Supporting Information

Synthesis of pyrrolo[3,4-*c*]pyridines *via* metal-free cross-coupling/cyclization cascades of β-ketothioamides with 2-aroylmalononitrile at room temperature

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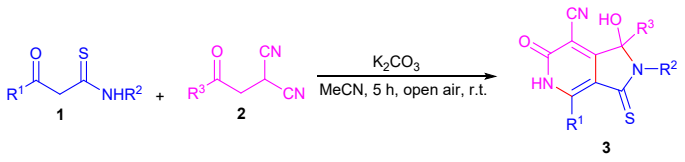
1. General Information. The commercially available solvents and reagents were used as received without any further purification. The β-ketothioamides were synthesized by the reported procedure[1] and 2-aroylmalononitrile were also synthesized by the reported procedure.[2] MeCN was purchased from Merck and K_2CO_3 was purchased from Sigma Aldrich. All the reactions were monitored by analytical thin layer chromatography (TLC) using Merck pre-coated aluminium sheets, and visualized by a UV lamp. Flash column chromatography was performed on silica gel (230-400 mesh). The ^1H and ^{13}C NMR spectra were recorded on a JEOL 500 FT-NMR spectrometer operating at 500 and 125 MHz, respectively and Bruker India Scientific, Avance Neo 600 MHz spectrometer operating at 600 and 150 MHz, respectively. Chemical shifts (δ) for ^1H and $^{13}C\{^1H\}$ NMR are given in parts per million (ppm) using the residual solvent peaks as a reference relative to tetramethylsilane (TMS). Coupling constant (J) values are reported in Hertz (Hz). High-resolution mass spectra (HRMS, m/z) were recorded in EI or ESI mode, on Sciex X500R QTOF and LC-MS (ESI)-QToF (Agilent 6546) instrument. The single crystal X-ray diffraction analysis of the representative compound **3d** was recorded on Rigaku XtaLAB Synergy-S. All the reactions were carried out using a single-neck round bottom (25 mL) borosilicate flask. Melting points have been determined with Büchi B-540 melting point apparatus and are uncorrected. IUPAC names were obtained using the ChemDraw (version 19.1) software.

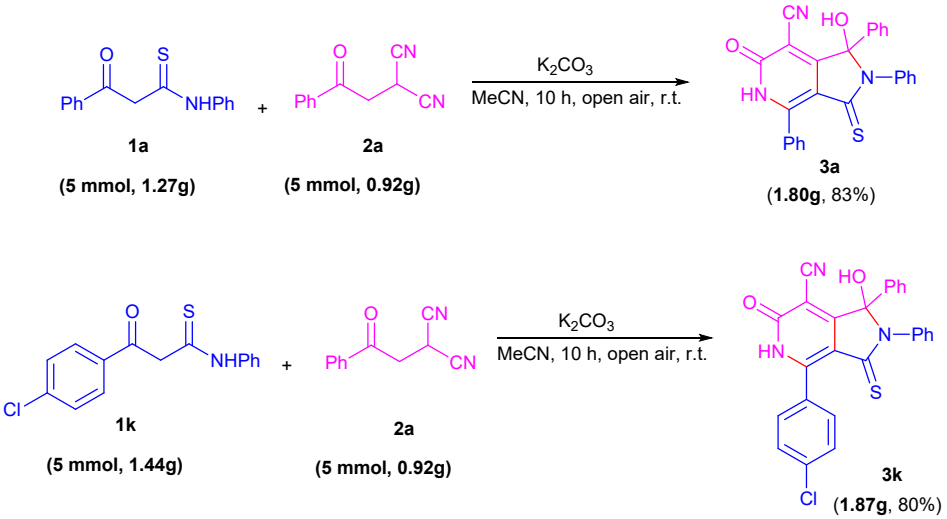
2. General Experimental Procedure for the Synthesis of Compounds 3.



β-Ketothioamides **1** (0.2 mmol), 2-aroylmalononitrile **2** (0.2 mmol) and K_2CO_3 (1.2 equiv.) were added into a 25 mL oven-dried single neck round bottom flask followed by addition of

2.0 mL of MeCN. The reaction mixture was allowed to stir at room temperature for 5 h in an open atmosphere. After completion of the reaction (monitored by TLC), the reaction was quenched with water (10 mL) followed by extraction with ethyl acetate (15 mL) and water (2×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude residue thus obtained was purified by silica gel column chromatography (4:1 hexane/ethyl acetate) to give the pure product **3**. The isolated product was dried under a vacuum and then the analytical studies were performed.

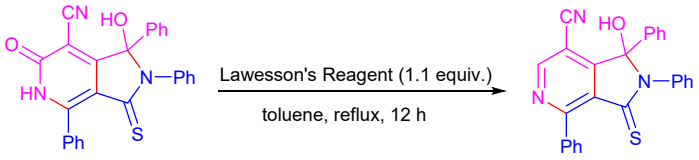
3. Scale-up Synthesis of Compounds 3a and 3k



β-Ketothioamide **1a** (5.0 mmol, 1.27 g), **1k** (5.0 mmol, 1.44g) and 2-aroylmalononitrile **2a** (5.0 mmol, 0.92 g) and K_2CO_3 (1.2 equiv.) were added into a 100 mL oven-dried single neck round bottom flask followed by addition of 20.0 mL of MeCN. The reaction mixture was allowed to stir at room temperature for 10 h in an open atmosphere. After completion of the reaction (monitored by TLC), the reaction was quenched with water (50 mL) followed by extraction with ethyl acetate (2×30 mL) and water (2×20 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude residue thus obtained was purified by silica gel column chromatography (4:1 hexane/ethyl acetate) to give the pure product **3a** (1.80g, 83%) and **3k** (1.87g, 80%).

4. Application of compound 3

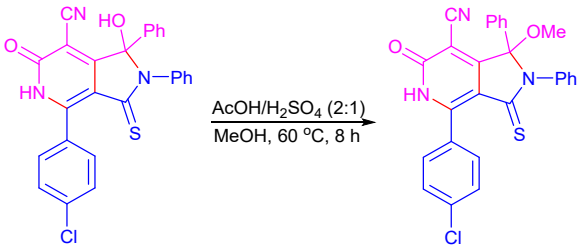
4.1 Synthesis of compound 4a



(**3a**, 0.2 mmol) (**4a**, 80%)

Pyrrolo[3,4-c]pyridines **3a** (0.2 mmol, 1.0 equiv.) was added into a 25 mL oven-dried single neck round bottom flask followed by the addition of 5.0 mL of toluene. After that, Lawesson's Reagent (0.22 mmol, 1.1 equiv.) was added at room temperature. Then, the reaction mixture was refluxed in a preheated oil bath for 12 h. After completion of the reaction (monitored by TLC), the reaction was quenched with water (10 mL) followed by extraction with ethyl acetate (15 mL) and water (2×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude residue thus obtained was purified by silica gel column chromatography (4:1 hexane/ethyl acetate) to give the pure product **4a** (80%). The isolated product was dried under a vacuum and then the analytical studies were performed.

4.2 Synthesis of compound 4b



(**3k**, 0.2 mmol) (**4b**, 93%)

Pyrrolo[3,4-c]pyridines **3k** (0.2 mmol) was added into a 25 mL oven-dried single neck round bottom flask followed by the addition of 5.0 mL of MeOH. After that, the mixture of $AcOH/H_2SO_4$ (2:1 v/v, 0.15 mL) was added at room temperature. Then, the reaction mixture

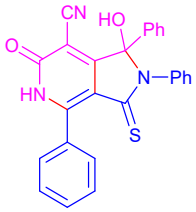
was allowed to stir at 60 ^{o}C for 8 h. After completion of the reaction (monitored by TLC), the reaction was quenched with water (10 mL) followed by extraction with ethyl acetate (15 mL) and water (2×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude residue thus obtained was purified by silica gel column chromatography (5:1 hexane/ethyl acetate) to give the pure product **4b** (93%). The isolated product was dried under a vacuum and then the analytical studies were performed.

5. References

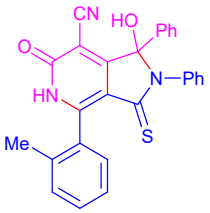
1. Zeng, X. M.; Meng, C. Y.; Bao, J. X.; Xu, D. C.; Xie J. W.; Zhu, W. D. Enantioselective Construction of Polyfunctionalized Spiroannulated Dihydrothiophenes via a Formal Thio [3+2] Cyclization. *J. Org. Chem*. **2015**, *80*, 11521-11528.

2. Sahoo, A. K.; Rakshit, A.; Dahiya, A.; Pan, A.; Patel, B. K. Visible-Light-Mediated Synthesis of Thio-Functionalized Pyrroles. *Org. Lett.* **2022**, *24*, 1918-1923.

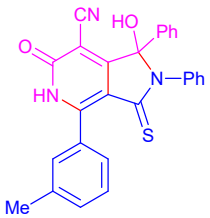
6. Characterization data of compounds 3 and 4



1-hydroxy-6-oxo-1,2,4-triphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3a**)**:** Isolated yield (75 mg, 86%); Yellow solid; m.p. 176-178 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.22 (s, 1H), 8.40 (s, 1H), 7.65 – 7.63 (m, 2H), 7.55 – 7.54 (m, 1H), 7.50 – 7.47 (m, 2H), 7.42 – 7.40 (m, 2H), 7.35 – 7.34 (m, 3H), 7.25 – 7.23 (m, 3H), 6.90 (d, J = 5.0 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.6, 165.0, 160.4, 155.0, 136.3, 136.0, 130.6, 129.8, 129.4, 129.0, 128.4, 128.1, 128.0, 127.4, 126.5, 114.4, 112.4, 95.0; HRMS (ESI-TOF, [M + H]$^{+}$): Calcd. for $C_{26}H_{17}N_3O_2S$, 436.1114, found 436.1135.

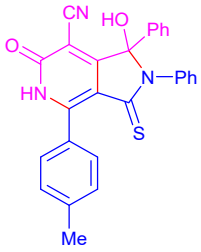


1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-4-(o-tolyl)-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3b**)**:** Isolated yield (79 mg, 88%); Yellow solid; m.p. 180-182 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.23 (s, 1H), 8.46 (d, J = 10.0 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.42 – 7.29 (m, 8H), 7.27 – 7.23 (m, 3H), 6.90 (t, J = 7.5 Hz, 2H), 2.32 – 2.23 (m, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 187.6, 164.9, 164.7, 160.8, 160.7, 154.9, 154.6, 136.5, 136.4, 136.4, 136.2, 136.1, 136.1, 130.8, 130.8, 130.3, 130.1, 129.7, 129.6, 129.5, 129.5, 129.3, 129.3, 129.3, 128.6, 128.6, 128.5, 128.5, 128.3, 128.3, 128.2, 126.6, 126.3, 125.7, 125.4, 115.3, 115.1, 112.7, 112.6, 95.5, 95.3, 95.3, 19.6, 19.5; HRMS (ESI-TOF, [M + H]$^{+}$): Calcd. for $C_{27}H_{19}N_3O_2S$, 450.1271, found 450.1258.

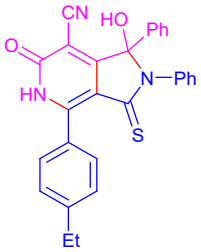


1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-4-(m-tolyl)-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3c**)**:** Isolated yield (75 mg, 83%); Yellow solid; m.p. 180-182 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.16 (s, 1H), 8.39 (s, 1H), 7.46 (s, 1H), 7.43 – 7.40 (m, 3H), 7.37 – 7.34 (m, 5H), 7.26 – 7.23 (m, 3H), 6.89 (d, J = 10.0 Hz, 2H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.7, 165.1, 160.3, 155.2, 136.5, 136.4, 136.0, 131.2, 129.7, 129.5, 129.0, 128.4, 128.1, 128.0, 127.4,

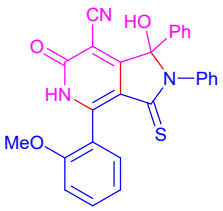
126.5, 114.3, 112.4, 94.9, 20.9; HRMS (ESI-TOF, [M + Na]$^+$): Calcd. for $C_{27}H_{19}N_3O_2S$, 472.1090, found 472.1087.



1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-4-(p-tolyl)-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3d**)**:** Isolated yield (81 mg, 90%); yellow solid; m.p. 170-172 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.46 (s, 1H), 7.53 (d, J = 10.0 Hz, 2H), 7.40 – 7.38 (m, 2H), 7.35 – 7.34 (m, 3H), 7.28 (d, J = 10.0 Hz, 2H), 7.25 – 7.23 (m, 3H), 6.89 – 6.87 (m, 2H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 187.8, 165.2, 160.5, 155.3, 140.6, 136.4, 136.0, 130.1, 129.5, 129.1, 128.4, 128.2, 128.1, 128.0, 126.9, 126.5, 114.4, 112.6, 94.9, 94.7, 21.2; HRMS (ESI-TOF, [M + H]$^+$): Calcd. for $C_{27}H_{19}N_3O_2S$, 450.1271, found 450.1288.

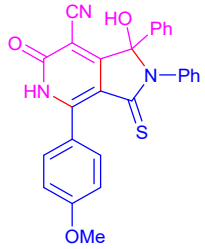


4-(4-ethylphenyl)-1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3e**)**:** Isolated yield (77 mg, 85%); Yellow solid; m.p. 195-197 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6 + $CDCl_3$) δ 13.07 (s, 1H), 8.35 (s, 1H), 7.59 – 7.57 (m, 2H), 7.42 – 7.41 (m, 2H), 7.35 – 7.31 (m, 5H), 7.25 – 7.22 (m, 3H), 6.92 – 6.91 (m, 2H), 2.71 (q, J = 6.6 Hz, 2H), 1.24 (t, J = 5.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6 + $CDCl_3$) δ 187.7, 165.0, 160.3, 155.1, 146.5, 136.3, 135.9, 130.0, 129.4, 128.9, 128.2, 128.1, 128.0, 127.9, 127.1, 126.7, 126.4, 114.2, 112.3, 94.8, 28.0, 15.1; HRMS (ESI-TOF, [M + H]$^+$): Calcd. for $C_{28}H_{21}N_3O_2S$, 464.1427, found 464.1433.

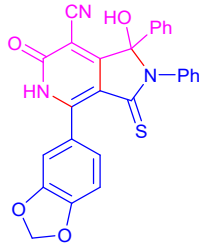


1-hydroxy-4-(2-methoxyphenyl)-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3f**)**:** Isolated yield (81 mg, 87%); Yellow solid; m.p. 205-207 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.21 (s, 1H), 8.48 – 8.45 (m, 1H), 7.53 – 7.48 (m, 2H), 7.40 – 7.32 (m, 5H), 7.26 – 7.23 (m, 3H), 7.12 (t, J = 7.5 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.93 – 6.89 (m, 2H), 3.83 – 3.78 (m, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 187.8, 187.7, 165.0, 164.7, 160.6,

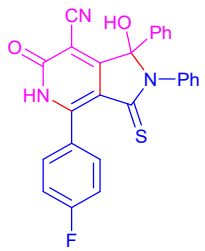
157.4, 156.8, 152.8, 152.2, 136.4, 136.2, 132.4, 132.1, 131.6, 129.8, 129.6, 129.5, 129.2, 129.1, 128.5, 128.5, 128.2, 128.1, 126.5, 126.1, 120.2, 119.7, 119.2, 115.2, 112.6, 111.4, 95.1, 94.9, 56.0, 55.7; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{27}H_{19}N_3O_3S$, 466.1220, found 466.1210.



1-hydroxy-4-(4-methoxyphenyl)-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3g**)**:** Isolated yield (84 mg, 90%); Yellow solid; m.p. 212-214 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.41 (s, 1H), 7.63 (d, J = 5.0 Hz, 2H), 7.41 – 7.39 (m, 2H), 7.35 – 7.34 (m, 3H), 7.25 – 7.24 (m, 3H), 7.01 (d, J = 10.0 Hz, 2H), 6.90 (d, J = 5.0 Hz, 2H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 188.1, 165.4, 161.5, 160.8, 155.4, 136.6, 136.1, 132.3, 129.7, 129.2, 128.5, 128.3, 128.2, 126.6, 121.8, 114.3, 112.9, 112.8, 95.0, 94.4, 55.4; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{27}H_{19}N_3O_3S$, 466.1220, found 466.1227.

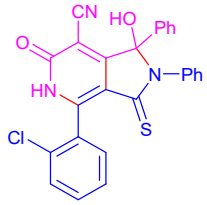


4-(benzo[d][1,3]dioxol-5-yl)-1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3h**)**:** Isolated yield (88 mg, 92%); Yellow solid; m.p. 178-180 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.13 (s, 1H), 8.36 (s, 1H), 7.43 – 7.41 (m, 2H), 7.35 – 7.34 (m, 3H), 7.27 – 7.23 (m, 4H), 7.16 (d, J = 10.0 Hz, 1H), 7.03 (d, J = 5.0 Hz, 1H), 6.91 (d, J = 5.0 Hz, 2H), 6.14 – 6.13 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.7, 165.1, 160.4, 154.5, 149.3, 146.3, 136.4, 135.9, 129.5, 129.0, 128.3, 128.1, 128.0, 126.5, 124.9, 123.1, 114.4, 112.4, 110.8, 107.5, 101.5, 94.9, 94.6, 79.1; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{27}H_{17}N_3O_4S$, 480.1013, found 480.1008.

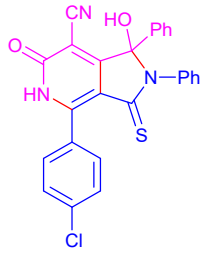


4-(4-fluorophenyl)-1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3i**)**:** Isolated yield (74 mg, 82%); Brown solid; m.p. 131-133 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-

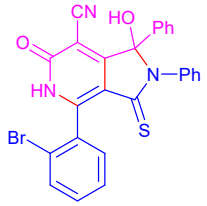
d_6 + $CDCl_3$) δ 13.17 (s, 1H), 8.29 (s, 1H), 7.67 (s, 2H), 7.40 (s, 2H), 7.31 (s, 3H), 7.20 (s, 5H), 6.93 – 6.92 (m, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 187.7, 165.1, 164.4, 162.8, 160.6, 154.2, 136.4, 136.0, 132.7, 129.5, 129.2, 128.5, 128.2, 126.6, 126.3, 114.7, 114.6, 114.5, 112.5, 95.1; ^{19}F NMR (470 MHz, DMSO-d_6): δ -109.86; HRMS (ESI-TOF, [M + H]$^+$): Calcd. for $C_{26}H_{16}FN_3O_2S$, 454.1020, found 454.1018.



4-(2-chlorophenyl)-1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3j**)**:** Isolated yield (74 mg, 79%); Yellow solid; m.p. 185-187 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^1H NMR (600 MHz, DMSO-d_6) δ 10.07 (d, J = 6.0 Hz, 1H), 8.43 (d, J = 6.0 Hz, 1H), 8.31 (s, 1H), 7.96 (t, J = 9.0 Hz, 1H), 7.78 (t, J = 6.0 Hz, 1H), 7.49 – 7.48 (m, 2H), 7.33 – 7.29 (m, 7H), 7.21 – 7.19 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 187.1, 164.7, 164.6, 160.6, 160.5, 151.5, 151.2, 136.2, 136.1, 136.1, 136.0, 132.4, 132.0, 131.9, 131.8, 131.7, 130.4, 130.1, 130.0, 129.4, 129.3, 129.3, 129.2, 129.0, 129.0, 128.6, 128.5, 128.3, 128.2, 127.2, 126.9, 126.7, 126.5, 126.1, 115.5, 115.5, 112.4, 112.2, 95.9, 95.8, 95.5; HRMS (ESI-TOF, [M + H]$^+$): Calcd. for $C_{26}H_{16}ClN_3O_2S$, 470.0725, found 470.0704.

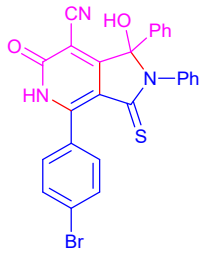


4-(4-chlorophenyl)-1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3k**)**:** Isolated yield (79 mg, 84%); Brown solid; m.p. 161-163 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^1H NMR (500 MHz, DMSO-d_6) δ 13.28 (s, 1H), 8.42 (s, 1H), 7.68 – 7.67 (m, 2H), 7.56 (d, J = 5.0 Hz, 2H), 7.42 – 7.40 (m, 2H), 7.35 – 7.34 (m, 3H), 7.26 – 7.24 (m, 3H), 6.89 (d, J = 5.0 Hz, 2H); $^{13}C\{^1H\}$ (125 MHz, DMSO-d_6) δ 187.5, 164.9, 160.5, 153.8, 136.3, 135.9, 135.4, 131.9, 129.4, 129.1, 128.8, 128.4, 128.1, 127.5, 126.5, 114.6, 112.4, 95.1; HRMS (ESI-TOF, [M + H]$^+$): Calcd. for $C_{26}H_{16}ClN_3O_2S$, 470.0725, found 470.0721.

