Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Electrochemical synthesis of versatile ammonium oxides under metal catalyst-, exogenous-oxidant-, and exogenous-electrolyte-free conditions

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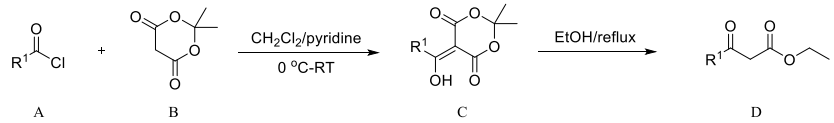
General information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). The anodic electrode was graphite rod (ϕ 6 mm) and cathodic electrode was platinum plate (15 mm×15 mm×0.3 mm). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 300-400 mesh silica gel in petroleum (boiling point is between 60-90 ℃). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they are listed as volume/volume ratios. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), 376 MHz (^{19}F NMR). All chemical shifts are reported relative to tetramethylsilane and solvent peaks. And all ^{1}H, ^{13}C and ^{19}F NMR data spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). GC-MS spectra were recorded on a Shimadzu GC-MS QP2010 Ultra.

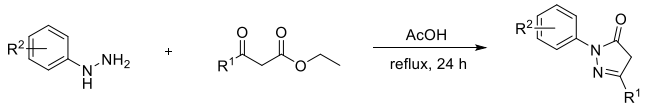
Experimental procedure

General procedure for synthesis of ethyl acetoacetate compounds [1]



To a solution of 2,2-dimethyl-1,3-dioxane-4,6-dione **B** (15.3 mmol, 1.0 equiv.) in CH_2Cl_2 (10.0 mL) at 0 ℃ in 100.0 mL round-bottomed flask equipped with an addition funnel was added pyridine (3.0 mL) over 5 min. To this solution was then added a solution of acyl chloride **A** (15.3 mmol, 1.0 equiv.) in CH_2Cl_2 (20.0 mL) over 10 min. This resulted in the formation of an orange solution. The reaction was stirred at 0 ℃ for 30 min and at RT for 1 h. CH_2Cl_2 (30.0 mL) was added and the solution was washed with water (40.0 mL x 4). The organic phase was dried over $MgSO_4$ and the solvent was removed to give compound **C** as an orange oil. This was dissolved in EtOH (40.0 mL) and heated at reflux for 3h. Evaporation of the solvent afforded compound β-ketoester **D** as an orange oil.

General procedure for synthesis of pyrazolones [2]



To 1.0 equiv. of β-ketoester in 50 mL of acetic acid was added 1.0 equiv. of substituted phenylhydrazine (for HCl salt 1.0 equiv. of triethylamine was added). The content was refluxed for 24 h, the contents cooled, and solvent was removed in vacuo. To the precipitate in flask was added ethylacetate to suspend the product and was then filtered to obtain pure compound. Thus obtained product was dried to yield substituted pyrazolone.

General procedure for the preparation of 3a - 3k, 3o, 3p

5-Methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one derivatives **1** (0.5 mmol) and ammonium thiocyanate **2a** (1.0 mmol) were combined and added into an oven-dried undivided three-necked bottle (25.0 mL) equipped with a stir bar. The bottle was equipped with graphite rod (ϕ 6.0 mm, about 17.0 mm immersion depth in solution) as the anode and platinum plate (15.0 mm×15.0 mm×0.3 mm) as the cathode. Under air conditions, MeCN (10.0 mL) were injected into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 12.0 mA at room temperature for 3 h. After

completion of the reaction, the pure compound **3a - 3k, 3o, 3p** was obtained by washed and filtered with 3.0 - 5.0 mL acetonitrile.

General procedure for the preparation of 3l, 3m, 3n, 3q - 3t

5-Methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one derivatives **1** (1.0 mmol) and ammonium thiocyanate **2a** (0.5 mmol) were combined and added into an oven-dried undivided three-necked bottle (25.0 mL) equipped with a stir bar. The bottle was equipped with graphite rod (ϕ 6.0 mm, about 17.0 mm immersion depth in solution) as the anode and platinum plate (15.0 mm×15.0 mm×0.3 mm) as the cathode. Under air conditions, MeCN (10.0 mL) were injected into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 12.0 mA at room temperature for 3 h. After completion of the reaction, the resulting mixture was concentrated under vacuum, add dichloromethane (3.0 mL), refrigerate for 10 minutes, the pure compound **3l, 3m, 3n, 3q - 3t** was obtained by washed and filtered with 1.0 - 2.0 mL acetone.

Procedure for gram scale synthesis of 3a

5-Methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one derivatives **1a** (10.0 mmol) and ammonium thiocyanate **2a** (20.0 mmol) were combined and added into an oven-dried beaker (250.0 mL) equipped with a stir bar. The beaker was equipped with graphite rod (ϕ 6.0 mm, about 17.0 mm immersion depth in solution) as the anode and platinum plate (15.0 mm×15.0 mm×0.3 mm) as the cathode. Under air conditions, MeCN (200.0 mL) were joined into the beaker. The reaction mixture was stirred and electrolyzed at a constant current of 24.0 mA at room temperature for 30 h. After completion of the reaction, the pure compound **3a** (1.9 g, 77%) was obtained by washed and filtered with 20.0 mL acetonitrile.

Procedure for the preparation of 4a

5-Methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **1a** (0.5 mmol) and potassium thiocyanate **2b** (1.0 mmol) were combined and added into an oven-dried undivided three-necked bottle (25.0 mL) equipped with a stir bar. The bottle was equipped with graphite rod (ϕ 6.0 mm, about 17.0 mm immersion depth in solution) as the anode and platinum plate (15.0 mm×15.0 mm×0.3 mm) as the cathode. Under the

protection of N_2, HFIP (1.0 mL) and MeCN (9.0 mL) were injected into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 12.0 mA at room temperature for 2 h. After completion of the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by silica gel column by using dichloromethane and methanol as a mixed eluent to provide the desired products **4a**.

Procedure for the preparation of 8a

3a (0.3 mmol), (bromomethyl)benzene (0.6 mmol) and triethylamine (0.6 mmol) were combined and added into an oven-dried undivided three-necked bottle (25.0 mL) equipped with a stir bar. Under air conditions, MeCN (10.0 mL) were injected into the tubes via syringes. The reaction mixture was stirred at room temperature for 6 h. After completion of the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by silica gel column by using petroleum ether and ethyl acetate as a mixed eluent to provide the desired products **8a**.

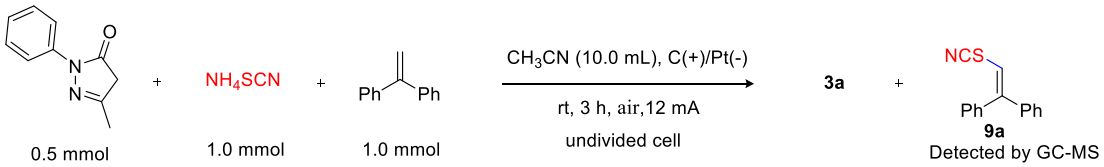
Procedure for the preparation of 8b

3a (0.3 mmol), 4-methylbenzoyl chloride (0.6 mmol) and triethylamine (0.6 mmol) were combined and added into an oven-dried undivided three-necked bottle (25.0 mL) equipped with a stir bar. Under air conditions, MeCN (10.0 mL) were injected into the tubes via syringes. The reaction mixture was stirred at room temperature for 6 h. After completion of the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by silica gel column by using petroleum ether and ethyl acetate as a mixed eluent to provide the desired products **8b**.

Procedure for the preparation of 8c

3a (0.3 mmol), benzenesulfonyl chloride (0.6 mmol) and triethylamine (0.6 mmol) were combined and added into an oven-dried undivided three-necked bottle (25.0 mL) equipped with a stir bar. Under air conditions, MeCN (10.0 mL) were injected into the tubes via syringes. The reaction mixture was stirred at room temperature for 6 h. After completion of the reaction, the resulting mixture was concentrated under vacuum and the residue was purified by silica gel column by using petroleum ether and ethyl acetate as a mixed eluent to provide the desired products **8c**.

Mechanism Studies



3-Methyl-1-phenyl-1H-pyrazol-5(4*H*)-one **1a** (0.5 mmol), ammonium thiocyanate **2a** (1.0 mmol) and ethene-1,1-diyldibenzene (1.0 mmol) were combined and added into an oven-dried undivided three-necked bottle (25.0 mL) equipped with a stir bar. The bottle was equipped with graphite rod (ϕ 6.0 mm, about 17.0 mm immersion depth in solution) as the anode and platinum plate (15.0 mm×15.0 mm×0.3 mm) as the cathode. Under air conditions, MeCN (10.0 mL) were injected into the tubes via syringes. After completion of the reaction, products were detected by GC-MS. Not only product **3a**, but also the SCN radical captured product **9a** could also be detected.

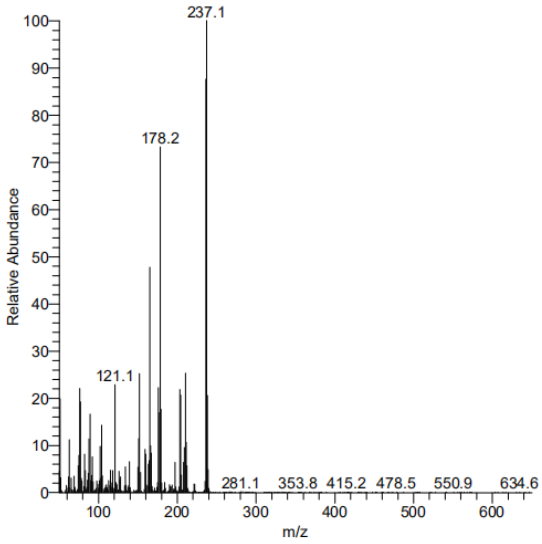
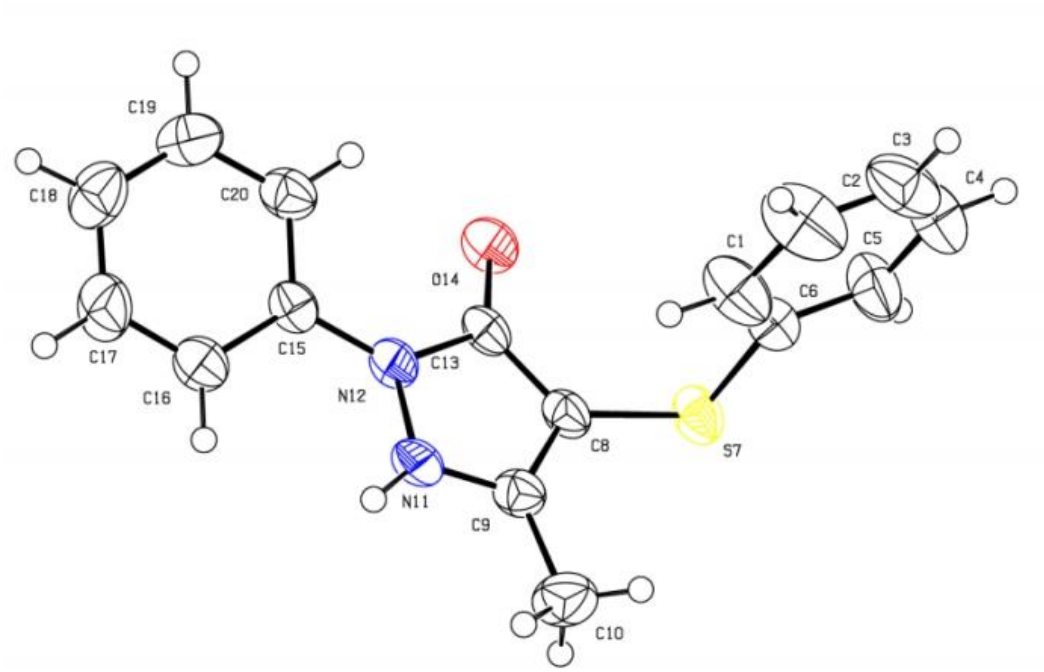


Figure S1. GC-MS of analysis of the **9a**

Crystal structure determination of compounds 6a (CCDC 2041170): Single crystals suitable for X-ray diffraction of **6a** were grown from dichloromethane. Intensity data were collected with a BRUKER Kappa-APEXII diffractometer with graphite-monochromated Cu-Kα radiation (λ = 0.71073 Å). Data collection were performed with APEX2 suite (BRUKER). Unitcell parameters refinement, integration and data reduction were carried out with SAINT program (BRUKER). SADABS (BRUKER) was used for scaling and multi-scan absorption corrections. In the WinGX suite

of programs, the structure were solved with Sir2014 program and refined by fullmatrix least-squares methods using SHELXL-14.

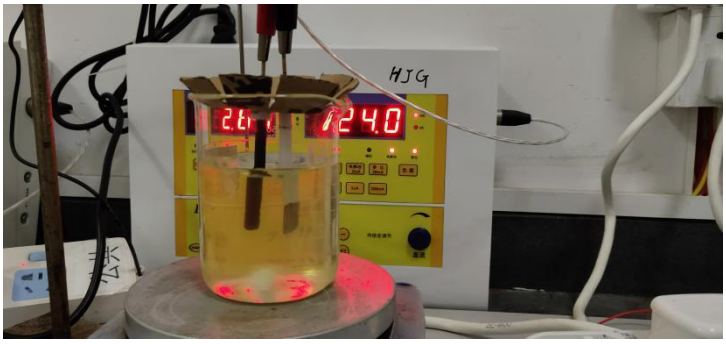
6a



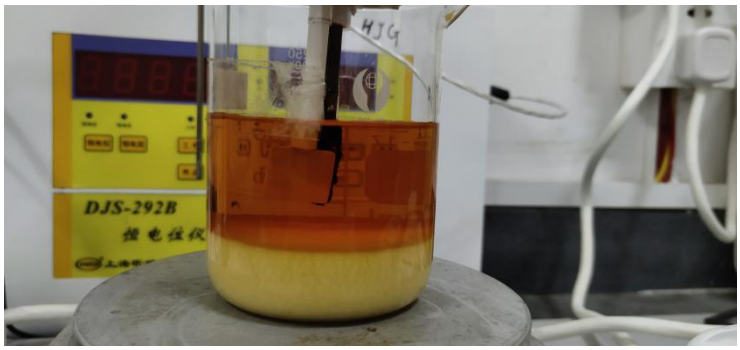
Empirical formula	$C_{16}H_{14}N_2OS$
Formula weight	282.37
Space group	P 1 c 1
a (Å)	9.6728(6)
b (Å)	6.3539(3)
c (Å)	11.8458(6)
α (deg)	90
β (deg)	101.244(6)
γ (deg)	90
V (Å3)	714.07(7)
Z	2
T (K)	295 K
ρ_{calcd} (g/cm^3)	1.313
μ (mm^{-1})	0.223
Significant reflections	2496

R[I > 2.5 (I)]	0.0322
R_w[I > 2.5 (I)]	0.0761

Picture of reaction process



A: before the reaction



B: after the reaction

C: suction filtration

D: pure compound **3a**

Procedure for cyclic voltammetry (CV)

Cyclic voltammetry was performed in a three-electrode cell connected to a Schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode while the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. A solvent (MeCN = 10.0 mL) containing $^{n}Bu_4NBF_4$ (0.1 mmol) was poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 0.10 V/s, ranging from 0.0 V to 3.0 V.

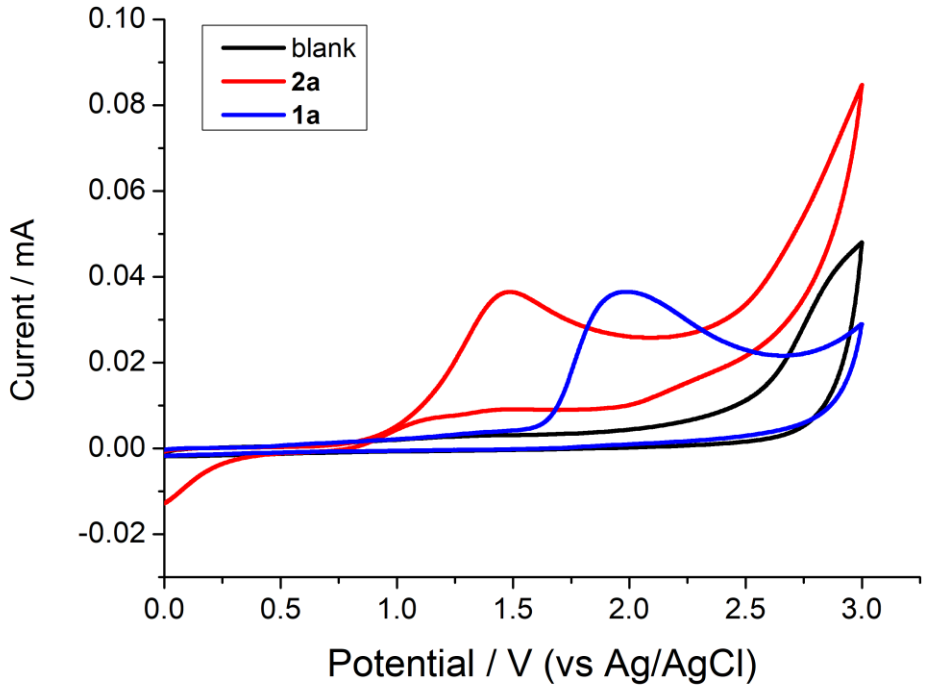
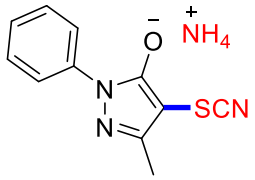
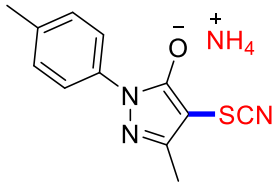


Figure S1. Cyclic voltammograms of related compounds (0.05 mmol) in corresponding solvent containing 0.1 mmol $^{n}Bu_4NBF_4$.

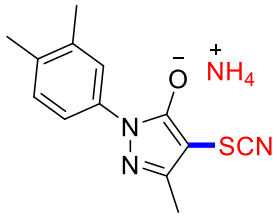
Detailed descriptions for products



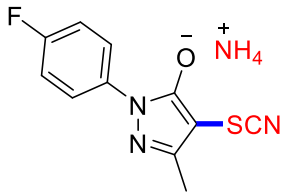
ammonium 3-methyl-1-phenyl-4-thiocyanato-1*H*-pyrazol-5-olate (3a). (White solid was obtained in 95% isolated yield, 117.8 mg). ^{1}H NMR (400 MHz, DMSO-D^{6}) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.43 (s, 4H), 7.29 (t, *J* = 8.0 Hz, 2H), 6.99 (t, *J* = 8.0 Hz, 1H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, DMSO-D^{6}) δ 164.78, 149.54, 141.44, 128.37, 122.28, 117.90, 114.35, 68.19, 13.65. HRMS (ESI) m/z: $[M+Na]^{+}$ Calcd for $C_{11}H_{12}N_4NaOS^{+}$; 271.0624, found 271.0630.



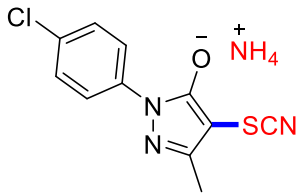
ammonium 3-methyl-4-thiocyanato-1-(p-tolyl)-1*H*-pyrazol-5-olate (3b). (White solid was obtained in 97% isolated yield, 127.1 mg).^{1}H NMR (400 MHz, DMSO-D^{6}) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.48 (s, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.27 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, DMSO-D^{6}) δ 164.09, 149.31, 138.88, 131.57, 129.01, 118.43, 114.25, 69.15, 20.70, 13.59. HRMS (ESI) m/z: $[M+H]^{+}$ Calcd for $C_{12}H_{15}N_4OS^{+}$; 263.0961, found 263.0959.



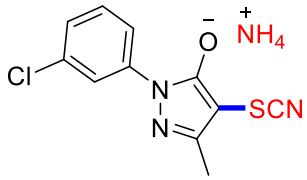
ammonium 1-(3,4-dimethylphenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-olate (3c). (White solid was obtained in 83% isolated yield, 114.6 mg). ^{1}H NMR (400 MHz, DMSO-D^{6}) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.45 (s, 4H), 7.03 (d, *J* = 8.0 Hz, 1H), 2.21 (s, 3H), 2.17 (s, 3H), 2.12 (s, 1H); ^{13}C NMR (100 MHz, DMSO-D^{6}) δ 163.08, 149.27, 138.70, 136.02, 130.74, 129.38, 119.92, 116.28, 114.01, 69.99, 19.84, 18.94, 13.34. HRMS (ESI) m/z: $[M+H]^{+}$ Calcd for $C_{13}H_{17}N_4OS^{+}$; 277.1118, found 277.1111.



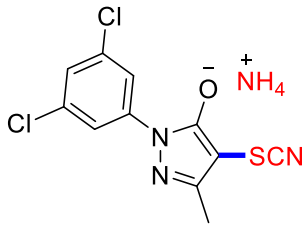
ammonium 1-(4-fluorophenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-olate (3d). (Yellow solid was obtained in 93% isolated yield, 123.7 mg). ^{1}H NMR (400 MHz, DMSO-D^{6}) δ 8.03 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.47 (s, 4H), 7.12 (t, *J* = 8.0 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, DMSO-D^{6}) δ 164.65, 157.97 (d, *J* = 238.0 Hz), 149.70, 137.95 (d, *J* = 2.0 Hz), 119.66 (d, *J* = 8.0 Hz), 115.07, 114.96 (d, *J* = 22.0 Hz), 68.64, 13.61; ^{19}F NMR (376 MHz, DMSO-D^{6}) δ -120.87. HRMS (ESI) m/z: [M+H]$^{+}$ Calcd for $C_{11}H_{12}FN_4OS^{+}$; 267.0710, found 267.0704.



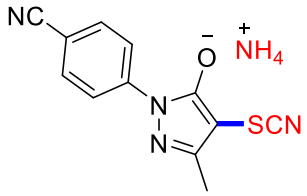
ammonium 1-(4-chlorophenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-olate (3e). (White solid was obtained in 82% isolated yield, 115.6 mg).^{1}H NMR (400 MHz, DMSO-D^{6}) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.44 (s, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D^{6}) δ 164.70, 150.25, 140.16, 128.38, 126.24, 119.37, 114.23, 69.07, 13.63. HRMS (ESI) m/z: [M+H]$^{+}$ Calcd for $C_{11}H_{12}ClN_4OS^{+}$; 283.0415, found 283.0414.



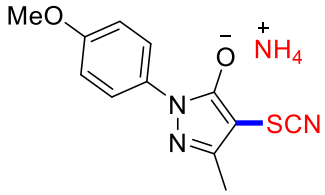
ammonium 1-(3-chlorophenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-olate (3f). (White solid was obtained in 81% isolated yield, 114.2 mg). ^{1}H NMR (400 MHz, DMSO-D^{6}) δ 8.21 (t, *J* = 4.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.37–7.14 (m, 5H), 7.00 (d, *J* = 8.0 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D^{6}) δ 164.96, 150.55, 142.59, 133.02, 130.09, 121.70, 116.91, 115.79, 114.17, 68.65, 13.59. HRMS (ESI) m/z: [M+H]$^{+}$ Calcd for $C_{11}H_{12}ClN_4OS^{+}$; 283.0415, found 283.0407.



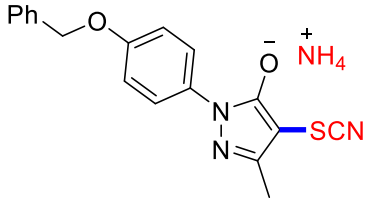
ammonium 1-(3,5-dichlorophenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-olatee (3g). (White solid was obtained in 70% isolated yield, 110.8 mg). ^{1}H NMR (400 MHz, DMSO-D^{6}) δ 8.15 (d, *J* = 4.0 Hz, 2H), 7.26 (s, 4H), 7.11 (t, *J* = 4.0 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D^{6}) δ 165.14, 151.57, 143.12, 134.06, 120.86, 115.05, 114.08, 68.82, 13.63. HRMS (ESI) m/z: [M+H]$^{+}$ Calcd for $C_{11}H_{11}Cl_2N_4OS^{+}$; 317.0025, found 317.0024.



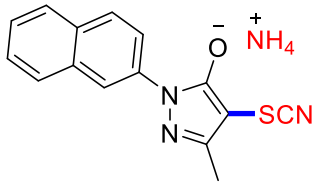
ammonium 1-(4-cyanophenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-olate (3h). (Yellow solid was obtained in 81% isolated yield, 110.6 mg). ^{1}H NMR (400 MHz, DMSO-D^{6}) δ 8.28 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.27 (s, 4H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, DMSO-D^{6}) δ 165.69, 151.89, 144.84, 132.93, 119.78, 116.98, 114.19, 103.15, 68.27, 13.74. HRMS (ESI) m/z: [M+H]$^{+}$ Calcd for $C_{12}H_{12}N_5OS^{+}$; 274.0757, found 274.0760.



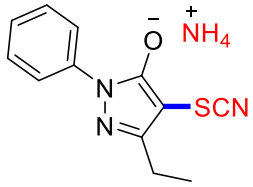
ammonium 1-(4-methoxyphenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-olate (3i). (White solid was obtained in 60% isolated yield, 83.4 mg). ^{1}H NMR (400 MHz, DMSO-D^{6}) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.44 (s, 4H), 6.88 (d, *J* = 12.0 Hz, 2H), 3.73 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D^{6}) δ 163.71, 155.12, 148.93, 134.77, 120.01, 114.23, 113.45, 68.89, 55.26, 13.46. HRMS (ESI) m/z: [M+H]$^{+}$ Calcd for $C_{12}H_{15}N_4O_2S^{+}$; 279.0910, found 279.0903.



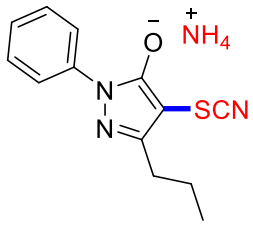
ammonium 1-(4-(benzyloxy)phenyl)-3-methyl-4-thiocyanato-1*H*-pyrazol-5-olate (3j). (White solid was obtained in 65% isolated yield, 115.2 mg). ^{1}H NMR (400 MHz, DMSO-D^{6}) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.52–7.21 (m, 9H), 7.01 (d, *J* = 12.0 Hz, 2H), 5.08 (s, 2H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D^{6}) δ 162.20, 154.67, 149.20, 137.33, 134.19, 128.50, 127.87, 127.77, 120.57, 114.67, 113.80, 70.72, 69.55, 13.22. HRMS (ESI) m/z: [M+H]$^{+}$ Calcd for $C_{18}H_{19}N_4O_2S^{+}$; 355.1223, found 355.1220.



ammonium 3-methyl-1-(naphthalen-2-yl)-4-thiocyanato-1*H*-pyrazol-5-olate (3k). (White solid was obtained in 74% isolated yield, 110.5 mg). ^{1}H NMR (400 MHz, DMSO-D^{6}) δ 8.48 (s, 1H), 8.35 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.84 (dd, *J* = 12.0, 8.0 Hz, 3H), 7.55–7.23 (m, 6H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D^{6}) δ 164.36, 150.10, 138.87, 138.84, 133.61, 129.62, 127.95, 127.55, 126.24, 124.30, 119.17, 114.16, 113.93, 69.41, 13.57. HRMS (ESI) m/z: [M+H]$^{+}$ Calcd for $C_{15}H_{15}N_4OS^{+}$; 299.0961, found 299.0957.

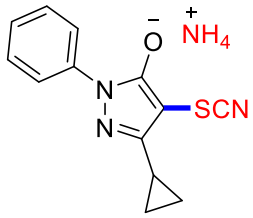


ammonium 3-ethyl-1-phenyl-4-thiocyanato-1*H*-pyrazol-5-olate (3l). (White solid was obtained in 61% isolated yield, 79.9 mg). ^{1}H NMR (400 MHz, DMSO-D^{6}) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 6H), 6.96 (t, *J* = 8.0 Hz, 1H), 2.49 (t, *J* = 16.0 Hz, 2H), 1.21 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-D^{6}) δ 164.17, 154.58, 141.13, 128.46, 122.77, 118.40, 114.32, 68.43, 21.26, 13.10. HRMS (ESI) m/z: [M+K]$^{+}$ Calcd for $C_{12}H_{14}KN_4OS^{+}$; 301.0520, found 301.0505.

