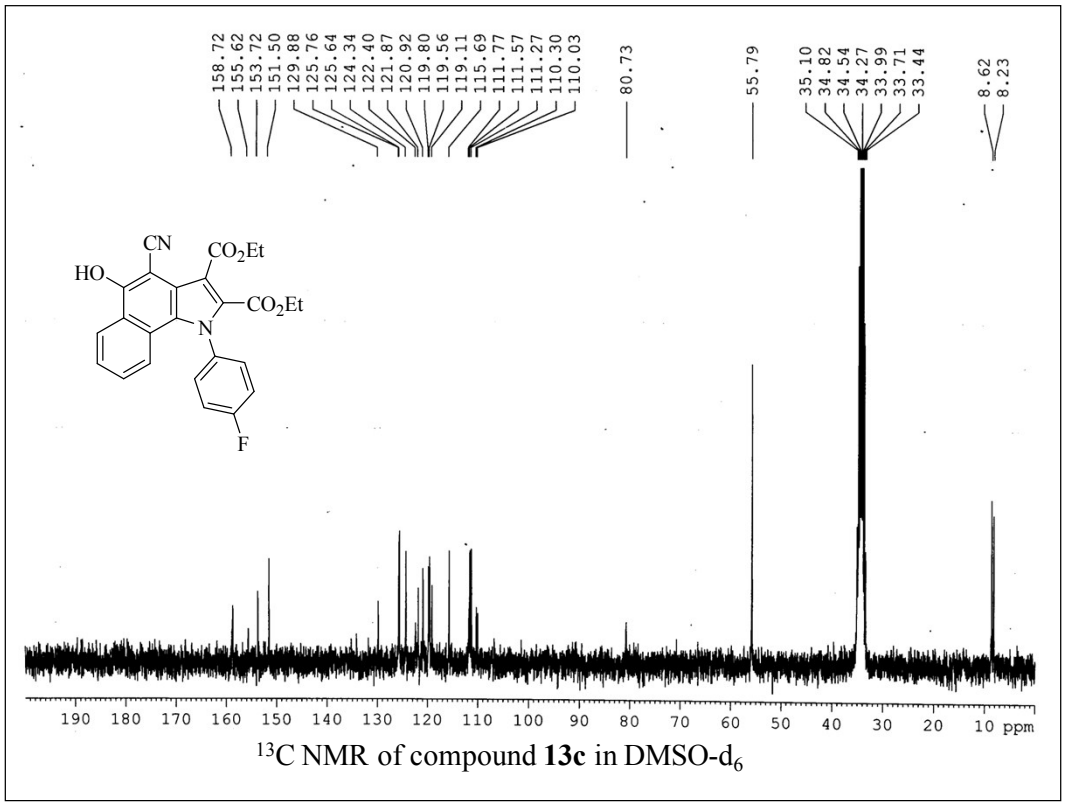
^{1}H NMR of compound **13b** in DMSO-d_6