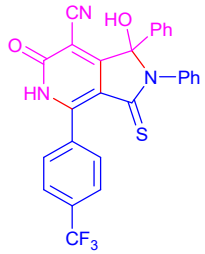


4-(2-bromophenyl)-1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3l**)**:** Isolated yield (77 mg, 75%); Yellow solid; m.p. 198-200 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^1H NMR (500 MHz, DMSO-

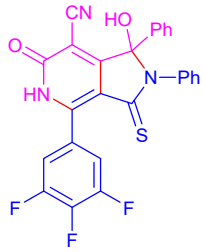
d_6) δ 8.64 – 8.57 (m, 1H), 7.76 – 7.69 (m, 1H), 7.54 – 7.47 (m, 3H), 7.40 – 7.34 (m, 5H), 7.27 – 7.24 (m, 3H), 6.91 (d, J = 5.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 187.0, 164.7, 160.5, 160.4, 152.7, 152.5, 136.2, 136.1, 136.1, 132.1, 132.0, 132.0, 131.8, 131.7, 130.4, 129.6, 129.4, 129.3, 129.3, 129.1, 128.6, 128.5, 128.3, 128.2, 127.6, 127.1, 126.5, 126.2, 122.4, 121.7, 115.3, 112.4, 112.2, 95.8, 95.5; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{26}H_{16}BrN_3O_2S$, 514.0219, found 514.0221.



4-(4-bromophenyl)-1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3m**)**:** Isolated yield (80 mg, 78%); Brown solid; m.p. 192-194 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^1H NMR (500 MHz, DMSO-d_6) δ 8.42 (s, 1H), 7.70 – 7.68 (m, 2H), 7.61 – 7.60 (m, 2H), 7.41 – 7.40 (m, 2H), 7.35 – 7.34 (m, 3H), 7.26 – 7.23 (m, 3H), 6.89 (d, J = 5.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 187.5, 164.9, 160.6, 153.9, 136.3, 135.9, 132.1, 130.4, 129.4, 129.2, 129.1, 128.4, 128.1, 126.5, 124.2, 114.6, 112.4, 95.1, 95.1; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{26}H_{16}BrN_3O_2S$, 514.0219, found 514.0220.

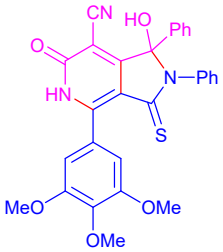


1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-4-(4-(trifluoromethyl)phenyl)-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3n**)**:** Isolated yield (81 mg, 80%); Brown solid; m.p. 143-145 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^1H NMR (500 MHz, DMSO-d_6) δ 8.47 (s, 1H), 7.87 (s, 4H), 7.42 (s, 2H), 7.35 (s, 3H), 7.26 – 7.24 (m, 3H), 6.90 – 6.88 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 187.3, 164.8, 160.4, 153.2, 136.2, 135.9, 134.2, 130.9, 130.4, 129.3, 129.1, 128.4, 128.2, 128.1, 126.5, 125.1, 124.4, 122.9, 114.8, 112.3, 95.7, 95.2; ^{19}F NMR (470 MHz, DMSO-d_6): δ -56.15; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{27}H_{16}F_3N_3O_2S$, 504.0988, found 504.0983.

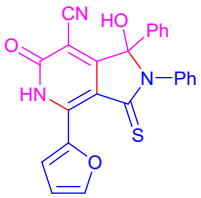


1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-4-(3,4,5-trifluorophenyl)-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3o**)**:** Isolated yield (73 mg, 75%); Brown solid; m.p.

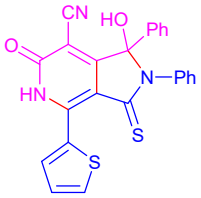
171-173 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.50 (s, 1H), 7.77 – 7.74 (m, 2H), 7.44 – 7.43 (m, 2H), 7.36 – 7.35 (m, 3H), 7.27 – 7.24 (m, 3H), 6.90 (d, J = 10.0 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.4, 164.9, 160.7, 151.4, 150.7, 136.3, 136.0, 129.5, 129.3, 128.6, 128.4, 128.3, 126.7, 115.8, 115.7, 115.0, 112.5, 95.8, 95.4; ^{19}F NMR (470 MHz, DMSO-d_6): δ -135.80, -158.92; HRMS (ESI-TOF, [M + H]$^{+}$): Calcd. for $C_{26}H_{14}F_3N_3O_2S$, 490.0832, found 490.0841.



1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-4-(3,4,5-trimethoxyphenyl)-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3p**)**:** Isolated yield (76 mg, 72%); Yellow solid; m.p. 162-164 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.07 (s, 1H), 8.40 (s, 1H), 7.42 – 7.41 (m, 2H), 7.36 – 7.35 (m, 3H), 7.28 – 7.24 (m, 3H), 7.03 (s, 2H), 6.92 (d, J = 6.0 Hz, 2H), 3.82 (s, 6H), 3.75 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 187.7, 165.3, 160.4, 154.6, 152.0, 139.6, 136.5, 136.0, 129.6, 129.1, 128.4, 128.2, 128.1, 126.6, 124.5, 114.3, 112.5, 108.5, 94.9, 94.8, 60.2, 59.8, 56.2; HRMS (ESI-TOF, [M + H]$^{+}$): Calcd. for $C_{29}H_{23}N_3O_5S$, 526.1431, found 526.1439.

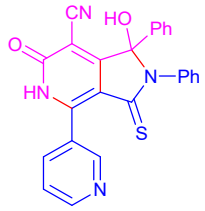


4-(furan-2-yl)-1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3q**)**:** Isolated yield (62 mg, 73%); Yellow solid; m.p. 191-193 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.39 (s, 1H), 8.05 (s, 1H), 7.72 – 7.71 (m, 1H), 7.38 – 7.36 (m, 2H), 7.34 – 7.33 (m, 3H), 7.29 – 7.26 (m, 3H), 6.93 (d, J = 5.0 Hz, 2H), 6.79 – 6.77 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.1, 165.3, 160.2, 146.7, 142.1, 141.5, 136.4, 135.8, 129.5, 129.1, 128.4, 128.1, 126.4, 120.1, 114.7, 112.3, 112.2, 95.1, 94.9; HRMS (ESI-TOF, [M + H]$^{+}$): Calcd. for $C_{24}H_{15}N_3O_3S$, 426.0907, found 426.0905.

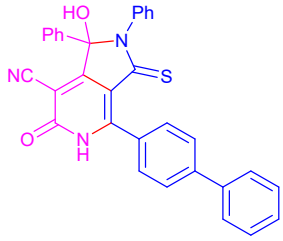


1-hydroxy-6-oxo-1,2-diphenyl-4-(thiophen-2-yl)-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3r**)**:** Isolated yield (66 mg, 75%); Brown solid; m.p. 180-182 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.38 (s, 1H), 7.92 – 7.91 (m, 1H), 7.62 (s, 1H), 7.39 – 7.37 (m, 2H), 7.35 – 7.33 (m, 3H), 7.27 – 7.24

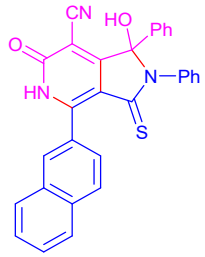
(m, 3H), 7.21 – 7.20 (m, 1H), 6.90 – 6.89 (m, 2H); $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6) δ 187.5, 164.9, 160.6, 148.5, 136.4, 136.0, 133.1, 131.0, 129.6, 129.3, 128.6, 128.3, 127.1, 126.6, 115.9, 112.5, 95.0; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{24}H_{15}N_3O_2S_2$, 442.0678, found 442.0682.



1-hydroxy-6-oxo-1,2-diphenyl-4-(pyridin-3-yl)-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3s**)**:** Isolated yield (61 mg, 70%); Yellow solid; m.p. 185-187 °C. Isolation: hexane/ethyl acetate (2/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.82 (s, 1H), 8.70 (d, J = 5.0 Hz, 1H), 8.51 (s, 1H), 8.07 – 8.05 (m, 1H), 7.54 – 7.52 (m, 1H), 7.43 – 7.41 (m, 2H), 7.36 – 7.35 (m, 3H), 7.26 – 7.25 (m, 3H), 6.89 – 6.88 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6) δ 187.6, 164.9, 160.6, 152.1, 151.1, 149.6, 137.7, 136.2, 135.9, 129.4, 129.2, 128.5, 128.3, 128.2, 126.6, 126.3, 122.6, 115.1, 112.4, 95.7, 95.3; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{25}H_{16}N_4O_2S$, 437.1067, found 437.1060.

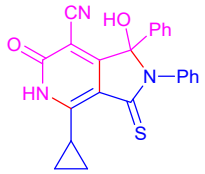


4-([1,1'-biphenyl]-4-yl)-1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3t**)**:** Isolated yield (74 mg, 72%); Yellow solid; m.p. 194-196 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.43 (s, 1H), 7.82 – 7.75 (m, 6H), 7.51 (t, J = 9.0 Hz, 2H), 7.43 – 7.41 (m, 3H), 7.36 - 7.35 (m, 3H), 7.27 – 7.23 (m, 3H), 6.92 (d, J = 6.0 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6) δ 187.7, 165.1, 160.5, 154.9, 142.1, 139.1, 136.4, 136.0, 129.5, 129.1, 128.9, 128.9, 128.5, 128.2, 128.1, 126.8, 126.6, 125.5, 114.5, 112.5, 95.0; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{32}H_{21}N_3O_2S$, 512.1427, found 512.1431.

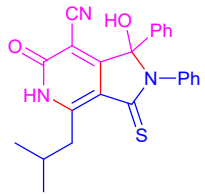


1-hydroxy-4-(naphthalen-2-yl)-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3u**)**:** Isolated yield (80 mg, 82%); Yellow solid; m.p. 225-227 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.31 (s, 1H), 8.44 (s, 1H), 8.23 (s, 1H), 8.05 – 7.97 (m, 3H), 7.77 – 7.76 (m, 1H), 7.66 – 7.59 (m, 2H), 7.46 – 7.44 (m, 2H), 7.37 – 7.36 (m, 3H), 7.27 – 7.23 (m, 3H), 6.91 (d, J =

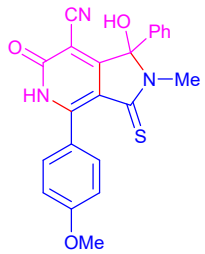
5.0 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6) δ 187.7, 165.2, 160.6, 155.1, 136.4, 136.0, 133.8, 131.9, 129.6, 129.2, 128.7, 128.5, 128.3, 128.2, 127.8, 127.7, 126.7, 126.6, 114.7, 112.6, 95.2; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{30}H_{19}N_3O_2S$, 486.1271, found 486.1274.



4-cyclopropyl-1-hydroxy-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3v**)**:** Isolated yield (67 mg, 84%); White solid; m.p. 226-228 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.05 (s, 1H), 8.30 (s, 1H), 7.31 (s, 5H), 7.29 – 7.27 (m, 3H), 6.93 – 6.92 (m, 2H), 4.74 – 4.71 (m, 1H), 1.58 – 1.54 (m, 1H), 1.47 - 1.40 (m, 1H), 1.36 – 1.33 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6) δ 189.0, 164.1, 163.4, 161.1, 136.3, 135.9, 129.7, 129.1, 128.5, 128.1, 126.4, 112.6, 94.9, 13.1, 12.9, 10.9; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{23}H_{17}N_3O_2S$, 400.1114, found 400.1082.

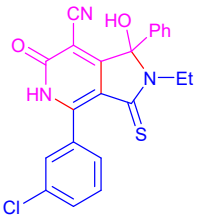


1-hydroxy-4-isobutyl-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3w**)**:** Isolated yield (65 mg, 78%); Yellow solid; m.p. 205-207 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.16 (s, 1H), 8.38 (s, 1H), 7.35 – 7.25 (m, 8H), 6.92 (d, J = 6.0 Hz, 2H), 3.61 (t, J = 6.4 Hz, 1H), 3.53 (dd, J = 11.7, 7.0 Hz, 1H), 2.32 – 2.27 (m, 1H), 1.00 (t, J = 6.8 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6) δ 188.4, 164.8, 160.5, 159.6, 136.2, 135.9, 129.5, 129.1, 128.5, 128.2, 126.3, 114.4, 112.5, 95.1, 93.8, 79.1, 36.7, 29.4, 22.1, 21.7; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{24}H_{21}N_3O_2S$, 416.1427, found 416.1439.

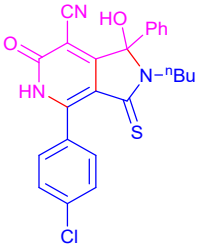


1-hydroxy-4-(4-methoxyphenyl)-2-methyl-6-oxo-1-phenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3x**)**:** Isolated yield (65 mg, 80%); Yellow solid ; m.p. 190-192 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.93 (s, 1H), 8.07 (s, 1H), 7.59 (d, J = 5.0 Hz, 2H), 7.46 – 7.41 (m, 5H), 7.02 (d, J = 10.0 Hz, 2H), 3.85 (s, 3H), 2.85 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6) δ 185.9, 165.0, 161.4, 160.3, 154.1, 135.6, 132.1, 129.2, 128.6, 126.1, 121.5, 114.0, 112.7, 112.6,

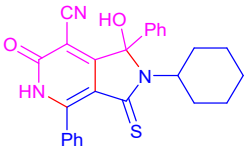
94.3, 93.6, 55.3, 28.9; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{22}H_{17}N_3O_3S$, 404.1063, found 404.1071.



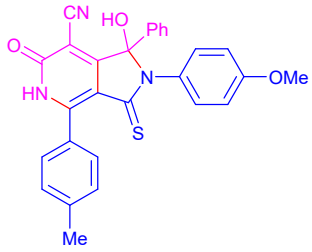
4-(3-chlorophenyl)-2-ethyl-1-hydroxy-6-oxo-1-phenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3y**)**:** Isolated yield (70 mg, 83%); Yellow solid; m.p. 179-181 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.14 (s, 1H), 7.73 (s, 1H), 7.62 – 7.61 (m, 1H), 7.52 – 7.51 (m, 2H), 7.49 – 7.44 (m, 5H), 3.31 – 3.27 (m, 2H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 184.7, 164.9, 160.2, 152.1, 136.0, 132.0, 131.7, 130.3, 129.8, 129.4, 129.3, 128.5, 126.4, 114.6, 112.4, 95.3, 94.2, 37.5, 12.4; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{22}H_{16}ClN_3O_2S$, 422.0725, found 422.0725.



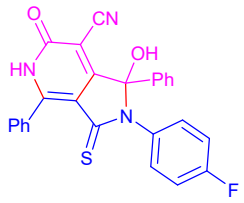
2-butyl-4-(4-chlorophenyl)-1-hydroxy-6-oxo-1-phenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3z**)**:** Isolated yield (71 mg, 79%); Yellow solid; m.p. 144-146 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.14 (s, 1H), 8.12 (s, 1H), 7.64 – 7.62 (m, 2H), 7.56 (d, J = 5.0 Hz, 2H), 7.47 – 7.44 (m, 5H), 3.57 – 3.52 (m, 2H), 3.20 – 3.17 (m, 2H), 1.10 – 1.08 (m, 2H), 0.70 (t, J = 5.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 185.1, 164.9, 160.2, 152.6, 136.0, 135.4, 131.9, 129.33, 128.6, 128.5, 127.5, 126.3, 114.6, 112.4, 95.1, 94.1, 42.5, 28.8, 19.7, 13.4; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{24}H_{20}ClN_3O_2S$, 450.1038, found 450.1034.



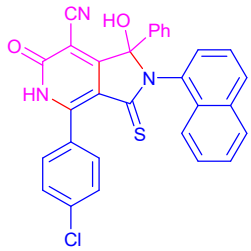
2-cyclohexyl-1-hydroxy-6-oxo-1,4-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3za**)**:** Isolated yield (71 mg, 80%); Yellow solid; m.p. 201-203 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.16 (s, 1H), 7.57 -7.53 (m, 4H), 7.49 – 7.47 (m, 2H), 7.45 – 7.42 (m, 4H), 1.56 – 1.54 (m, 3H), 1.45 – 1.23 (m, 4H), 1.07 – 0.87 (m, 4H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 185.0, 165.2, 160.3, 154.2, 136.6, 130.5, 130.2, 129.2, 128.3, 127.4, 126.5, 112.5, 94.9, 56.7, 28.6, 25.8, 25.7, 24.9; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{26}H_{23}N_3O_2S$, 442.1584, found 442.1576.



1-hydroxy-2-(4-methoxyphenyl)-6-oxo-1-phenyl-3-thioxo-4-(p-tolyl)-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3zb**)**:** Isolated yield (78 mg, 81%); Brown solid; m.p. 195-197 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.10 (s, 1H), 8.30 (s, 1H), 7.54 (d, J = 5.0 Hz, 2H), 7.41 – 7.39 (m, 2H), 7.35 – 7.34 (m, 3H), 7.29 – 7.27 (m, 2H), 6.79 (s, 4H), 3.67 (s, 3H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 188.0, 165.3, 160.5, 158.7, 155.2, 140.6, 136.1, 130.6, 130.1, 129.1, 128.8, 128.2, 128.0, 126.9, 126.6, 114.4, 113.7, 112.6, 94.8, 55.1, 21.2; HRMS (ESI-TOF, [M + H]$^{+}$): Calcd. for $C_{28}H_{21}N_3O_3S$, 480.1376, found 480.1378.

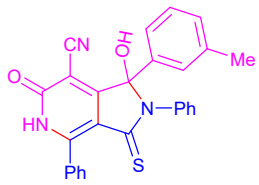


2-(4-fluorophenyl)-1-hydroxy-6-oxo-1,4-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3zc**)**:** Isolated yield (70 mg, 77%); Yellow solid; m.p. 188-190 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.23 (s, 1H), 8.42 (s, 1H), 7.64 – 7.63 (m, 2H), 7.57 – 7.54 (m, 1H), 7.50 – 7.47 (m, 2H), 7.42 – 7.41 (m, 2H), 7.37 – 7.35 (m, 3H), 7.11 (t, J = 10.0 Hz, 2H), 6.93 – 6.90 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 188.2, 165.1, 162.4, 160.7, 160.7, 155.5, 136.0, 132.7, 131.8, 131.8, 130.9, 130.0, 129.4, 128.5, 127.7, 126.7, 115.7, 115.6, 114.5, 112.7, 95.2, 95.1; ^{19}F NMR (470 MHz, DMSO-d_6): δ -108.39; HRMS (ESI-TOF, [M + H]$^{+}$): Calcd. for $C_{26}H_{16}FN_3O_2S$, 454.1020, found 454.1026.

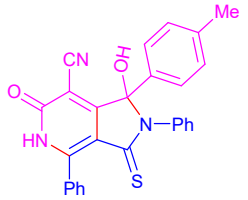


4-(4-chlorophenyl)-1-hydroxy-2-(naphthalen-1-yl)-6-oxo-1-phenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3zd**)**:** Isolated yield (78 mg, 75%); Yellow solid; m.p. 170-172 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.34 (s, 1H), 8.37 (s, 1H), 7.92 – 7.88 (m, 2H), 7.85 – 7.83 (m, 1H), 7.74 – 7.71 (m, 2H), 7.56 (t, J = 7.5 Hz, 2H), 7.51 – 7.47 (m, 2H), 7.46 – 7.43 (m, 4H), 7.16 (t, J = 7.5 Hz, 1H), 7.05 – 7.03 (m, 1H), 6.20 (d, J = 5.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.8, 165.0, 160.4, 153.8, 136.4, 135.5, 133.7, 133.3, 132.0, 131.1, 129.4, 128.9, 128.6, 128.3, 127.9, 127.5, 126.9, 126.8, 126.5, 126.2, 126.1, 124.8, 124.7, 114.3,

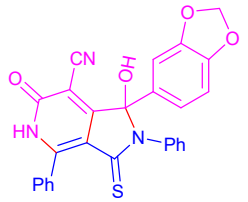
112.5, 96.3; HRMS (ESI-TOF, [M + H]$^+$): Calcd. for $C_{30}H_{18}ClN_3O_2S$, 520.0881, found 520.0886.



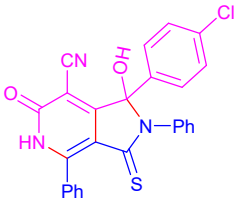
1-hydroxy-6-oxo-2,4-diphenyl-3-thioxo-1-(m-tolyl)-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3ze**)**:** Isolated yield (72 mg, 80%); Yellow solid; m.p. 177-179 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.21 (s, 1H), 8.35 (s, 1H), 7.64 – 7.63 (m, 2H), 7.56 – 7.54 (m, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.26 – 7.21 (m, 6H), 7.16 – 7.15 (m, 1H), 6.90 (d, J = 10.0 Hz, 2H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.7, 165.0, 160.4, 155.0, 137.3, 136.4, 135.8, 130.6, 129.9, 129.7, 129.5, 128.4, 128.0, 127.4, 126.9, 123.7, 114.4, 112.5, 95.0, 79.1, 21.0; HRMS (ESI-TOF, [M + H]$^+$): Calcd. for $C_{27}H_{19}N_3O_2S$, 450.1271, found 450.1267.



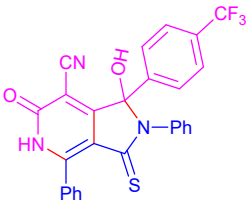
1-hydroxy-6-oxo-2,4-diphenyl-3-thioxo-1-(p-tolyl)-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3zf**)**:** Isolated yield (76 mg, 85%); Yellow solid; m.p. 249-251 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.39 (s, 1H), 7.63 – 7.61 (m, 2H), 7.56 – 7.53 (m, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.29 – 7.28 (m, 2H), 7.26 – 7.23 (m, 3H), 7.15 (d, J = 10.0 Hz, 2H), 6.91 (d, J = 10.0 Hz, 2H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.7, 165.3, 160.5, 155.1, 138.5, 136.5, 133.2, 130.7, 130.0, 129.6, 128.8, 128.5, 128.2, 127.5, 126.5, 114.5, 112.6, 95.2, 95.0, 20.8; HRMS (ESI-TOF, [M + H$^+$): Calcd. for $C_{27}H_{19}N_3O_2S$, 450.1271, found 450.1271.