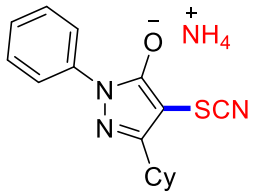


ammonium 1-phenyl-3-propyl-4-thiocyanato-1*H*-pyrazol-5-olate (3m). (White solid was obtained in 60% isolated yield, 82.8 mg). ^{1}H NMR (400 MHz, DMSO-D^{6}) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.45 (s, 4H), 7.29 (t, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 8.0 Hz, 1H), 2.51–2.45 (m, 2H), 1.75–1.62 (m, 2H), 0.97 (t, *J*

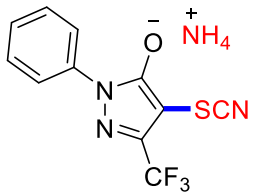
= 8.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-D^6) δ 161.18, 153.67, 139.74, 128.67, 124.21, 119.62, 113.50, 72.67, 29.38, 21.45, 14.02. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}N_4OS^+$; 277.1118, found 277.1116.



ammonium 3-cyclopropyl-1-phenyl-4-thiocyanato-1*H*-pyrazol-5-olate (3n). (White solid was obtained in 58% isolated yield, 79.5 mg).^{1}H NMR (400 MHz, DMSO-D^6) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 4H), 7.28 (t, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 8.0 Hz, 1H), 1.93–1.78 (m, 1H), 0.93–0.74 (m, 4H). ^{13}C NMR (100 MHz, DMSO-D^6) δ 164.86, 153.63, 141.42, 128.32, 122.28, 117.96, 114.48, 68.25, 8.76, 6.69. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}N_4OS^+$; 275.0961, found 275.0953.

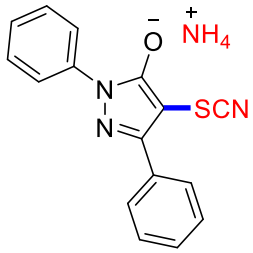


ammonium 3-cyclohexyl-1-phenyl-4-thiocyanato-1*H*-pyrazol-5-olate (3o). (White solid was obtained in 63% isolated yield, 99.6 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.40 (s, 4H), 7.29 (t, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 8.0 Hz, 1H), 2.73–2.59 (m, 1H), 1.85 (dd, *J* = 24.0, 12.0 Hz, 4H), 1.77–1.54 (m, 3H), 1.46–1.21 (m, 3H). ^{13}C NMR (100 MHz, DMSO-D^6) δ 163.33, 157.17, 140.81, 128.44, 123.05, 118.77, 114.22, 68.96, 37.34, 31.38, 26.25, 25.99. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}N_4OS^+$; 317.1431, found 317.1426.

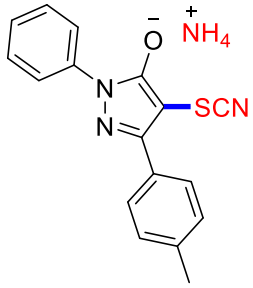


ammonium 1-phenyl-4-thiocyanato-3-(trifluoromethyl)-1*H*-pyrazol-5-olate (3p). (White solid was obtained in 90% isolated yield, 135.9 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.16 (s, 4H), 7.11 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-D^6) δ 164.51, 140.62, 140.55 (q, *J* = 51.0 Hz), 128.62, 123.92, 121.62(q, *J* = 402.0 Hz), 118.70, 113.50,

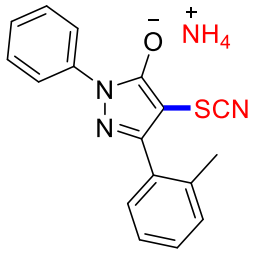
66.20. ^{19}F NMR (376 MHz, DMSO-D^6) δ -62.24. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{10}F_3N_4OS^+$; 303.0522, found 303.0525.



ammonium 1,3-diphenyl-4-thiocyanato-1*H*-pyrazol-5-olate (3q). (White solid was obtained in 74% isolated yield, 114.7 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 12.0 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 3H), 7.44–7.18 (m, 6H), 7.13 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-D^6) δ 163.95, 150.21, 140.68, 133.91, 128.67, 128.50, 128.12, 127.34, 123.81, 119.20, 114.40, 69.48. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}N_4OS^+$; 311.0961, found 311.0958.

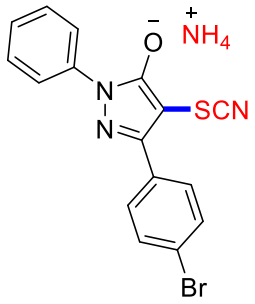


ammonium 1-phenyl-4-thiocyanato-3-(p-tolyl)-1*H*-pyrazol-5-olate (3r). (White solid was obtained in 72% isolated yield, 116.6 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.43–7.13 (m, 8H), 7.03 (t, *J* = 8.0 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D^6) δ 165.39, 149.89, 141.39, 136.93, 131.64, 128.85, 128.35, 127.01, 122.54, 118.07, 114.74, 66.64, 20.98. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_4OS^+$; 325.1118, found 325.1120.

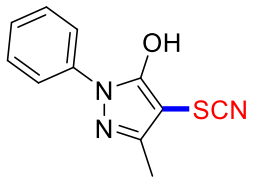


ammonium 1-phenyl-4-thiocyanato-3-(o-tolyl)-1*H*-pyrazol-5-olate (3s). (White solid was obtained in 70% isolated yield, 113.5 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 4H), 7.35–7.23 (m, 6H), 7.04 (t, *J* = 8.0 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz,

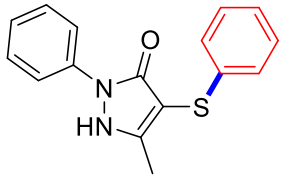
DMSO-D^6) δ 164.79, 152.49, 141.44, 136.71, 134.09, 130.16, 130.03, 128.42, 127.87, 125.33, 122.65, 118.13, 114.49, 68.73, 20.16. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_4OS^+$; 325.1118, found 325.1113.



ammonium 3-(4-bromophenyl)-1-phenyl-4-thiocyanato-1*H*-pyrazol-5-olate (3t). (White solid was obtained in 71% isolated yield, 137.7 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.89 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.67 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.49–7.11 (m, 6H), 7.08 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-D^6) δ 164.97, 148.59, 141.04, 133.47, 131.33, 128.95, 128.46, 123.11, 121.05, 118.46, 114.39, 67.53. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}BrN_4OS^+$; 389.0066, found 389.0064.

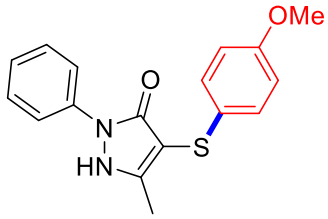


3-methyl-1-phenyl-4-thiocyanato-1*H*-pyrazol-5-ol (4a).[3] (White solid was obtained in 56% isolated yield, 64.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.10 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.27–7.18 (m, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.87, 151.41, 134.80, 129.22, 127.62, 122.17, 110.72, 82.53, 11.58.

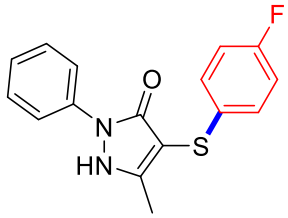


5-methyl-2-phenyl-4-(phenylthio)-1,2-dihydro-3*H*-pyrazol-3-one (6a). (White solid was obtained in 88% isolated yield, 124.2 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 12.27 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 3H), 7.12 (t, *J* = 8.0 Hz, 3H), 2.16 (s, 3H). ^{13}C NMR

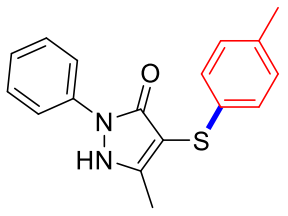
(100 MHz, DMSO-D^6) δ 156.42, 152.13, 138.51, 138.28, 129.15, 129.07, 125.86, 125.04, 125.02, 120.88, 87.08, 12.43. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}N_2OS^+$; 283.0900, found 283.0898.



4-((4-methoxyphenyl)thio)-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (6b). (White solid was obtained in 64% isolated yield, 99.8 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 12.01 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 12.0 Hz, 2H), 3.69 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D^6) δ 157.73, 156.87, 152.04, 138.30, 129.09, 128.82, 127.93, 125.80, 120.81, 114.94, 89.68, 55.30, 12.47. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2O_2S^+$; 313.1005, found 313.1007.

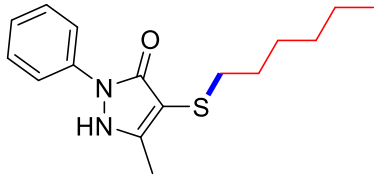


4-((4-fluorophenyl)thio)-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (6c). (White solid was obtained in 80% isolated yield, 120.1 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 12.22 (s, 1H), 7.76 (d, *J* = 4.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.13 (dd, *J* = 8.0, 4.0 Hz, 4H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D^6) δ 161.67, 159.27, 152.07, 138.21, 133.95 (d, *J* = 3.0 Hz), 129.08, 127.35 (d, *J* = 7.0 Hz), 125.89, 120.88, 116.17 (d, *J* = 22.0 Hz), 88.59, 12.39. ^{19}F NMR (376 MHz, DMSO-D^6) δ -118.01. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}FN_2OS^+$; 301.0805, found 301.0802.

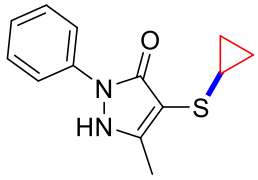


5-methyl-2-phenyl-4-(p-tolylthio)-1,2-dihydro-3*H*-pyrazol-3-one (6d). (White solid was obtained in 72% isolated yield, 106.6 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 12.18 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H),

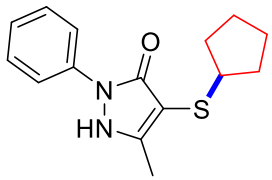
2.22 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D^6) δ 156.81, 152.15, 138.31, 134.91, 134.47, 129.81, 129.08, 125.83, 125.47, 120.86, 88.03, 20.55, 12.46. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2OS^+$; 297.1056, found 297.1054.



4-(hexylthio)-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (6e). (White solid was obtained in 55% isolated yield, 79.8 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 11.66 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 1H), 2.53 (t, *J* = 8.0 Hz, 2H), 2.20 (s, 3H), 1.49–1.42 (m, 2H), 1.38–1.31 (m, 2H), 1.27–1.20 (m, 4H), 0.84 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-D^6) δ 157.60, 151.90, 138.31, 129.00, 125.43, 120.37, 91.34, 35.18, 31.04, 29.09, 27.78, 22.15, 14.01, 12.49. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}N_2OS^+$; 291.1526, found 291.1527.

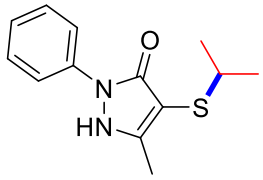


4-(cyclopropylthio)-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (6f). (White solid was obtained in 59% isolated yield, 72.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.12 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 2.23 (s, 3H), 1.92–1.79 (m, 1H), 0.67–0.57 (m, 2H), 0.53–0.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.70, 151.80, 136.06, 128.77, 126.06, 121.24, 96.17, 16.29, 11.71, 8.27. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}N_2OS^+$; 247.0900, found 247.0899.

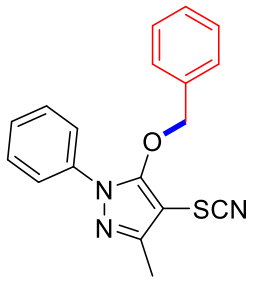


4-(cyclopentylthio)-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (6g). (White solid was obtained in 52% isolated yield, 71.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.07 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 3.20–2.91 (m, 1H), 2.23 (s, 3H), 1.80–1.57 (m, 4H), 1.46–1.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.05, 152.19, 136.13, 128.74, 125.92,

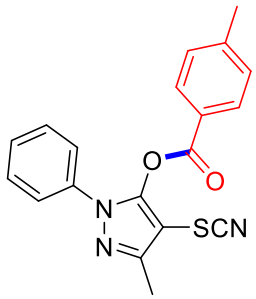
121.06, 95.48, 77.48, 77.16, 76.84, 47.64, 33.11, 24.49, 11.77. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2OS^+$; 275.1213, found 275.1210.



4-(isopropylthio)-5-methyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (6h). (White solid was obtained in 70% isolated yield, 86.8 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 11.69 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 1H), 3.05–2.92 (m, 1H), 2.19 (s, 3H), 1.15 (d, *J* = 4.0 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-D^6) δ 156.26, 152.29, 138.39, 129.00, 125.48, 120.52, 90.44, 38.51, 22.86, 12.62. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{17}N_2OS^+$; 249.1056, found 249.1046.

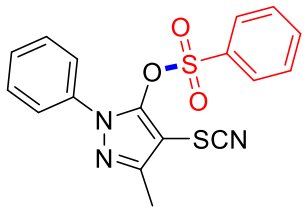


5-(benzyloxy)-3-methyl-1-phenyl-4-thiocyanato-1*H*-pyrazole (8a). (Colorless liquid was obtained in 65% isolated yield, 62.6 mg). ^{1}H NMR (400 MHz, DMSO-D^6) δ 7.50 (t, *J* = 8.0 Hz, 2H), 7.45–7.40 (m, 1H), 7.30–7.21 (m, 5H), 6.91–6.84 (m, 2H), 5.03 (s, 2H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D^6) δ 162.88, 157.59, 134.36, 133.87, 129.44, 128.80, 128.28, 128.20, 126.95, 126.17, 111.65, 85.62, 50.13, 12.04. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{16}N_3OS^+$; 322.1009, found 322.1008.



3-methyl-1-phenyl-4-thiocyanato-1*H*-pyrazol-5-yl 4-methylbenzoate (8b). (Colorless liquid was obtained in 82% isolated yield, 85.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.33 (dd, *J* = 8.0, 4.0 Hz, 3H), 2.49 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.22, 151.90, 146.85, 146.55, 137.31, 131.04, 129.92, 129.53, 128.51,

123.88, 123.18, 110.01, 88.90, 22.04, 12.97. HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_{19}H_{15}KN_3O_2S^+$; 388.0517, found 388.0519.



3-methyl-1-phenyl-4-thiocyanato-1*H*-pyrazol-5-yl benzenesulfonate (8c). (Colorless liquid was obtained in 91% isolated yield, 101.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 12.0, 8.0 Hz, 3H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.29–7.21 (m, 5H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.94, 143.97, 136.73, 135.40, 134.03, 129.49, 129.18, 128.36, 128.31, 123.30, 109.74, 90.53, 13.00. HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_{17}H_{13}KN_3O_3S_2^+$; 410.0030, found 410.0028.

References:

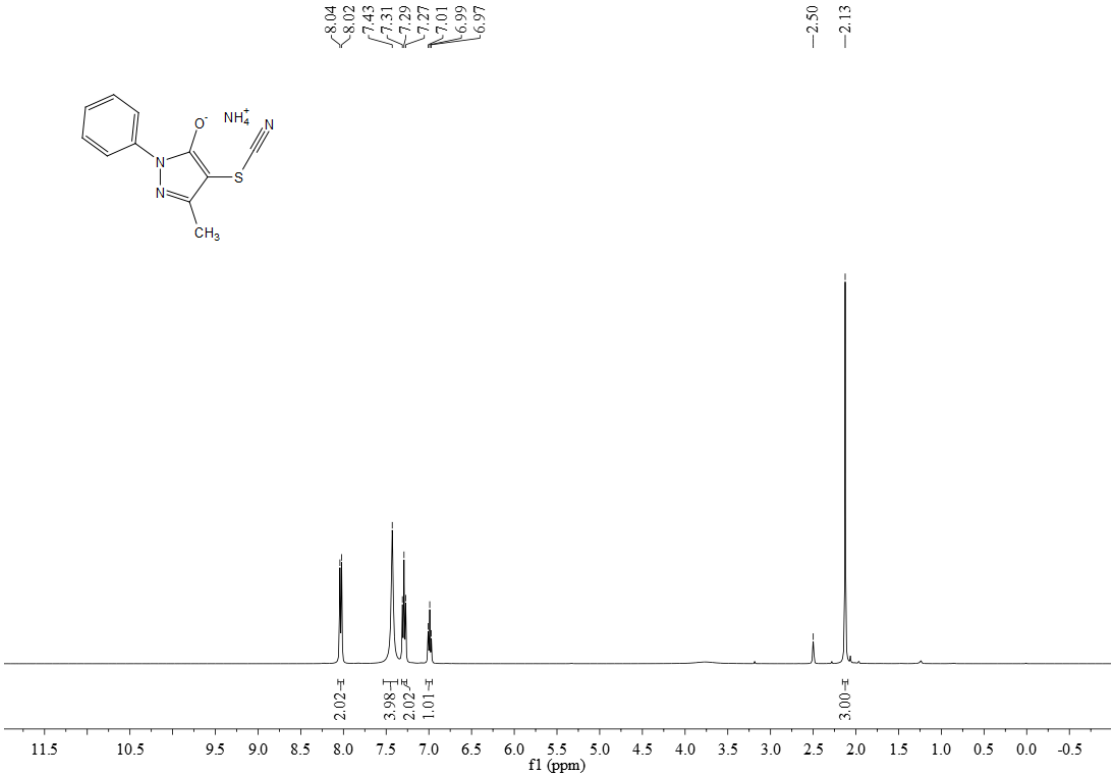
1. Yuan, P.-F.; Zhang, Q.-B.; Jin, X.-L.; Lei, W.-L.; Wu, L.-Z.; Liu, Q., Visible-light-promoted aerobic metal-free aminothiocyanation of activated ketones. *Green Chem.* **2018,** *20*, 5464-5468.

2. Kumar, V.; Chang, C.-K.; Tan, K.-P.; Jung, Y.-S.; Chen, S.-H.; Cheng, Y.-S. E.; Liang, P.-H., Identification, Synthesis, and Evaluation of New Neuraminidase Inhibitors. *Org. Lett.* **2014,** *16*, 5060-5063.

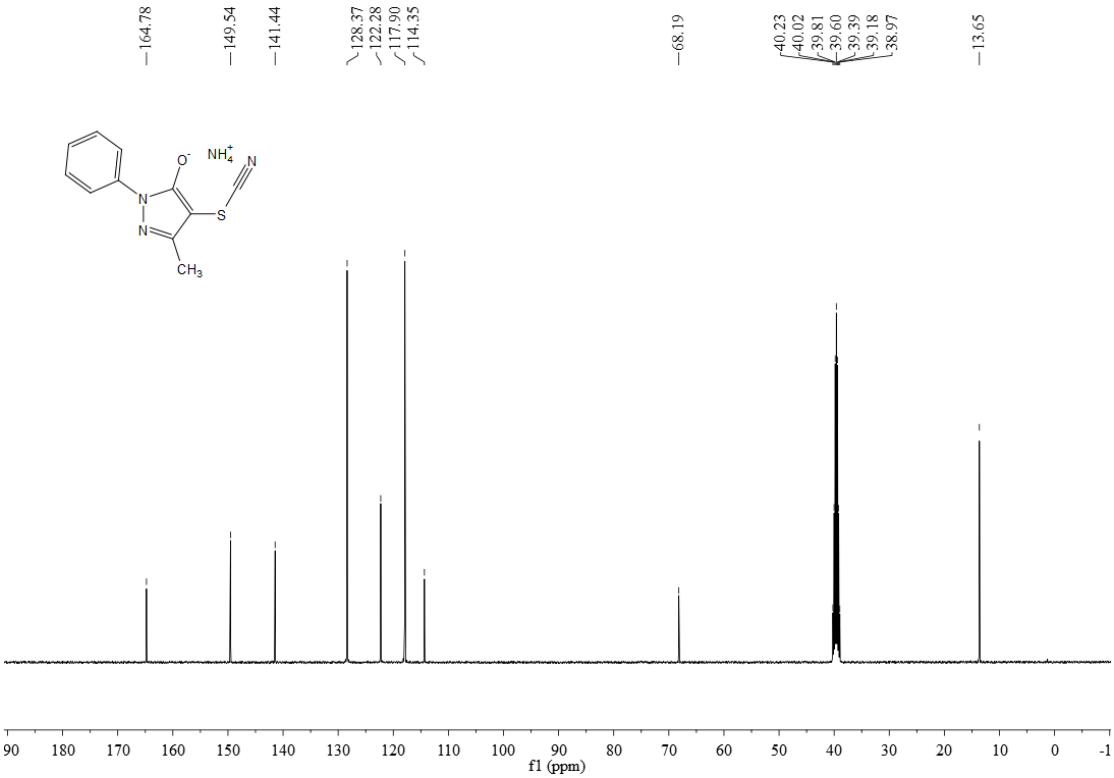
3. Mao, X.; Ni, J.; Xu, B.; Ding, C., $K_2S_2O_8$-promoted direct thiocyanation of pyrazolin-5-ones with ammonium thiocyanate at room temperature. *Org. Chem. Front.* **2020,** *7*, 350-354.

Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra

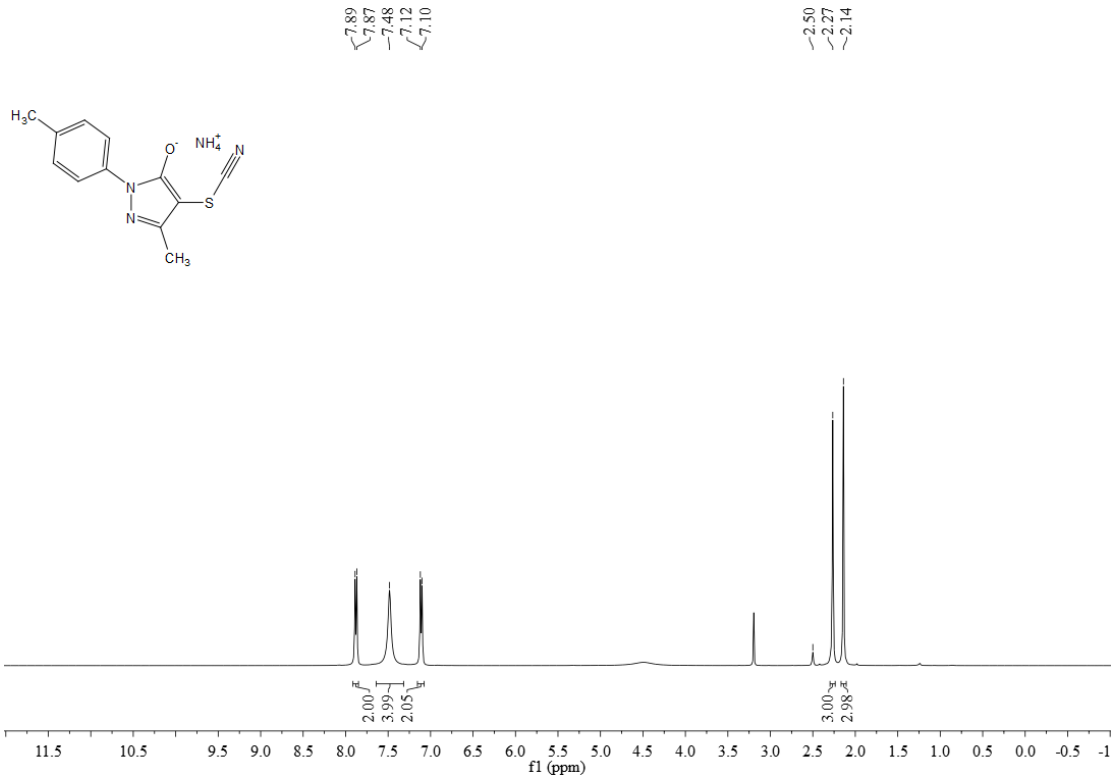
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3a



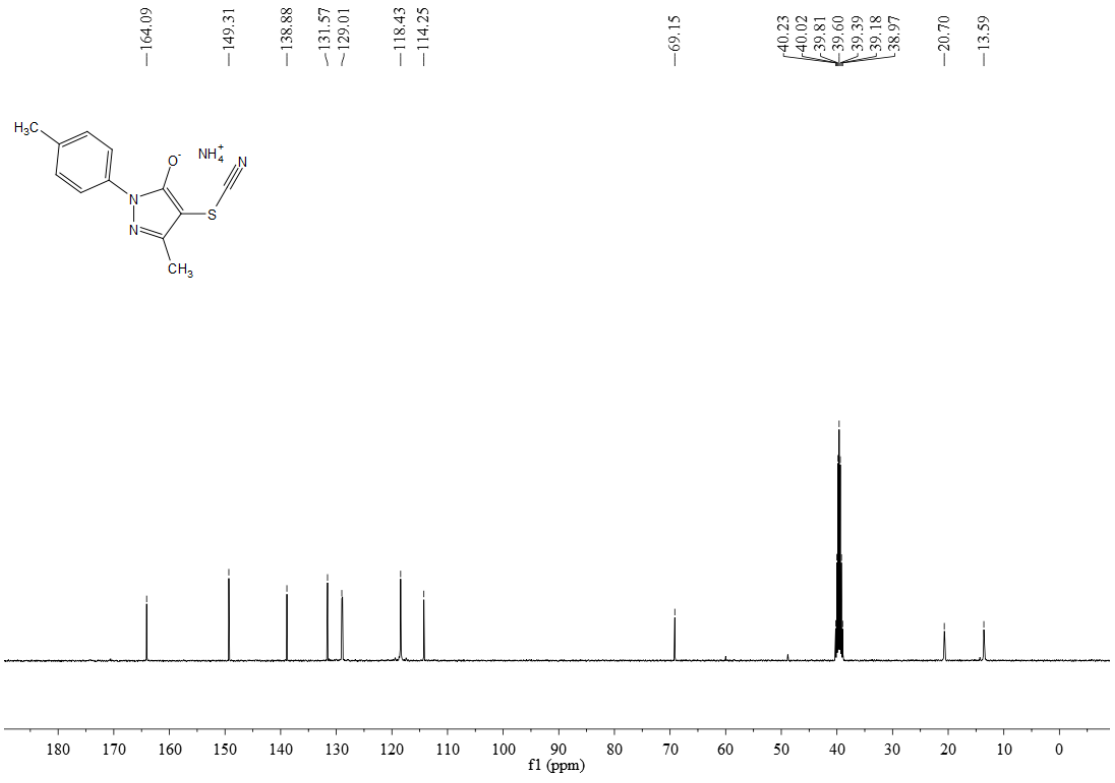
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3a



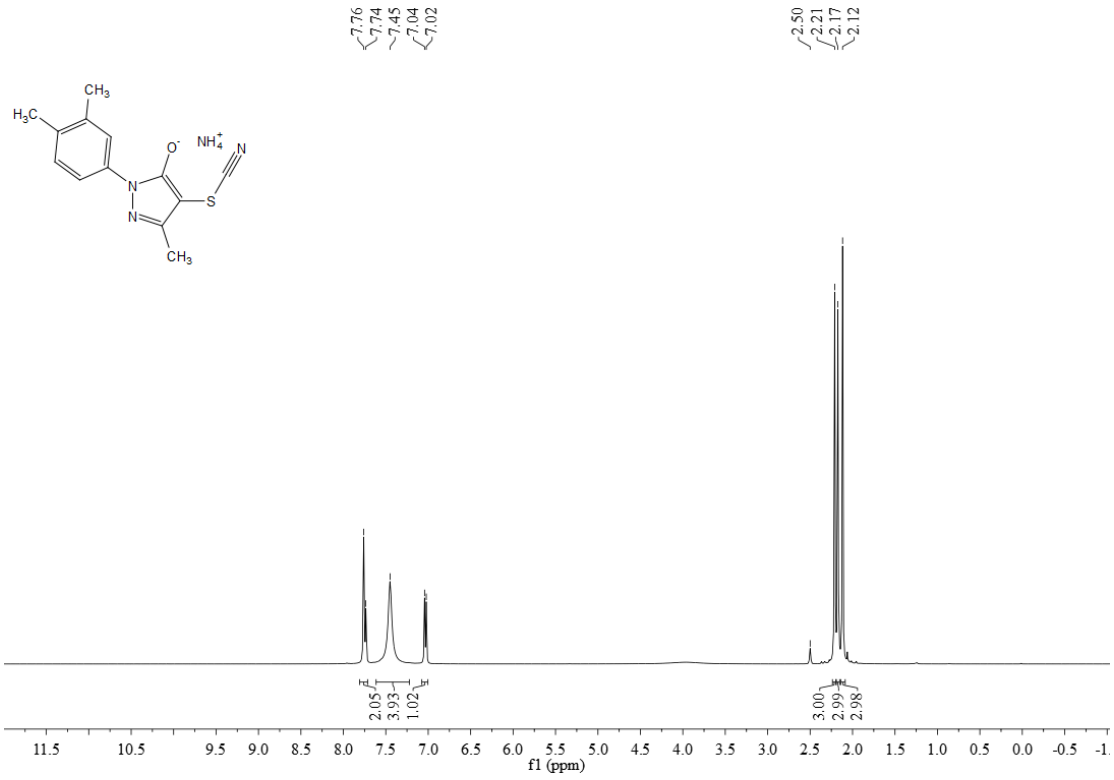
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3b