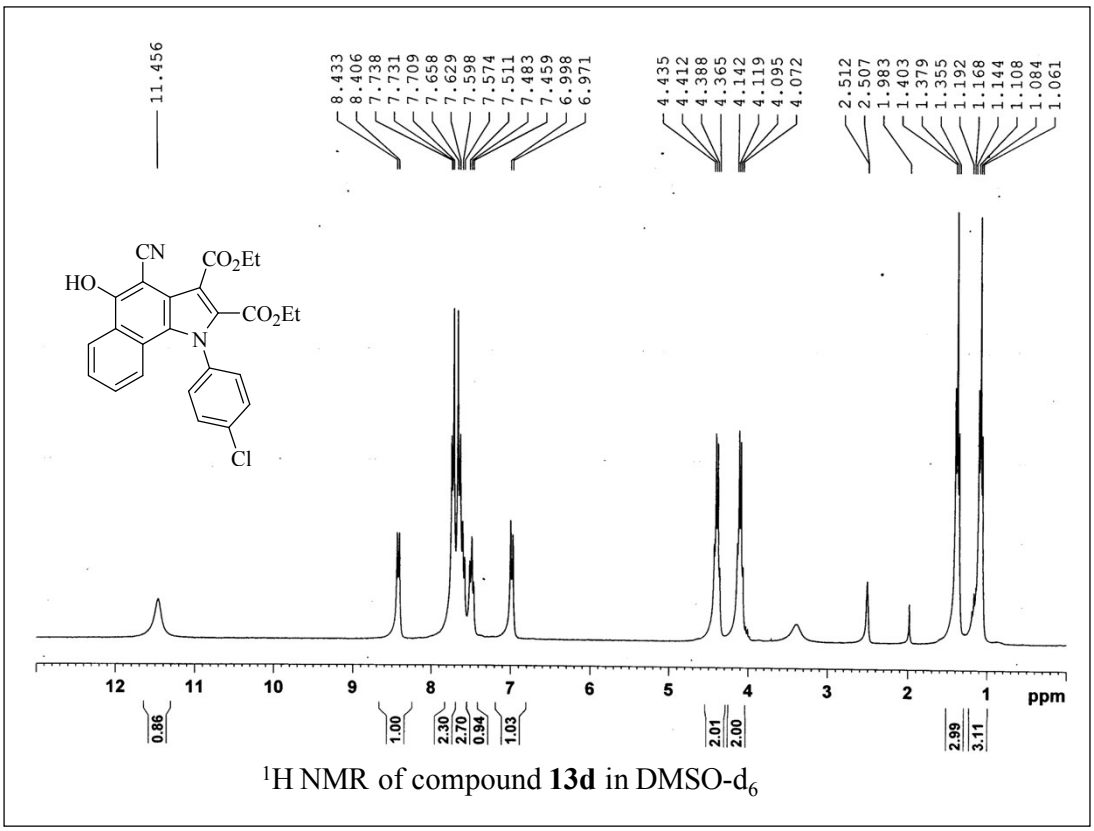
^{13}C NMR of compound **13b** in DMSO-d_6



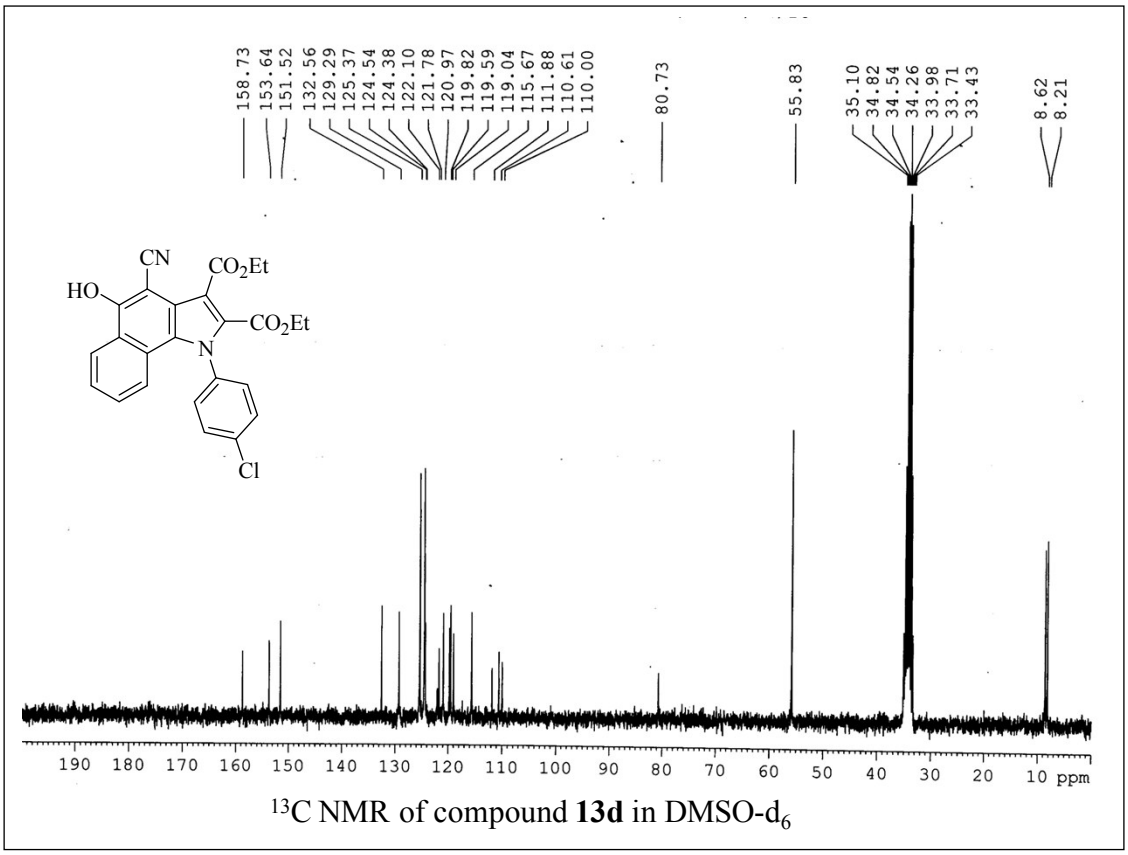
^{1}H NMR of compound **13c** in DMSO-d_6