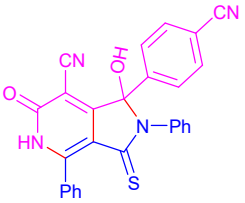
1-(benzo[d][1,3]dioxol-5-yl)-1-hydroxy-6-oxo-2,4-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3zg**)**:** Isolated yield (86 mg, 90%); Yellow solid; m.p. 160-162 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.19 (s, 1H), 8.36 (s, 1H), 7.64 – 7.62 (m, 2H), 7.56 – 7.53 (m, 1H), 7.47 (t, J = 10.0 Hz, 2H), 7.31 – 7.26 (m, 3H), 6.93 – 6.91 (m, 4H), 6.87 – 6.85 (m, 1H), 6.06 (s, 1H), 6.02 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.5, 164.9, 160.5, 155.1, 147.6, 147.0, 136.4, 130.6, 129.9, 129.9, 129.4, 128.4, 128.1, 127.4, 120.7, 114.4, 112.6, 107.8, 106.9, 101.4, 94.8, 94.7; HRMS (ESI-TOF, [M + H]$^+$): Calcd. for $C_{27}H_{17}N_3O_4S$, 480.1013, found 480.1014.



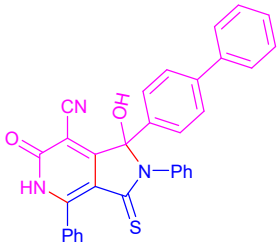
1-(4-chlorophenyl)-1-hydroxy-6-oxo-2,4-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3zh**)**:** Isolated yield (69 mg, 73%); Brown solid; m.p. 145-147 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.53 (s, 1H), 7.64 – 7.63 (m, 2H), 7.57 – 7.54 (m, 1H), 7.50 – 7.47 (m, 2H), 7.45 – 7.40 (m, 4H), 7.30 – 7.25 (m, 3H), 6.92 (d, J = 10.0 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.8, 164.5, 160.3, 155.2, 136.2, 135.1, 133.7, 130.6, 129.8, 129.5, 128.6, 128.5, 128.2, 127.4, 114.4, 112.7, 112.4, 95.0, 94.4; HRMS (ESI-TOF, [M + H]$^{+}$): Calcd. for $C_{26}H_{16}ClN_3O_2S$, 470.0725, found 470.0730.



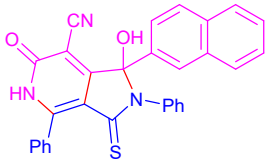
1-hydroxy-6-oxo-2,4-diphenyl-3-thioxo-1-(4-(trifluoromethyl)phenyl)-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3zi**)**:** Isolated yield (83 mg, 82%); Yellow solid; m.p. 183-185 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.30 (s, 1H), 8.67 (s, 1H), 7.74 – 7.72 (m, 2H), 7.67 – 7.63 (m, 4H), 7.57 – 7.55 (m, 1H), 7.51 – 7.48 (m, 2H), 7.29 – 7.25 (m, 3H), 6.93 (d, J = 10.0 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 188.0, 164.3, 160.3, 155.4, 140.5, 136.1, 130.7, 129.8, 129.7, 129.5, 129.5, 129.3, 128.5, 128.2, 127.6, 127.5, 125.1, 125.0, 122.8, 114.4, 112.4, 95.0, 94.3, 79.1; ^{19}F NMR (470 MHz, DMSO-d_6): δ -56.18; HRMS (ESI-TOF, [M + H]$^{+}$): Calcd. for $C_{27}H_{16}F_3N_3O_2S$, 504.0988, found 504.0987.



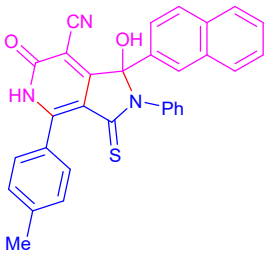
1-(4-cyanophenyl)-1-hydroxy-6-oxo-2,4-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3zj**)**:** Isolated yield (69 mg, 75%); Brown solid; m.p. 188-190 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.58 (s, 1H), 8.06 (s, 1H), 7.91 (t, J = 7.5 Hz, 3H), 7.68 – 7.67 (m, 1H), 7.56 – 7.53 (m, 2H), 7.52 – 7.48 (m, 3H), 7.42 (d, J = 10.0 Hz, 1H), 7.21 – 7.19 (m, 2H), 6.92 (d, J = 10.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.9, 164.9, 160.5, 155.3, 136.4, 133.3, 132.9, 132.2, 130.7, 129.9, 129.5, 128.6, 128.5, 128.1, 128.1, 127.6, 127.5, 127.0, 126.6, 126.4, 123.7, 114.6, 112.5, 95.1; HRMS (ESI-TOF, [M + H]$^{+}$): Calcd. for $C_{27}H_{16}N_4O_2S$, 461.1067, found 461.1071.



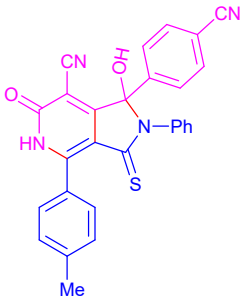
1-([1,1'-biphenyl]-4-yl)-1-hydroxy-6-oxo-2,4-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3zk**)**:** Isolated yield (84 mg, 82%); Yellow solid; m.p. 171-173 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.46 (s, 1H), 7.69 – 7.67 (m, 4H), 7.66 – 7.64 (m, 2H), 7.57 – 7.55 (m, 1H), 7.51 – 7.45 (m, 6H), 7.38 (t, J = 7.5 Hz, 1H), 7.29 – 7.24 (m, 3H), 6.96 (d, J = 5.0 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.7, 165.0, 160.4, 155.2, 140.4, 139.0, 136.4, 135.1, 130.6, 129.9, 129.5, 129.0, 128.5, 128.1, 127.8, 127.4, 127.2, 126.6, 126.2, 114.4, 112.5, 94.9; HRMS (ESI-TOF, [M + H]$^+$): Calcd. for $C_{32}H_{21}N_3O_2S$, 512.1427, found 512.1426.



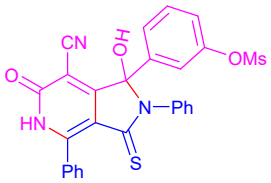
1-hydroxy-1-(naphthalen-2-yl)-6-oxo-2,4-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3zl**)**:** Isolated yield (78 mg, 80%); Brown solid; m.p. 164-166 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.56 (s, 1H), 8.06 (s, 1H), 7.91 (t, J = 7.5 Hz, 3H), 7.69 – 7.67 (m, 2H), 7.57 – 7.53 (m, 2H), 7.52 – 7.49 (m, 3H), 7.42 (d, J = 10.0 Hz, 1H), 7.21 – 7.18 (m, 3H), 6.92 (d, J = 10.0 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.9, 164.9, 160.4, 155.2, 136.4, 133.2, 132.9, 132.1, 130.7, 129.9, 129.4, 128.5, 128.4, 128.1, 128.0, 127.5, 127.5, 126.9, 126.5, 126.4, 123.7, 114.6, 112.4, 95.1; HRMS (ESI-TOF, [M + H]$^+$): Calcd. for $C_{30}H_{19}N_3O_2S$, 486.1271, found 486.1278.



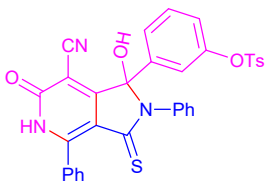
1-hydroxy-1-(naphthalen-2-yl)-6-oxo-2-phenyl-3-thioxo-4-(p-tolyl)-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3zm**)**:** Isolated yield (83 mg, 83%); Yellow solid; m.p. 175-177 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.53 (s, 1H), 8.06 (s, 1H), 7.93 – 7.89 (m, 3H), 7.60 – 7.59 (m, 2H), 7.55 – 7.52 (m, 2H), 7.42 (d, J = 10.0 Hz, 1H), 7.31 (d, J = 10.0 Hz, 2H), 7.23 – 7.18 (m, 3H), 6.93 (d, J = 5.0 Hz, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 188.0, 164.9, 160.5, 155.4, 140.6, 136.4, 133.2, 132.9, 132.1, 130.1, 129.5, 128.5, 128.4, 128.0, 128.0, 127.5, 126.9, 126.5, 126.4, 123.7, 114.5, 112.5, 95.0, 94.8, 21.1; HRMS (ESI-TOF, [M + H]$^+$): Calcd. for $C_{31}H_{21}N_3O_2S$, 500.1427, found 500.1440.



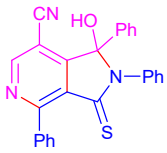
1-(4-cyanophenyl)-1-hydroxy-6-oxo-2-phenyl-3-thioxo-4-(p-tolyl)-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**3zn**)**:** Isolated yield (74 mg, 78%); Yellow solid ; m.p. 196-198 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. 1H NMR (500 MHz, DMSO-d_6) δ 8.69 (s, 1H), 7.84 – 7.82 (m, 2H), 7.62 – 7.61 (m, 2H), 7.55 (d, J = 10.0 Hz, 2H), 7.30 – 7.26 (m, 5H), 6.90 (d, J = 10.0 Hz, 2H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 188.2, 164.2, 160.4, 155.8, 141.3, 140.7, 136.1, 132.3, 130.1, 129.6, 128.6, 128.3, 128.0, 127.8, 126.8, 118.4, 114.4, 112.5, 111.9, 94.8, 94.1, 21.1; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{28}H_{18}N_4O_2S$, 475.1223, found 475.1224.



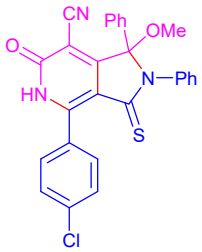
3-(7-cyano-1-hydroxy-6-oxo-2,4-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridin-1-yl)phenyl methanesulfonate (**3zo**)**:** Isolated yield (77 mg, 73%); Yellow solid; m.p. 139-141 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^1H NMR (500 MHz, DMSO-d_6) δ 8.63 (s, 1H), 8.30 (s, 1H), 7.65 – 7.63 (m, 2H), 7.57 – 7.54 (m, 1H), 7.51 – 7.47 (m, 3H), 7.43 – 7.40 (m, 2H), 7.34 (d, J = 10.0 Hz, 1H), 7.27 – 7.25 (m, 2H), 6.93 (d, J = 5.0 Hz, 2H), 3.24 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 187.9, 164.4, 160.4, 155.4, 148.9, 138.6, 136.2, 130.7, 130.2, 129.8, 129.5, 128.5, 128.2, 127.5, 125.7, 123.2, 120.3, 114.4, 112.6, 95.0, 94.2, 79.2, 36.9; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{27}H_{19}N_3O_5S_2$, 530.0839, found 530.0850.



3-(7-cyano-1-hydroxy-6-oxo-2,4-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridin-1-yl)phenyl 4-methylbenzenesulfonate (**3zp**)**:** Isolated yield (92 mg, 76%); Brown solid; m.p. 141-143 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^1H NMR (500 MHz, DMSO-d_6) δ 8.51 (s, 1H), 7.63 – 7.61 (m, 4H), 7.58 – 7.55 (m, 1H), 7.53 – 7.50 (m, 2H), 7.35 – 7.34 (m, 4H), 7.27 – 7.24 (m, 3H), 7.05 – 7.03 (m, 1H), 6.99 (s, 1H), 6.69 – 6.68 (m, 2H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 187.6, 164.2, 160.3, 155.3, 148.8, 145.9, 138.4, 136.0, 130.8, 130.7, 130.1, 129.9, 129.8, 129.4, 128.4, 128.2, 127.5, 125.6, 123.1, 120.1, 114.4, 112.3, 95.0, 94.0, 79.1, 21.2; HRMS (ESI-TOF, $[M + H]^+$): Calcd. for $C_{33}H_{23}N_3O_5S_2$, 606.1152, found 606.1161.



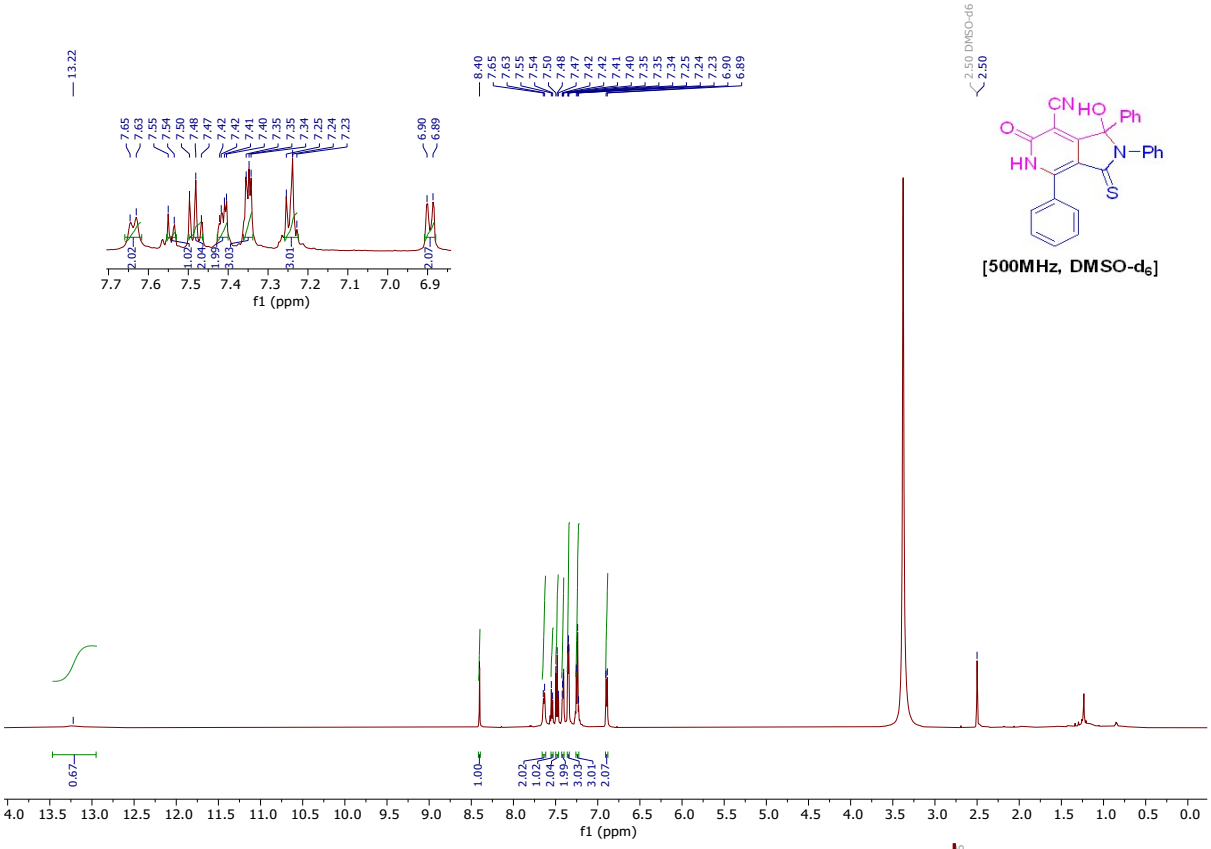
1-hydroxy-1,2,4-triphenyl-3-thioxo-2,3-dihydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**4a**)**:** Isolated yield (67 mg, 80%); Brown solid; m.p. 151-153 °C. Isolation: hexane/ethyl acetate (4/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.23 (s, 1H), 7.66 – 7.64 (m, 2H), 7.56 – 7.53 (m, 1H), 7.50 – 7.47 (m, 2H), 7.33 – 7.29 (m, 9H), 7.21 – 7.18 (m, 1H), 6.81 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 187.6, 165.0, 160.4, 155.0, 136.3, 135.9, 130.6, 130.2, 129.8, 129.5, 129.0, 128.7, 128.4, 128.2, 128.1, 128.0, 127.7, 127.4, 126.9, 126.5, 123.1, 112.4, 94.9; HRMS (ESI-TOF, [M + H]$^{+}$): Calcd. for $C_{26}H_{17}N_3OS$, 420.1165, found 420.1182.

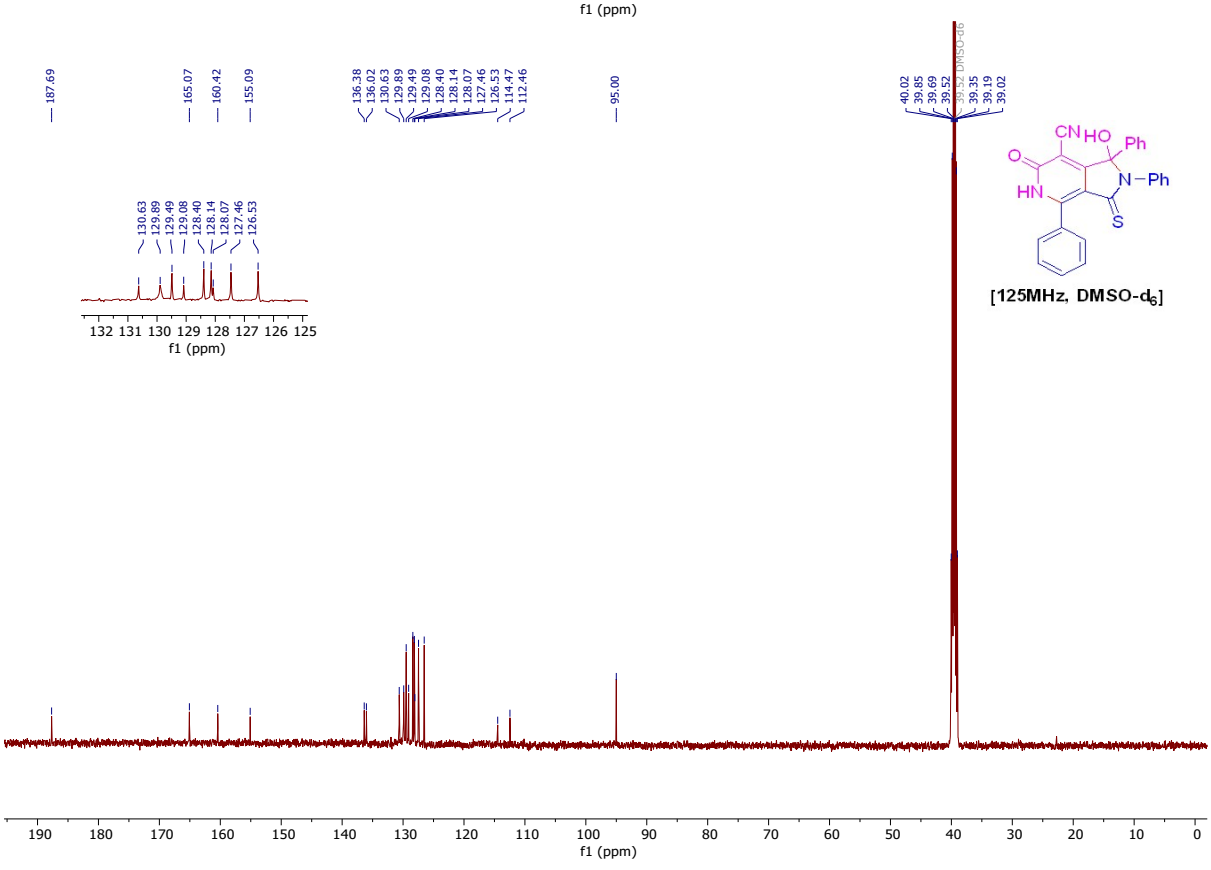


4-(4-chlorophenyl)-1-methoxy-6-oxo-1,2-diphenyl-3-thioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridine-7-carbonitrile (**4b**)**:** Isolated yield (90 mg, 93%); Yellow solid; m.p. 170-172 °C. Isolation: hexane/ethyl acetate (5/1) as the eluent. ^{1}H NMR (500 MHz, DMSO-d_6 + $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.40 – 7.37 (m, 2H), 7.33 – 7.31 (m, 2H), 7.29 (s, 1H), 7.26 – 7.25 (m, 2H), 7.18 – 7.16 (m, 3H), 6.89 – 6.86 (m, 2H), 3.45 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6 + $CDCl_3$) δ 188.5, 160.2, 160.0, 153.8, 136.7, 135.6, 134.5, 131.1, 129.0, 128.2, 128.0, 127.8, 127.4, 126.1, 114.8, 111.1, 99.4, 96.2, 51.4; HRMS (ESI-TOF, [M + Na]$^{+}$): Calcd. for $C_{27}H_{18}ClN_3O_2S$, 506.0700, found 506.0695.