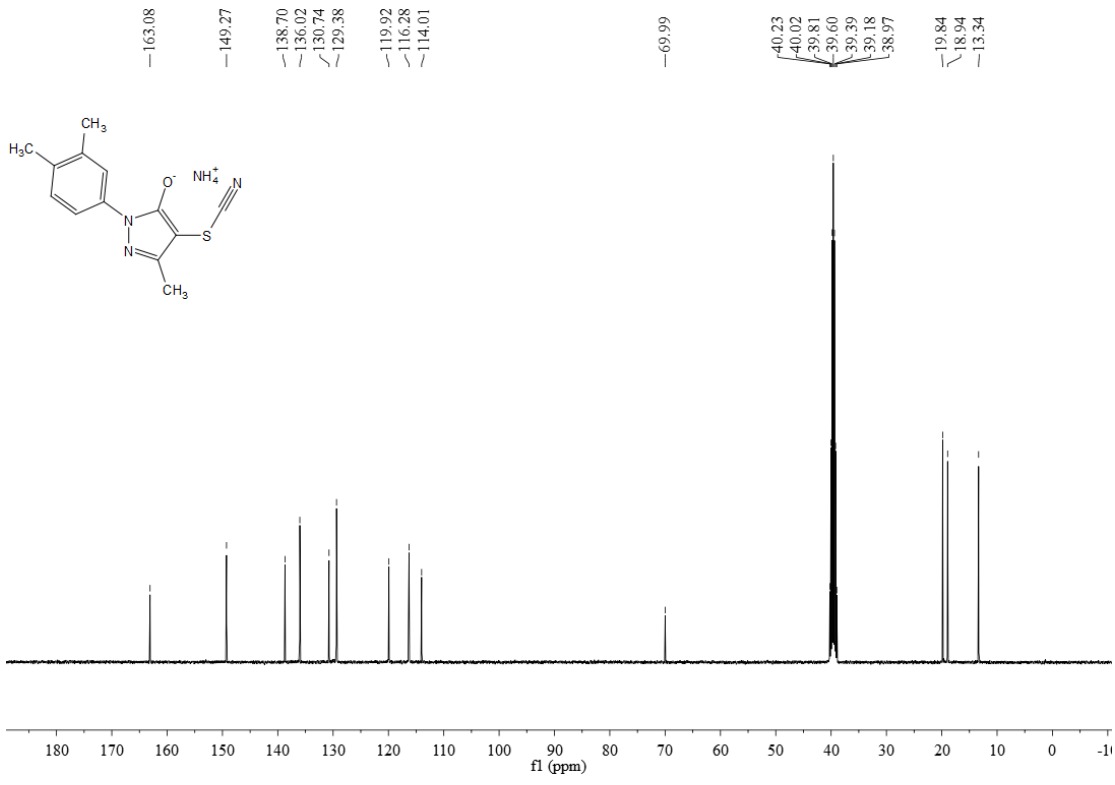
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3b



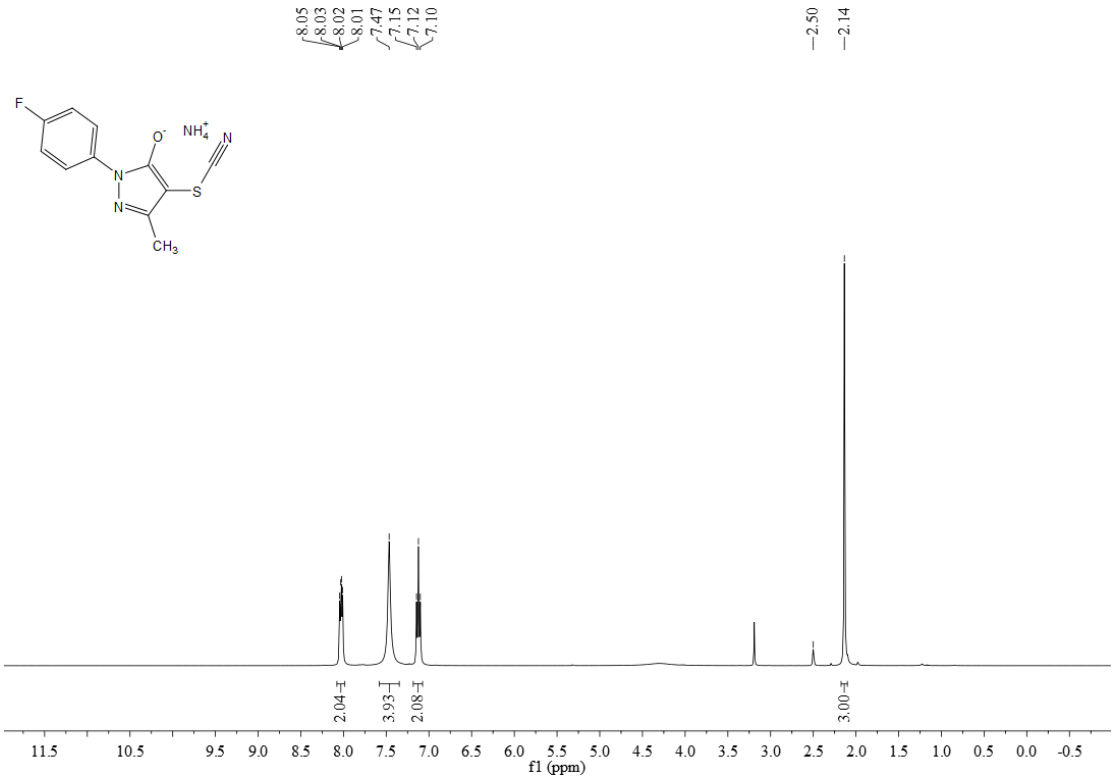
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3c



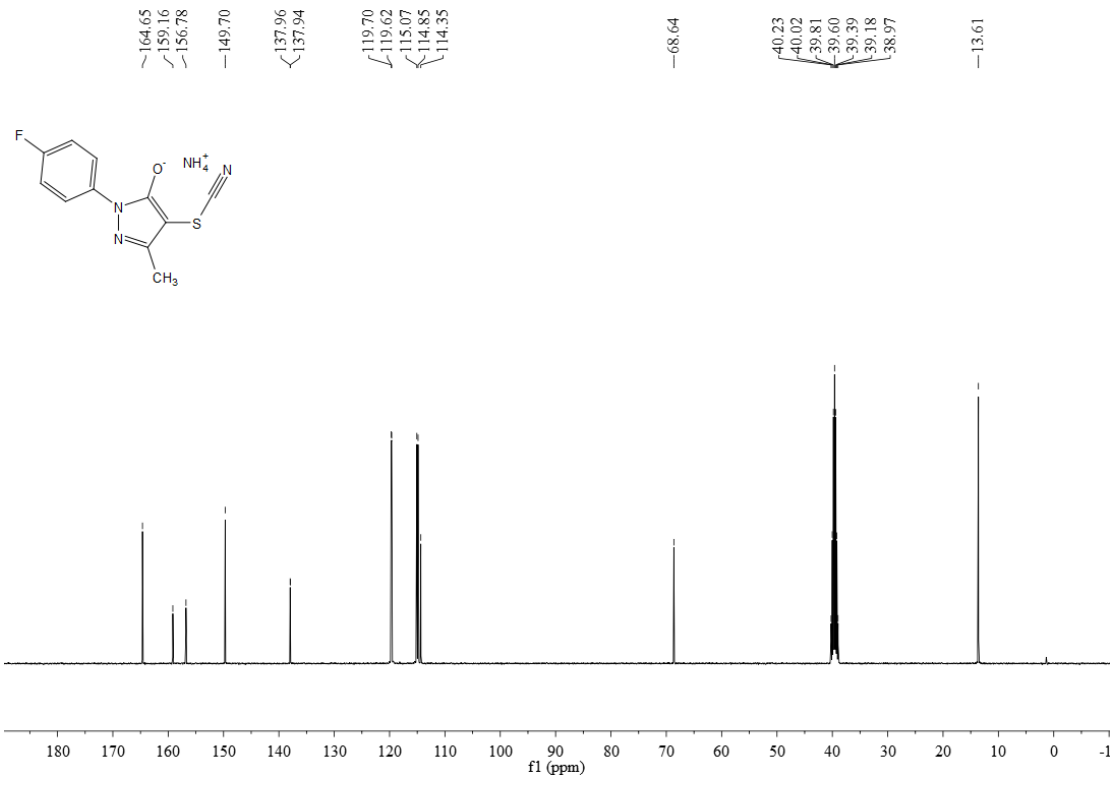
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3c



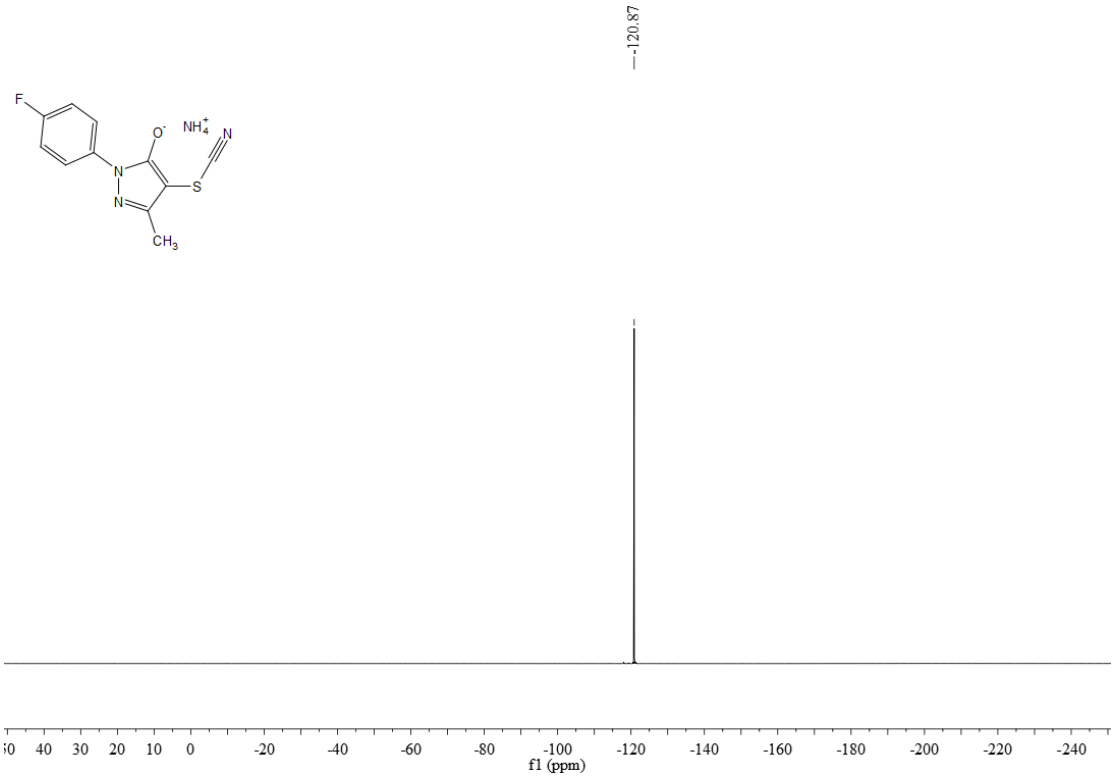
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3d



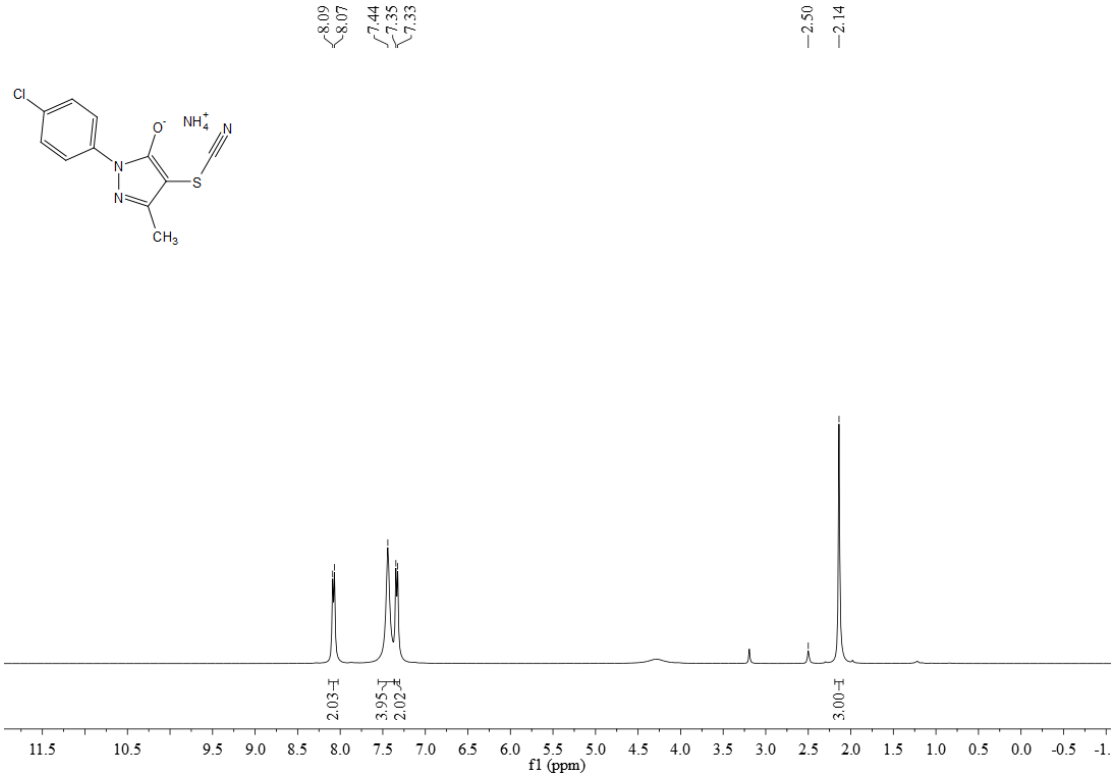
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3d



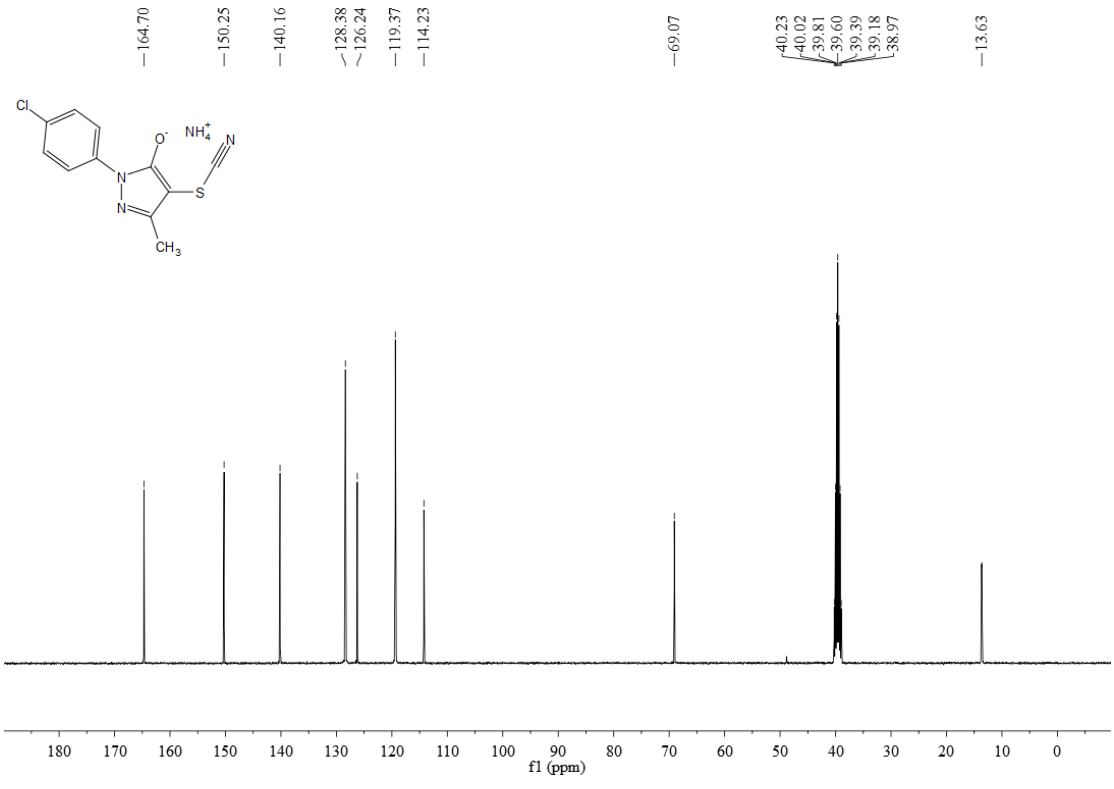
^{19}F NMR (376 MHz, DMSO-D^{6}) spectrum of 3d



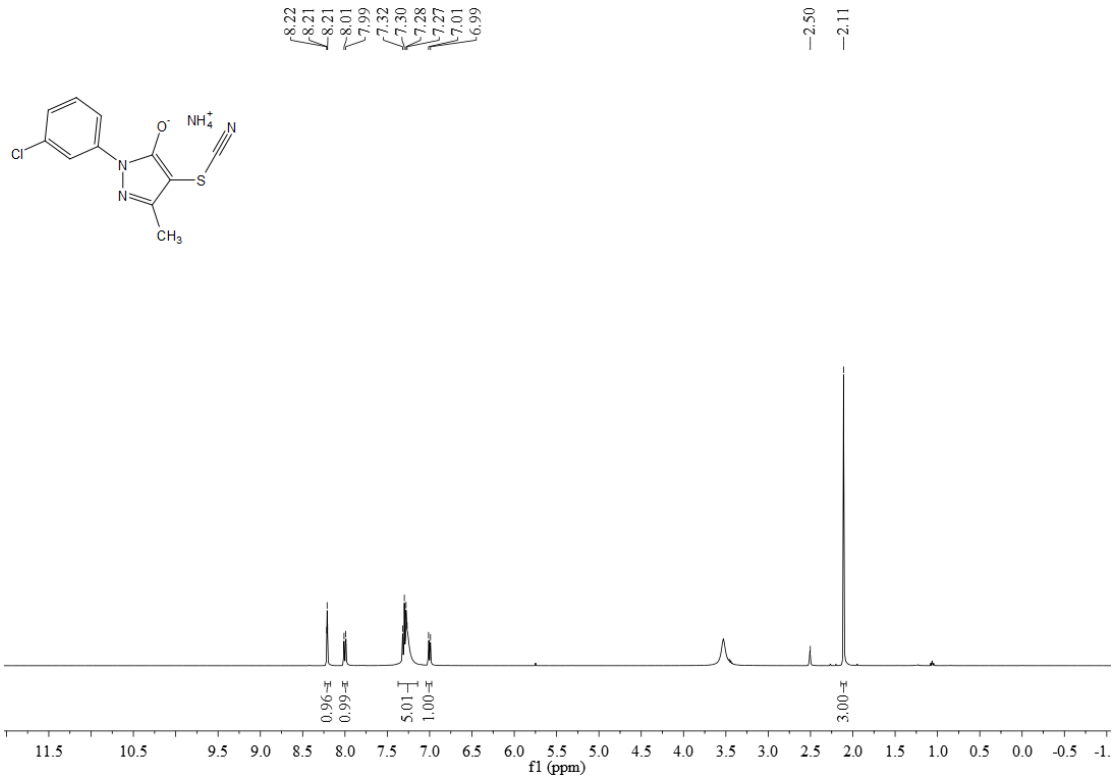
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3e



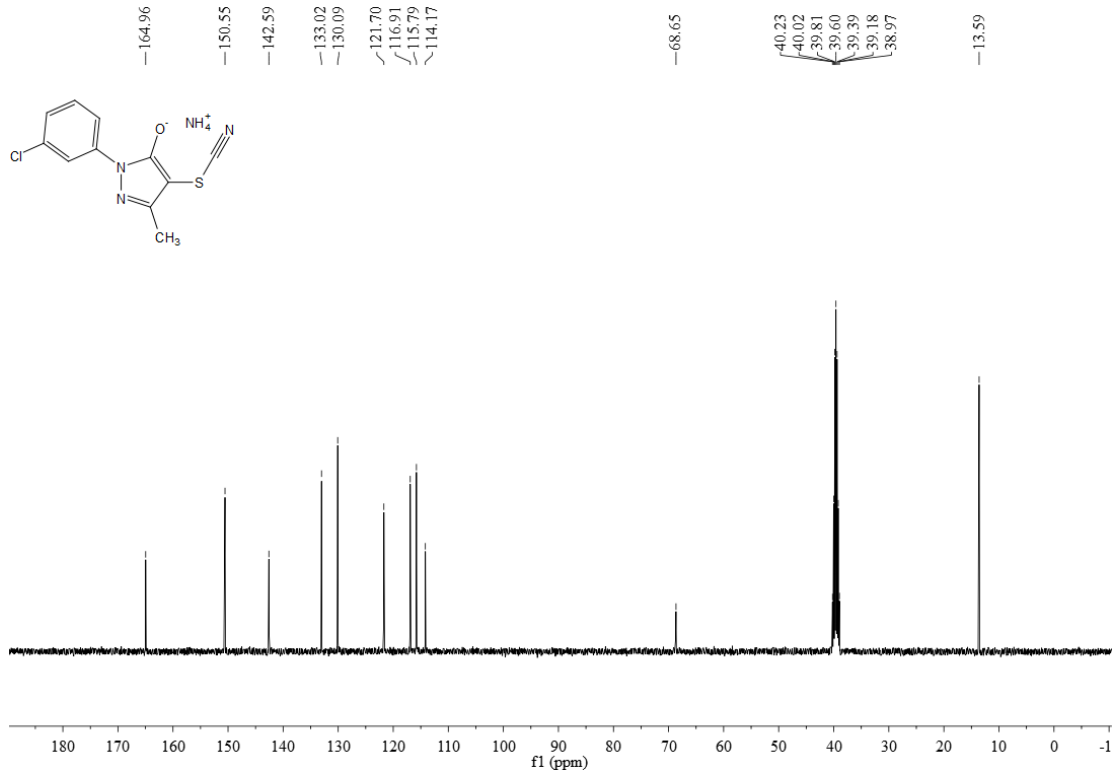
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3e



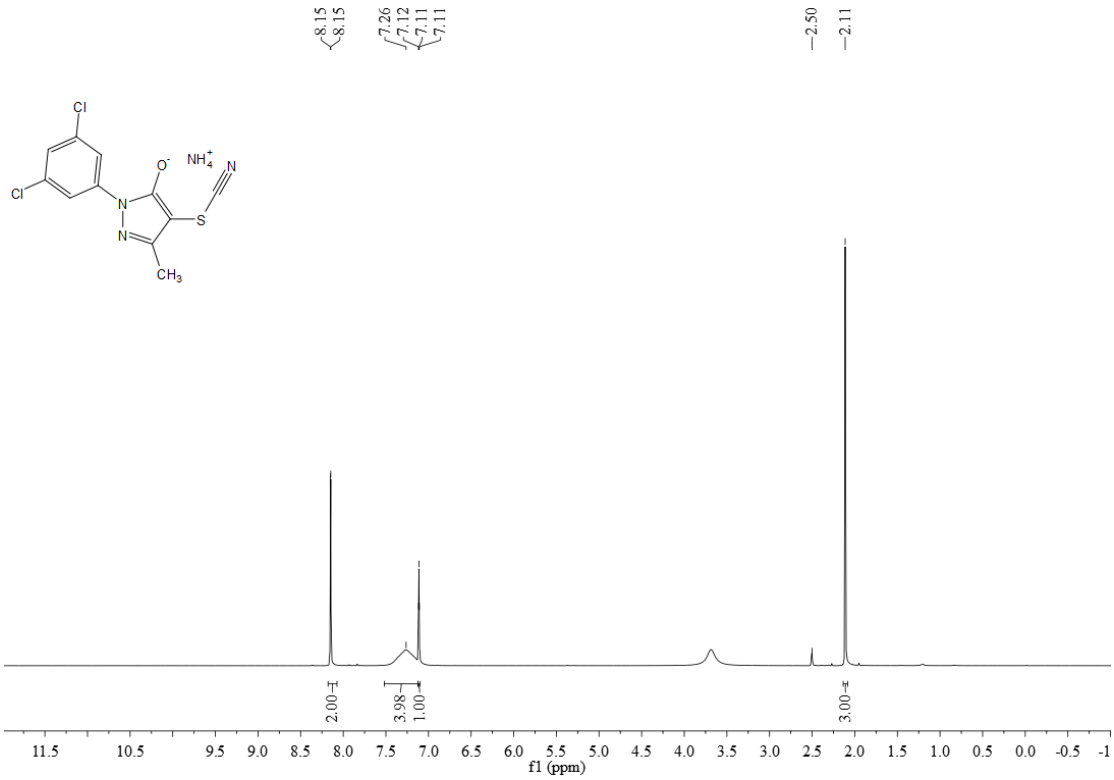
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3f



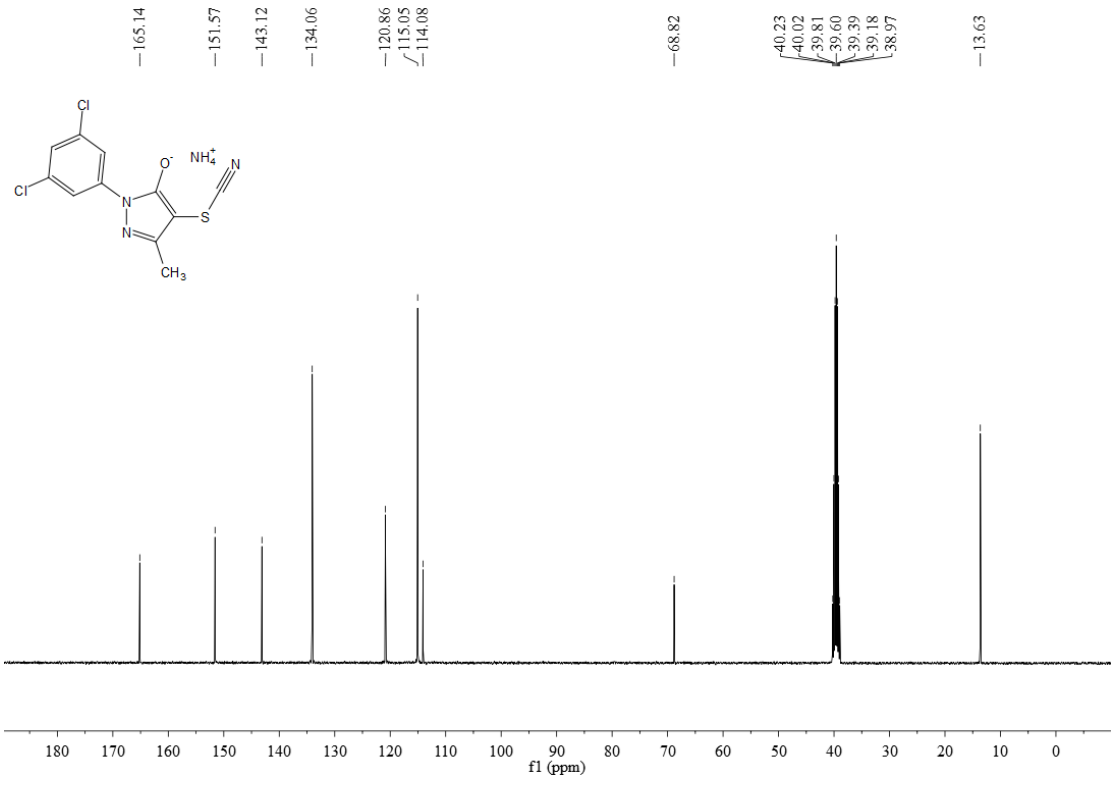
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3f