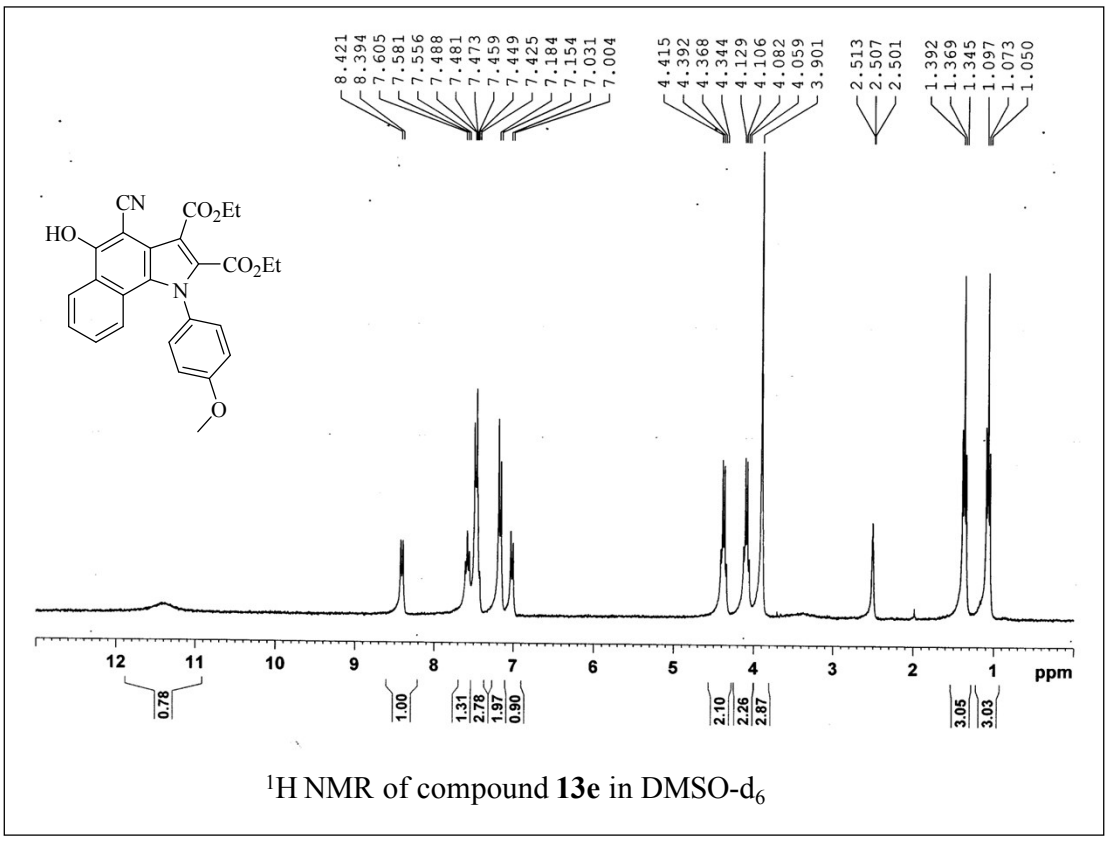
^{13}C NMR of compound **13c** in DMSO-d_6