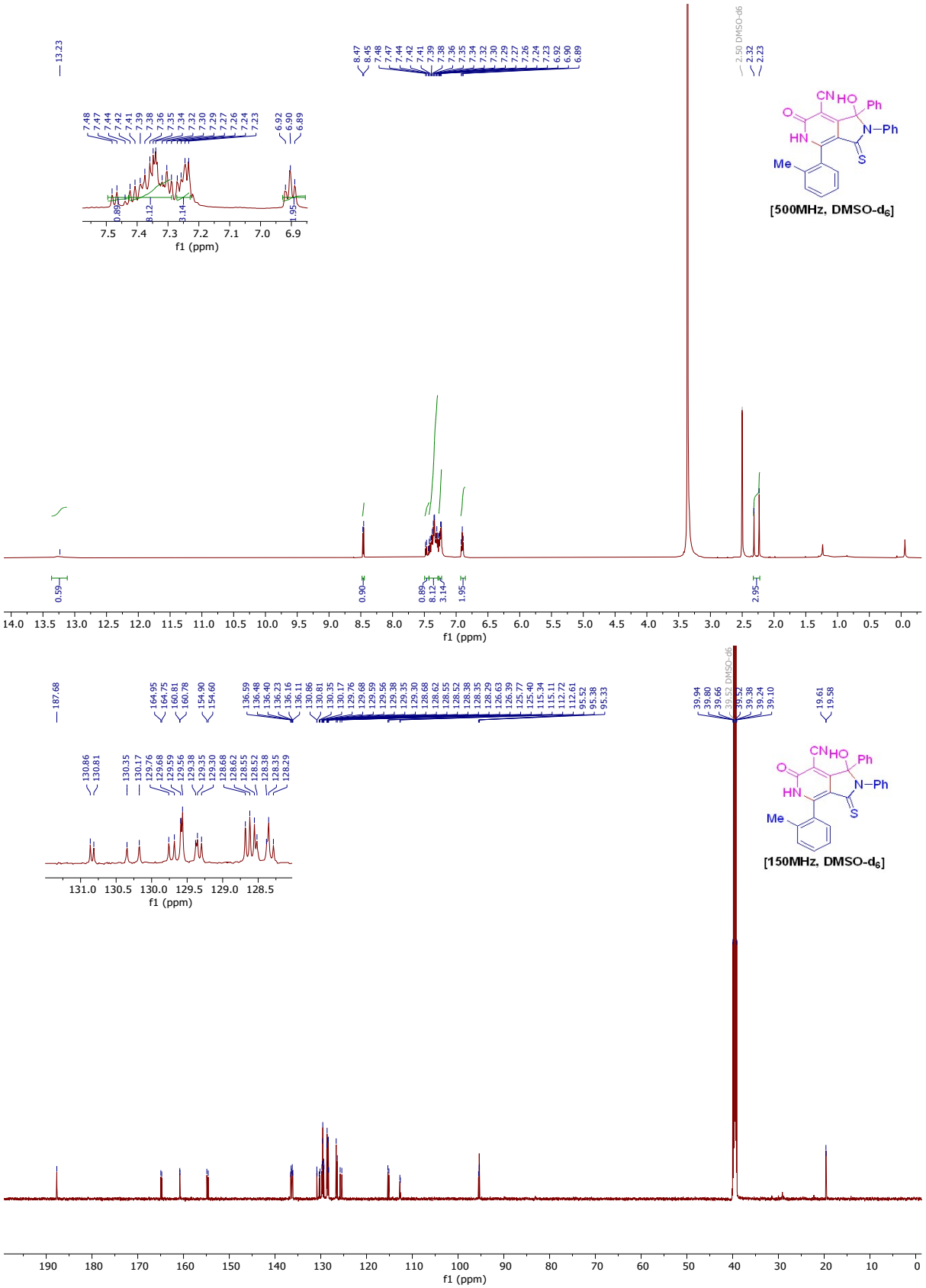
7. Copies of ^{1}H and ^{13}C NMR Spectra

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3a

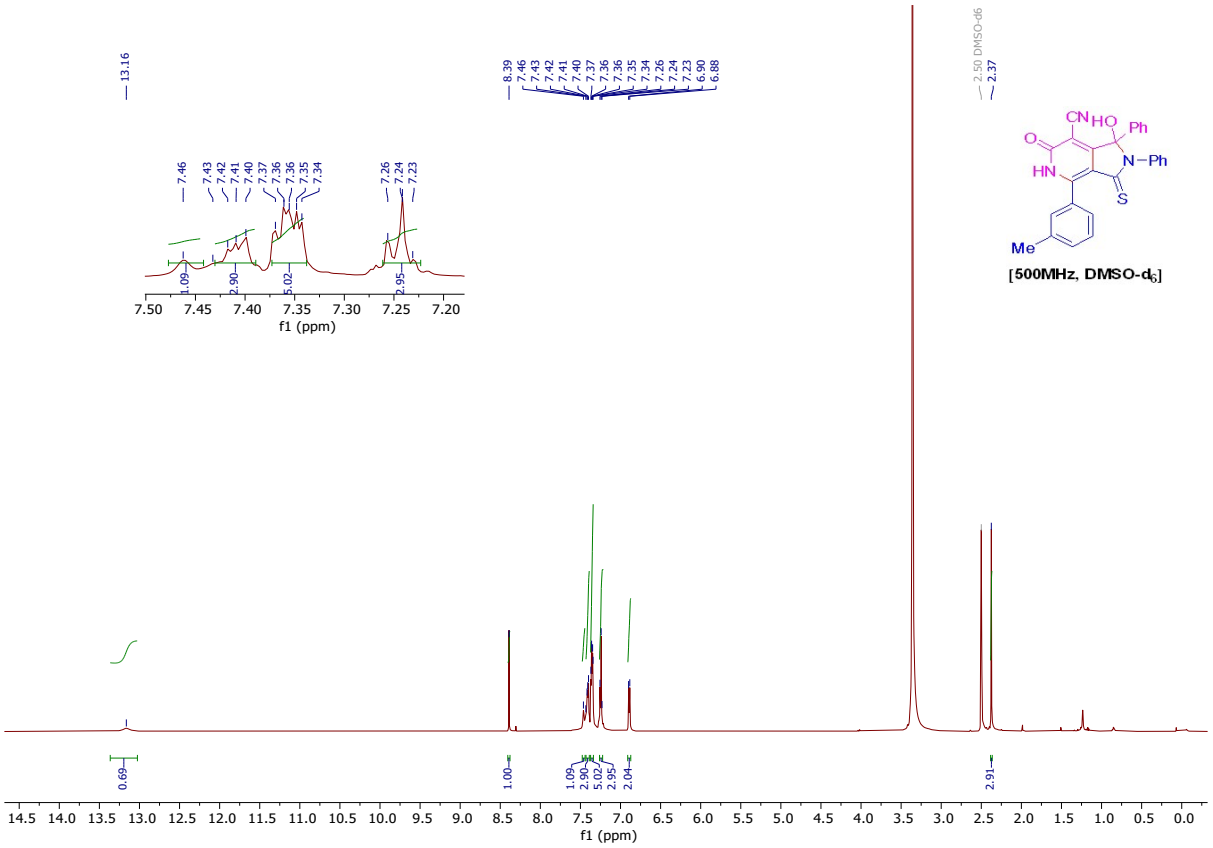


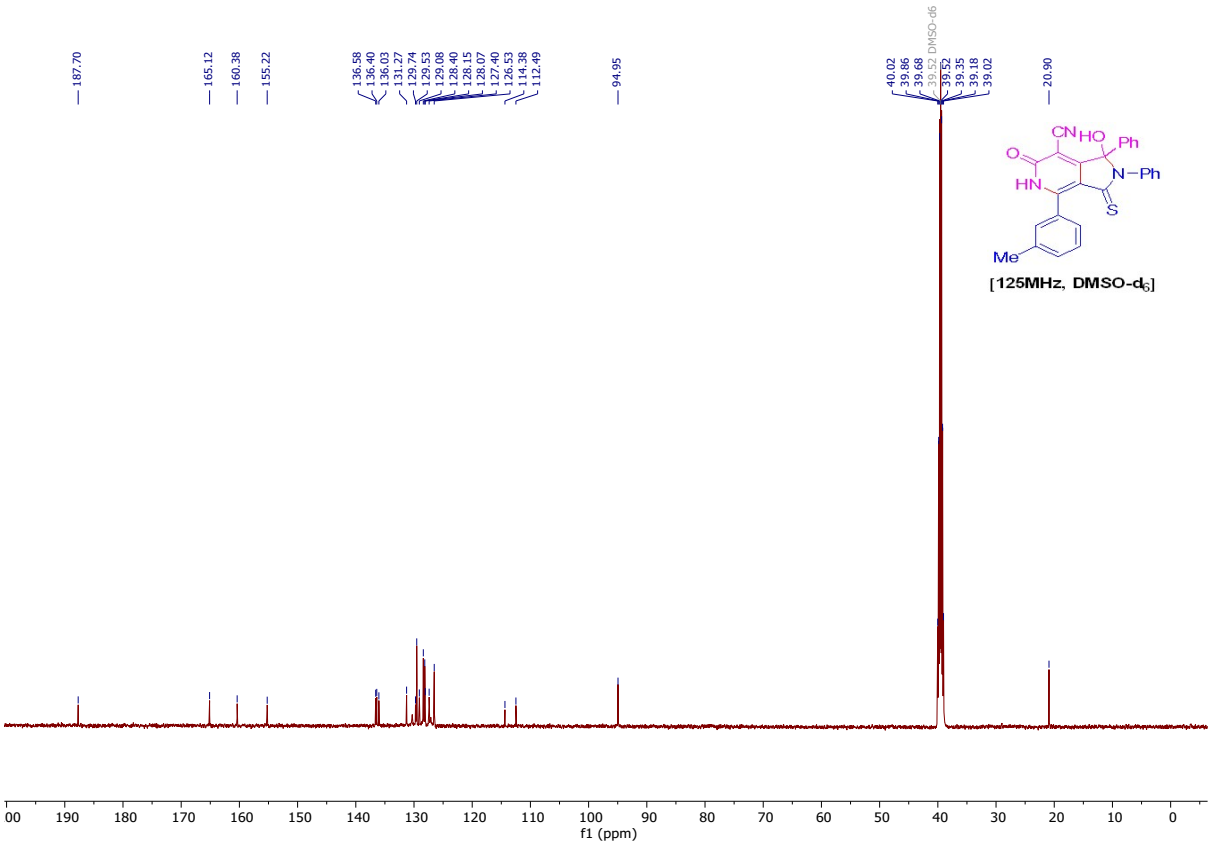


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3b

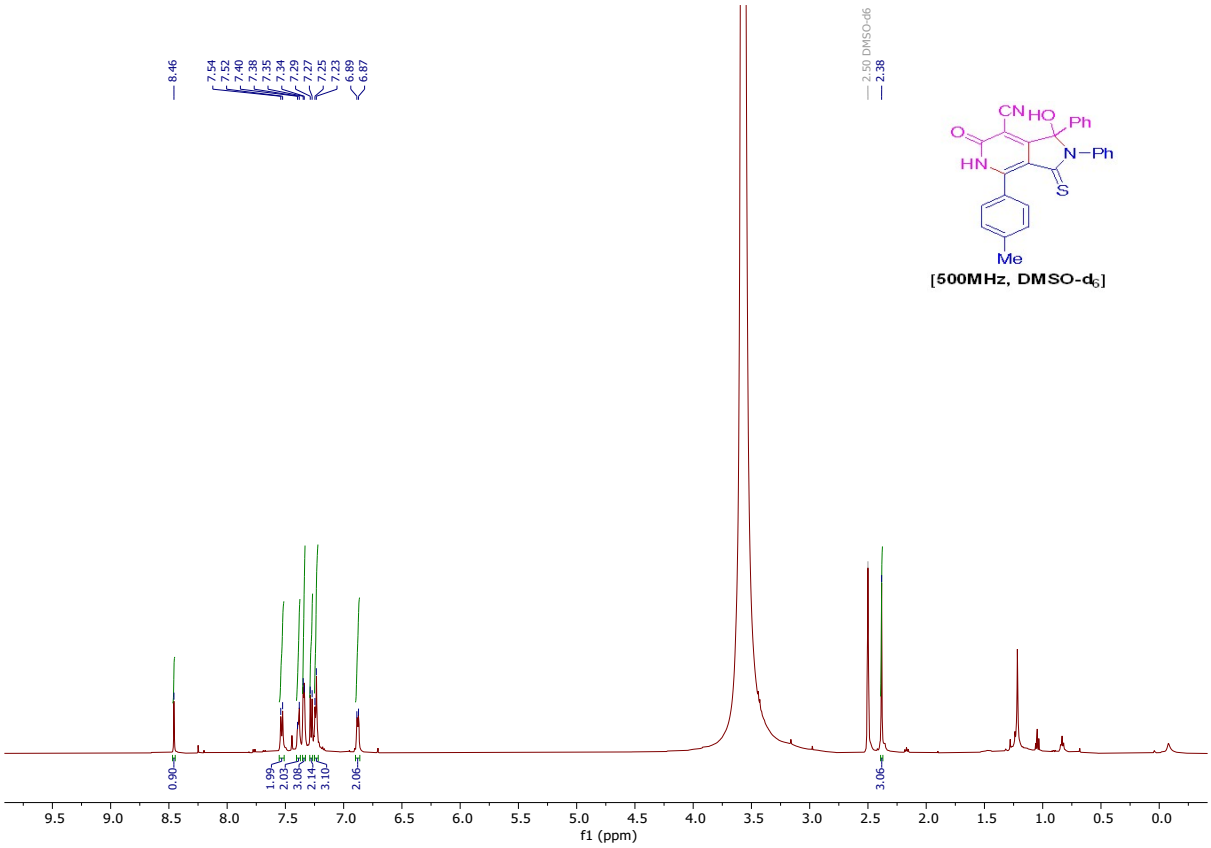


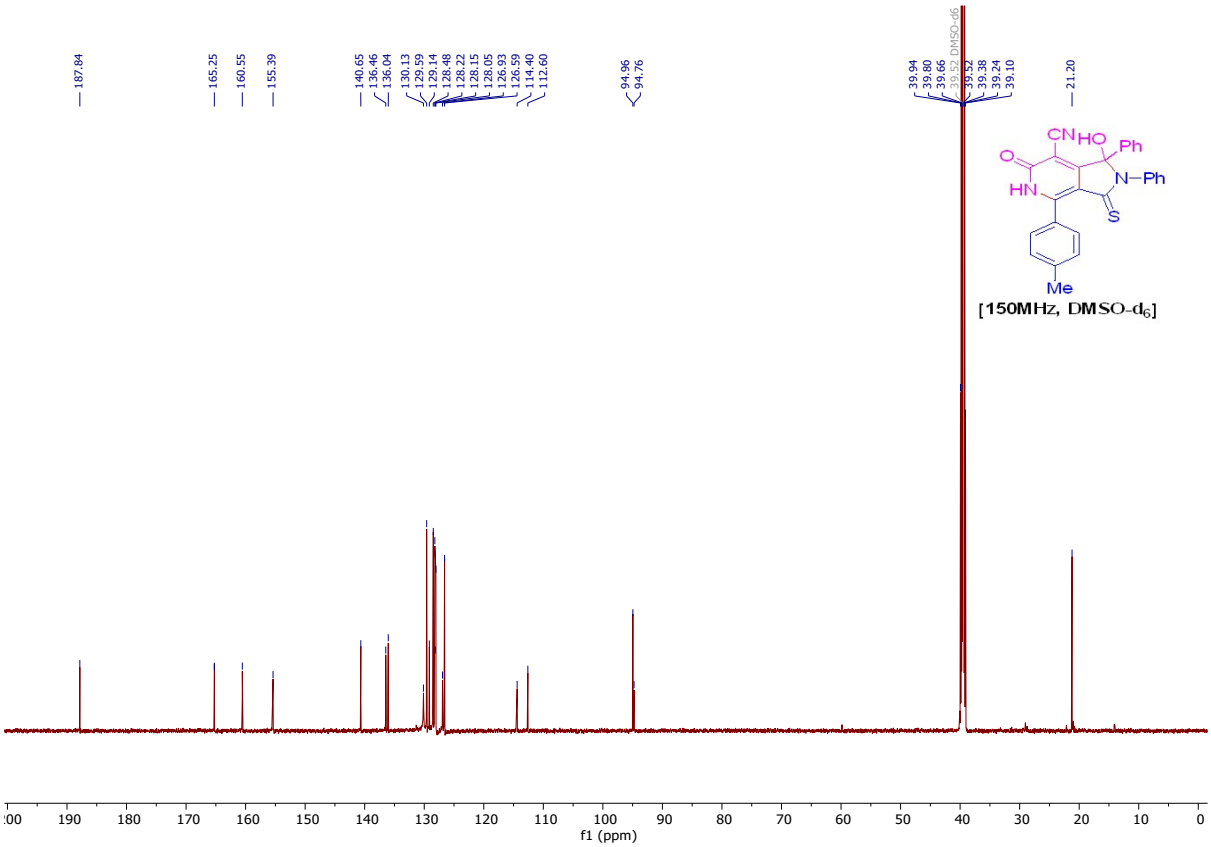
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3c



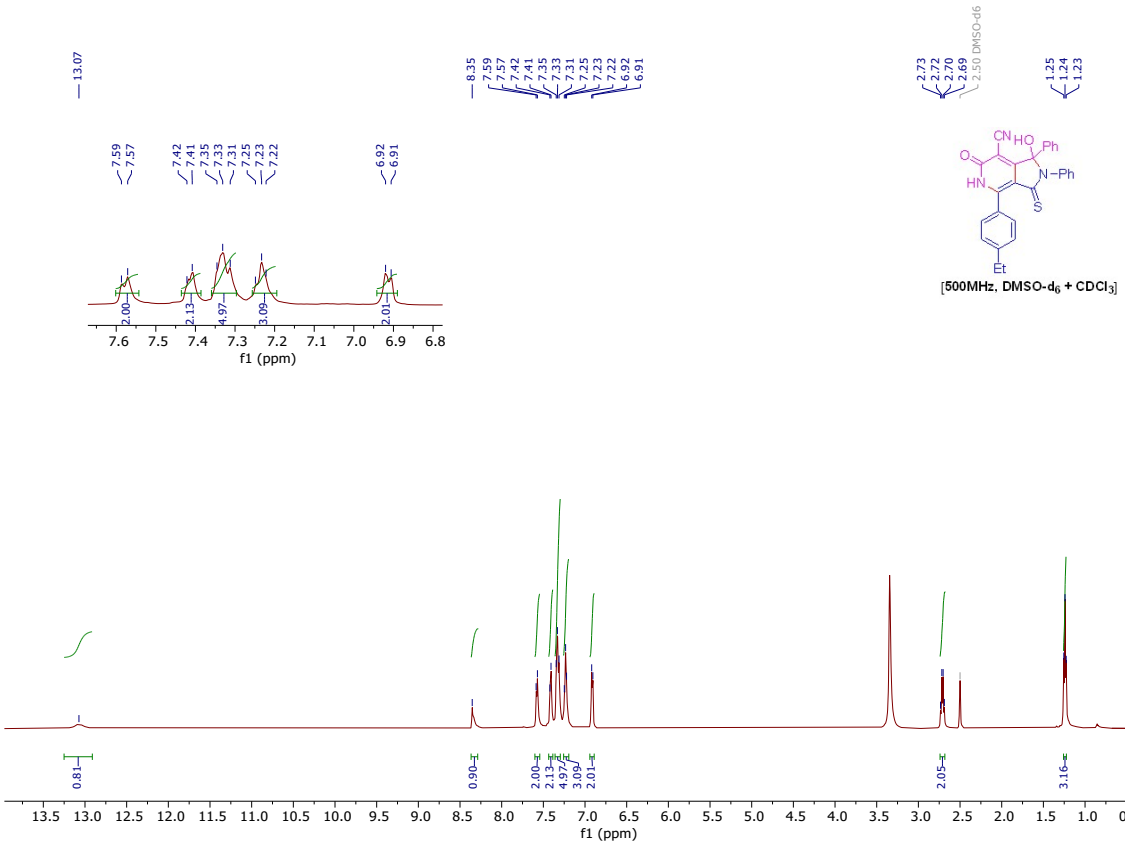


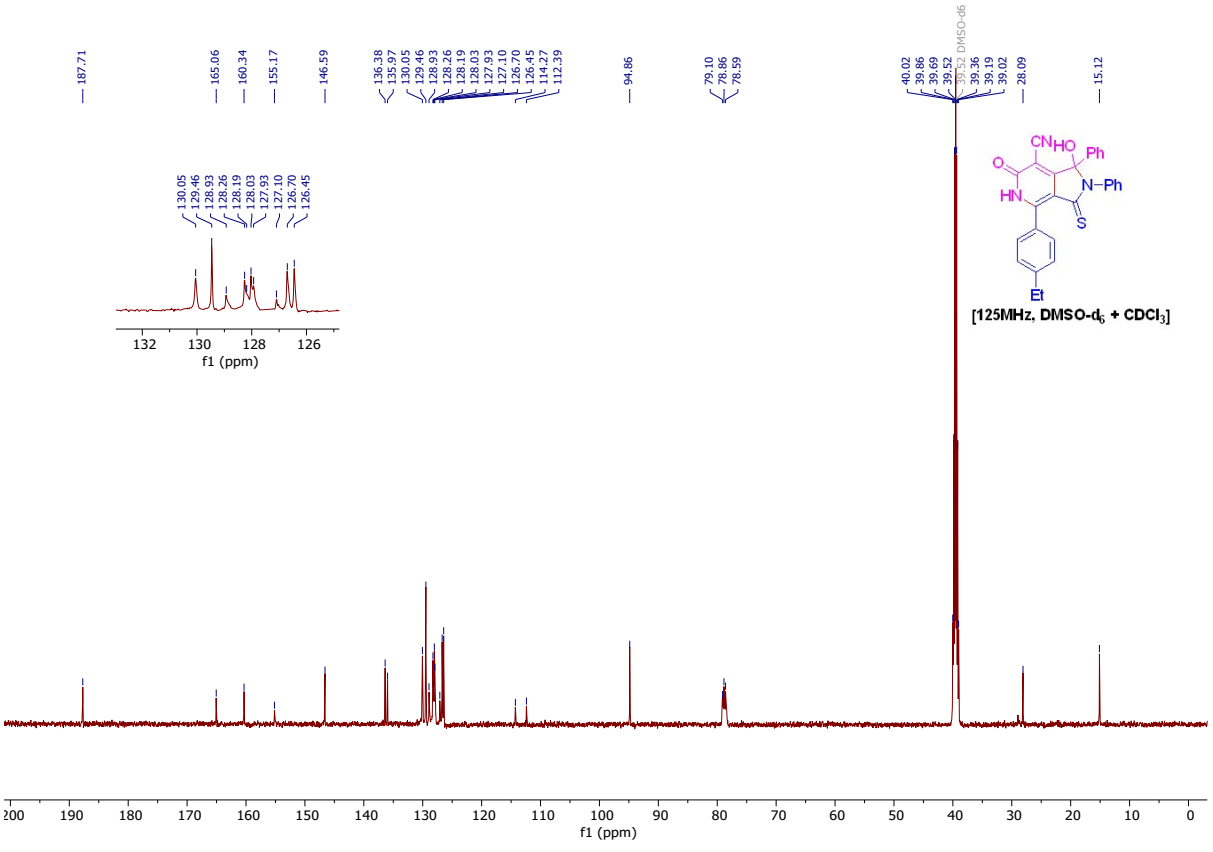
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3d