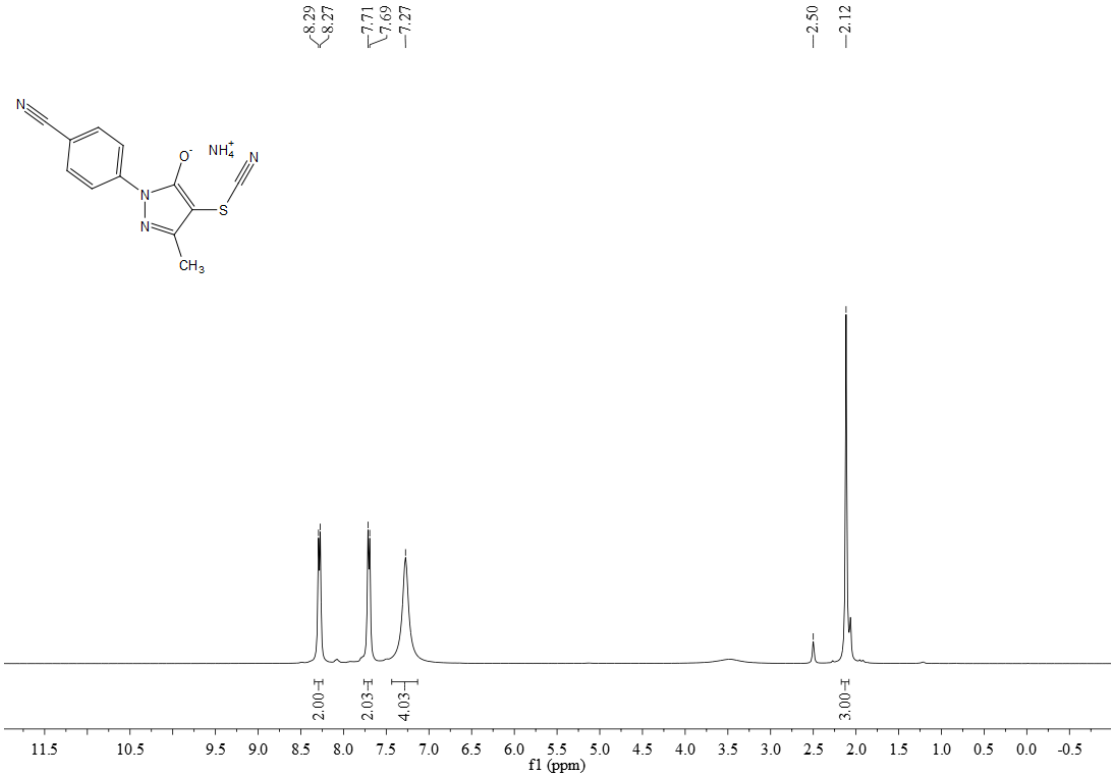
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3g



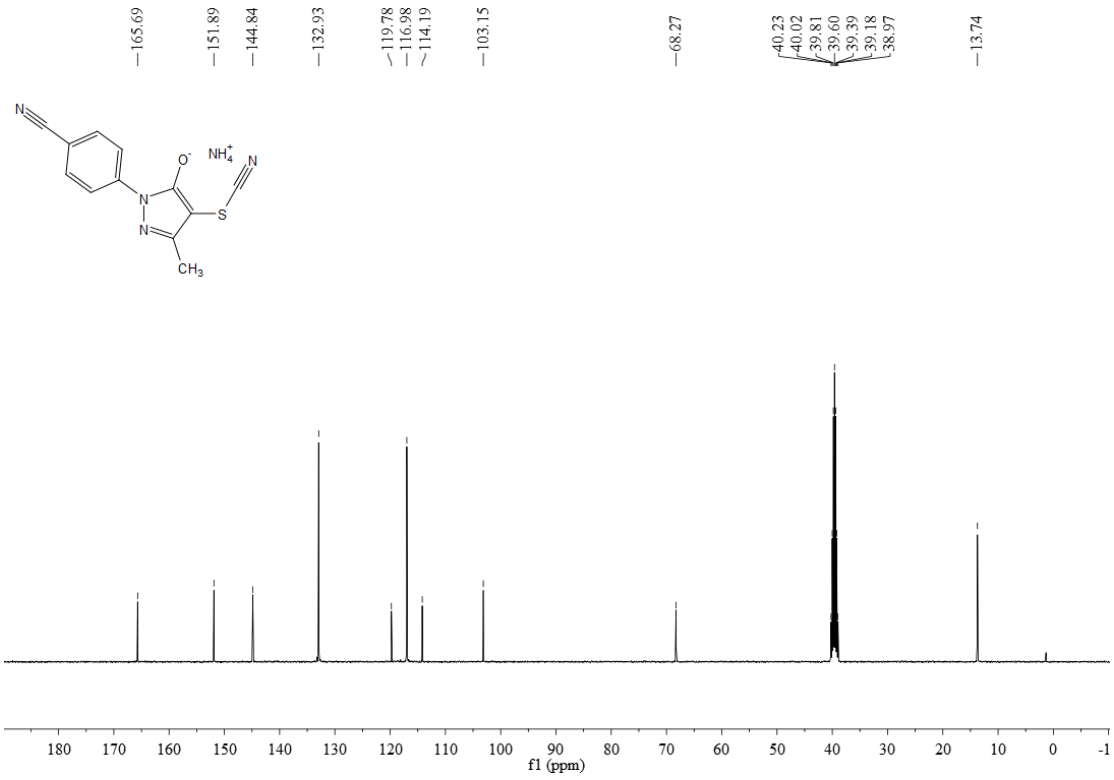
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3g



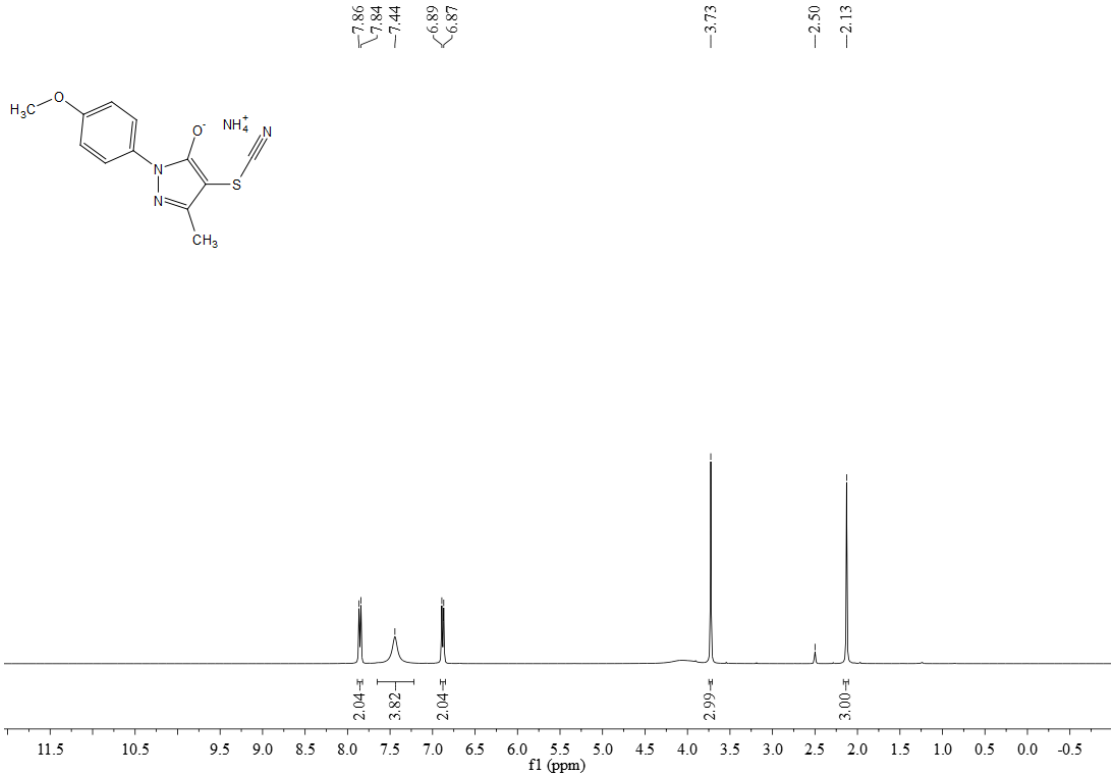
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3h



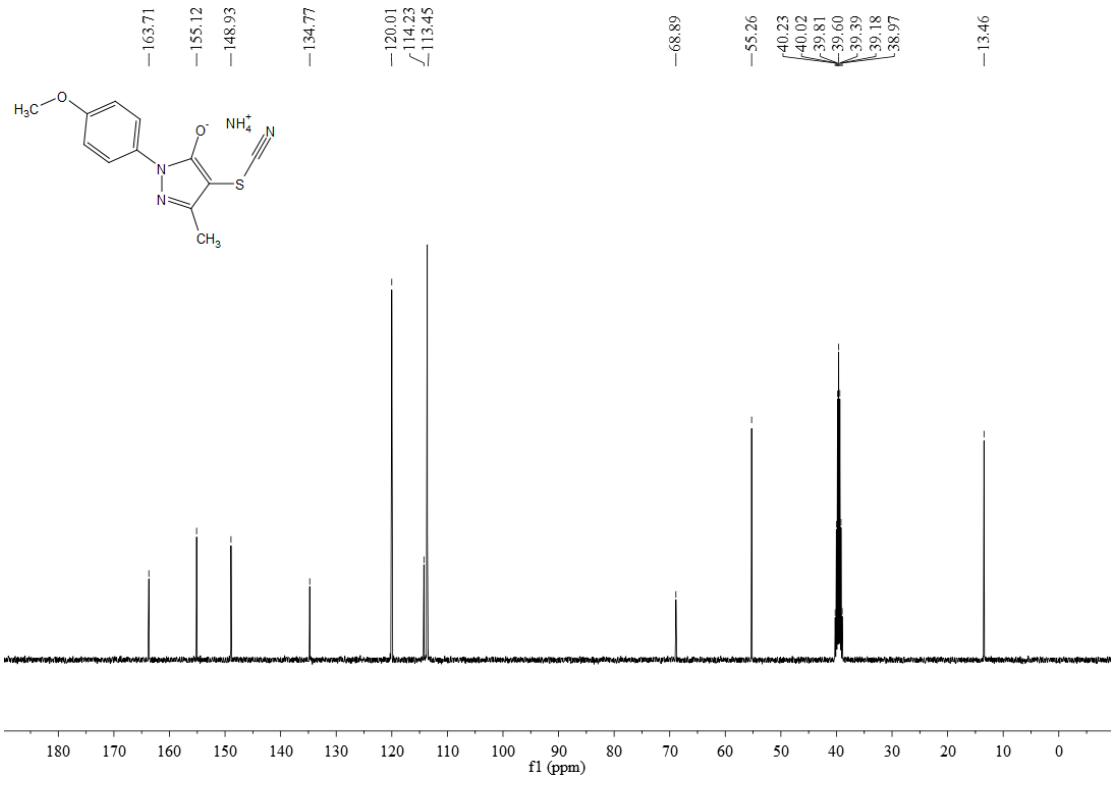
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3h



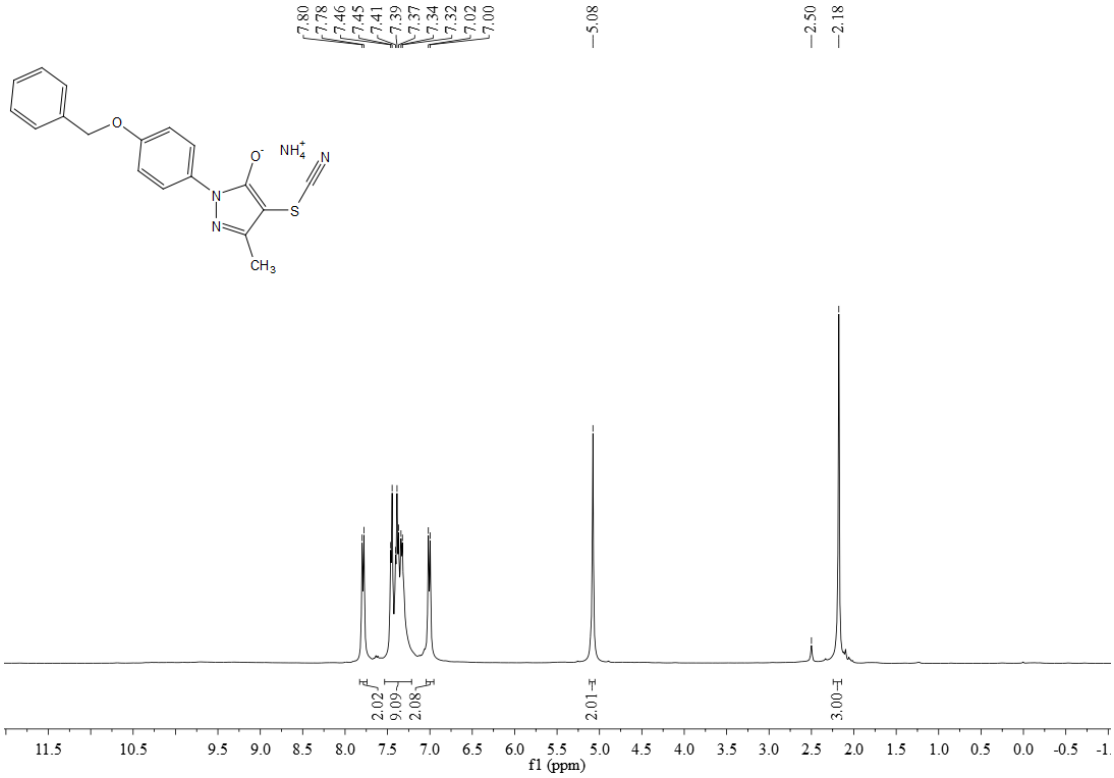
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3i



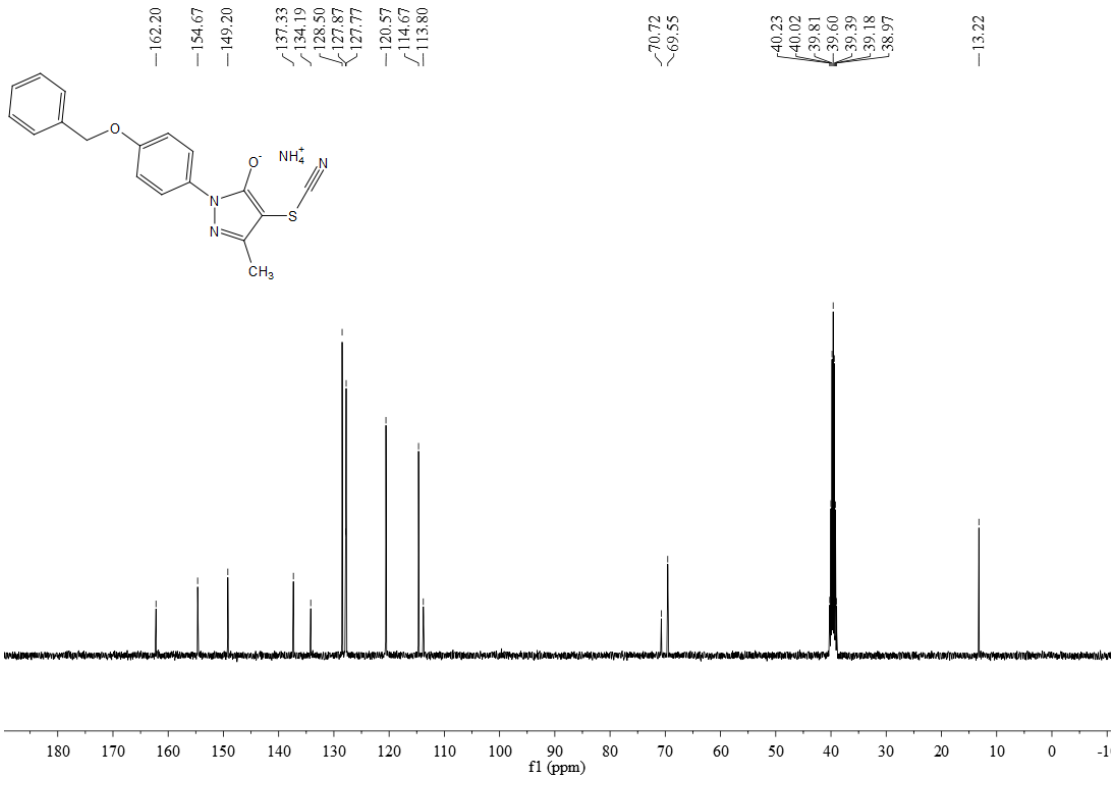
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3i



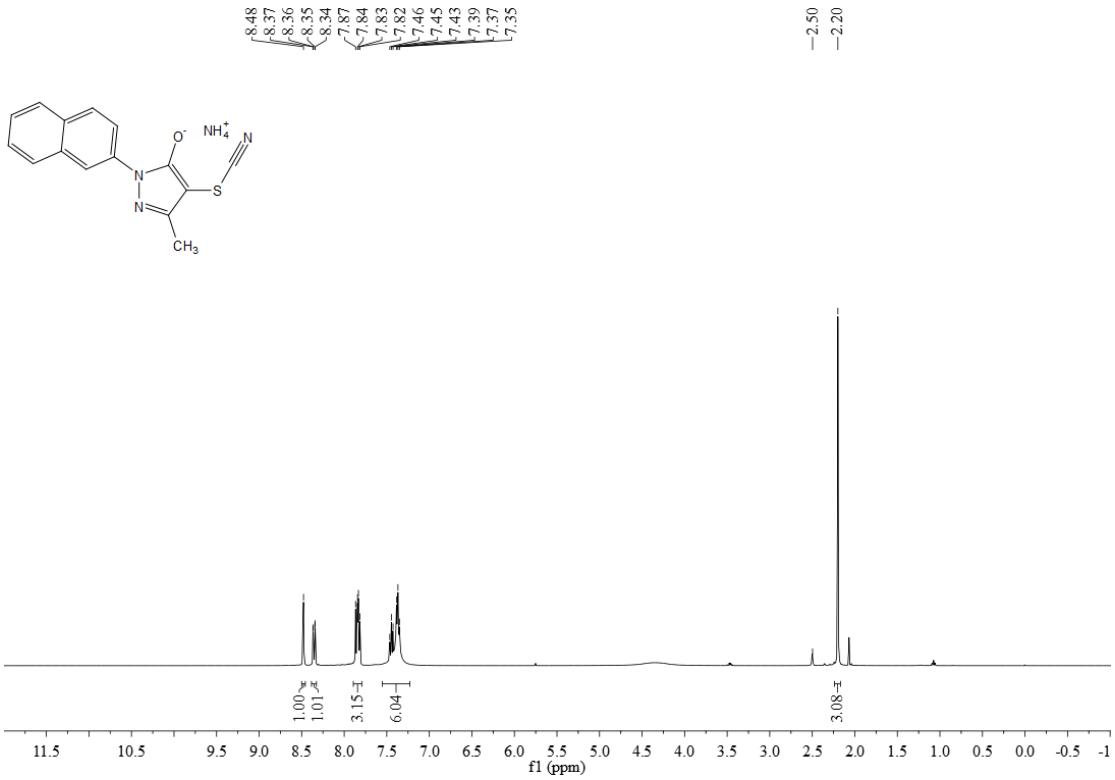
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3j



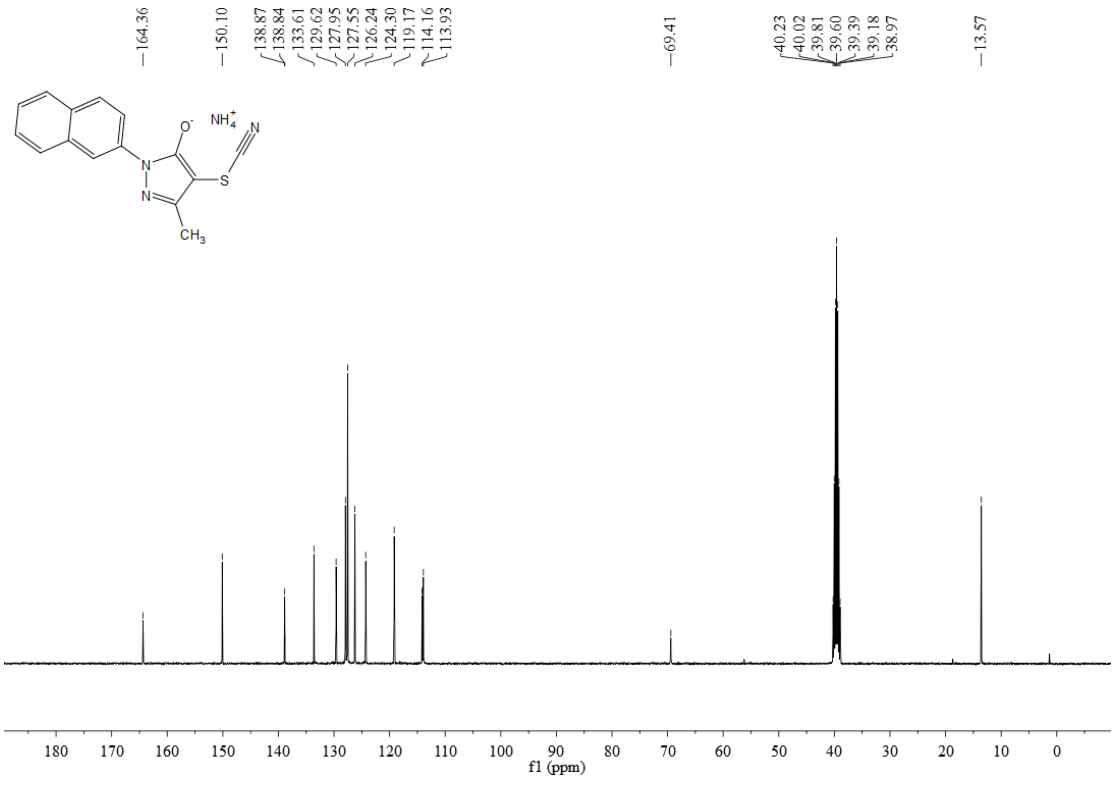
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3j



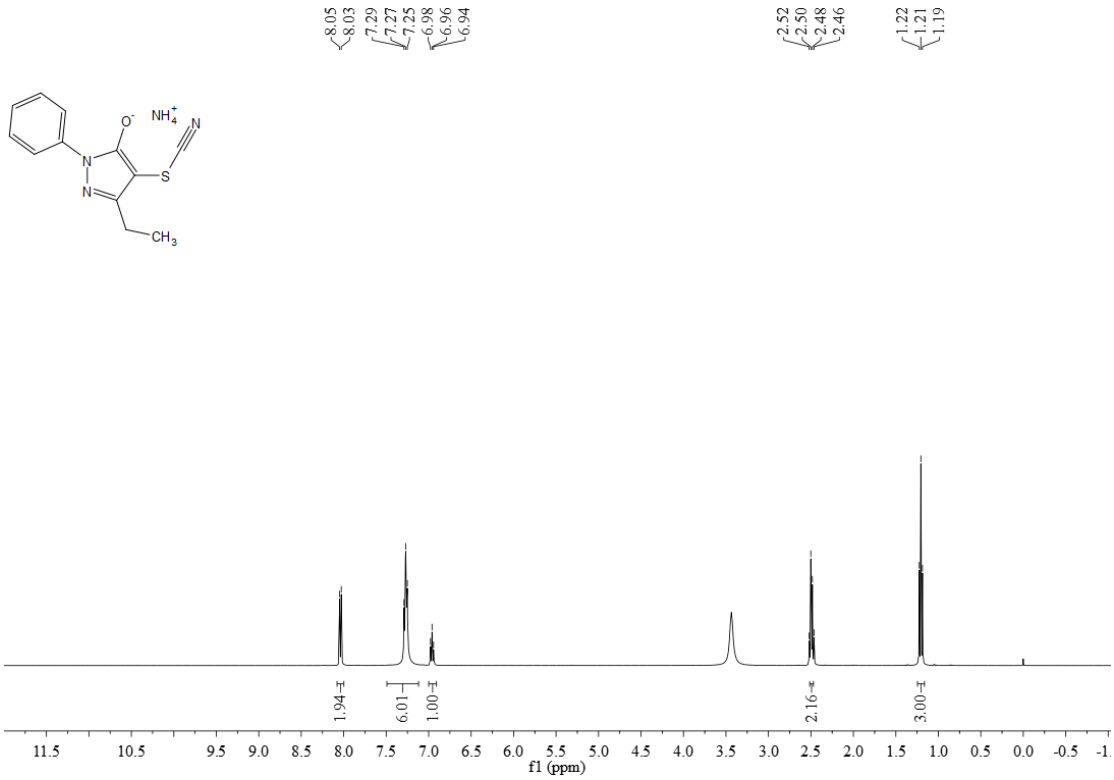
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3k



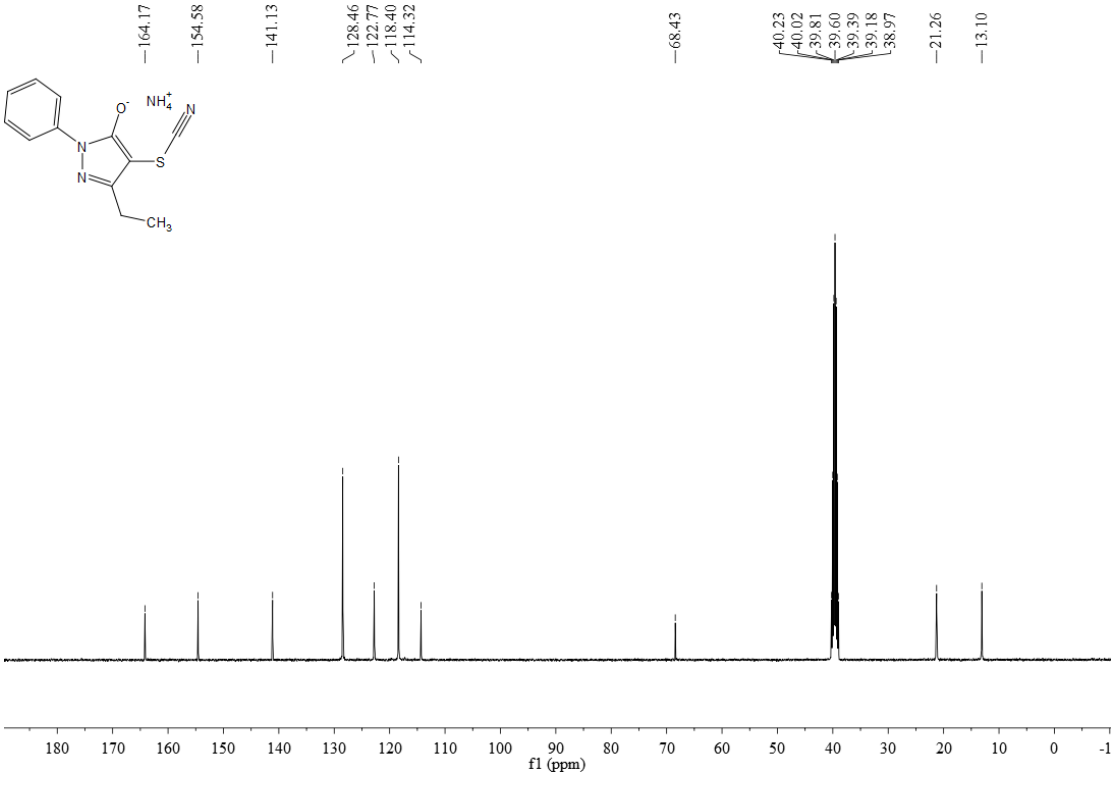
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3k