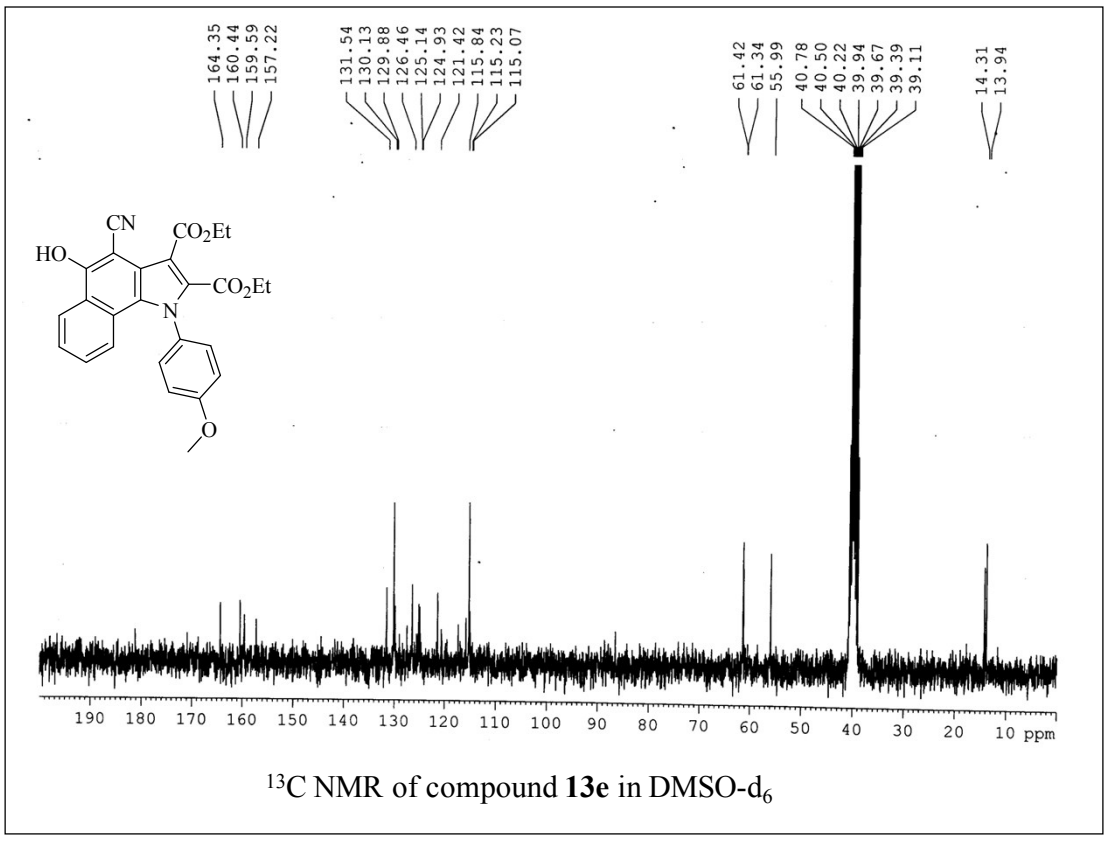
^{1}H NMR of compound **13d** in DMSO-d_6