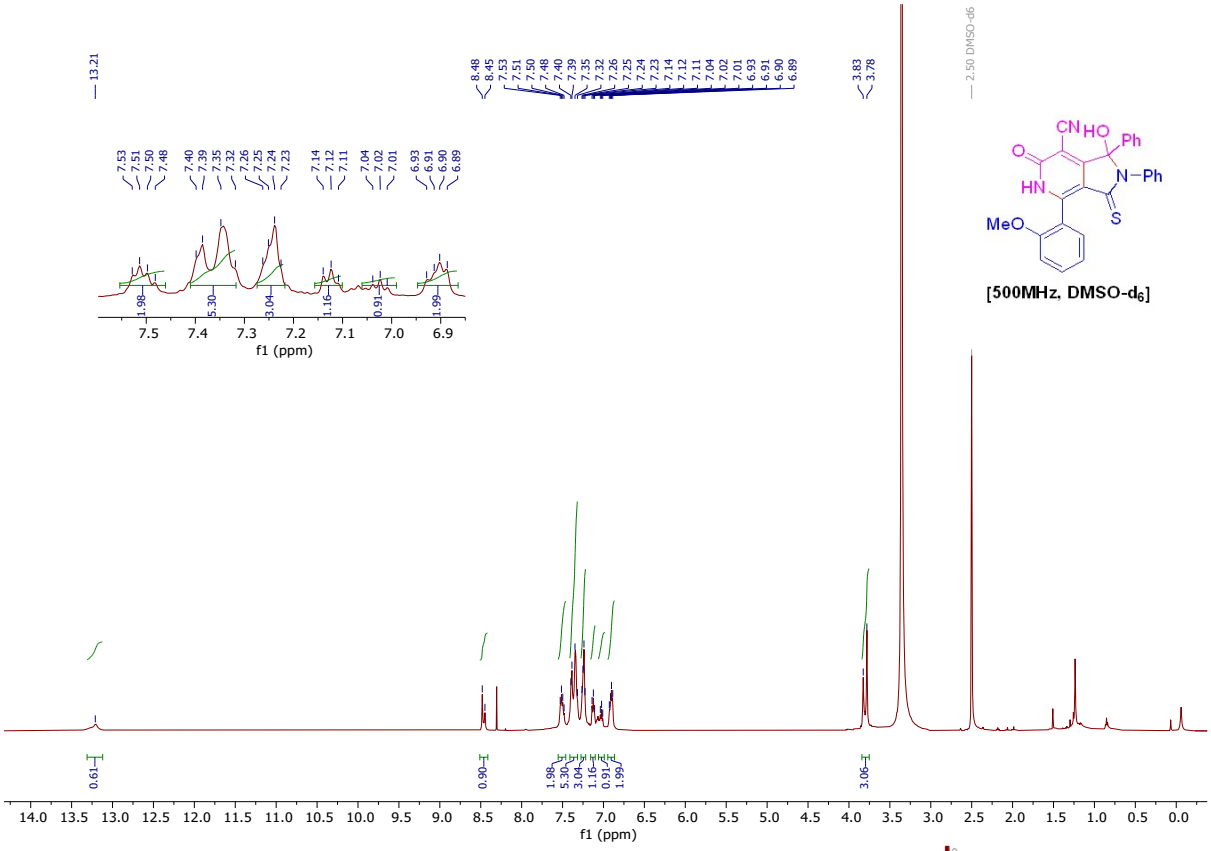


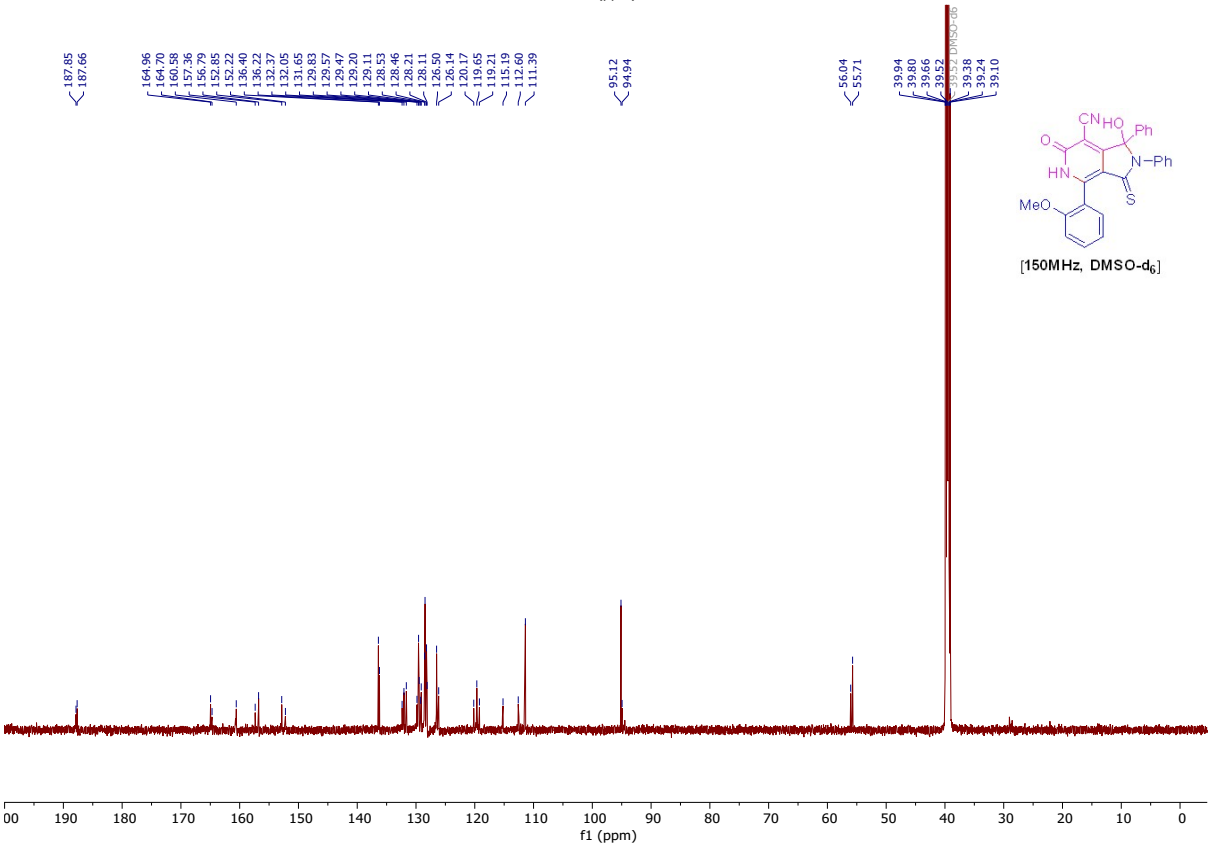
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3e



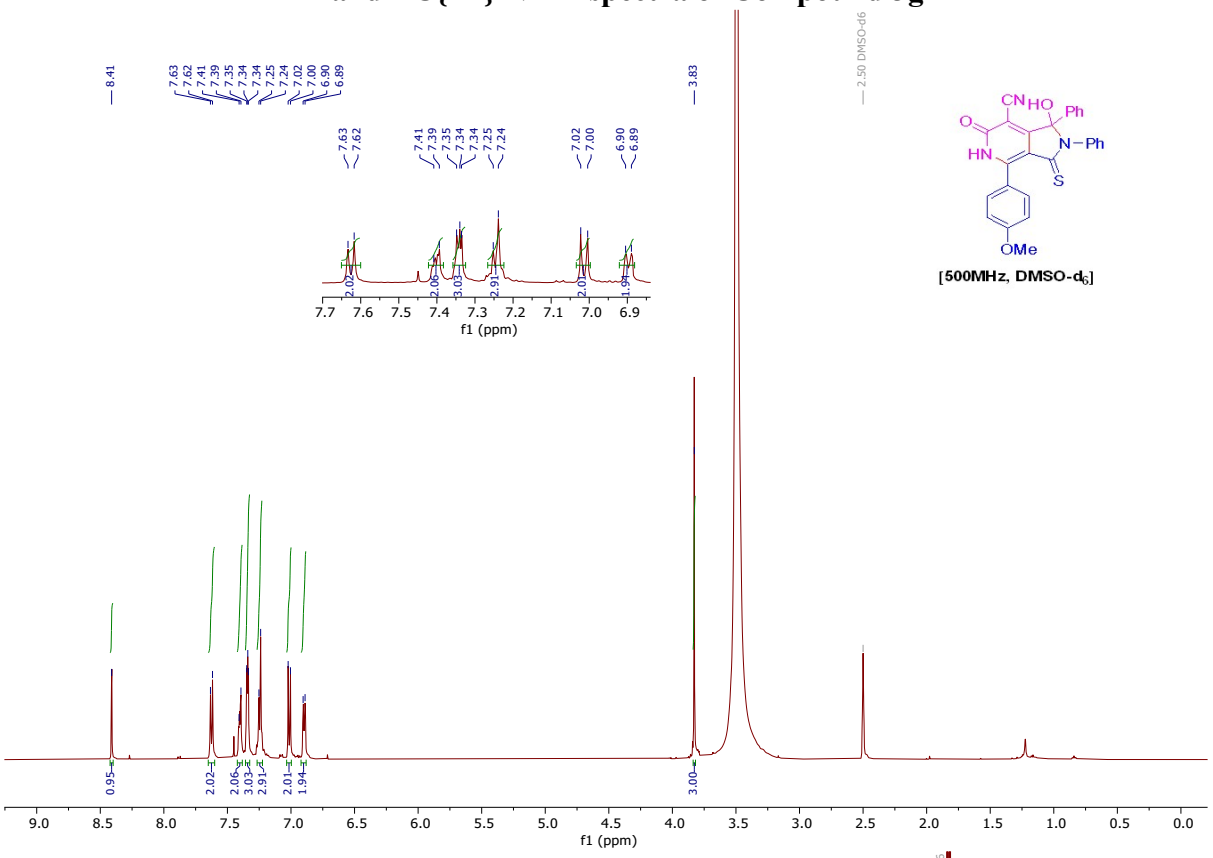


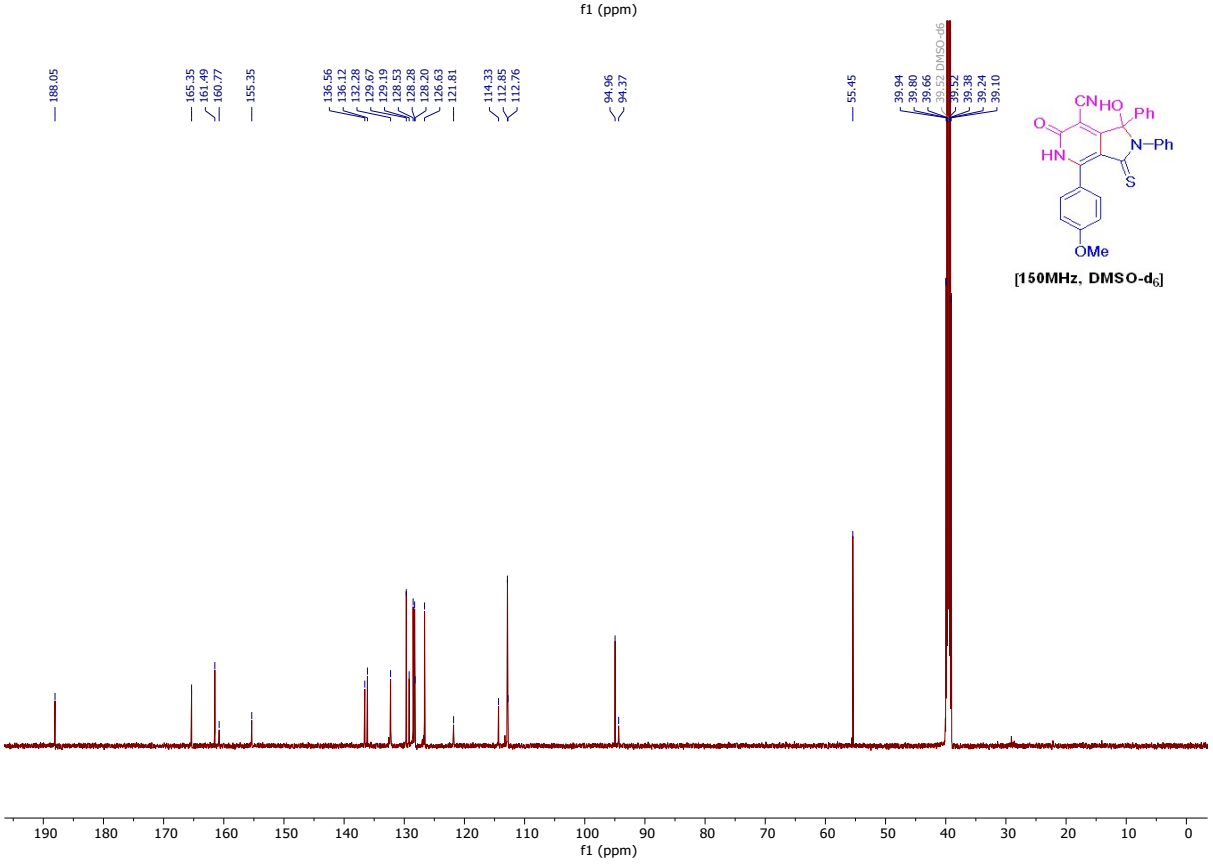
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3f



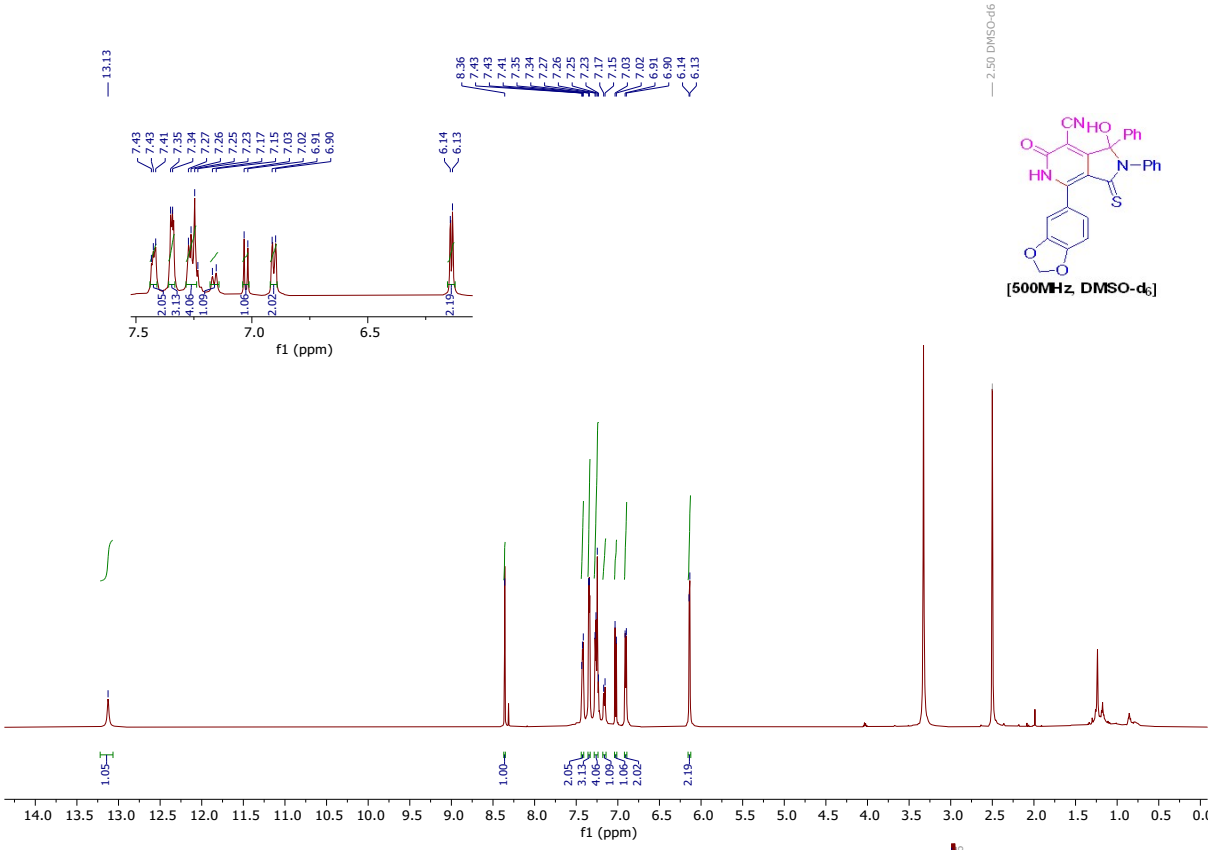


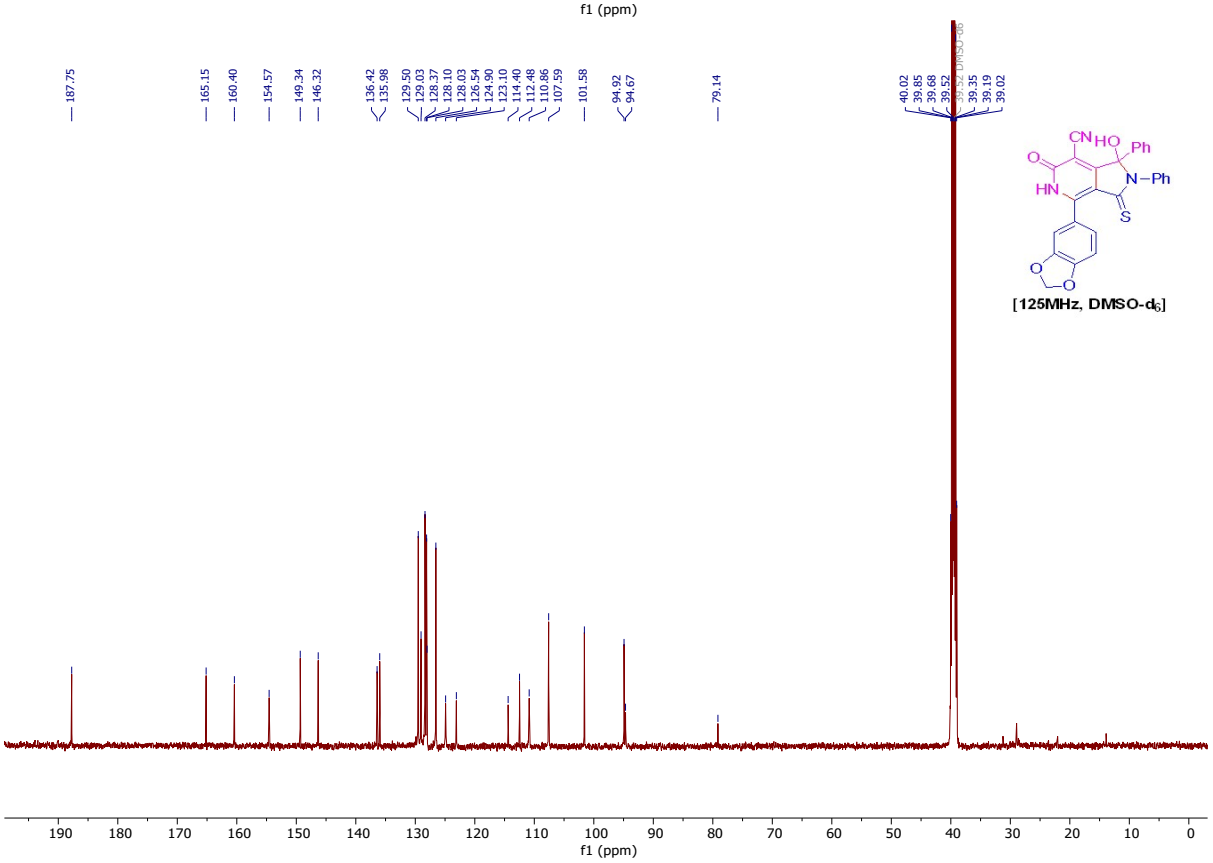
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3g