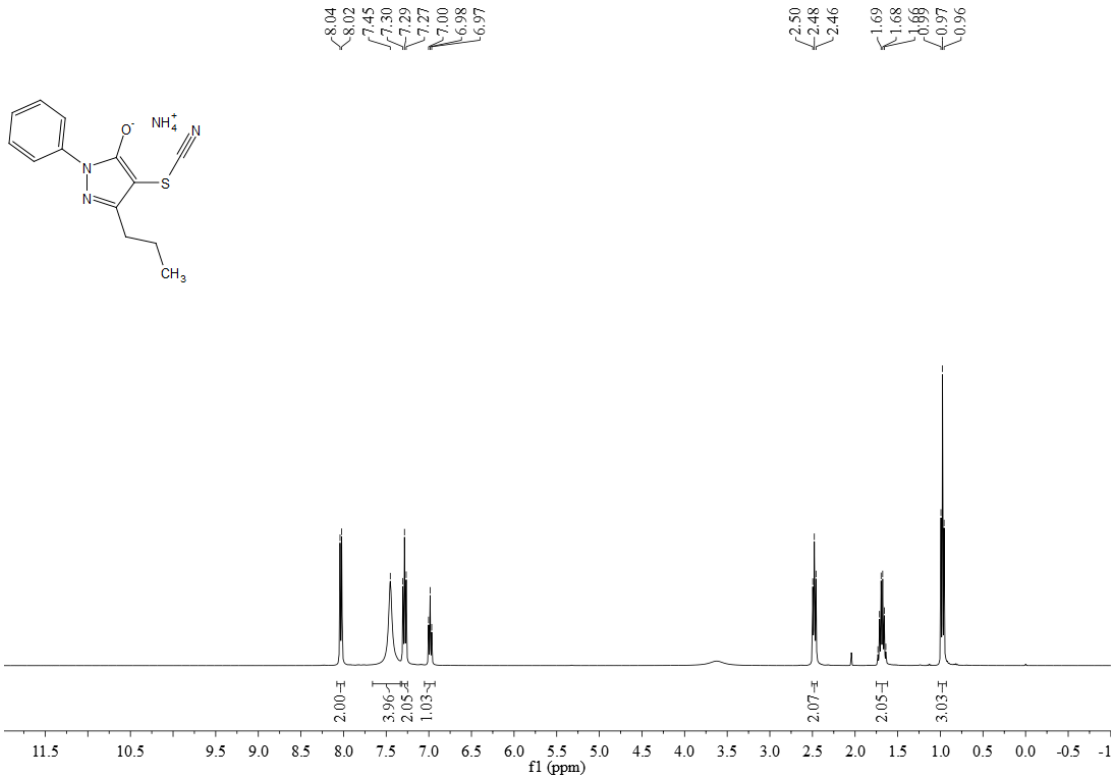
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3l



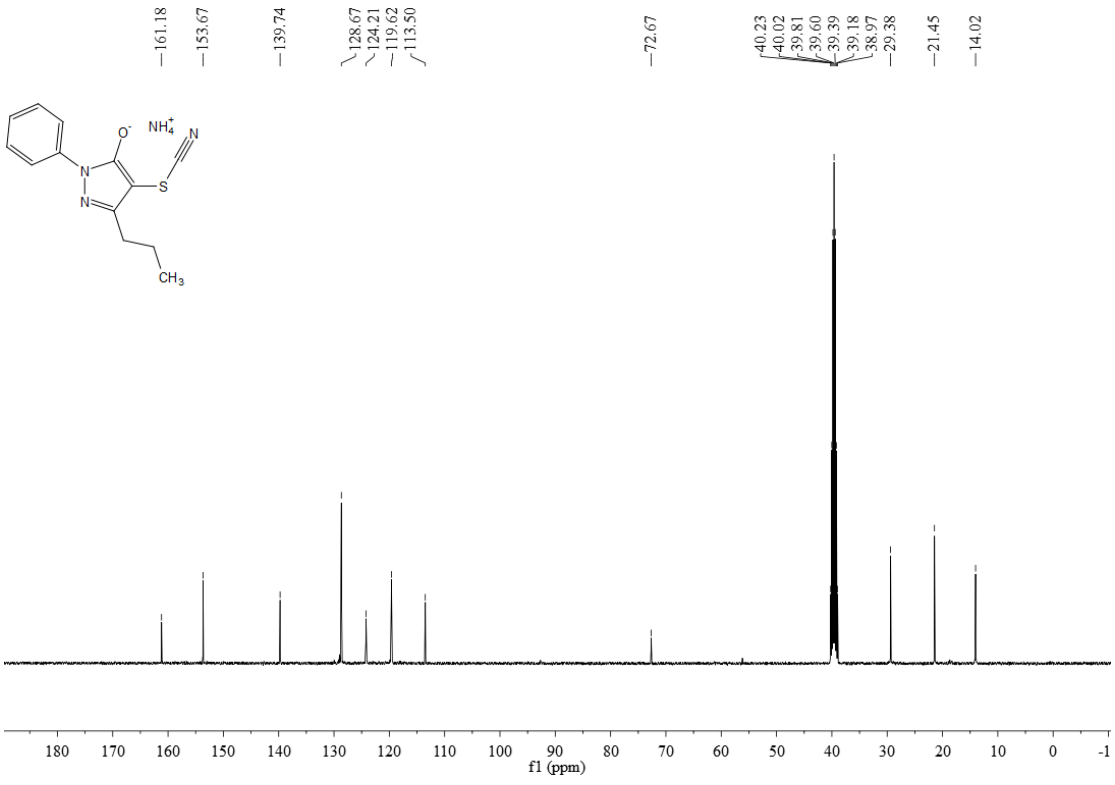
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3l



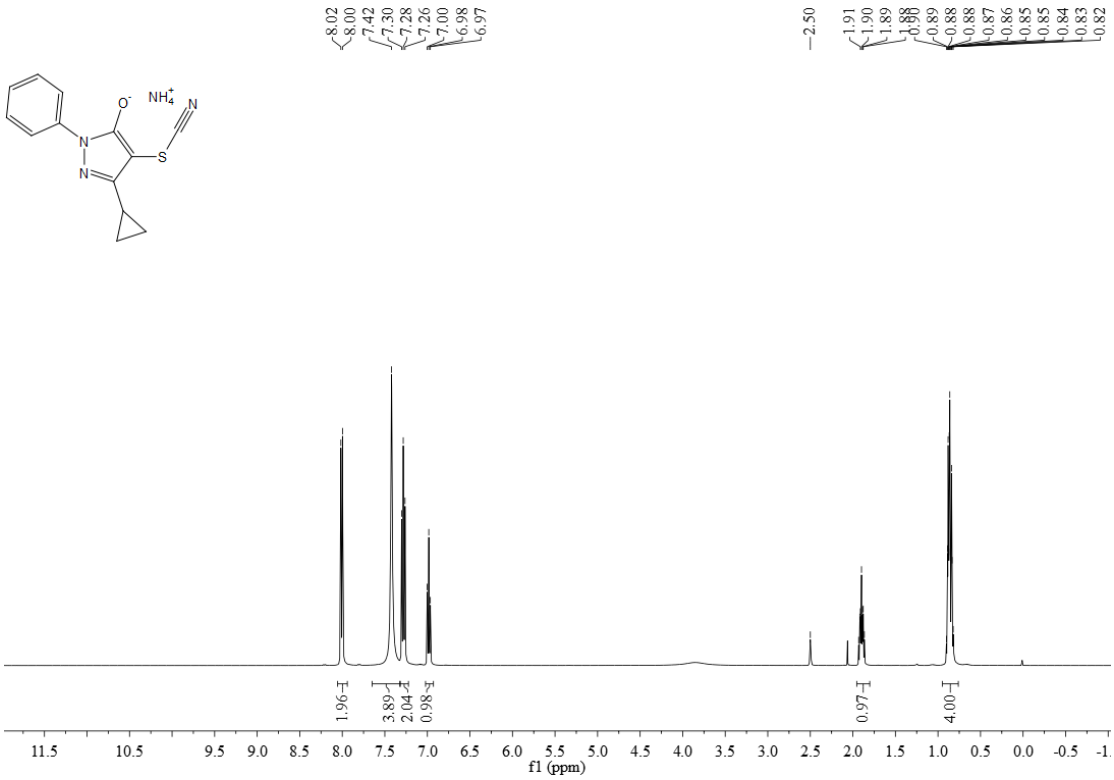
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3m



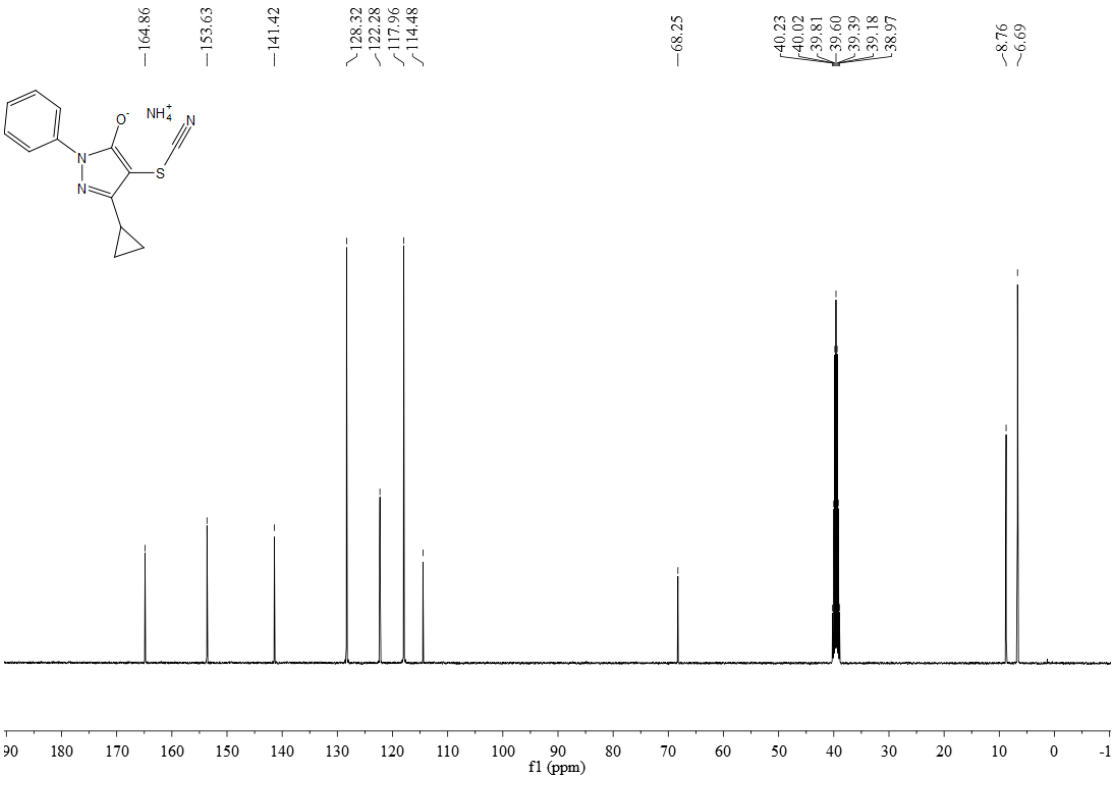
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3m



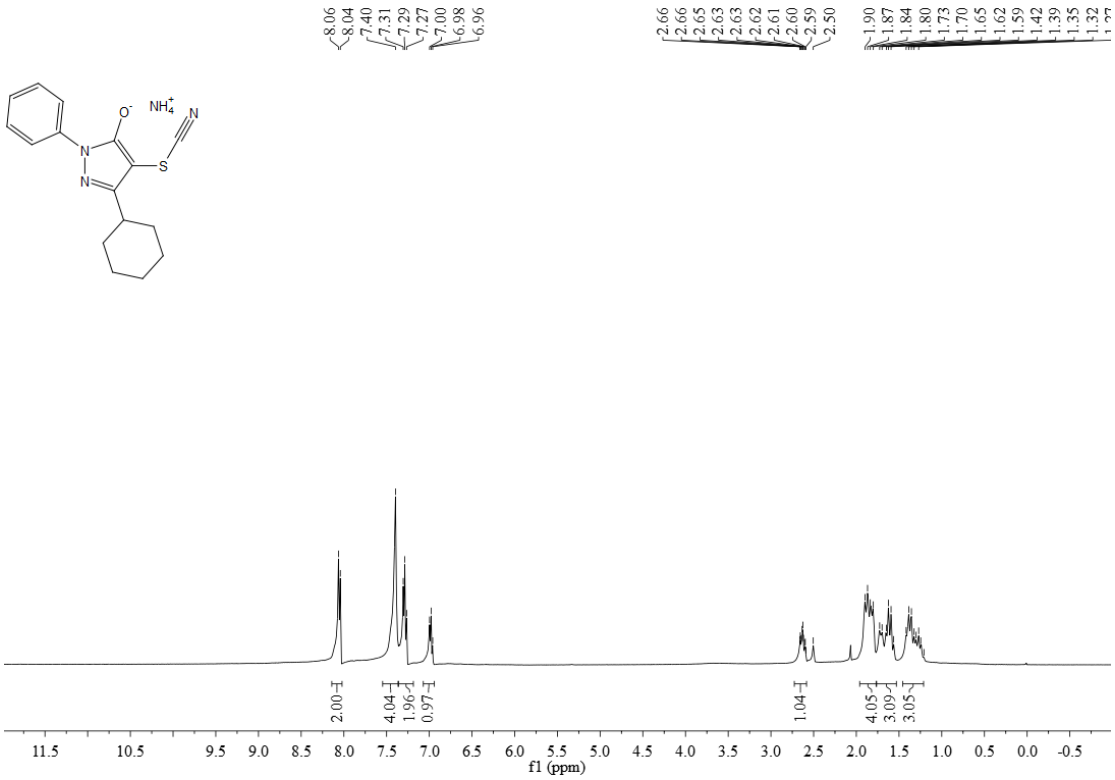
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3n



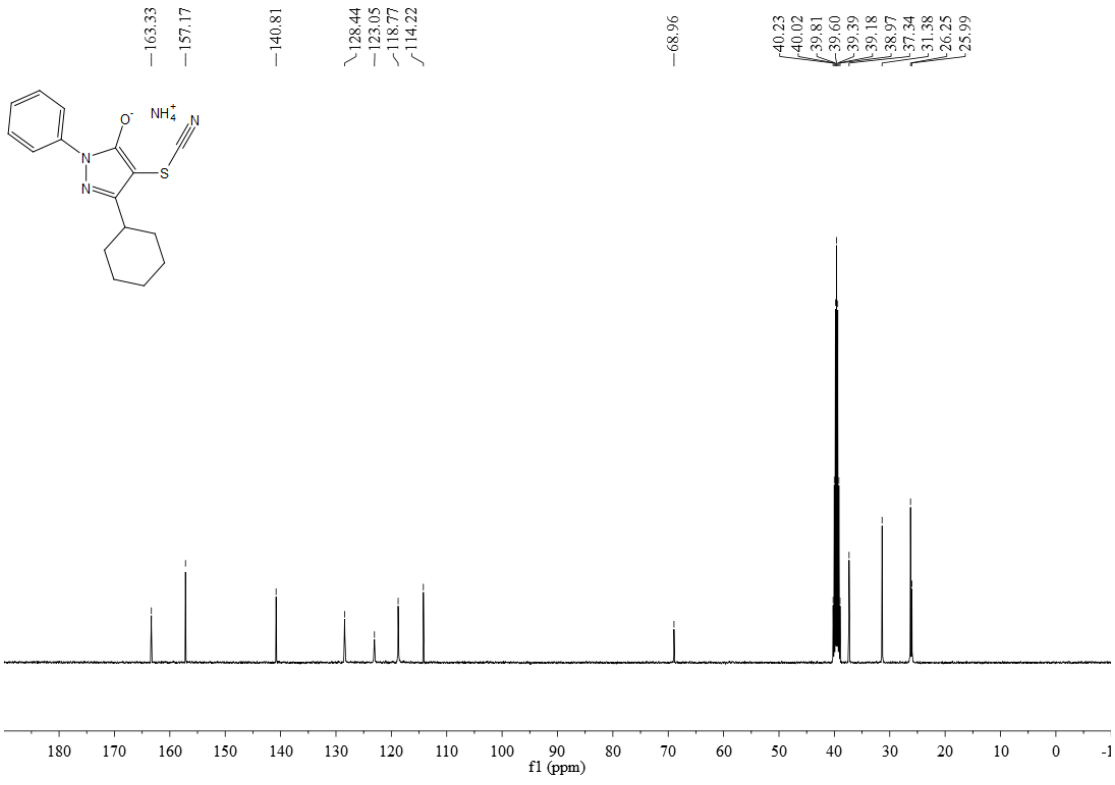
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3n



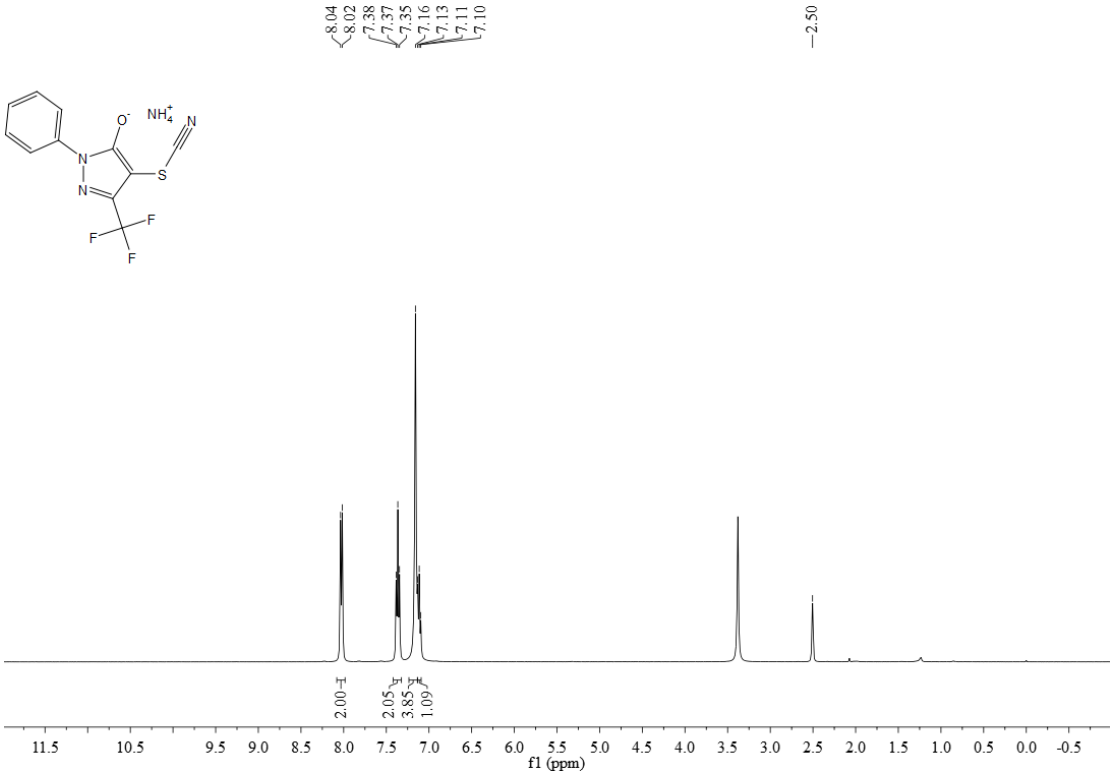
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3o



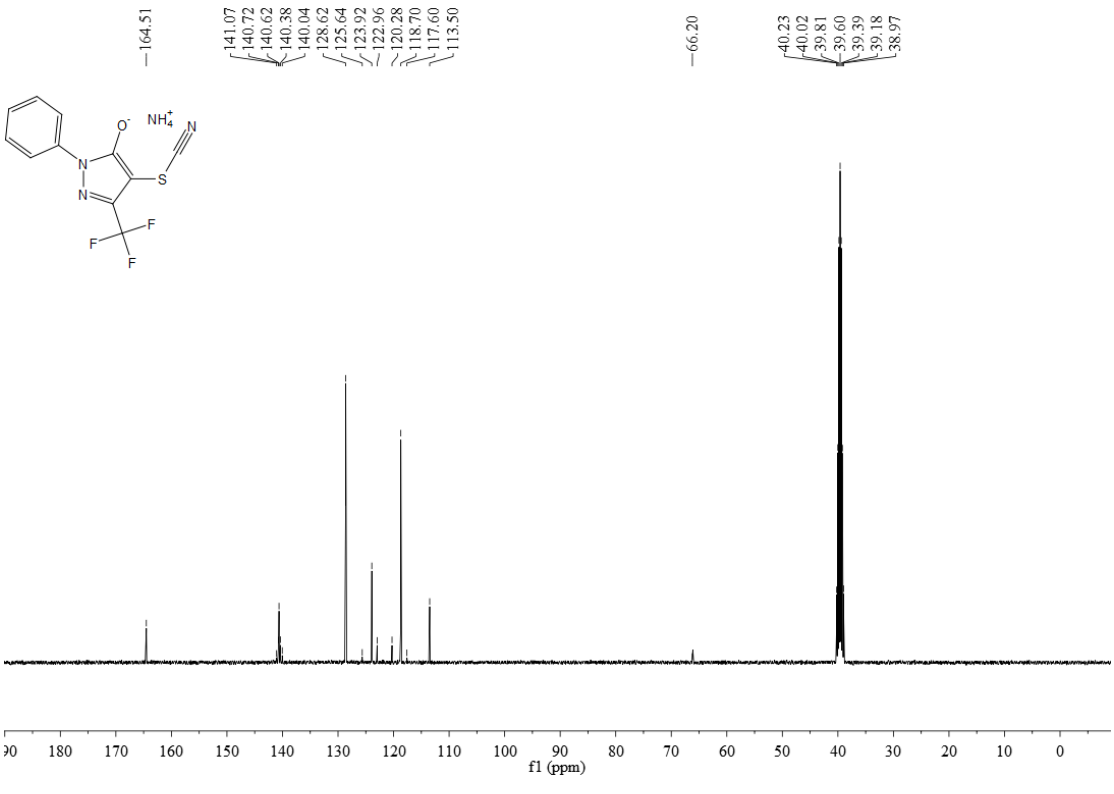
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3o



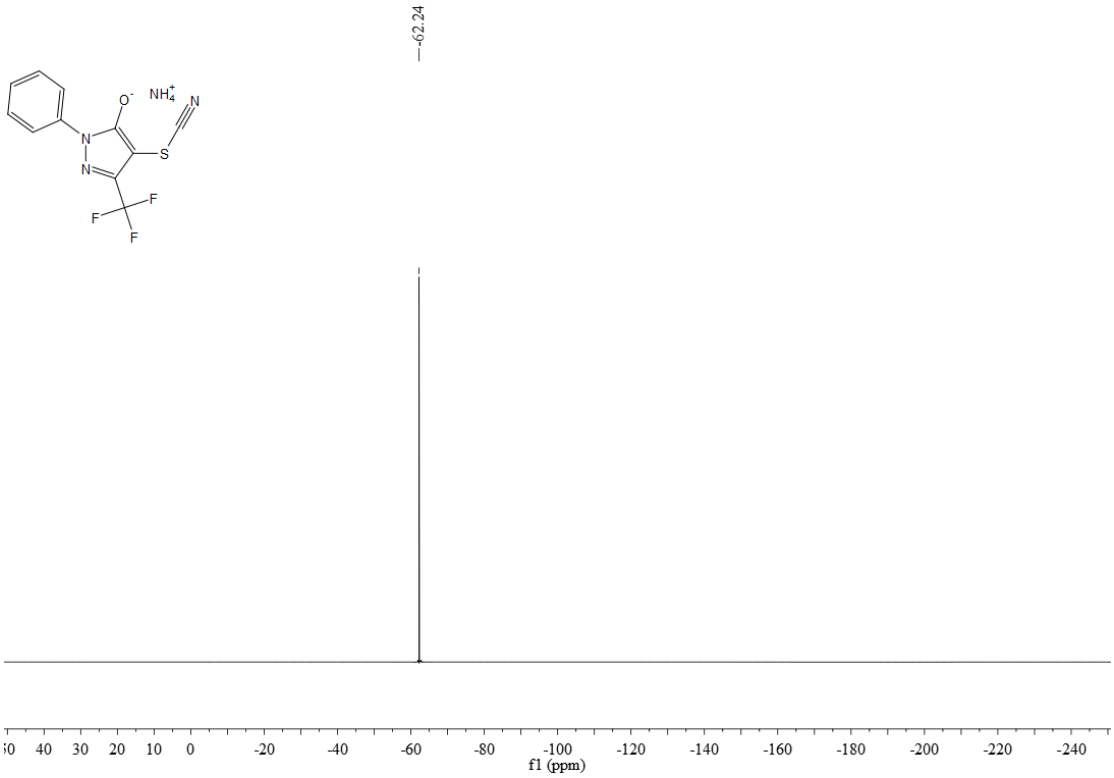
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3p



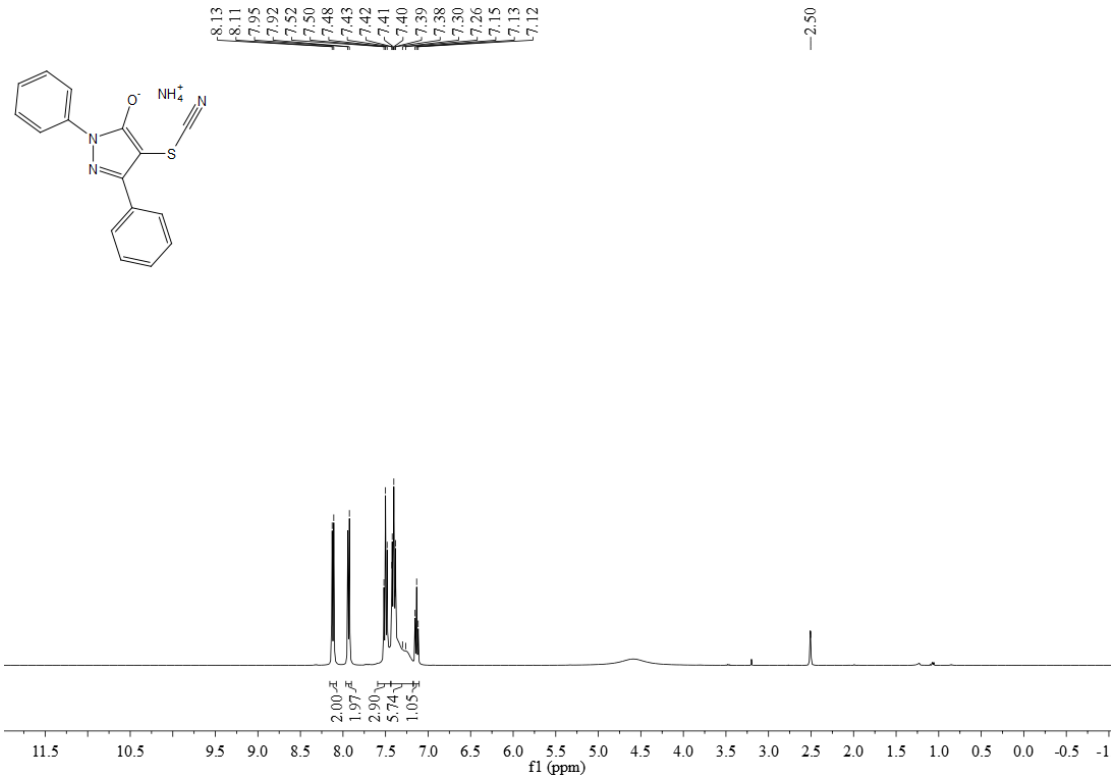
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3p