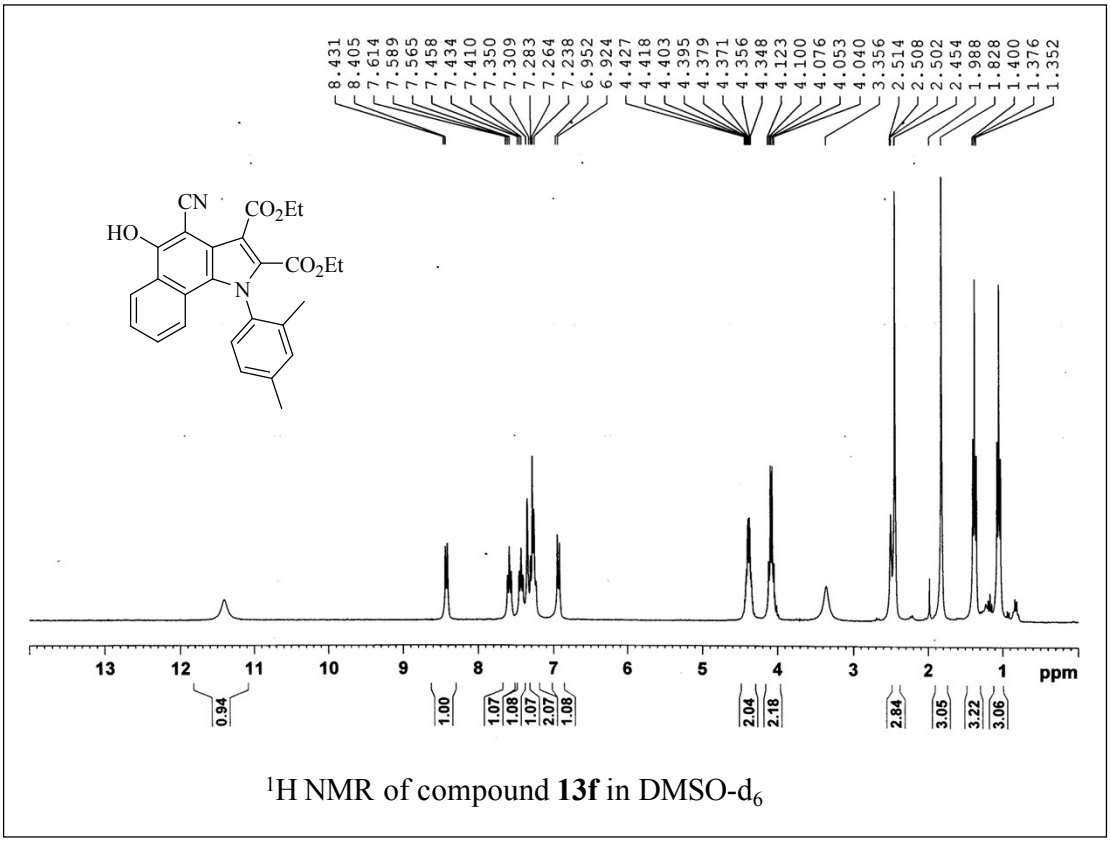
^{13}C NMR of compound **13d** in DMSO-d_6



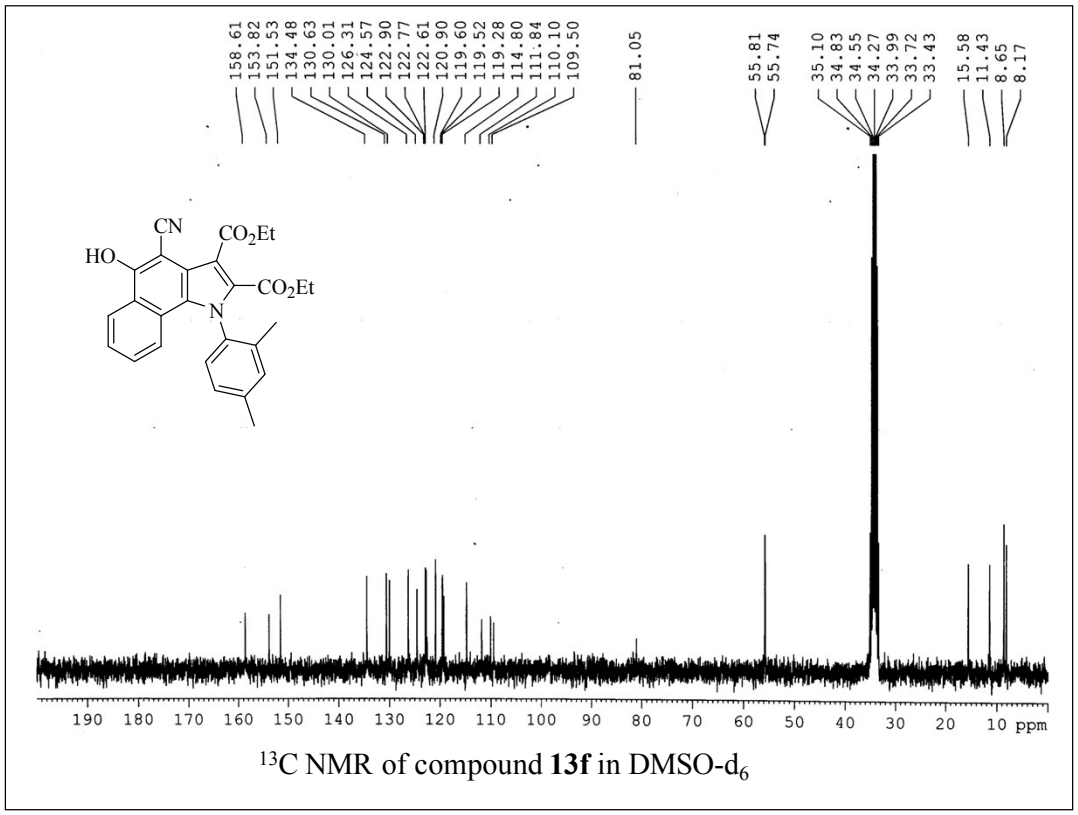
^{1}H NMR of compound **13e** in DMSO-d_6