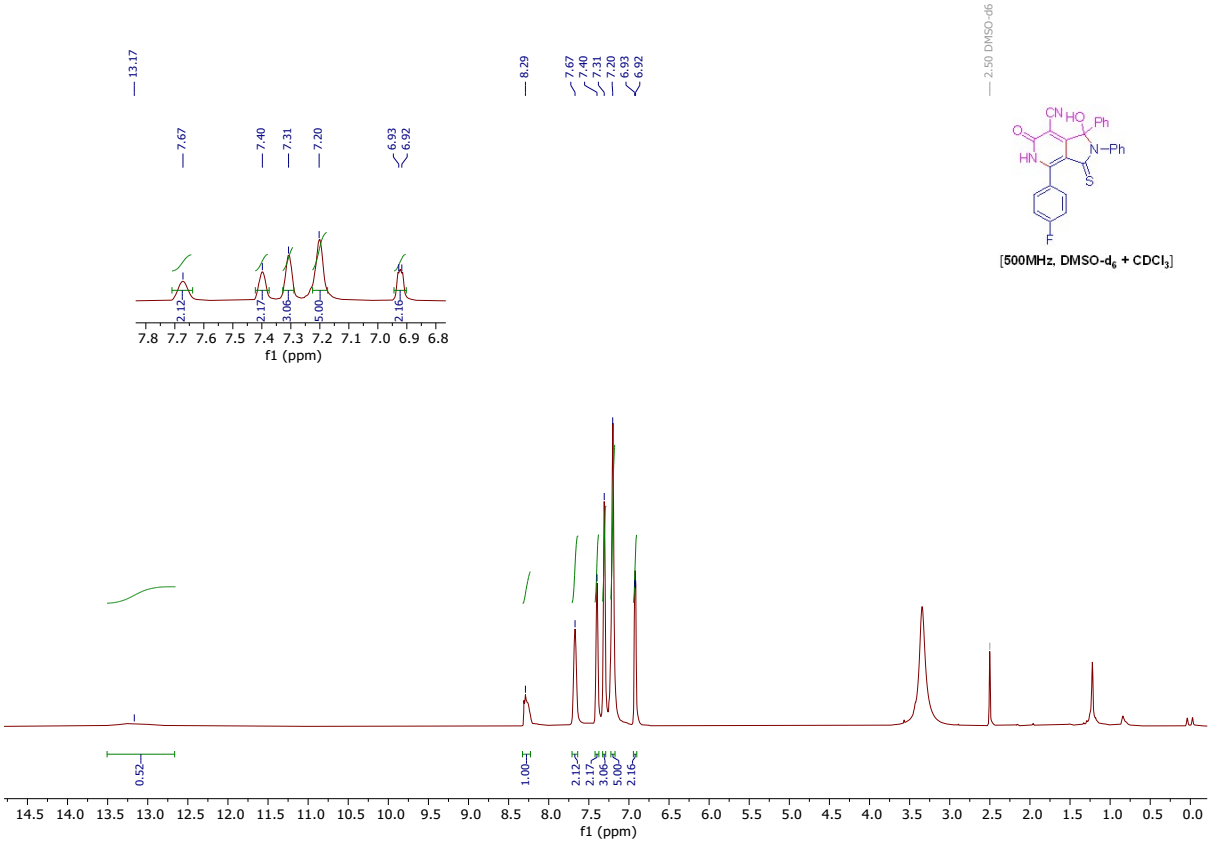


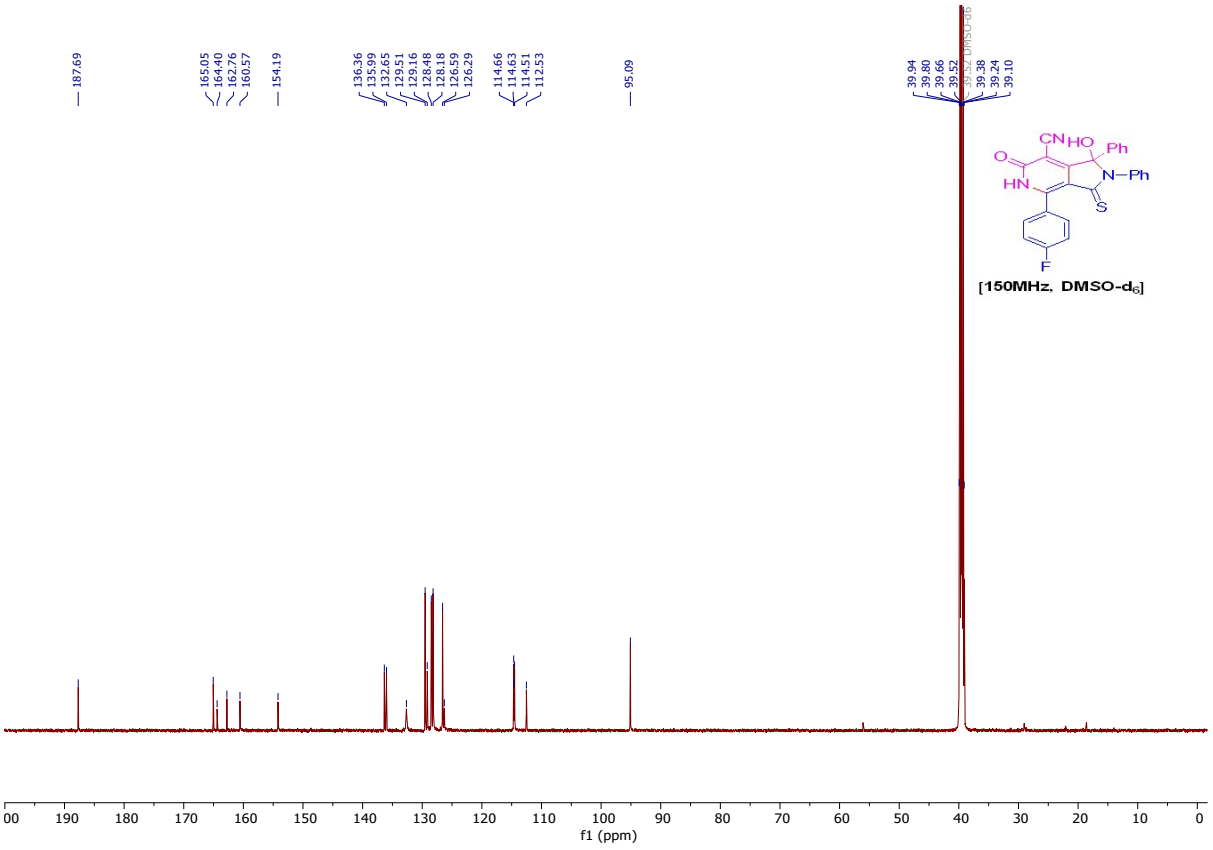
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3h



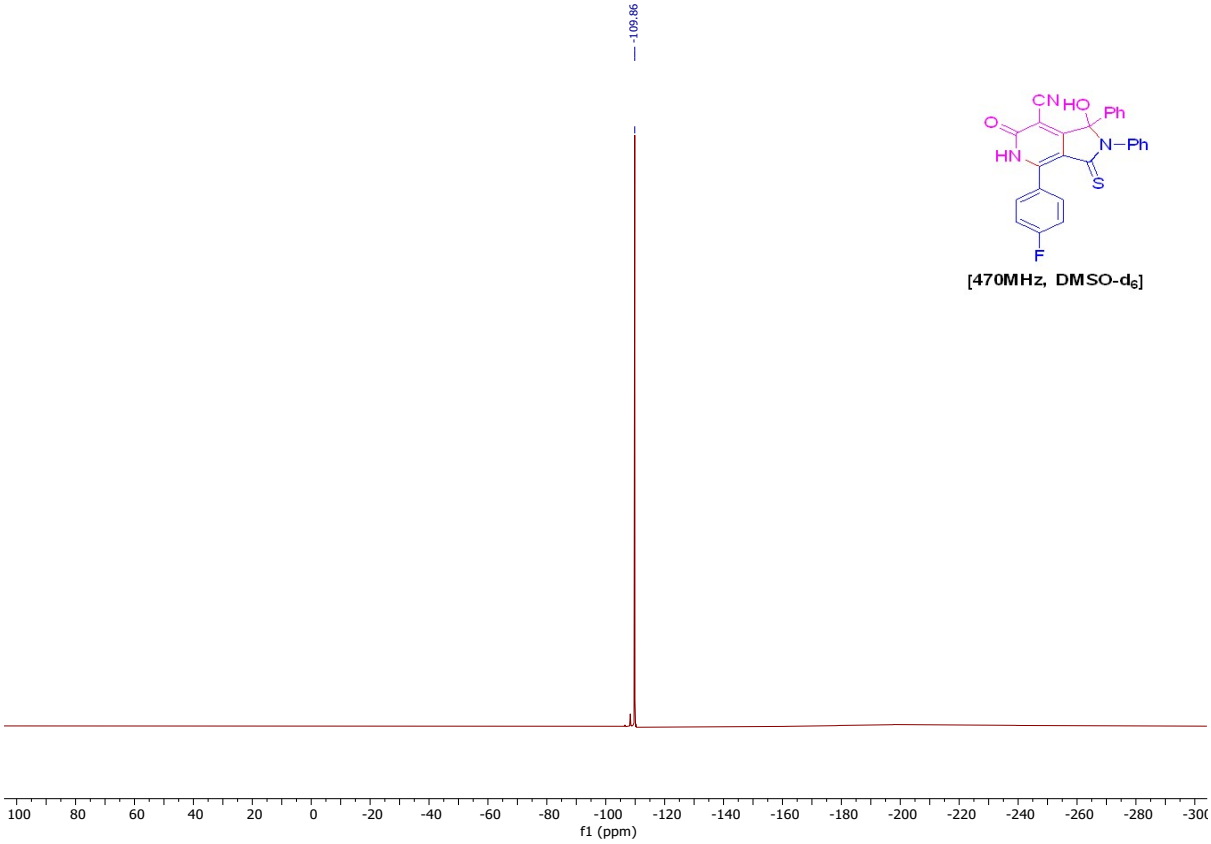


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3i

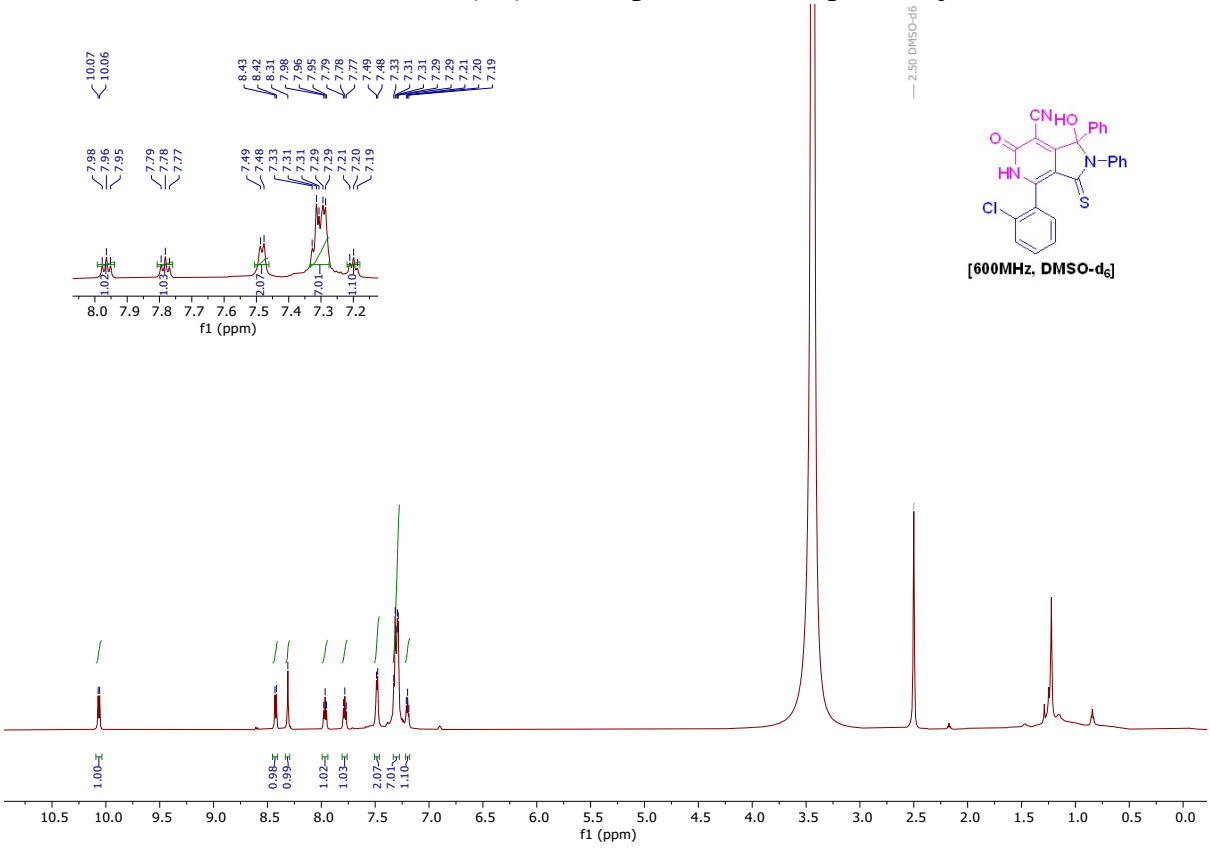


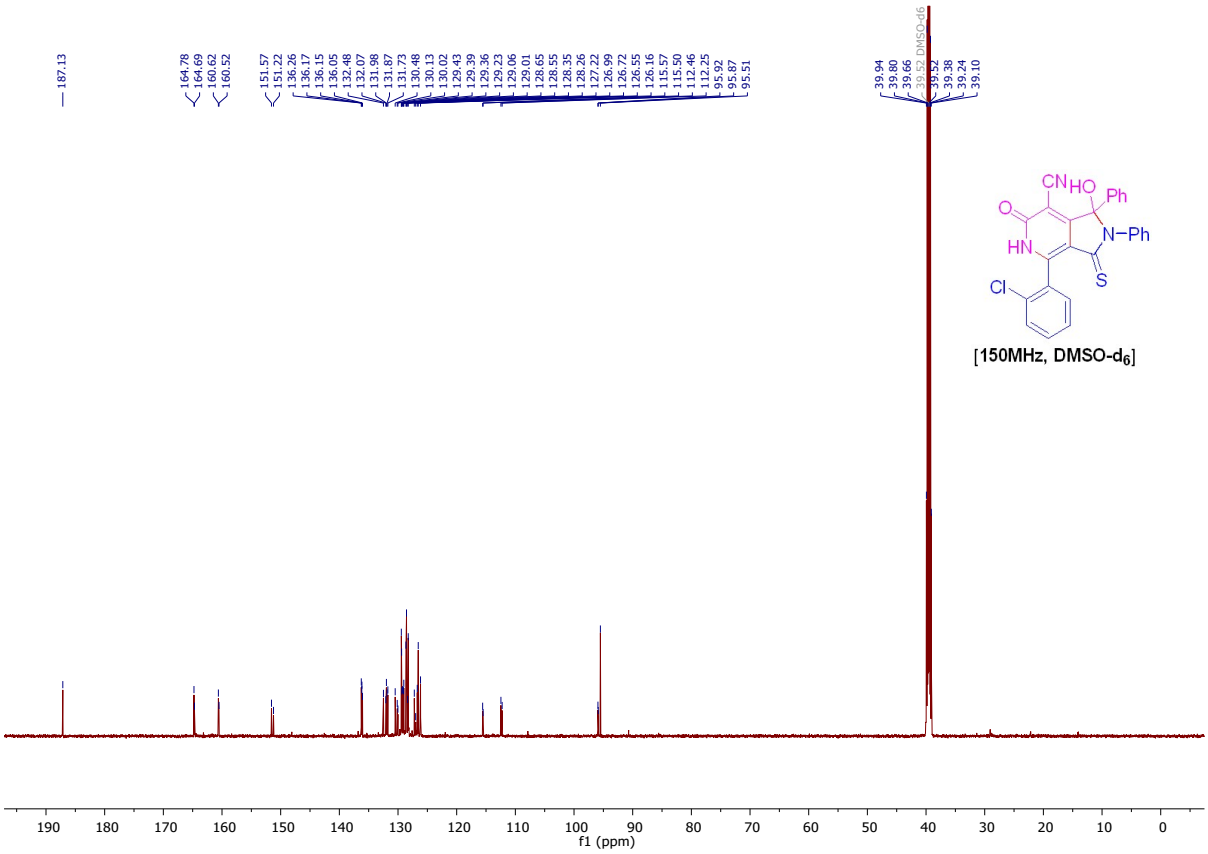


^{19}F NMR spectra of Compound 3i

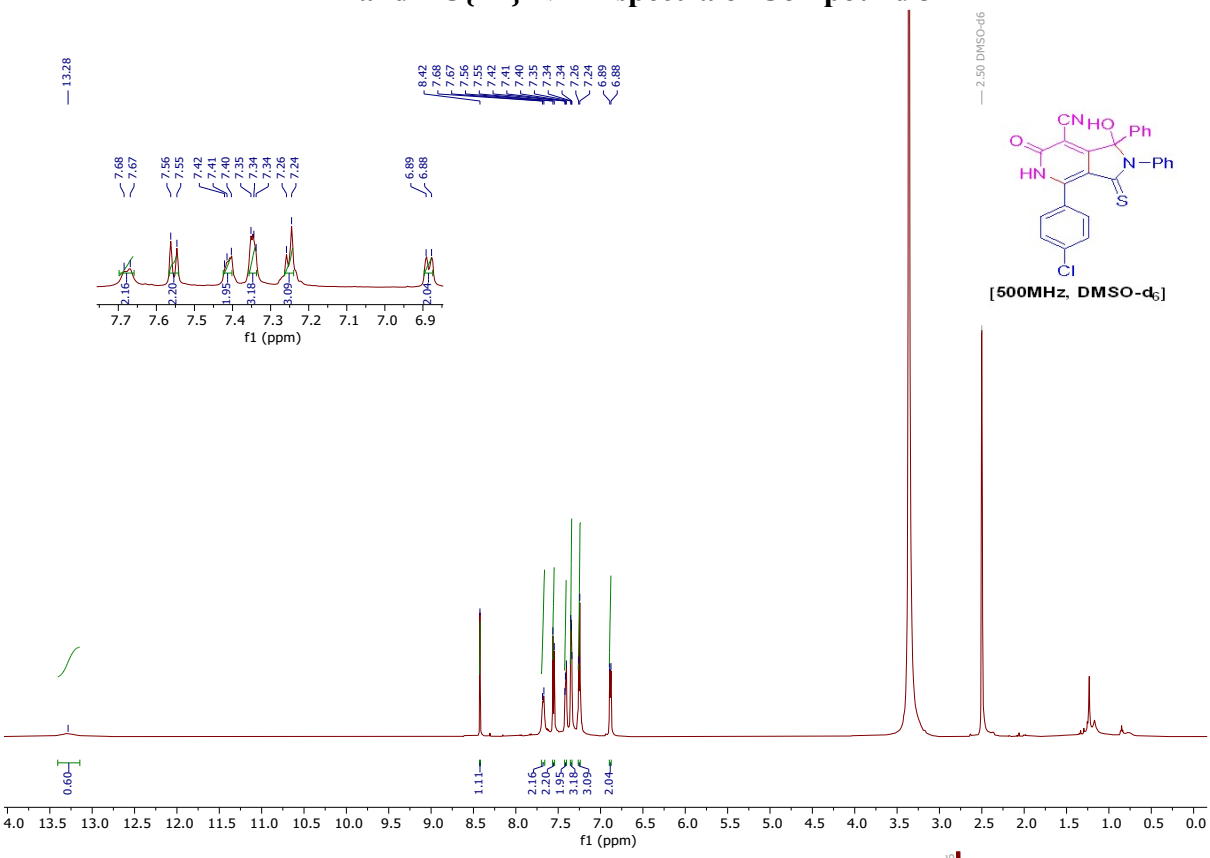


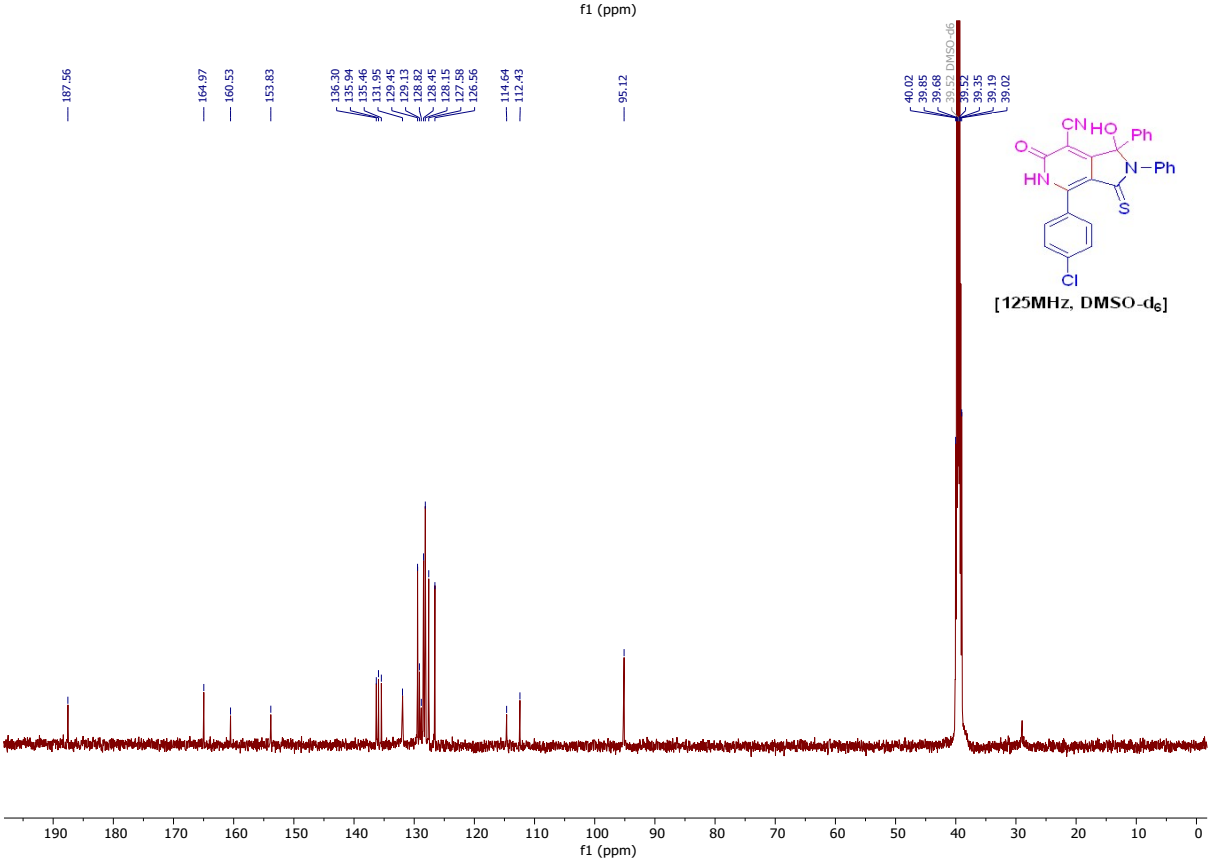
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3j