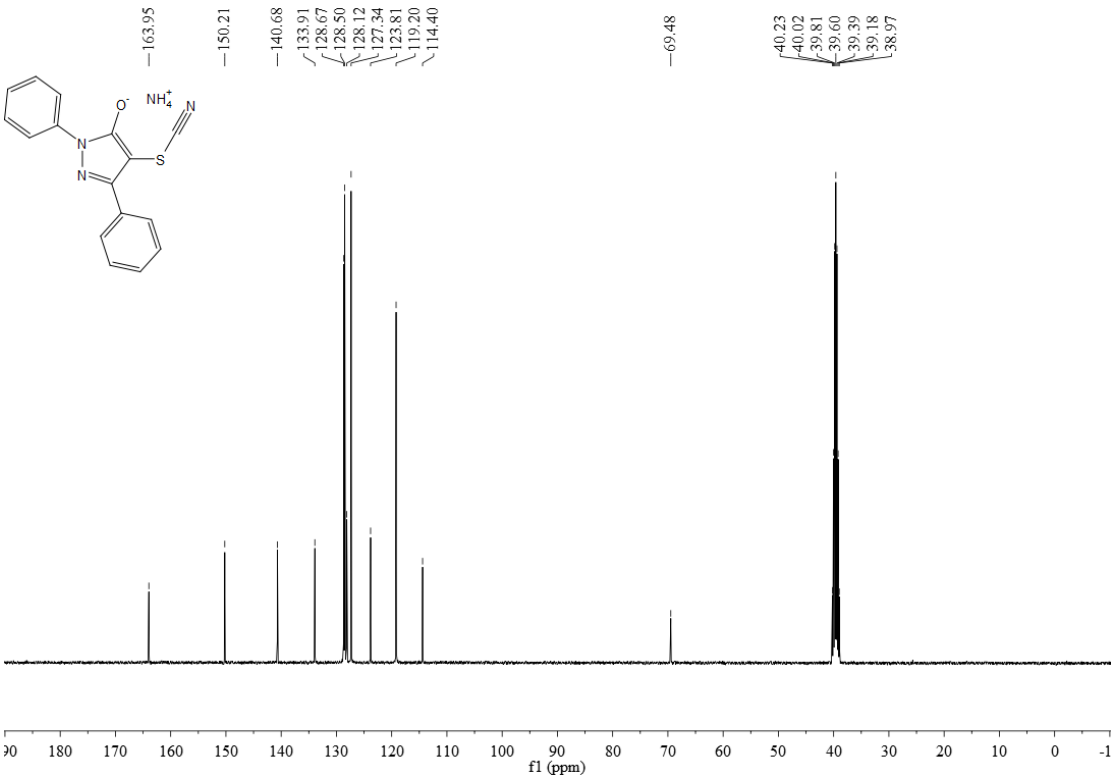
^{19}F NMR (376 MHz, DMSO-D^{6}) spectrum of 3p



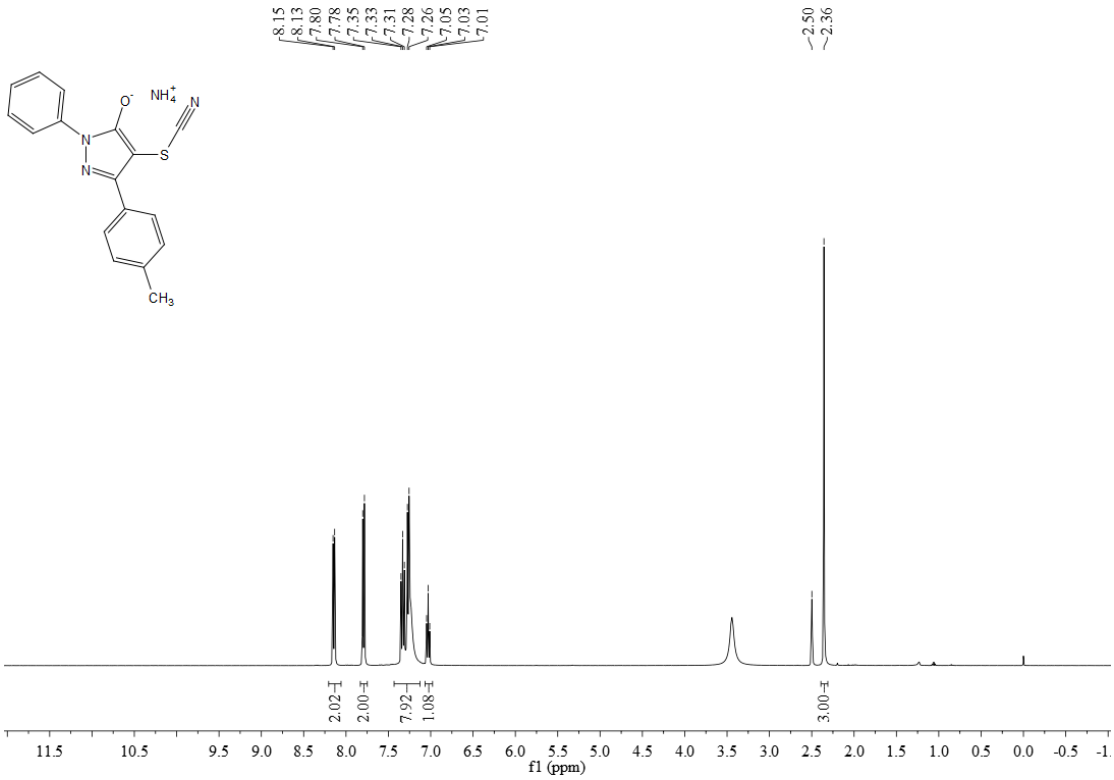
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3q



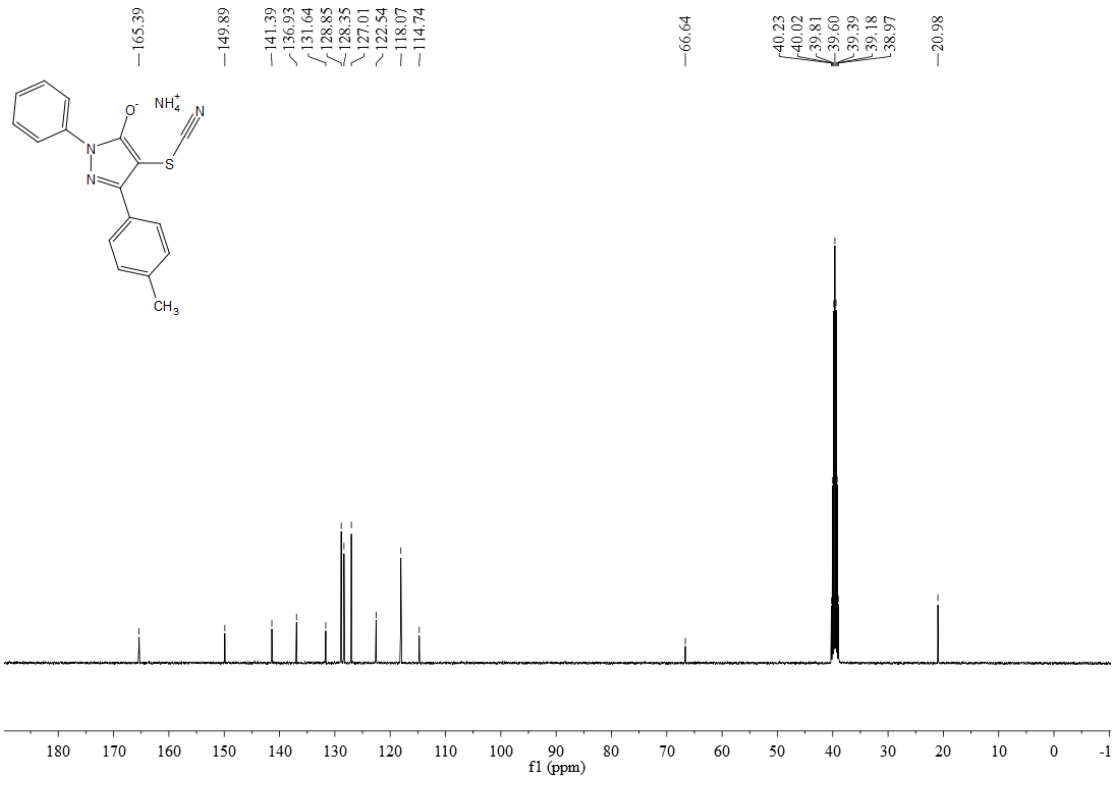
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3q



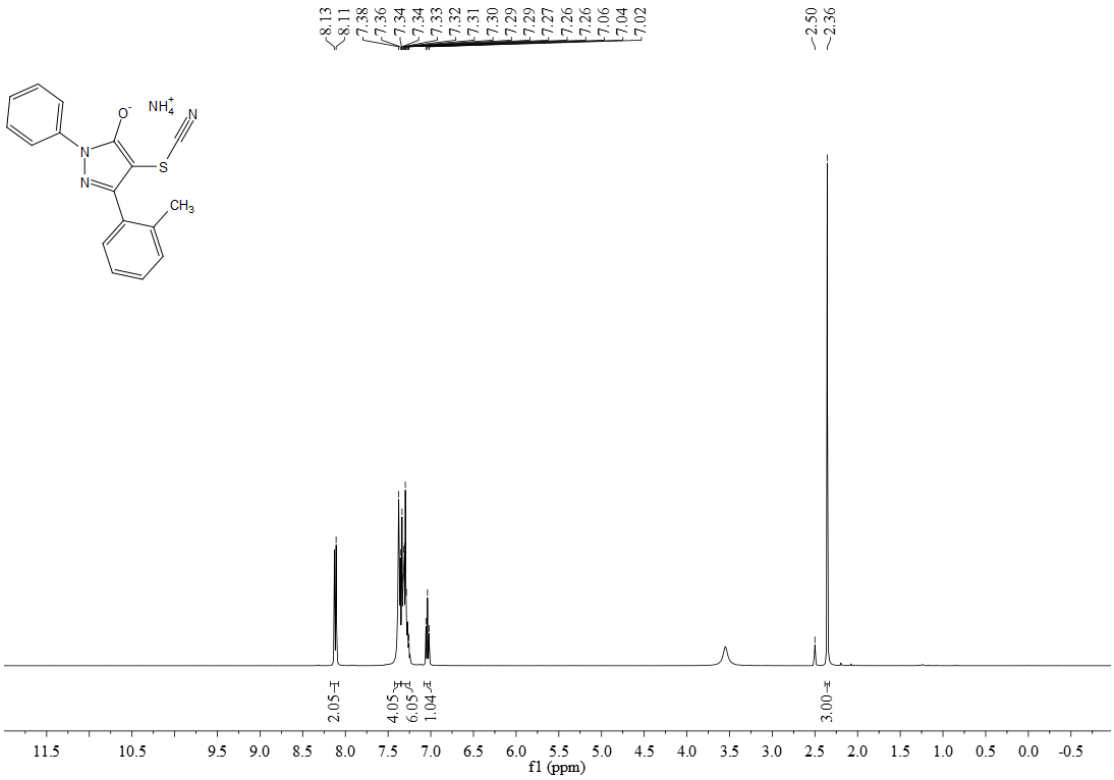
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3r



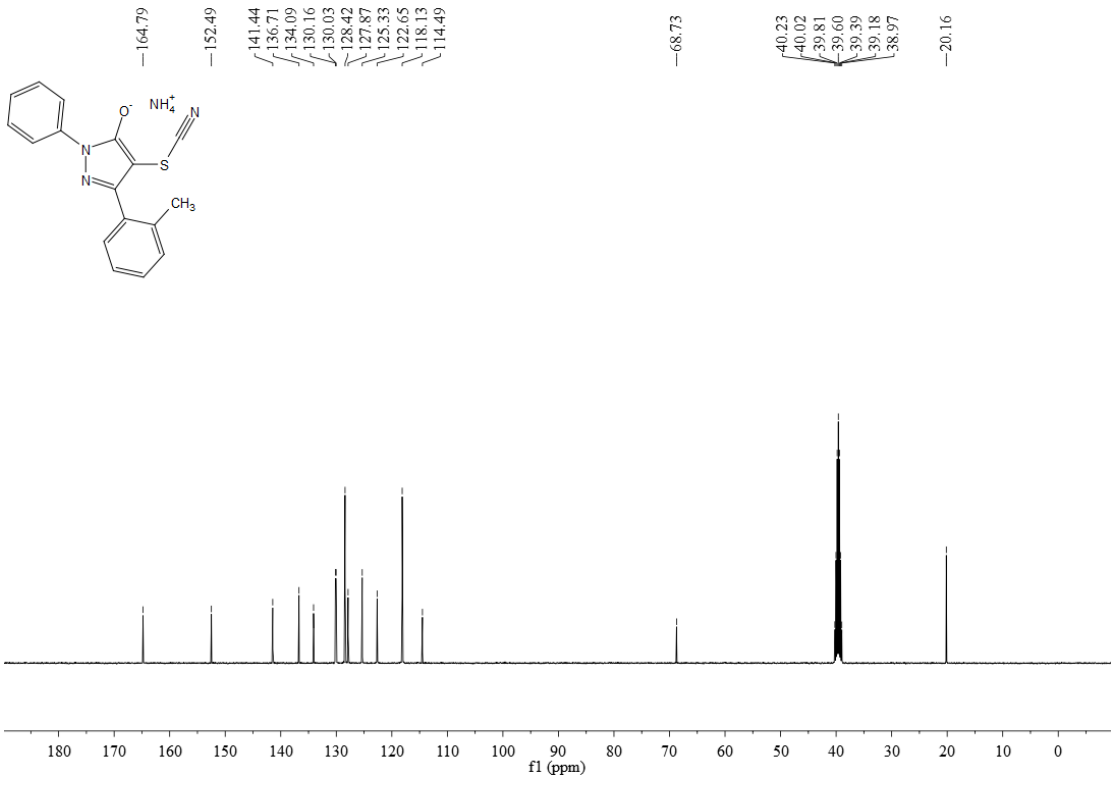
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3r



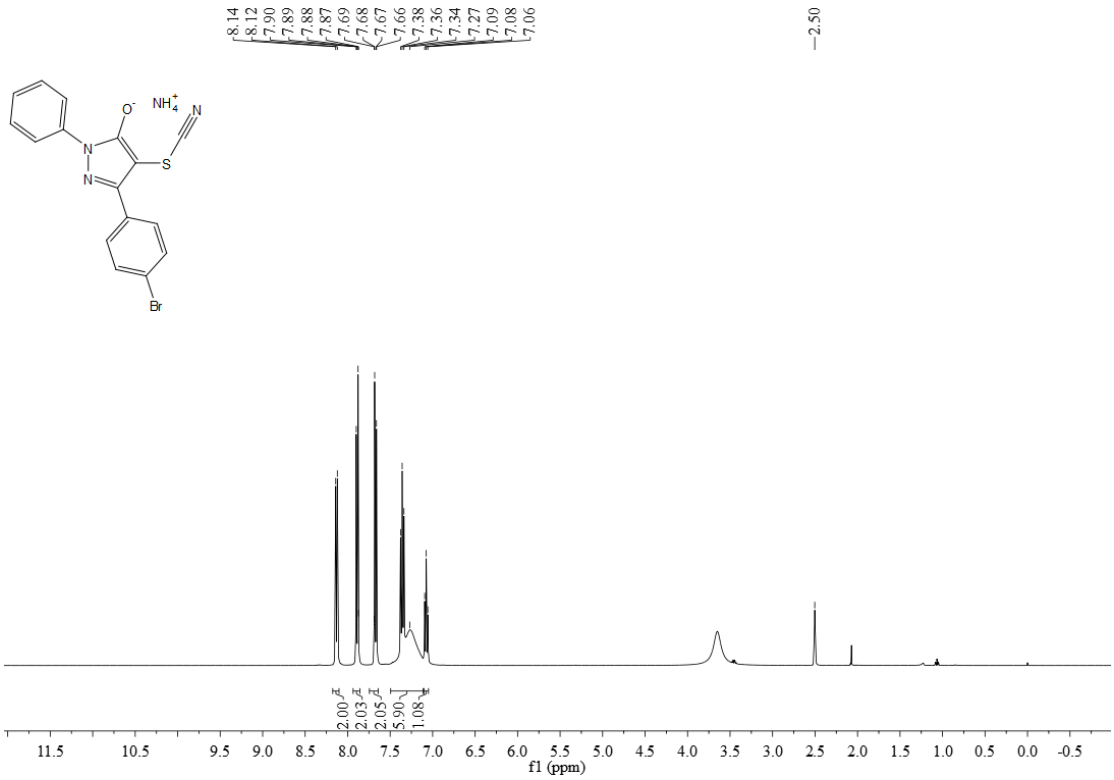
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3s



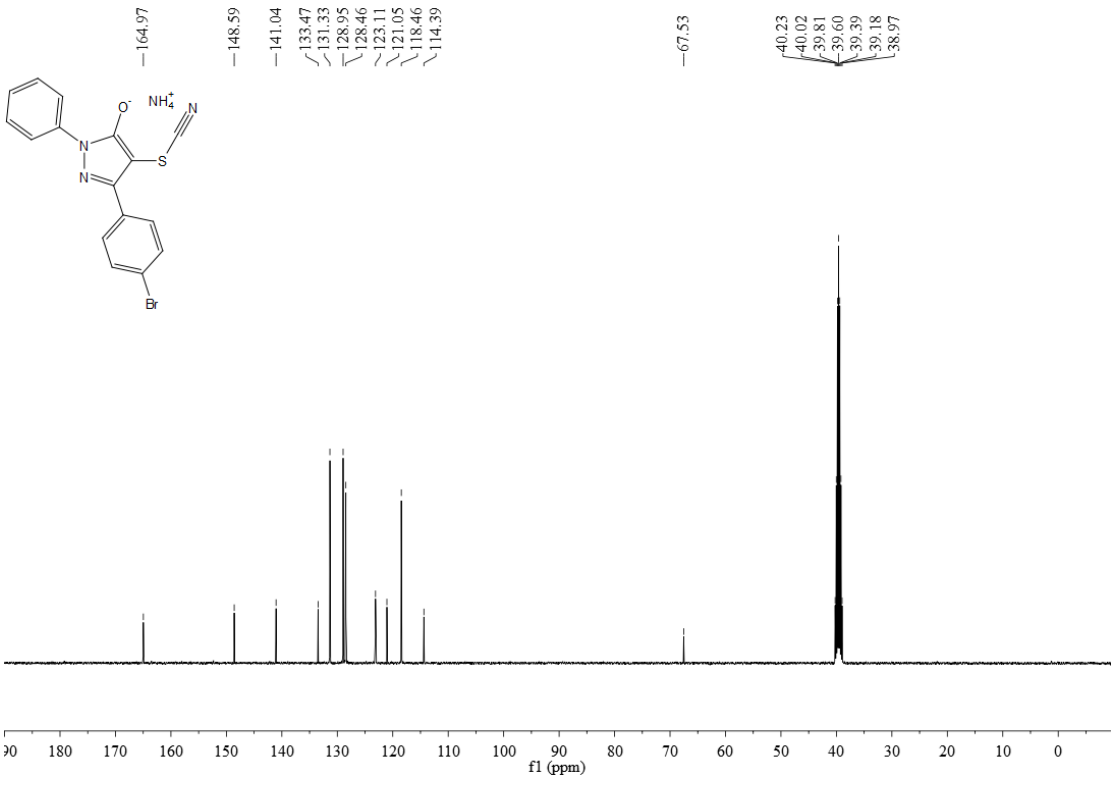
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3s



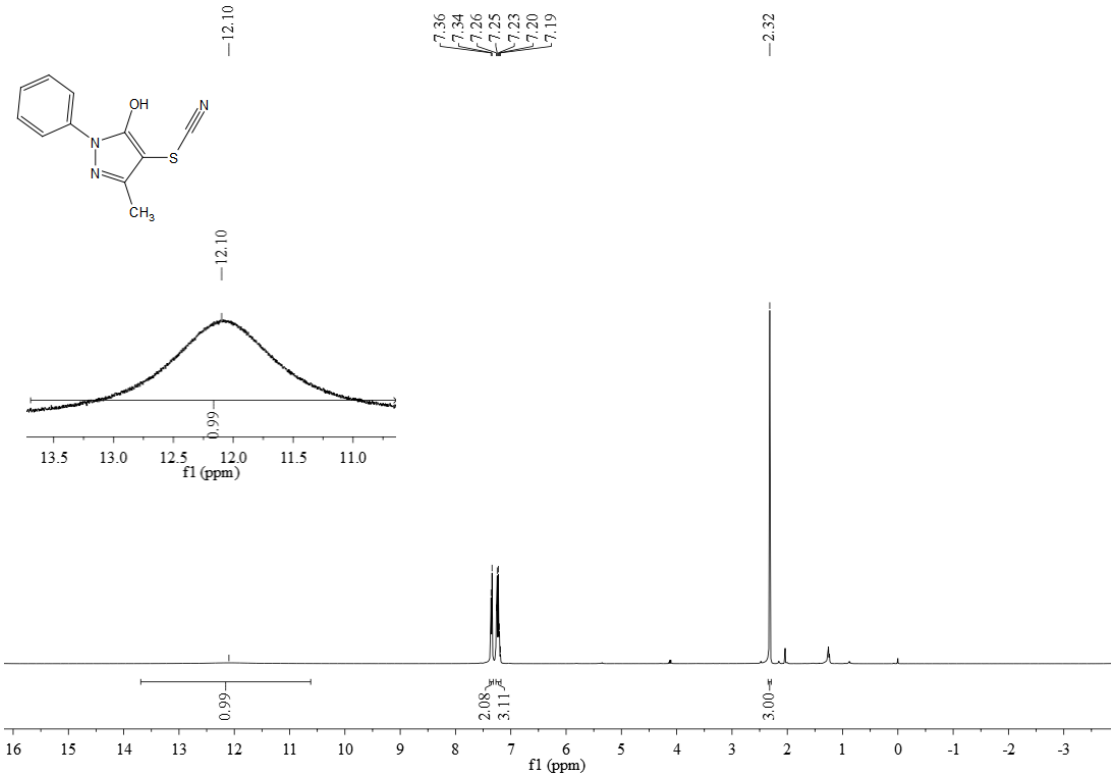
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 3t



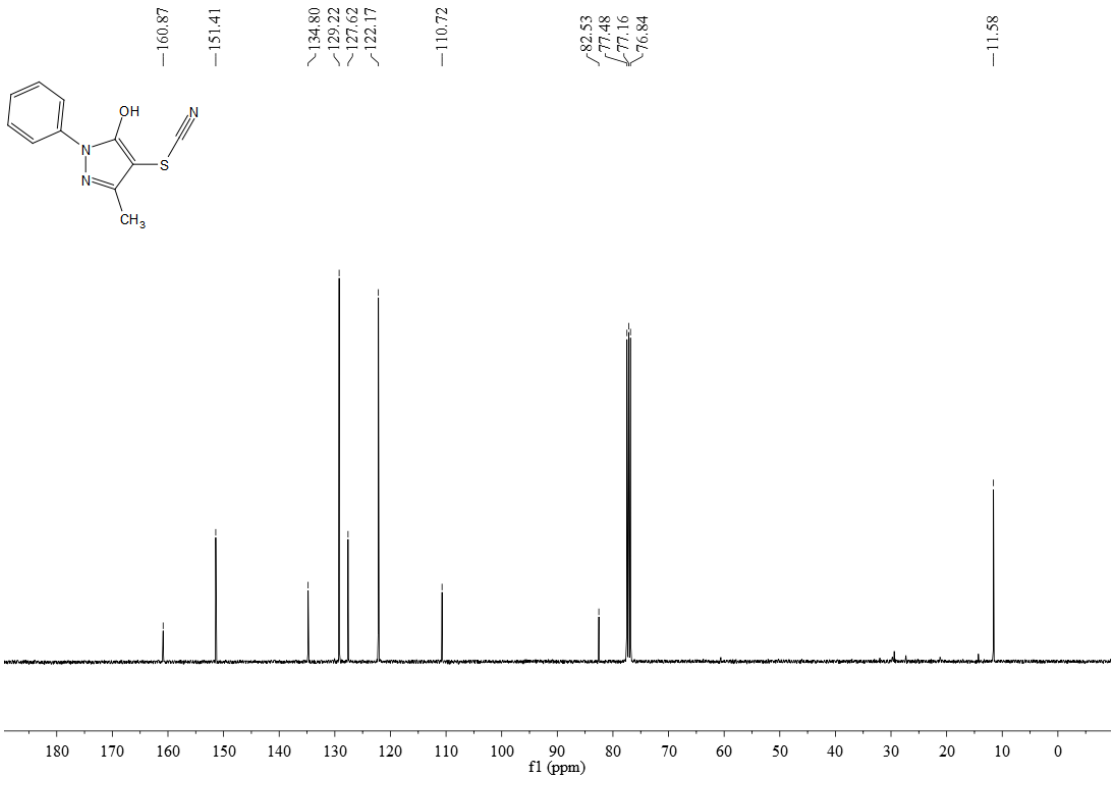
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 3t



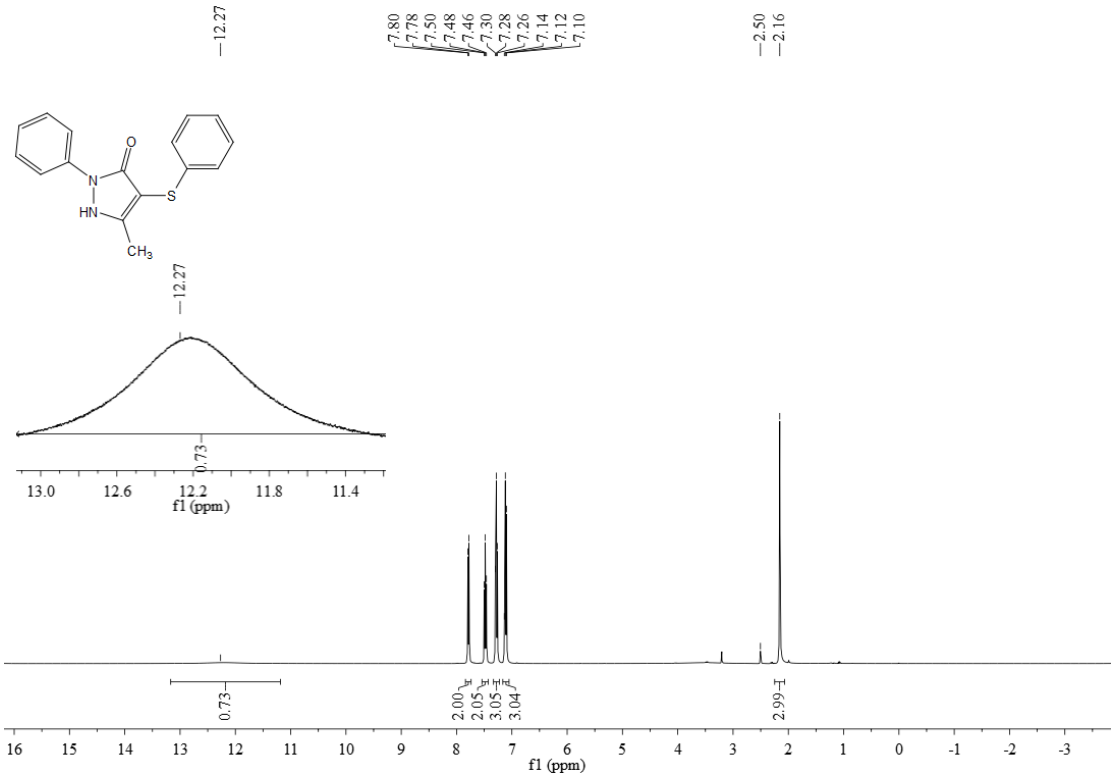
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4a



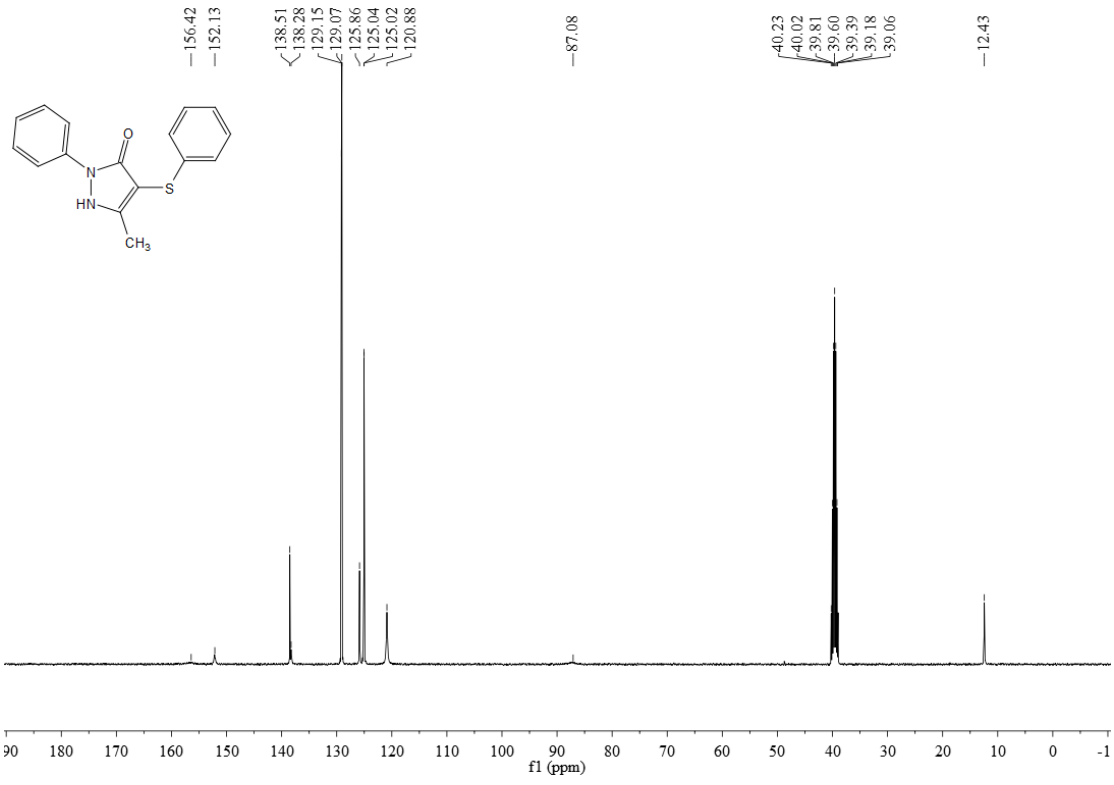
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4a