^{13}C NMR of compound **13e** in DMSO-d_6



^{1}H NMR of compound **13f** in DMSO-d_6



^{13}C NMR of compound **13f** in DMSO-d_6

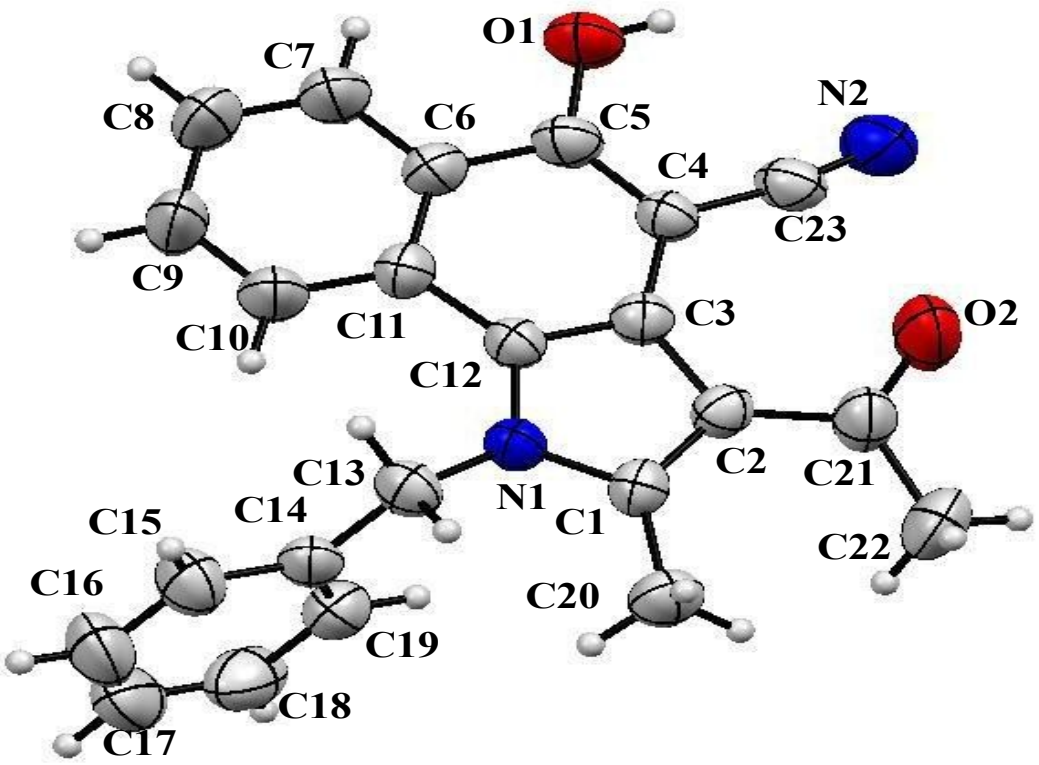


Fig S9. Crystal Structure of **11g** (CCDC 1025252)