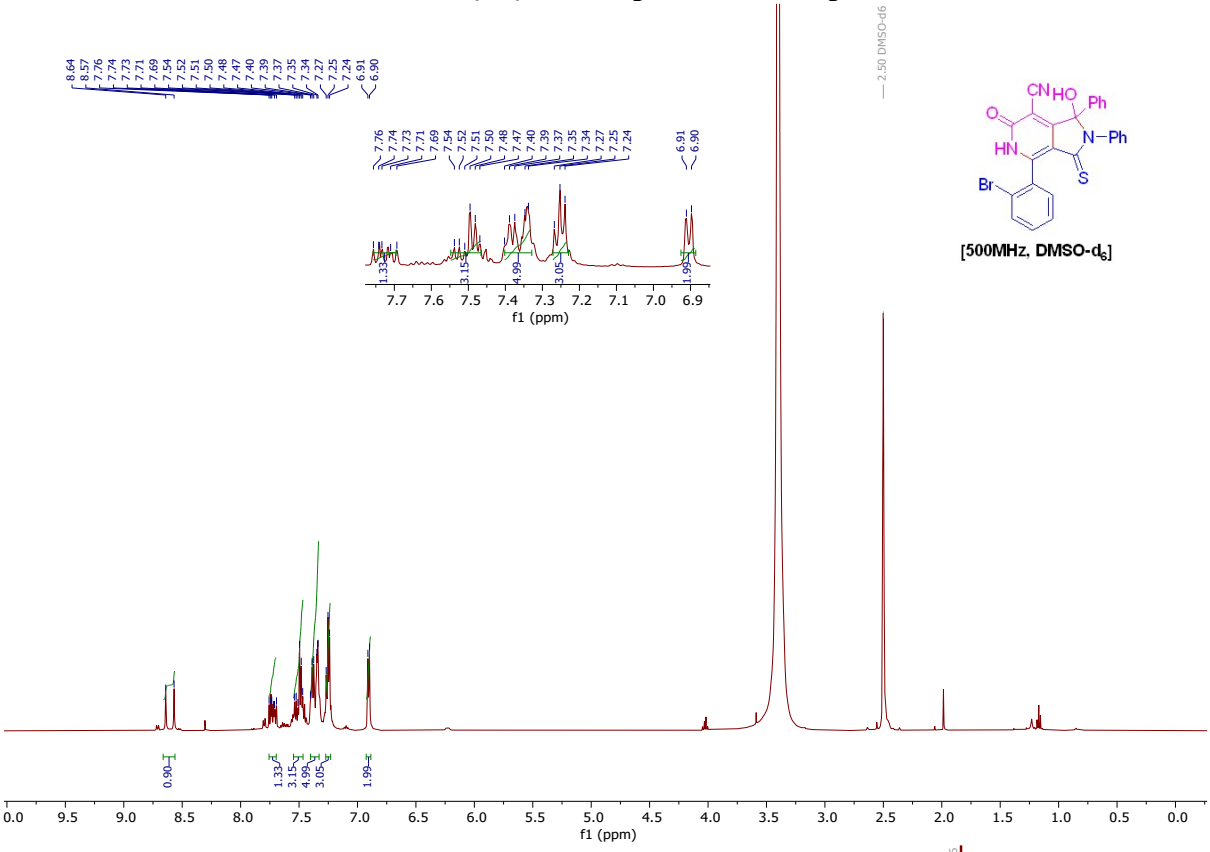


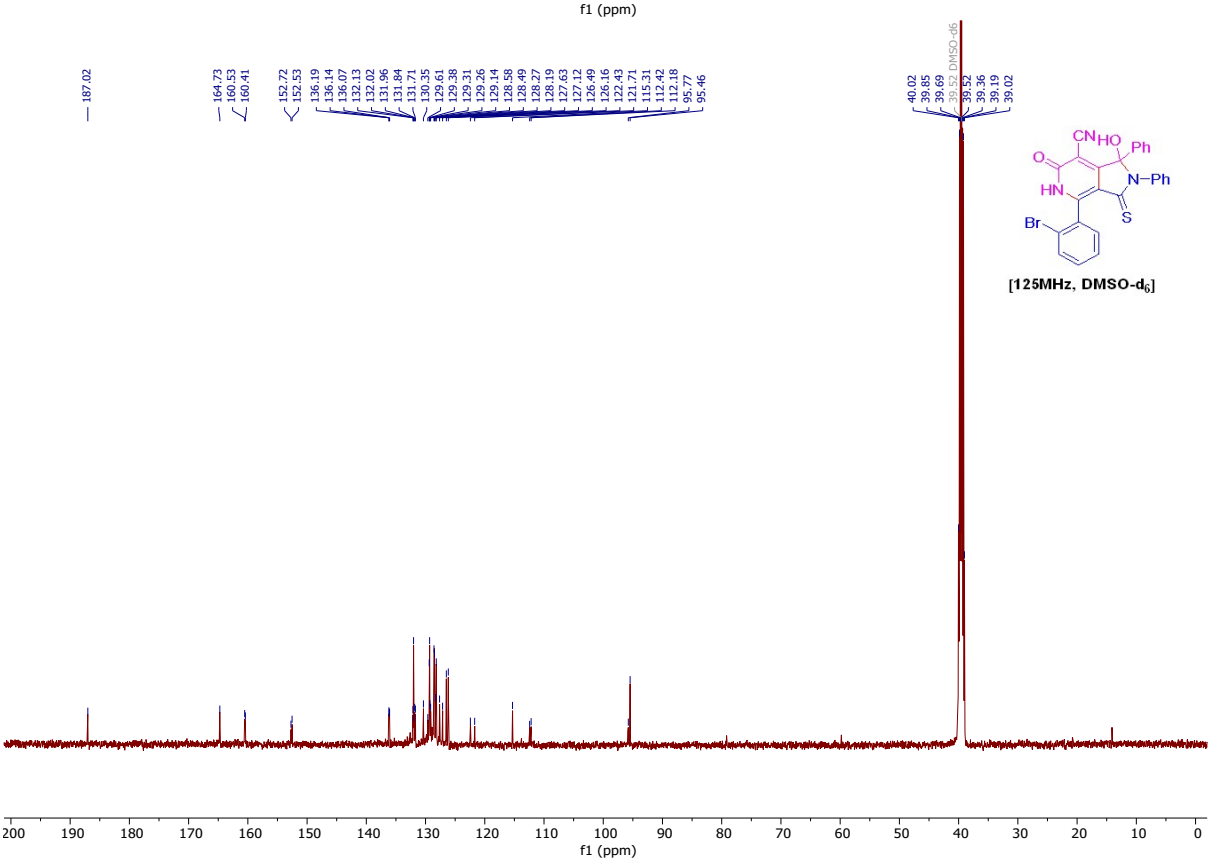
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3k



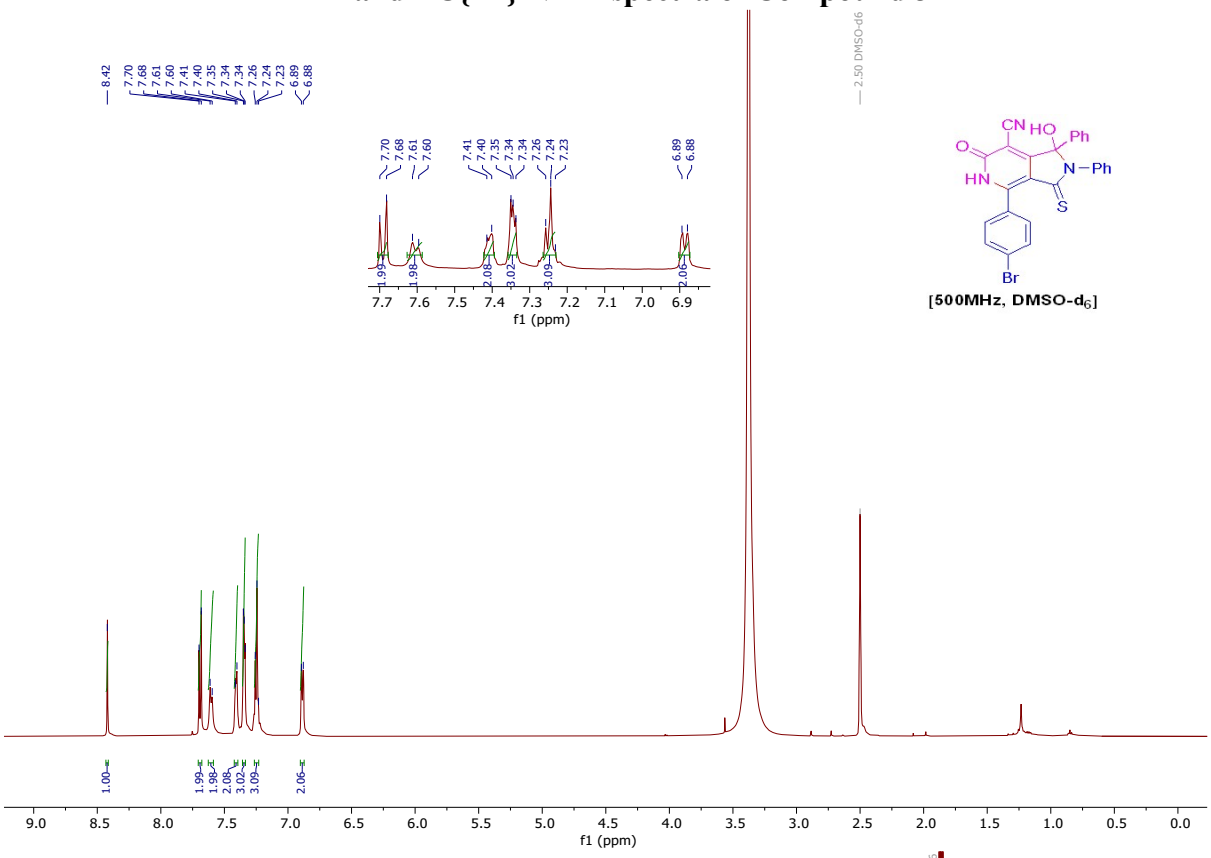


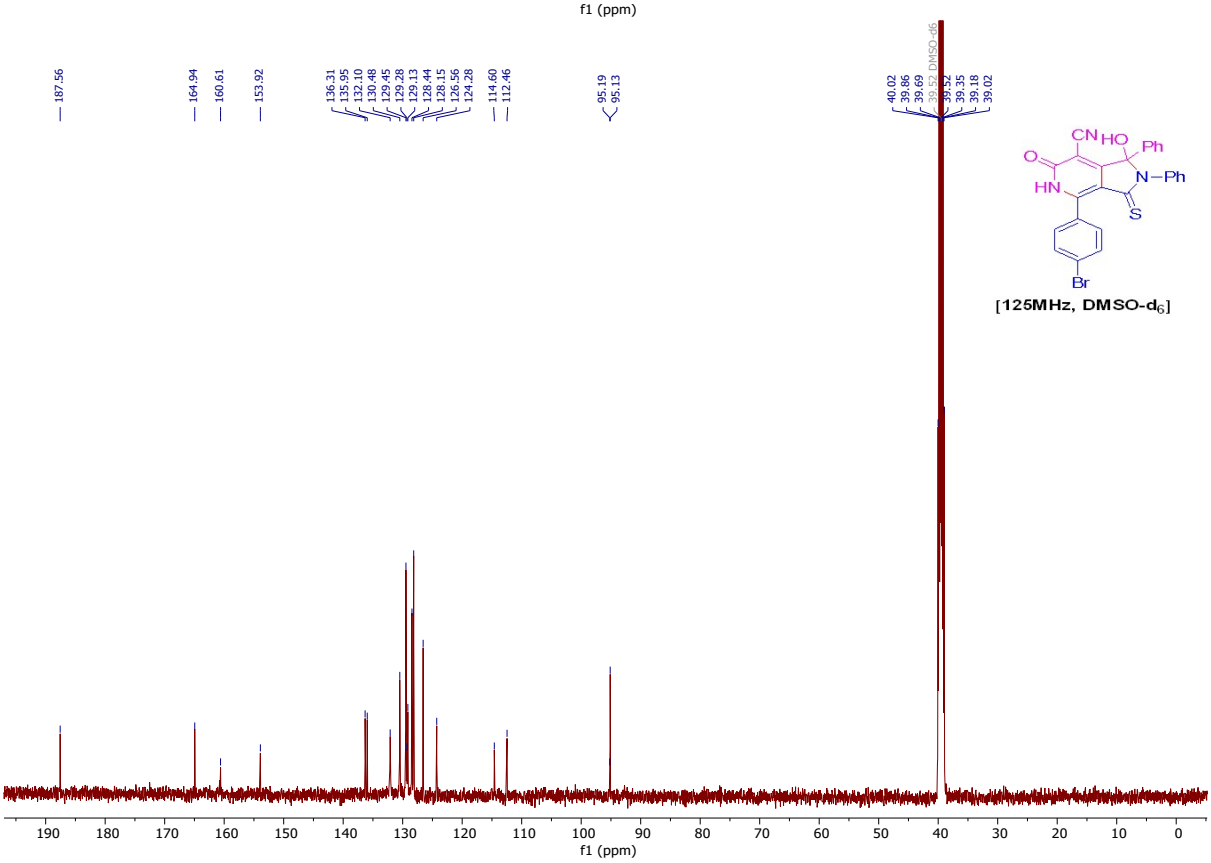
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3l



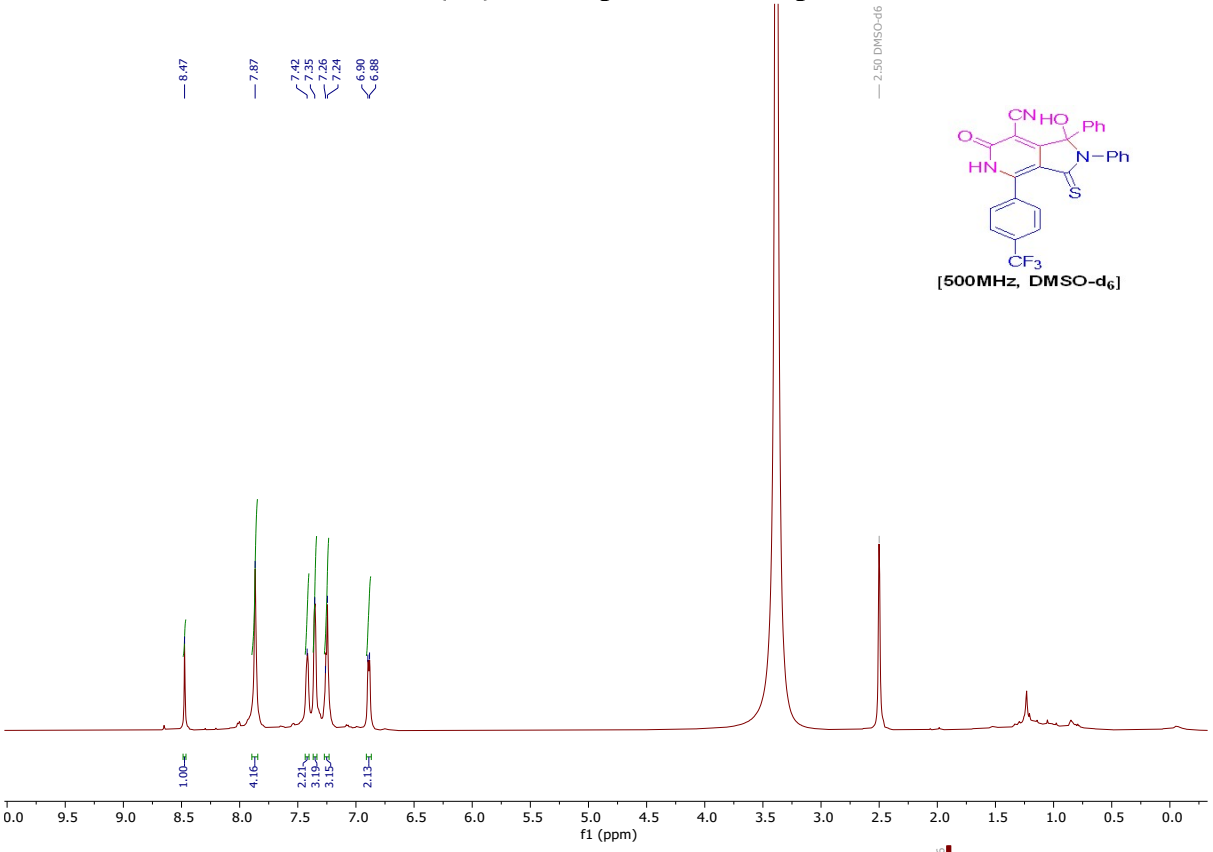


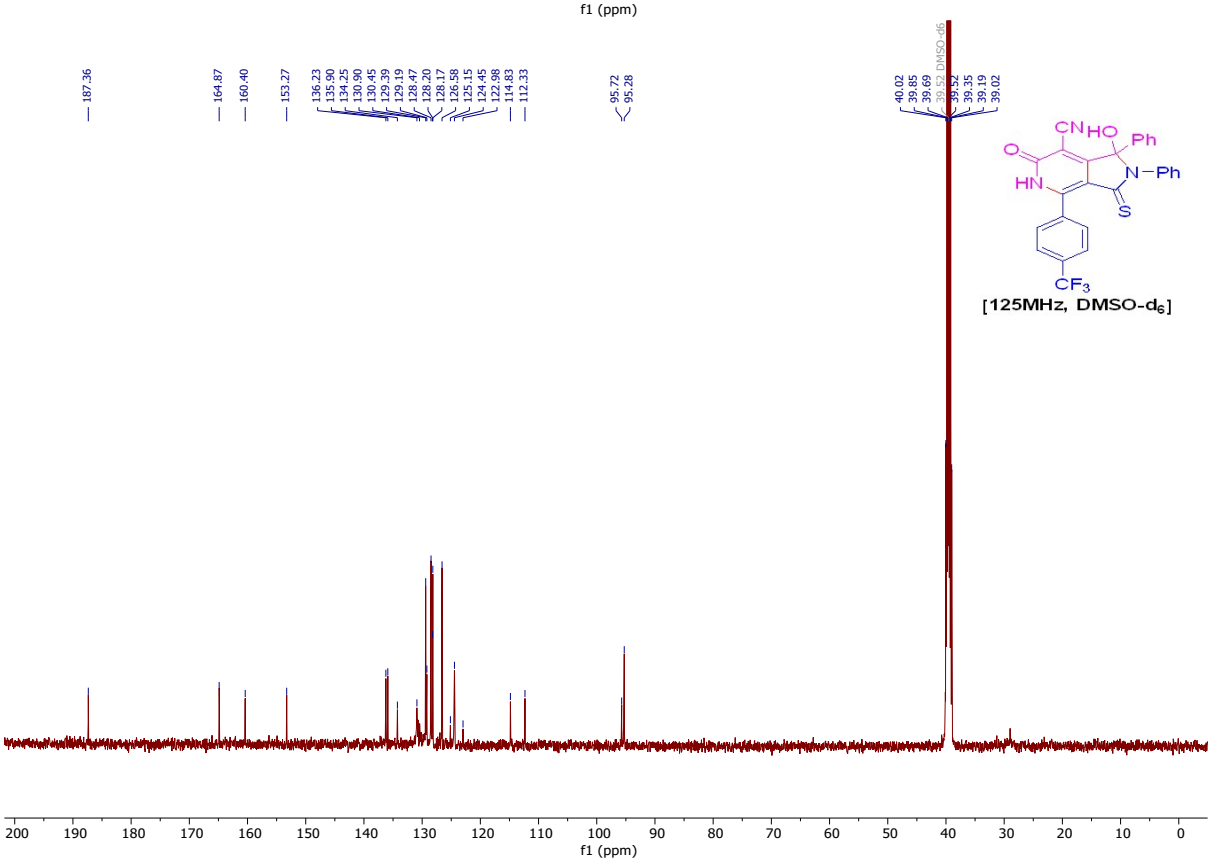
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3m