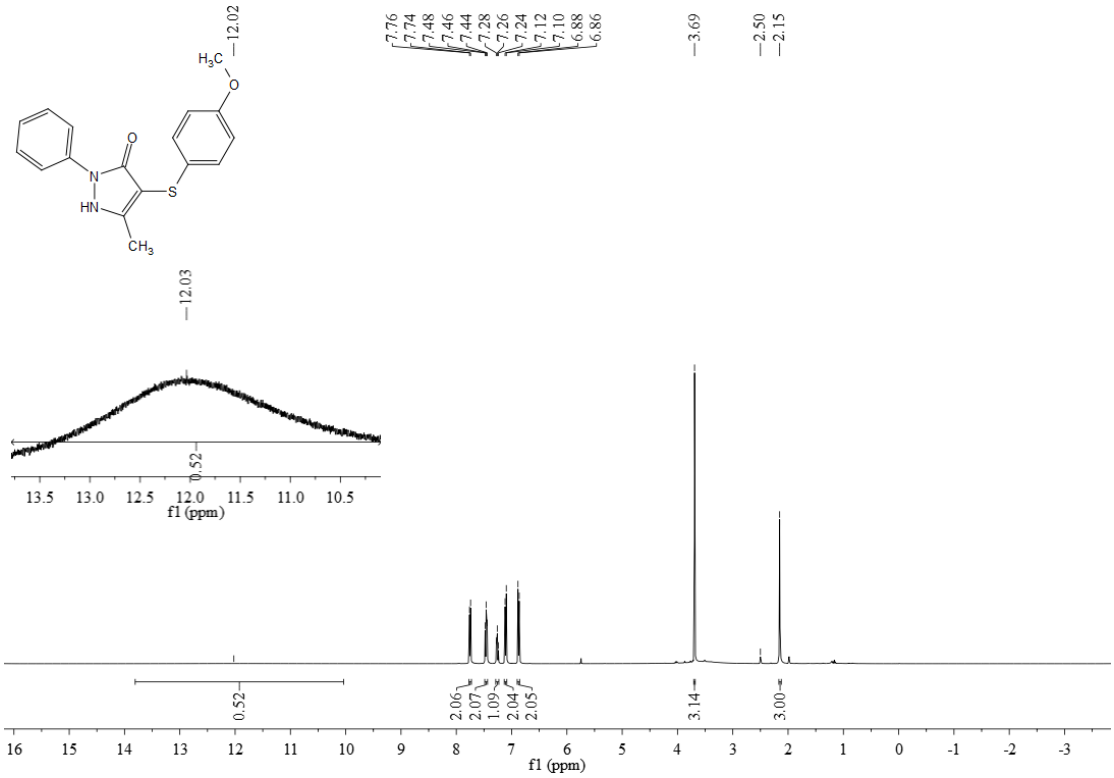
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 6a



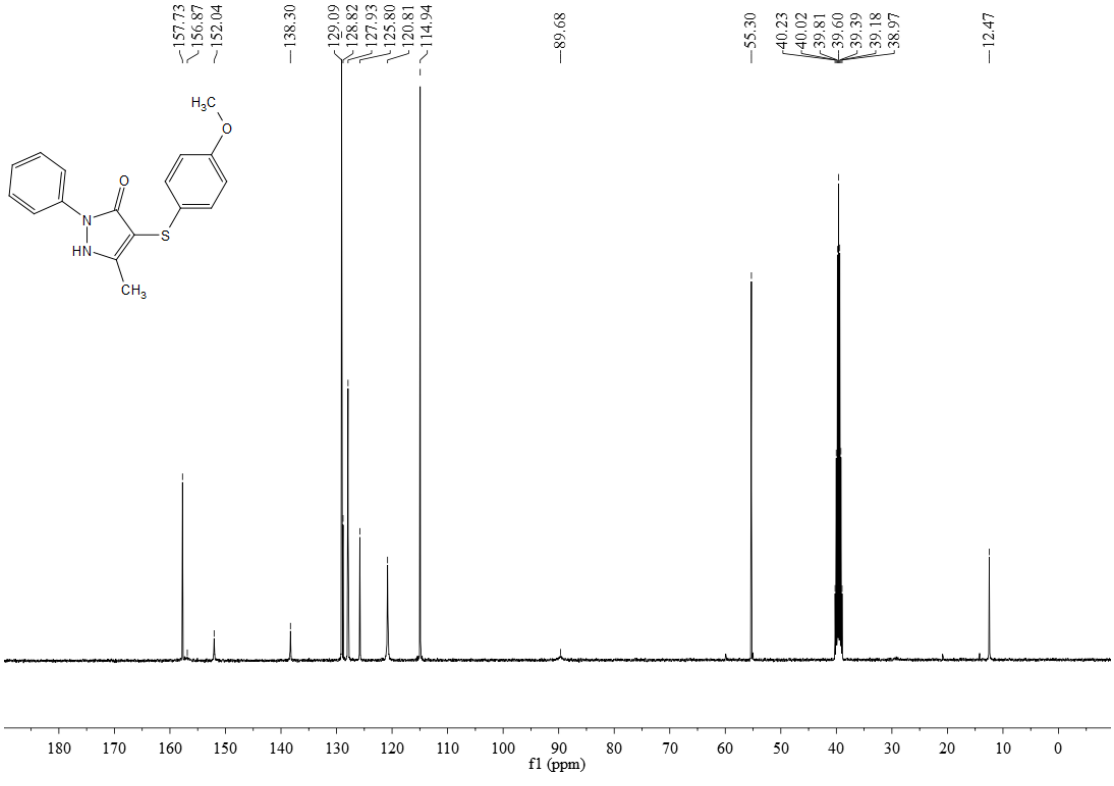
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 6a



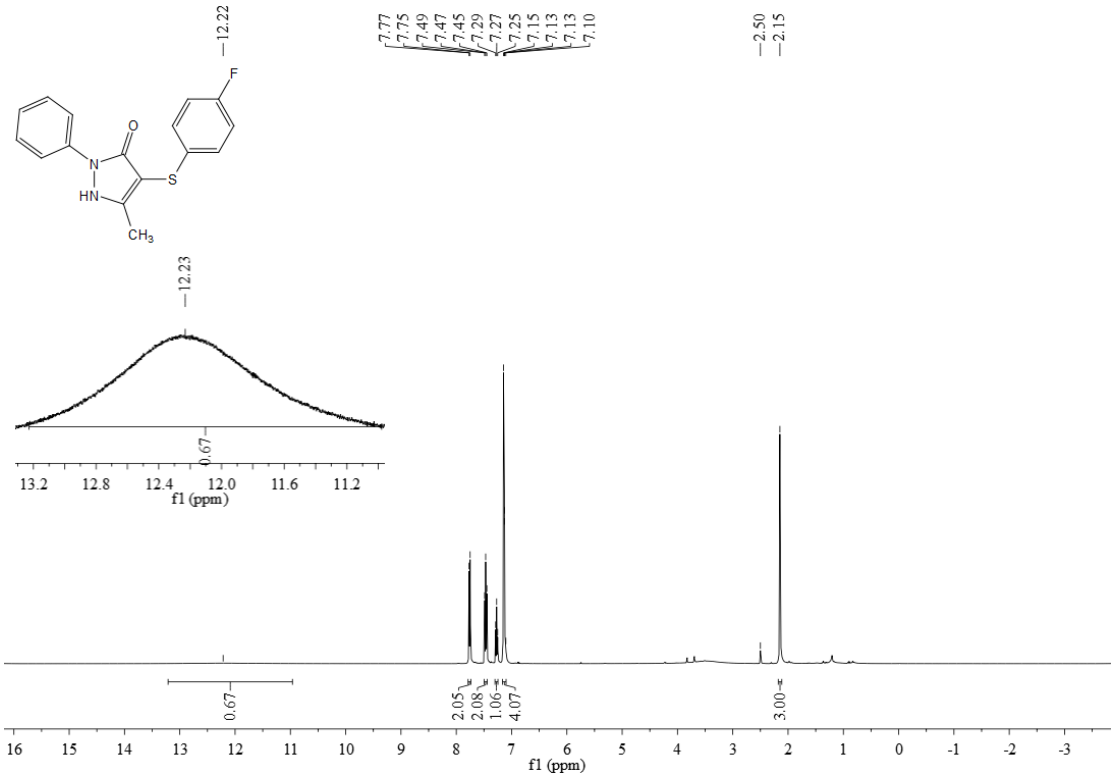
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 6b



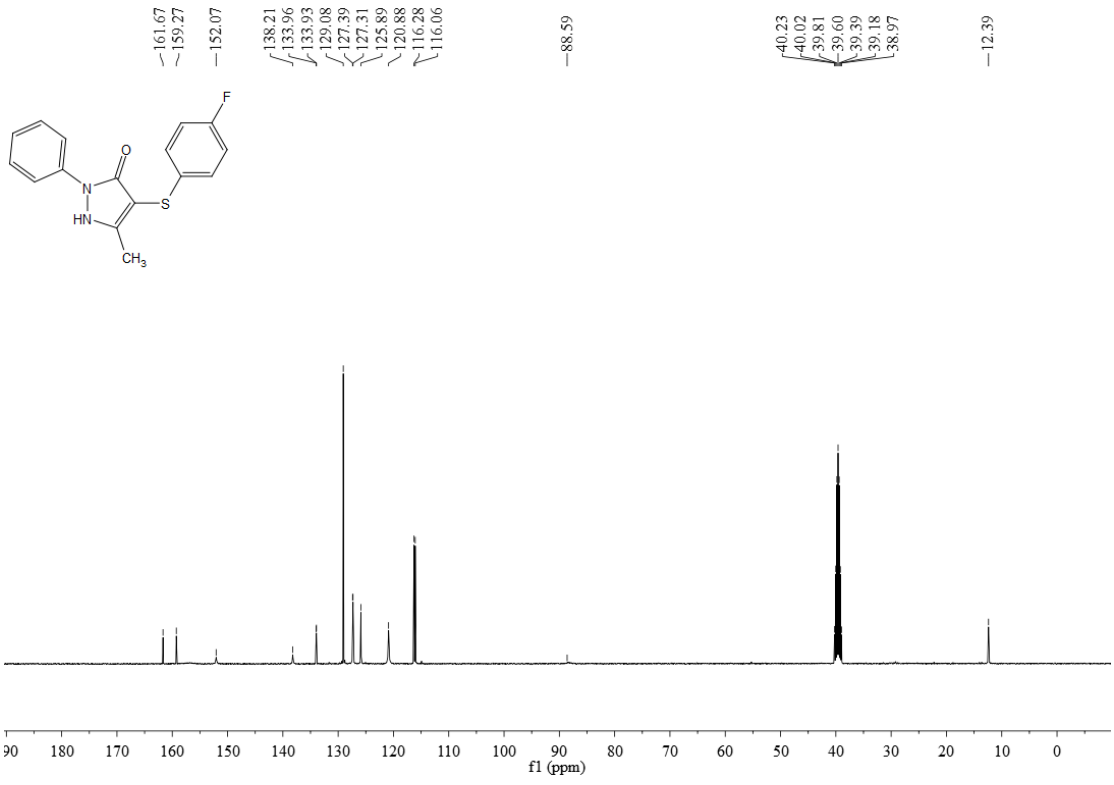
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 6b



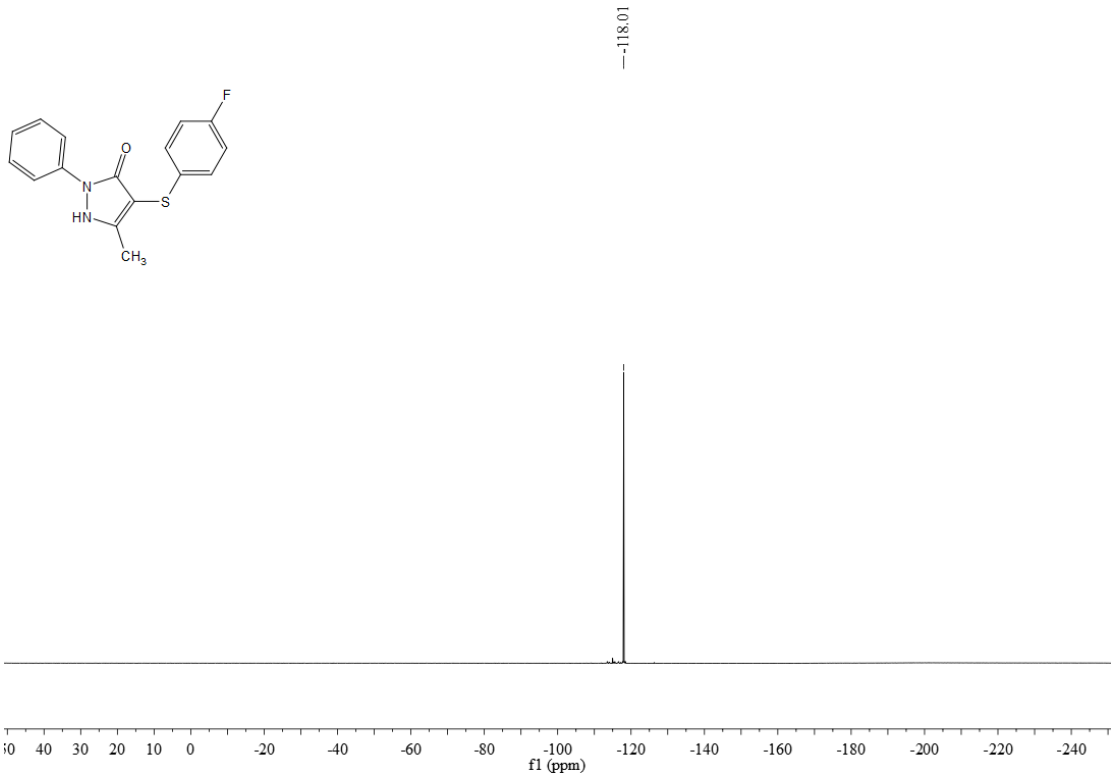
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 6c



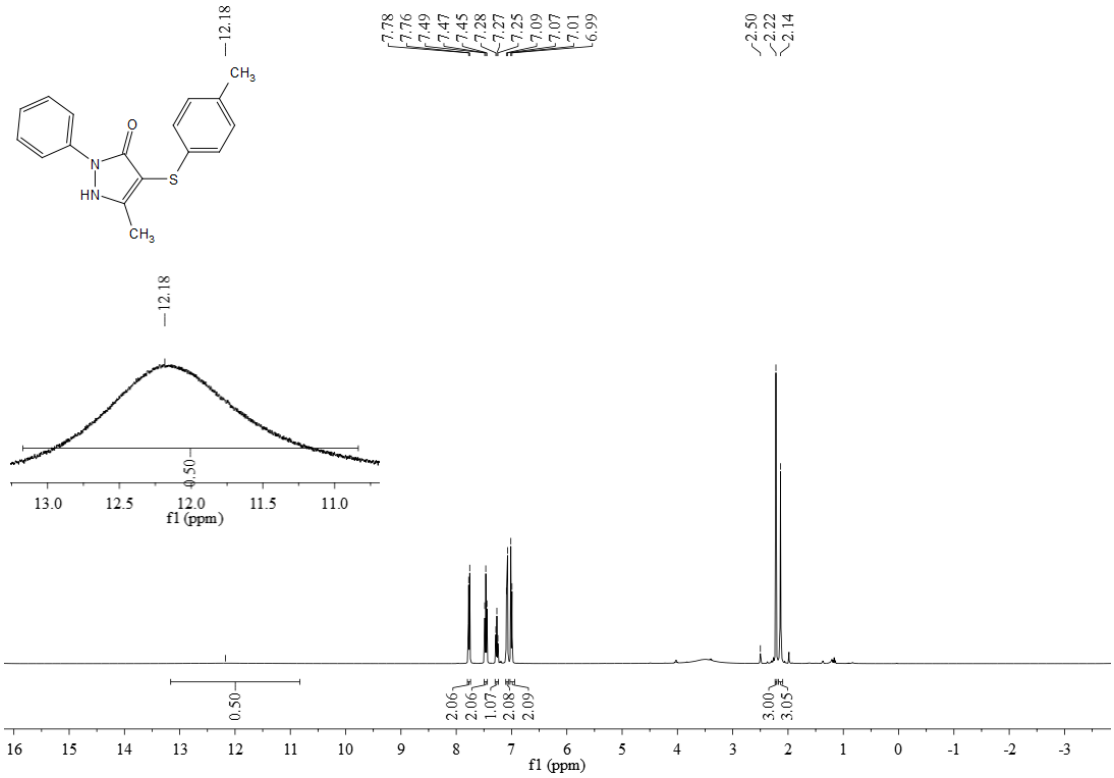
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 6c



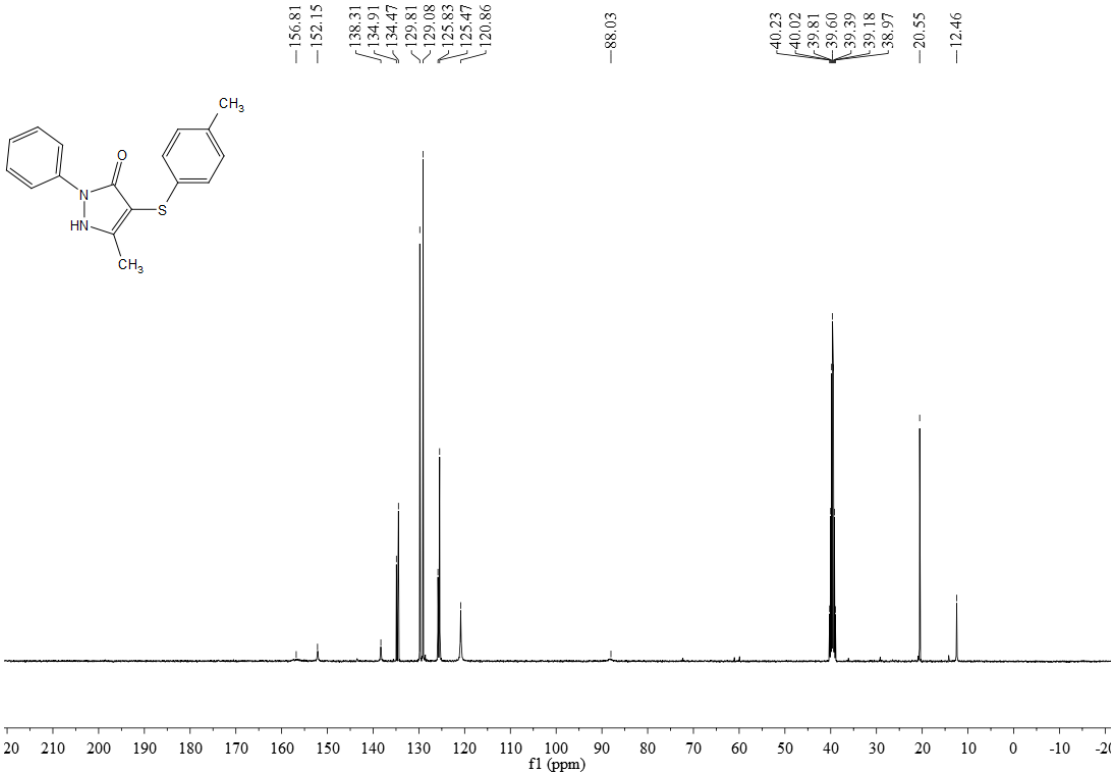
^{19}F NMR (376 MHz, DMSO-D^{6}) spectrum of 6c



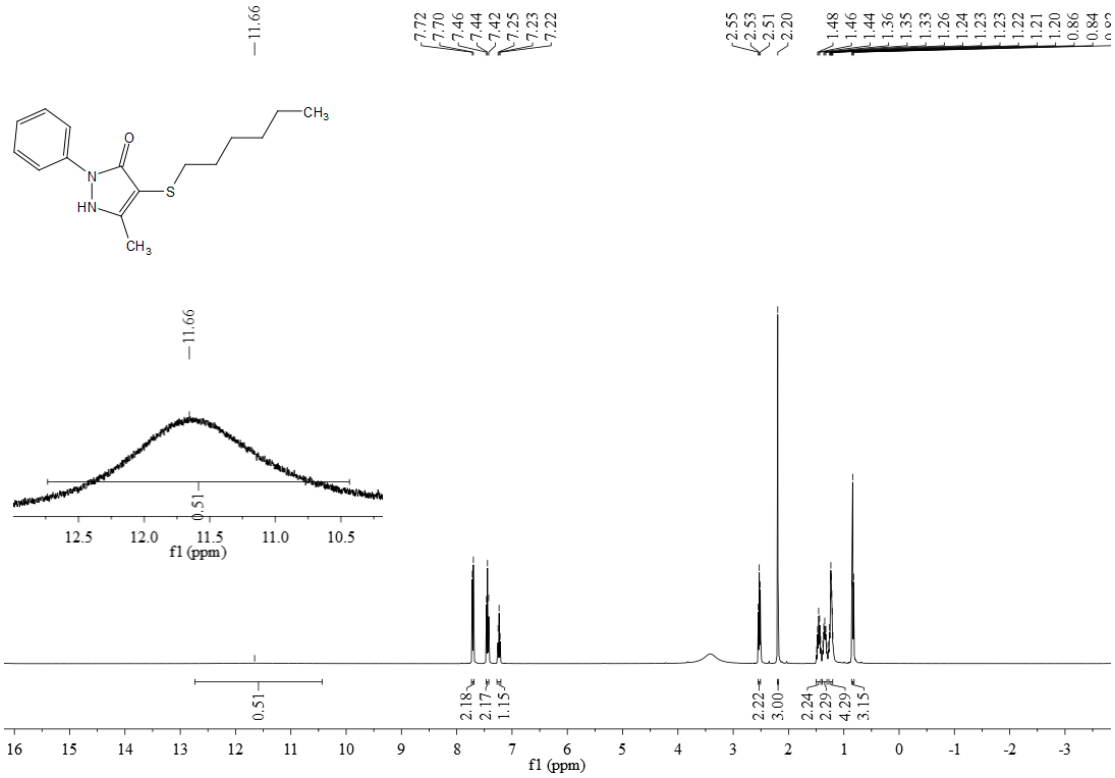
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 6d



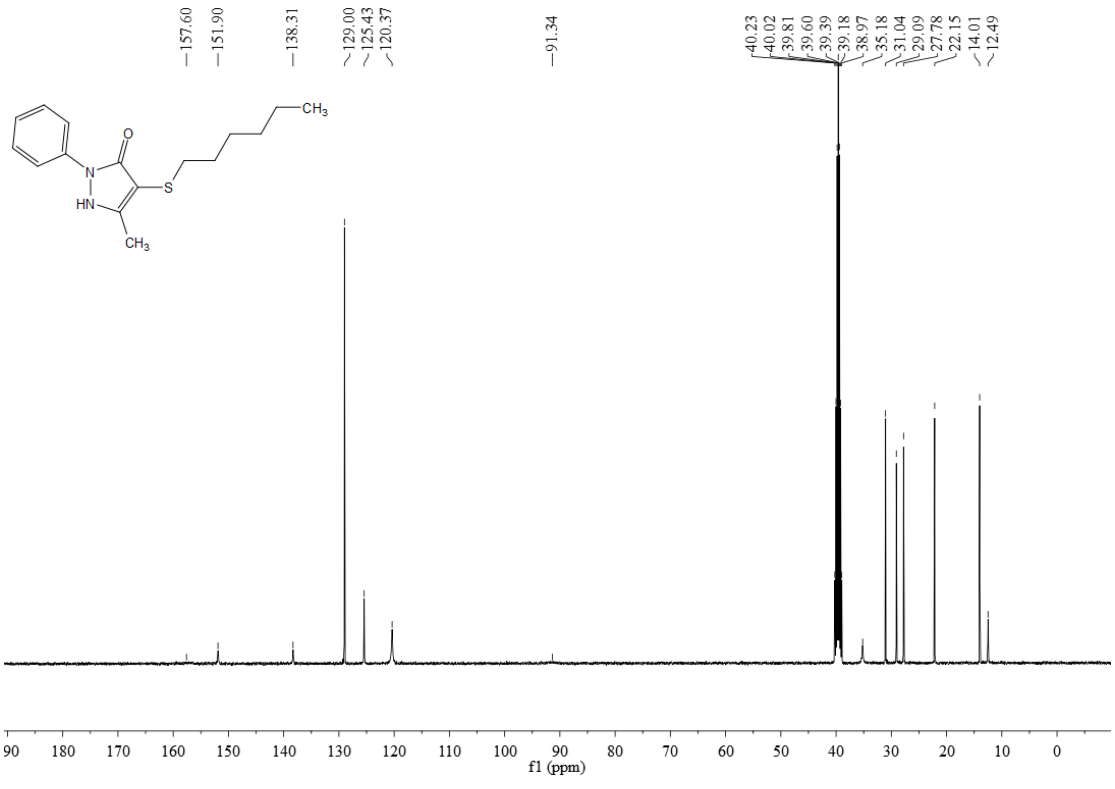
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 6d



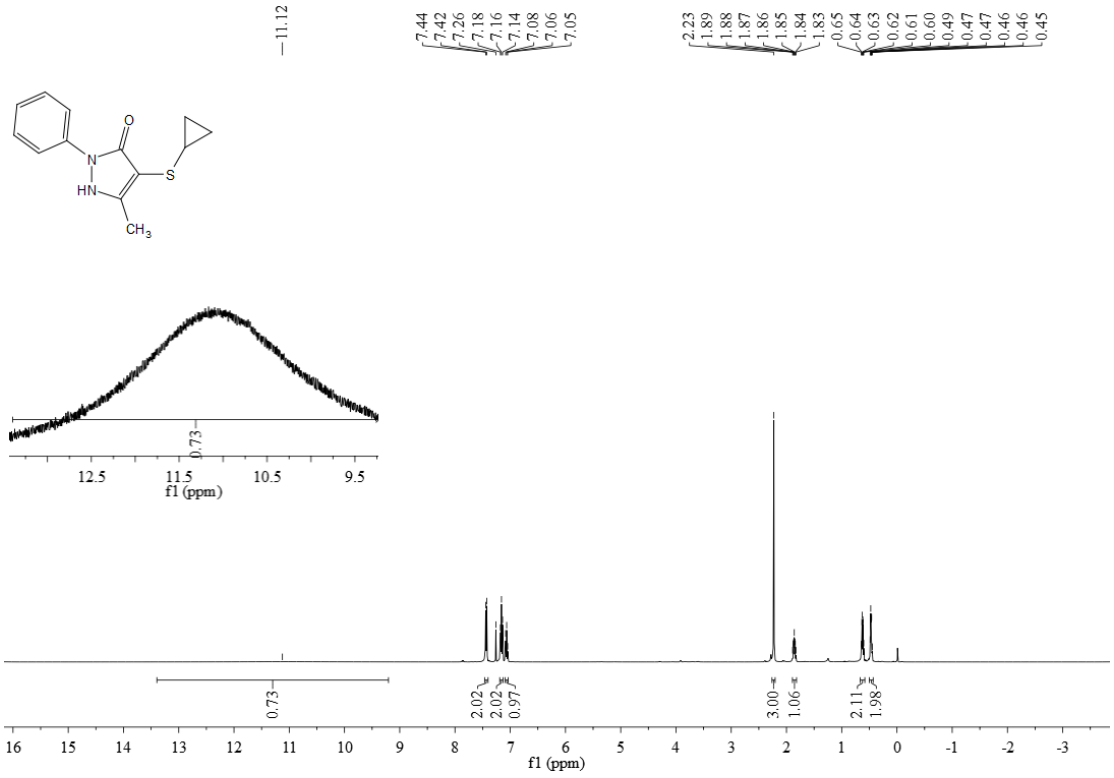
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 6e