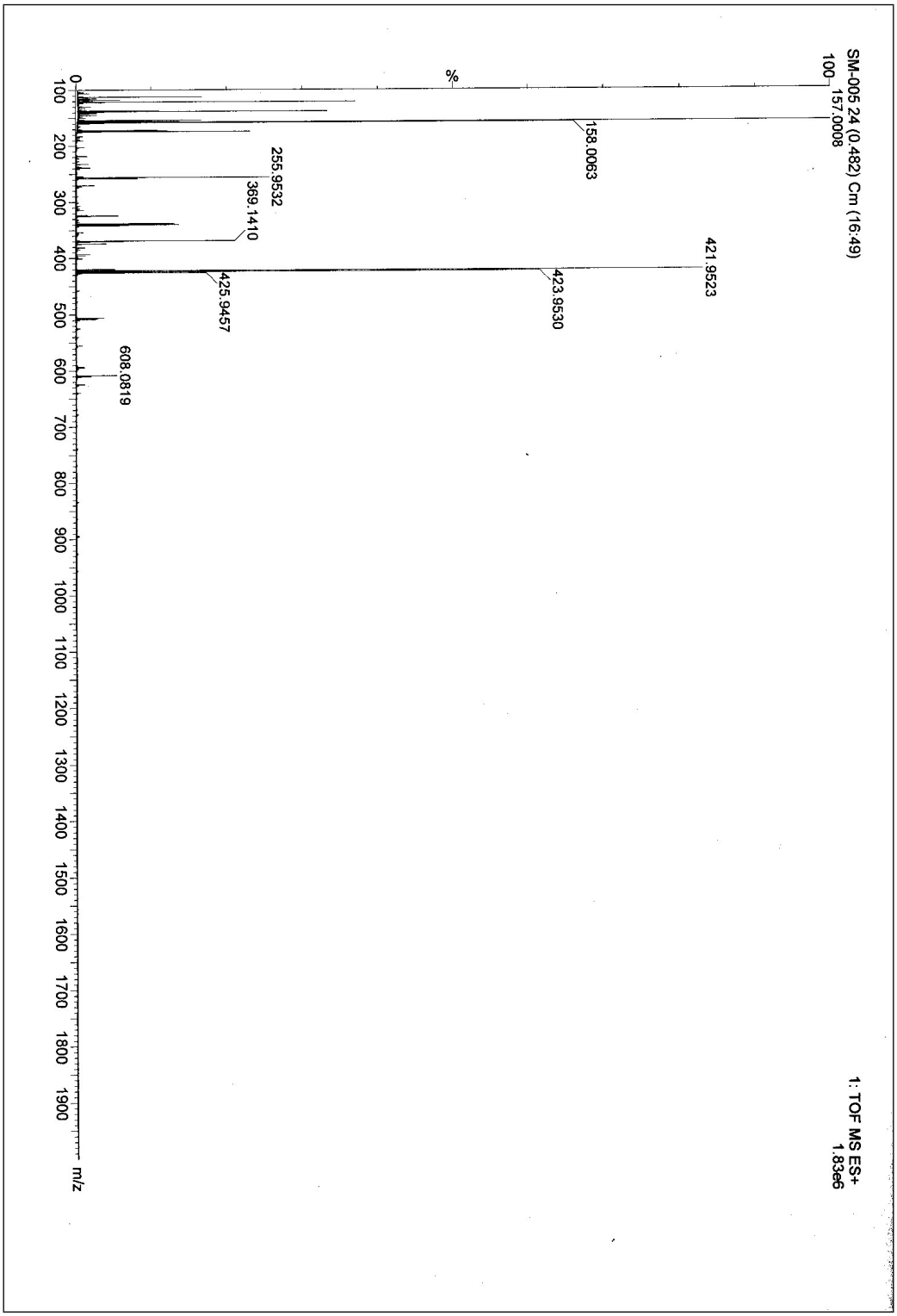


Fig S10. Mass spectrum of complex between **11u** & Fe^{3+} ion