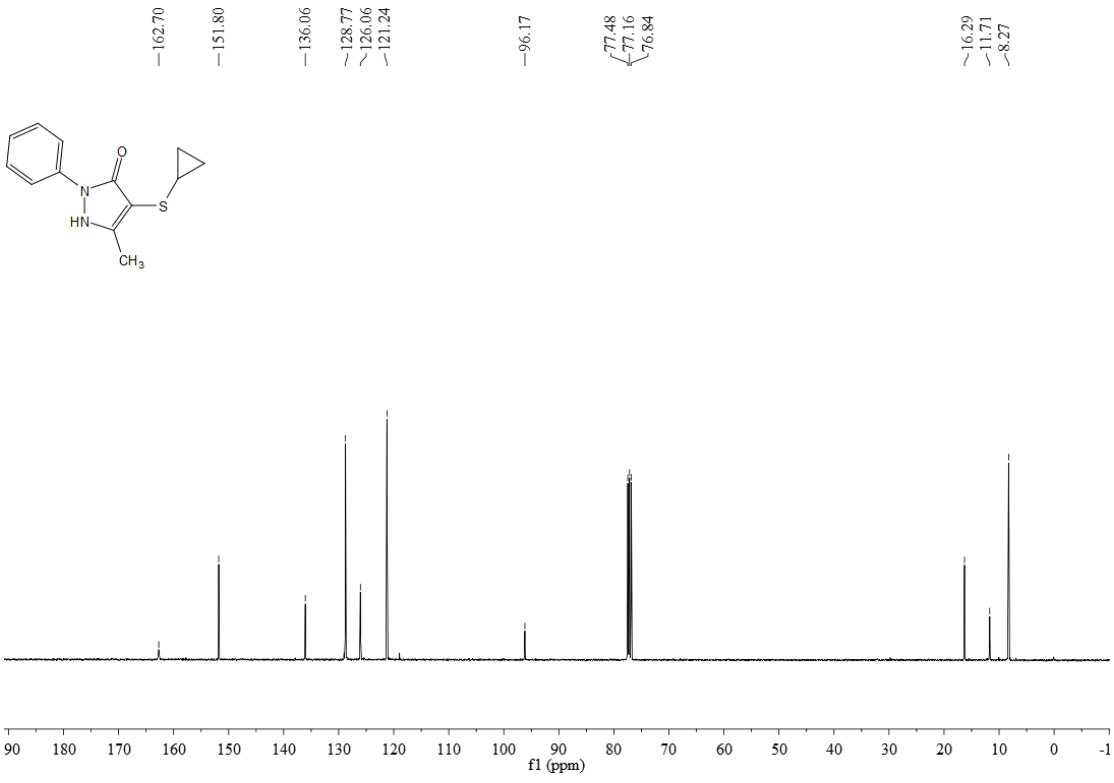
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 6e



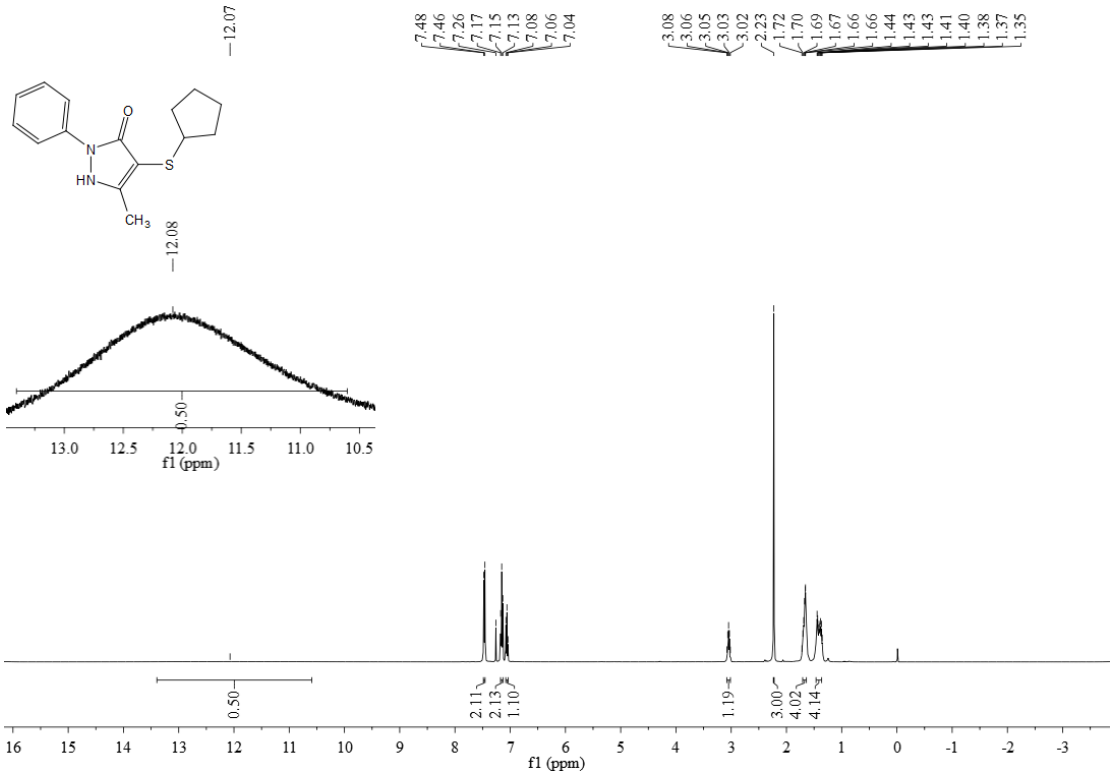
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6f



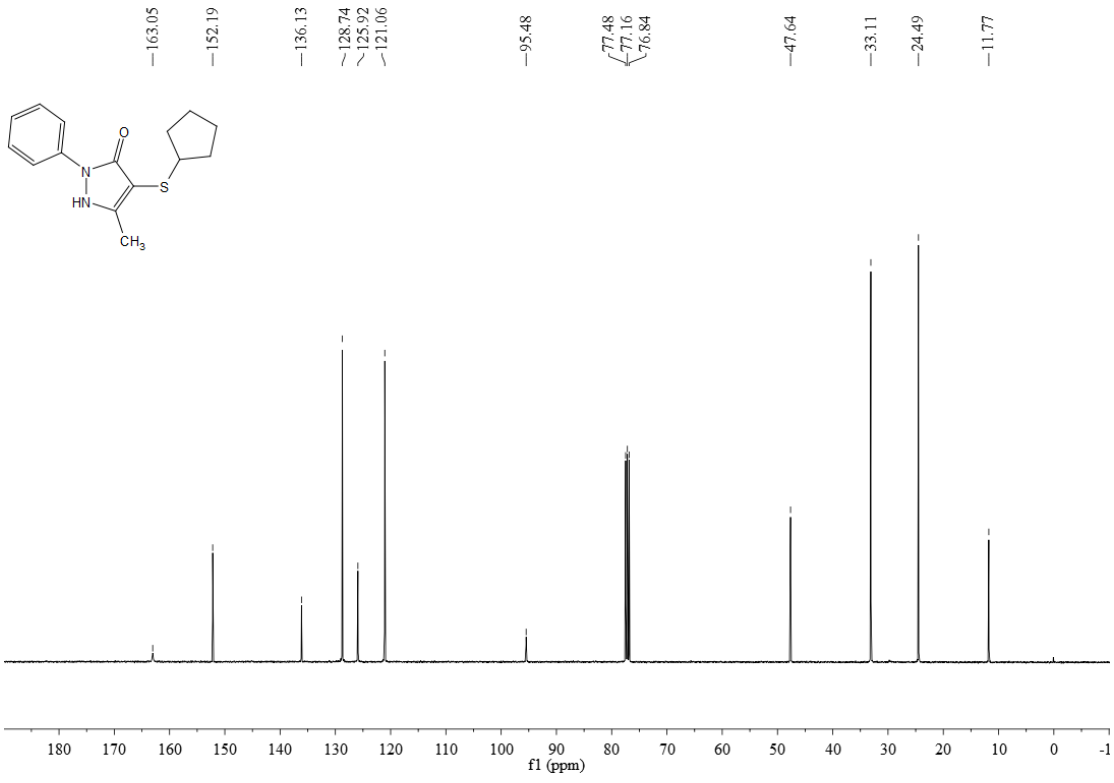
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6f



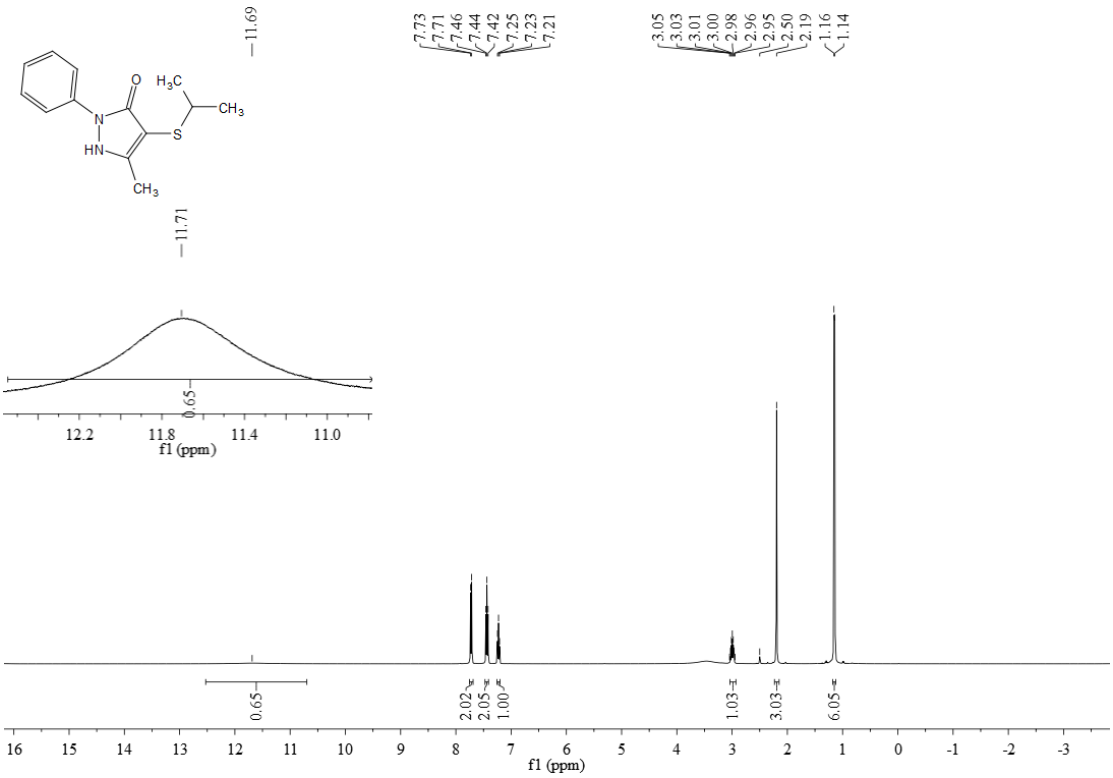
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6g



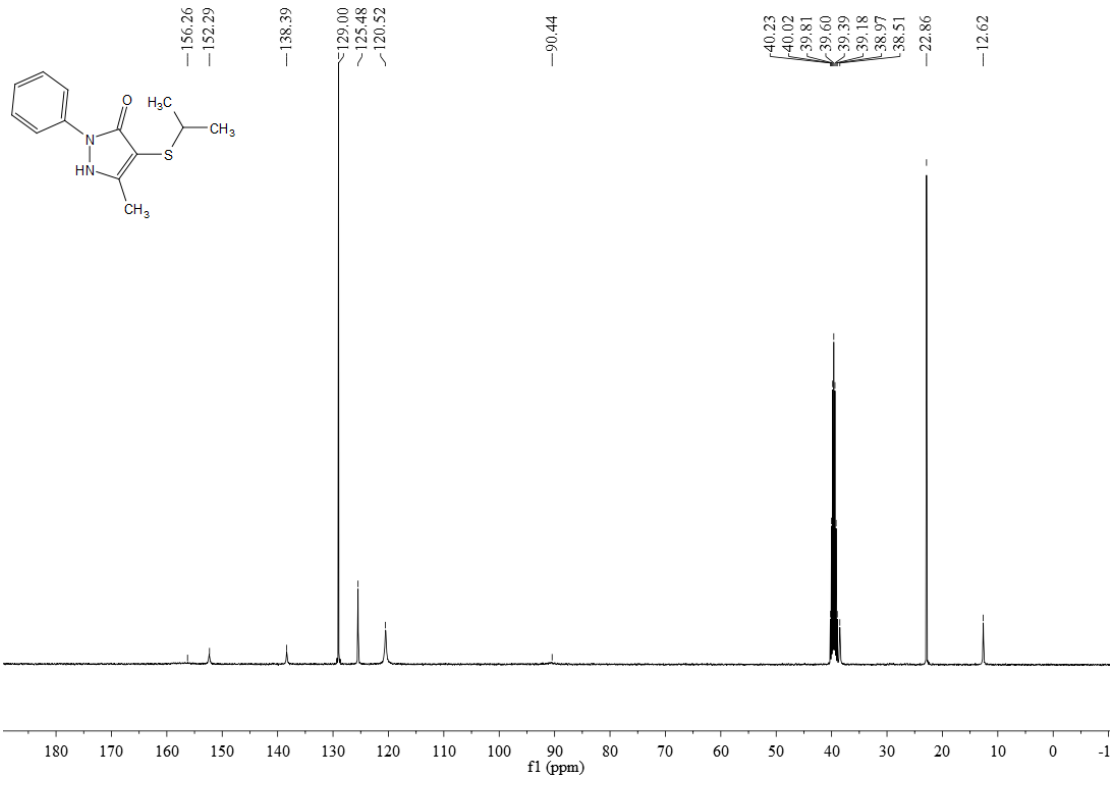
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6g



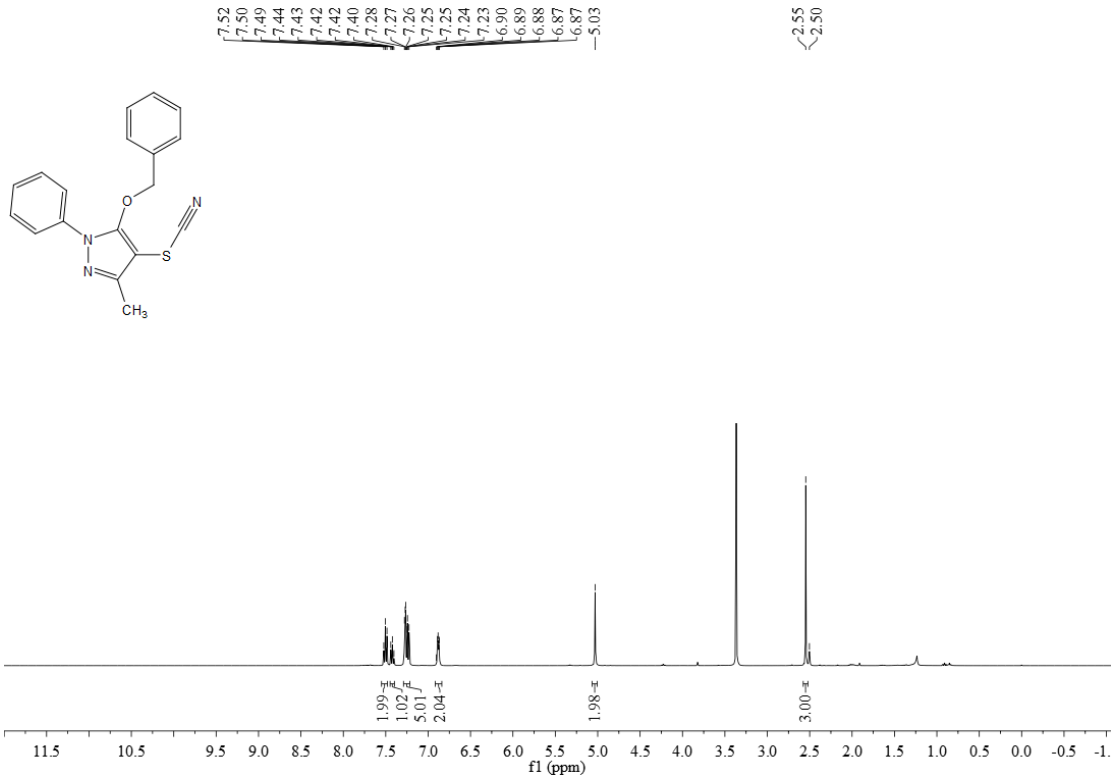
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 6h



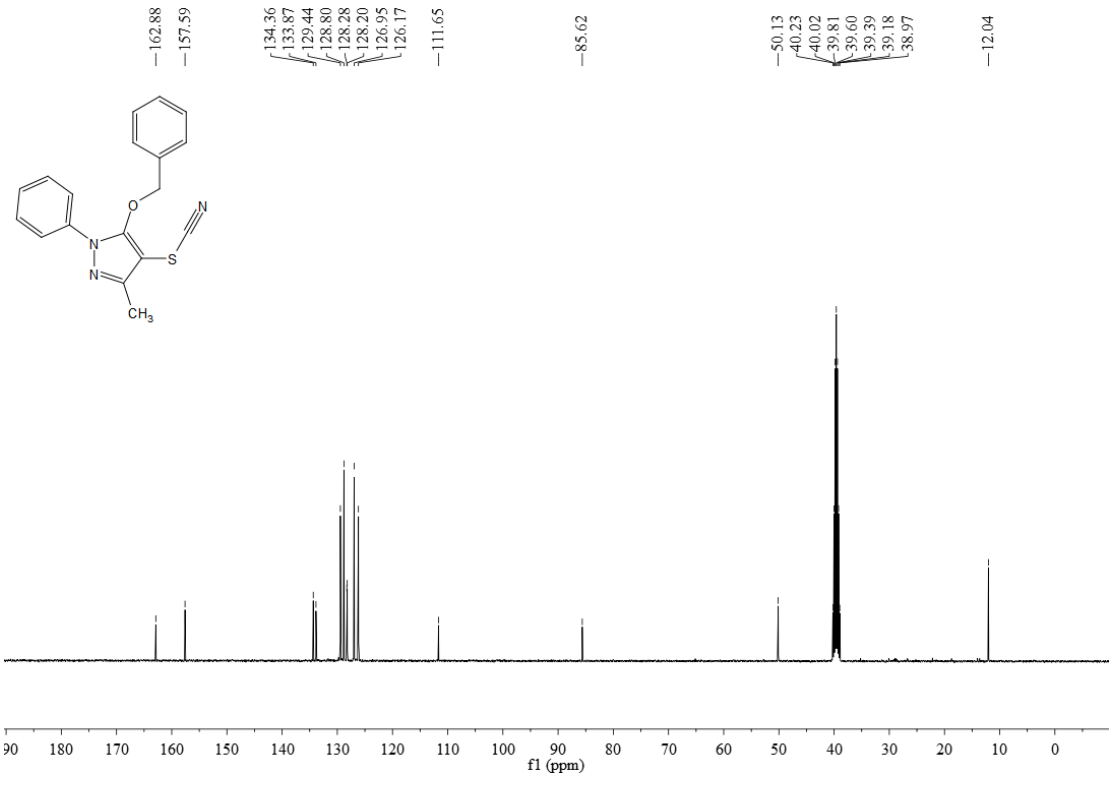
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 6h



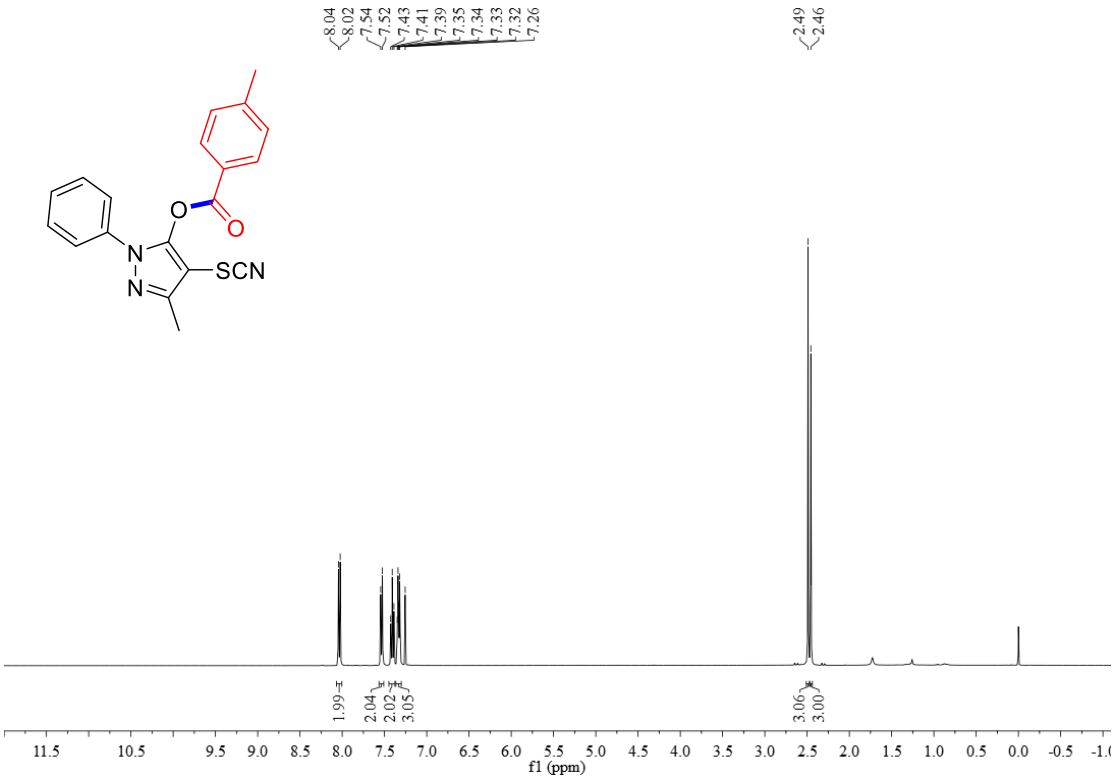
^{1}H NMR (400 MHz, DMSO-D^{6}) spectrum of 8a



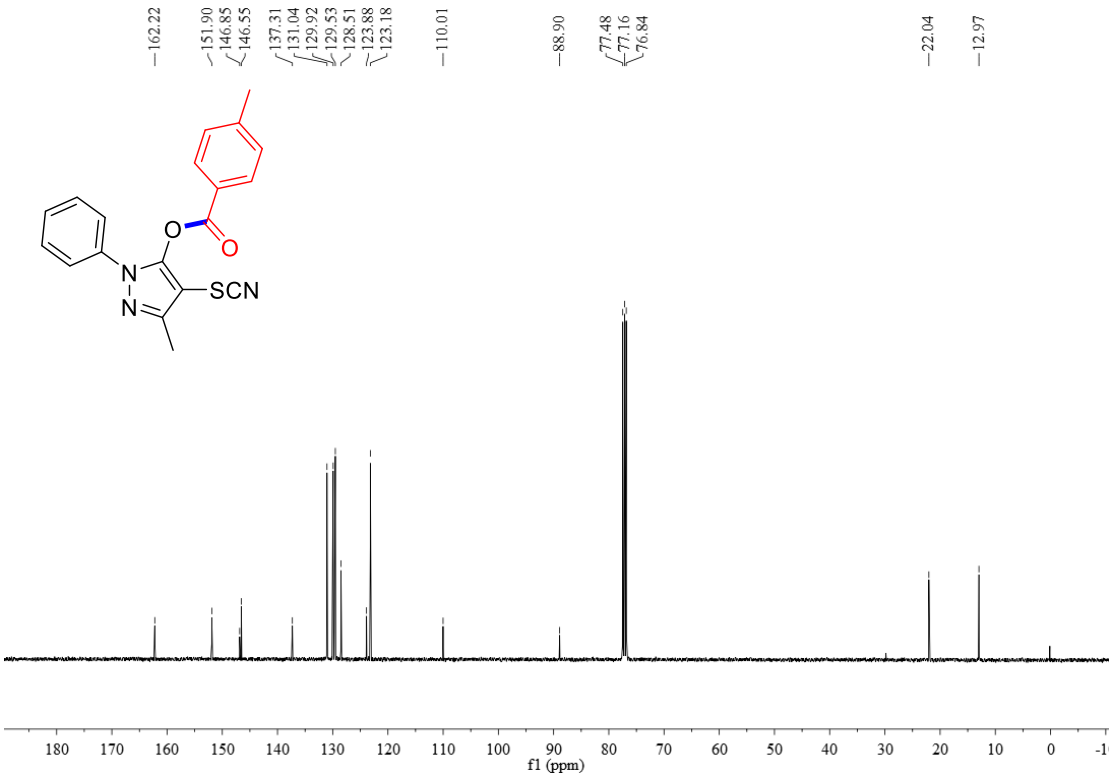
^{13}C NMR (100 MHz, DMSO-D^{6}) spectrum of 8a



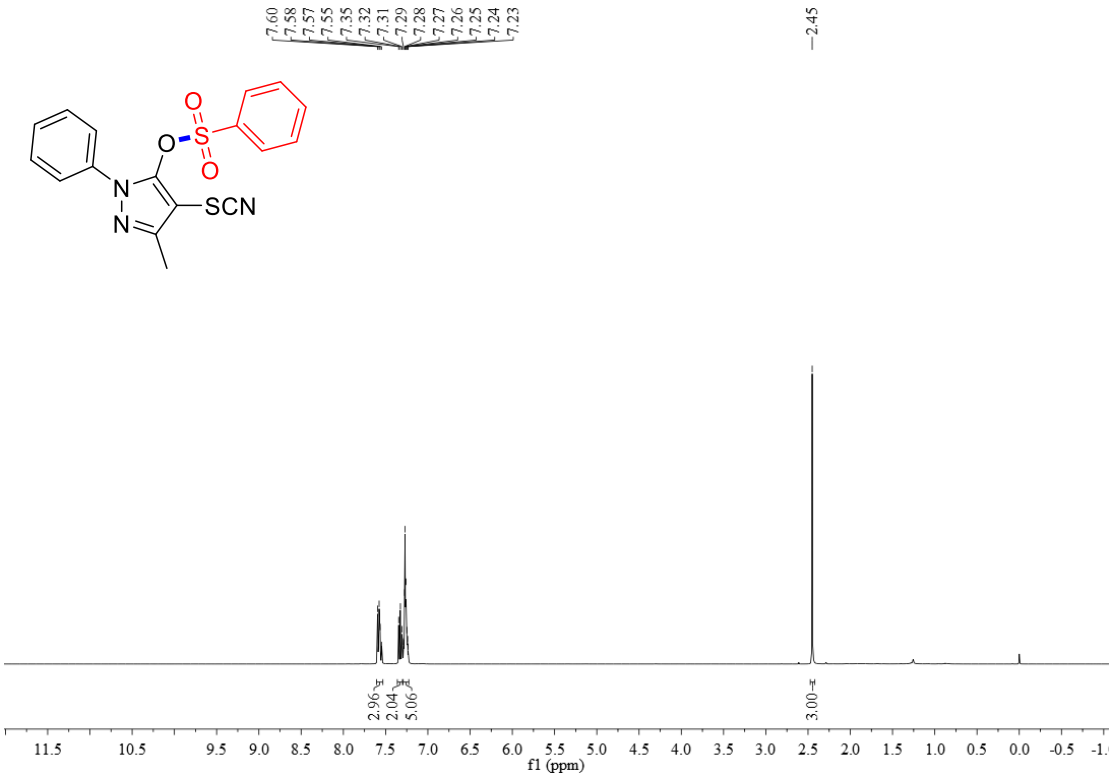
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 8b



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 8b



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



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 8c