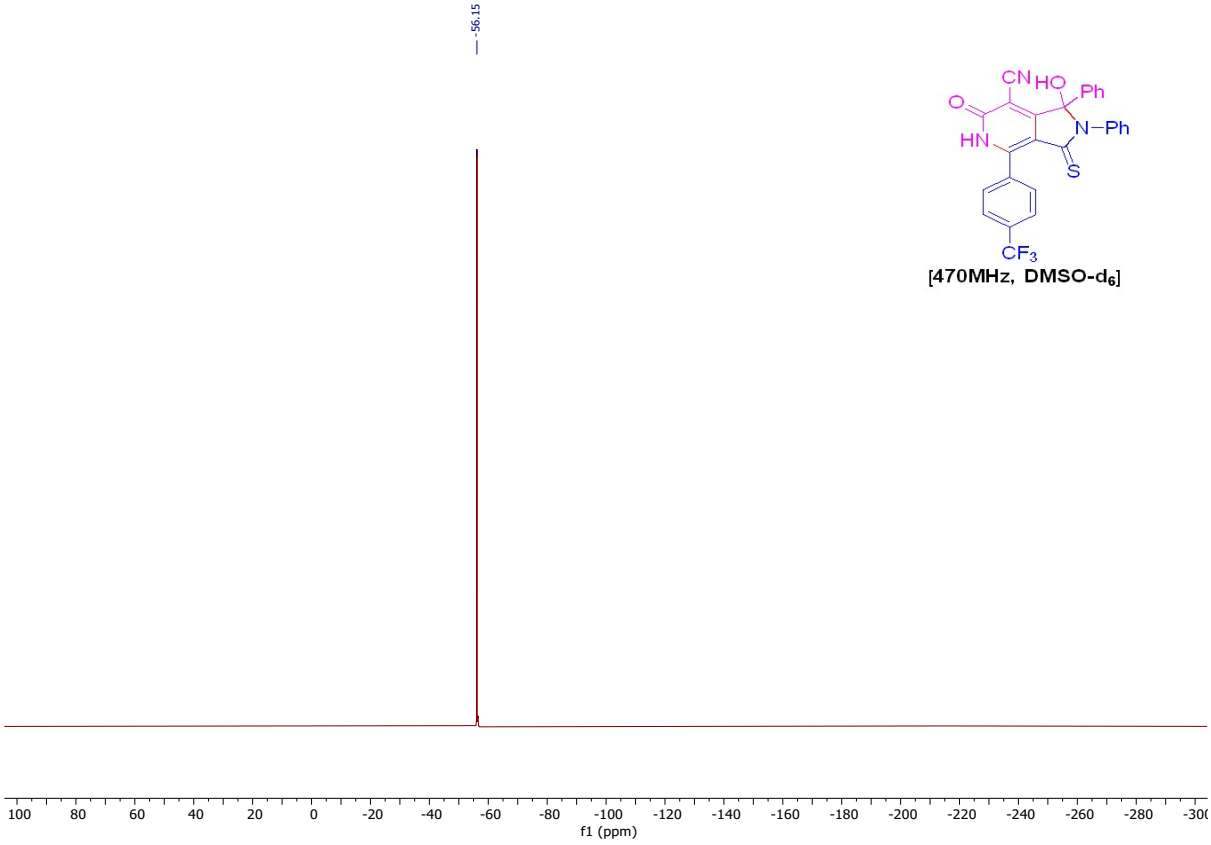


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3n

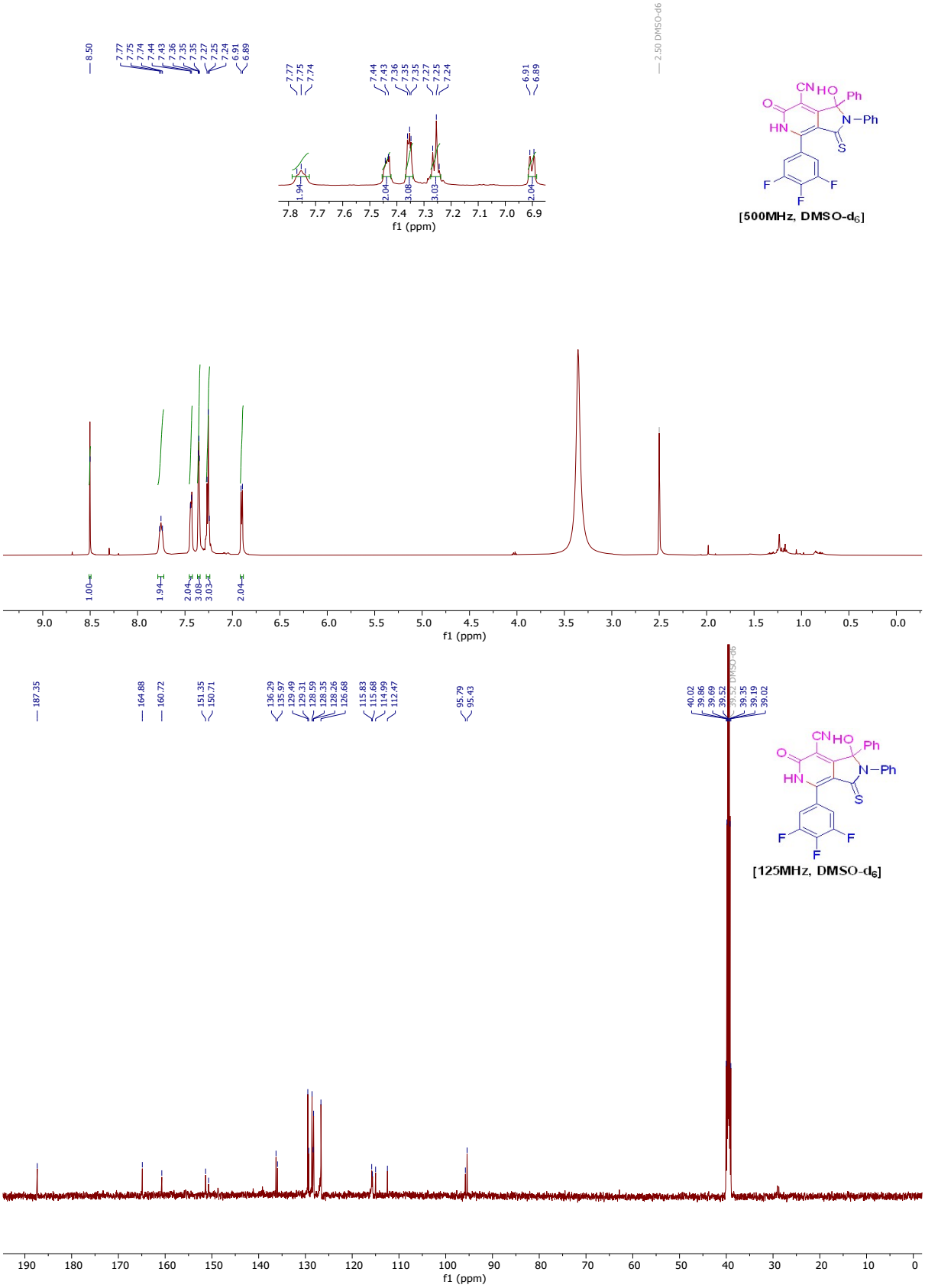




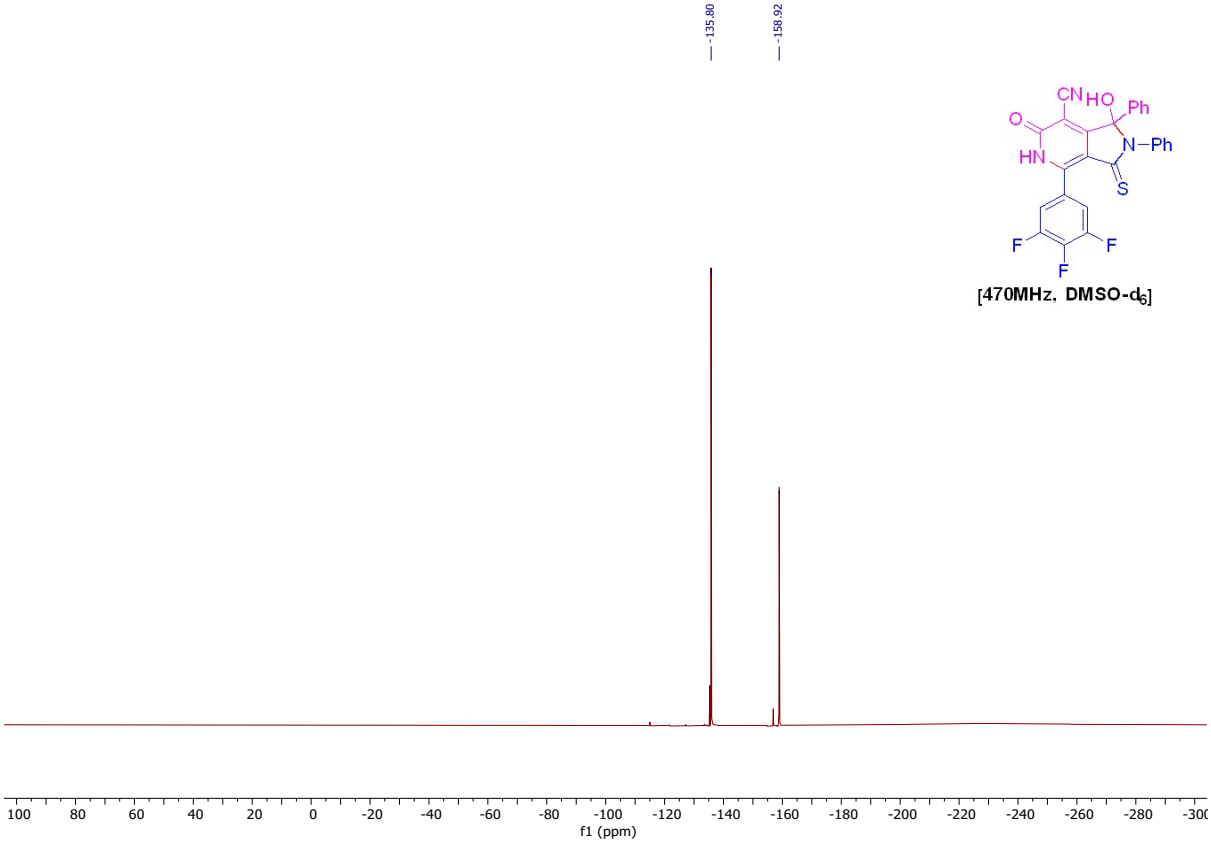
^{19}F NMR spectra of Compound 3n



^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3o

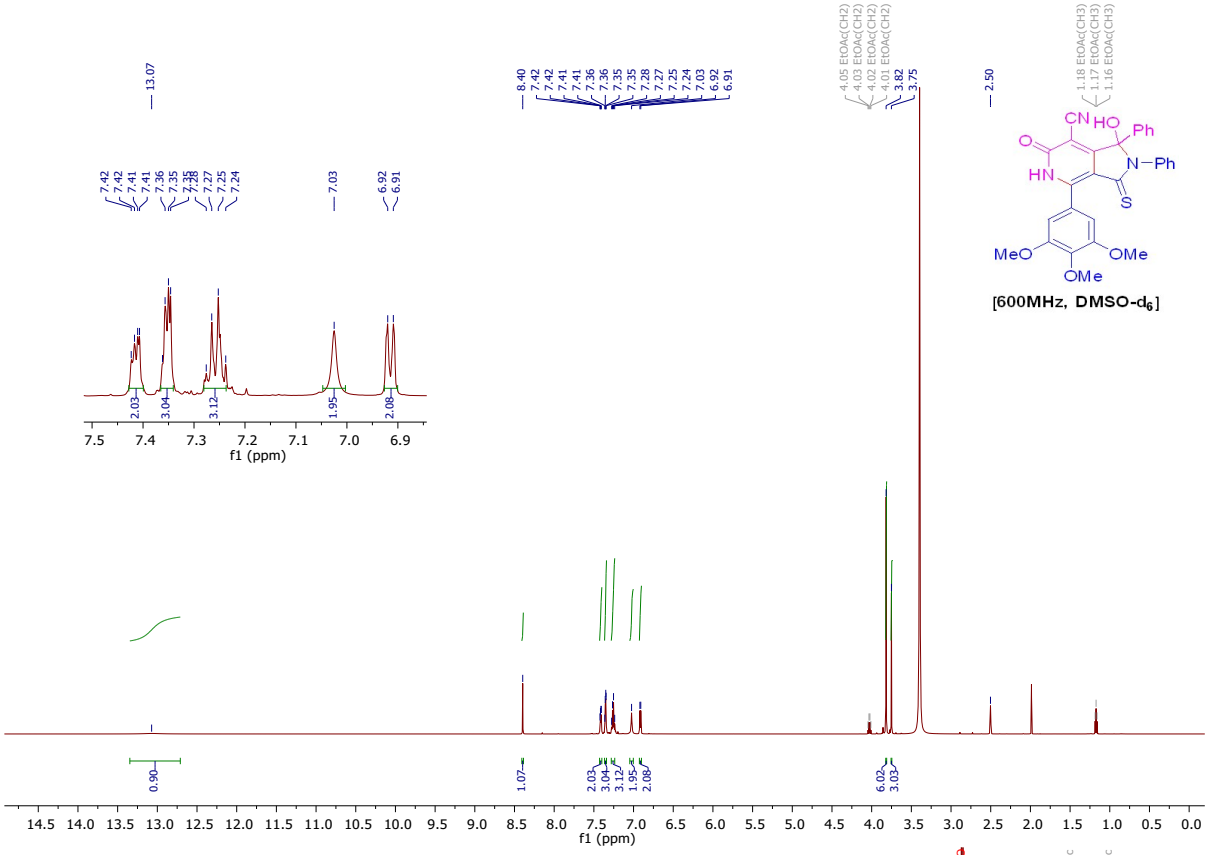


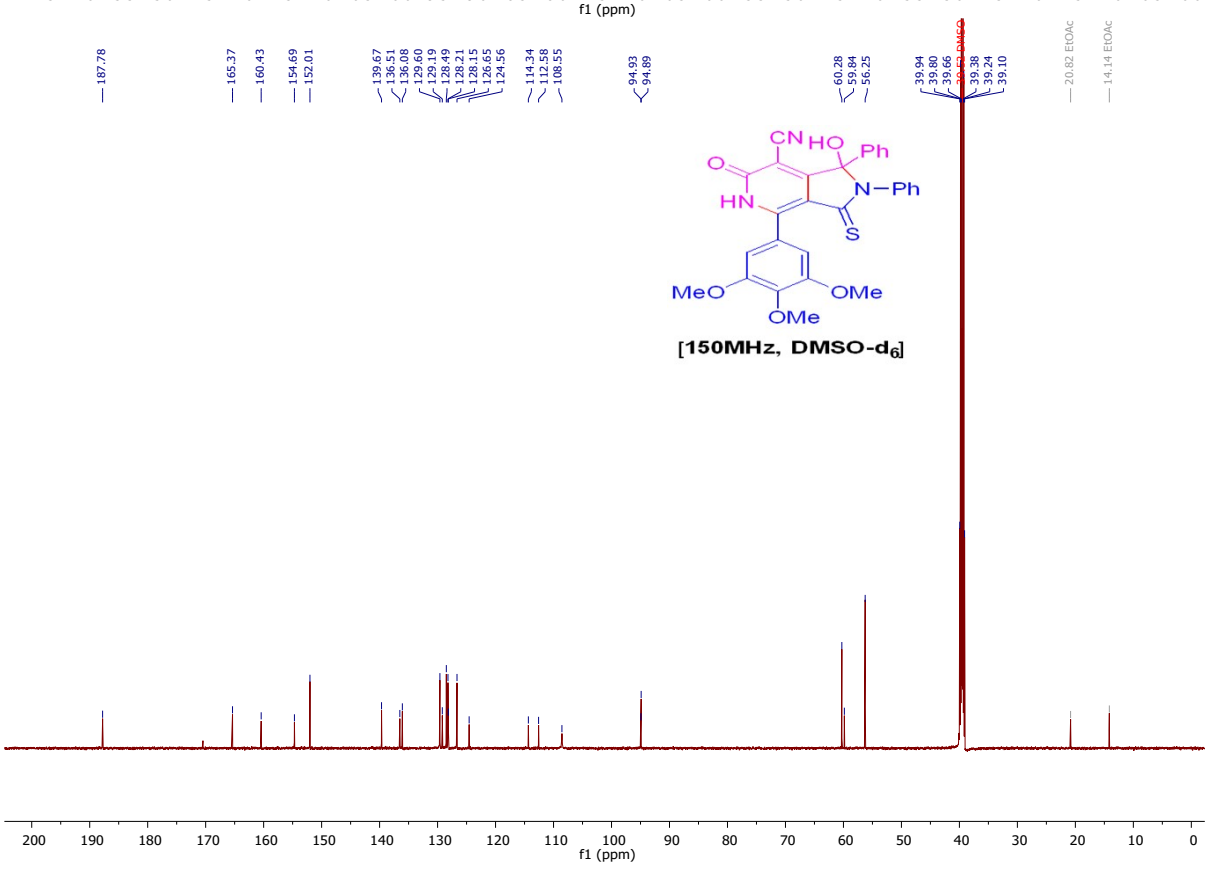
^{19}F NMR spectra of Compound 3o



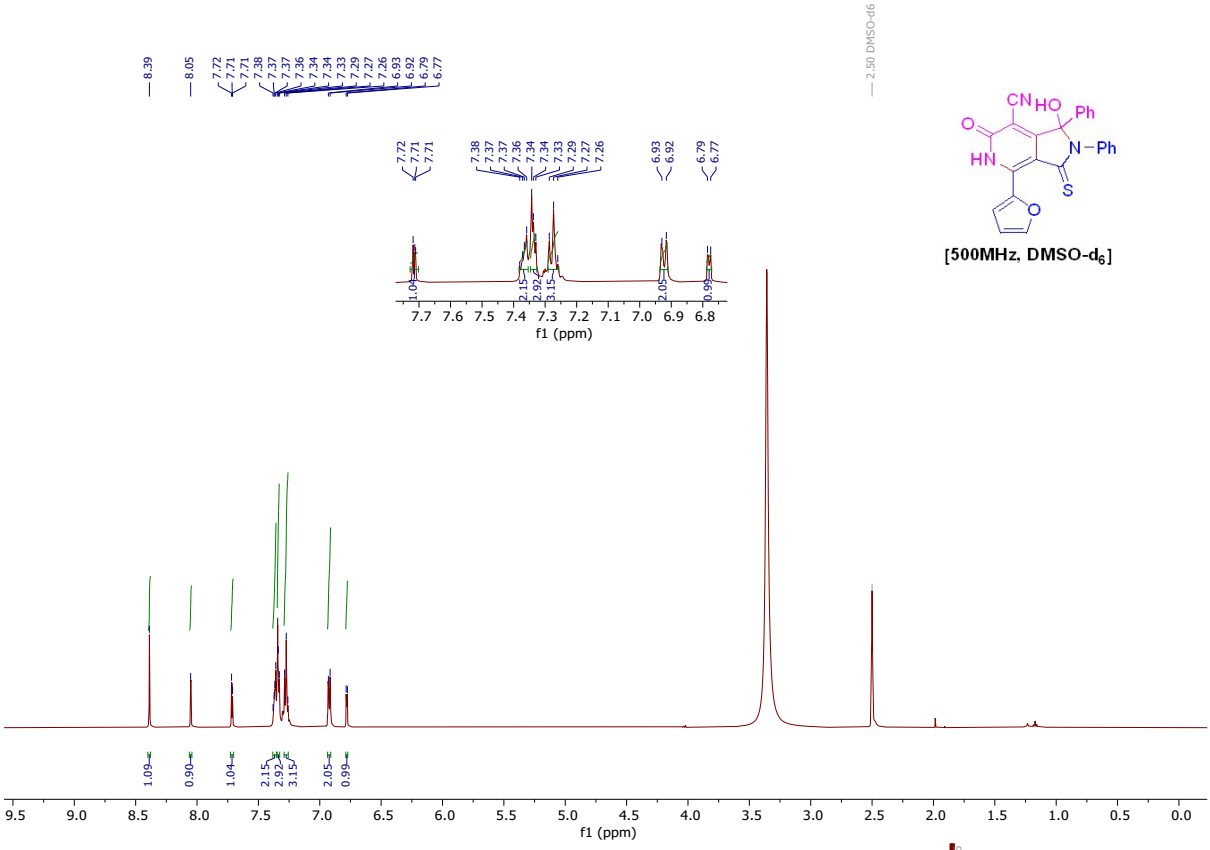
[470MHz, DMSO-d_6]

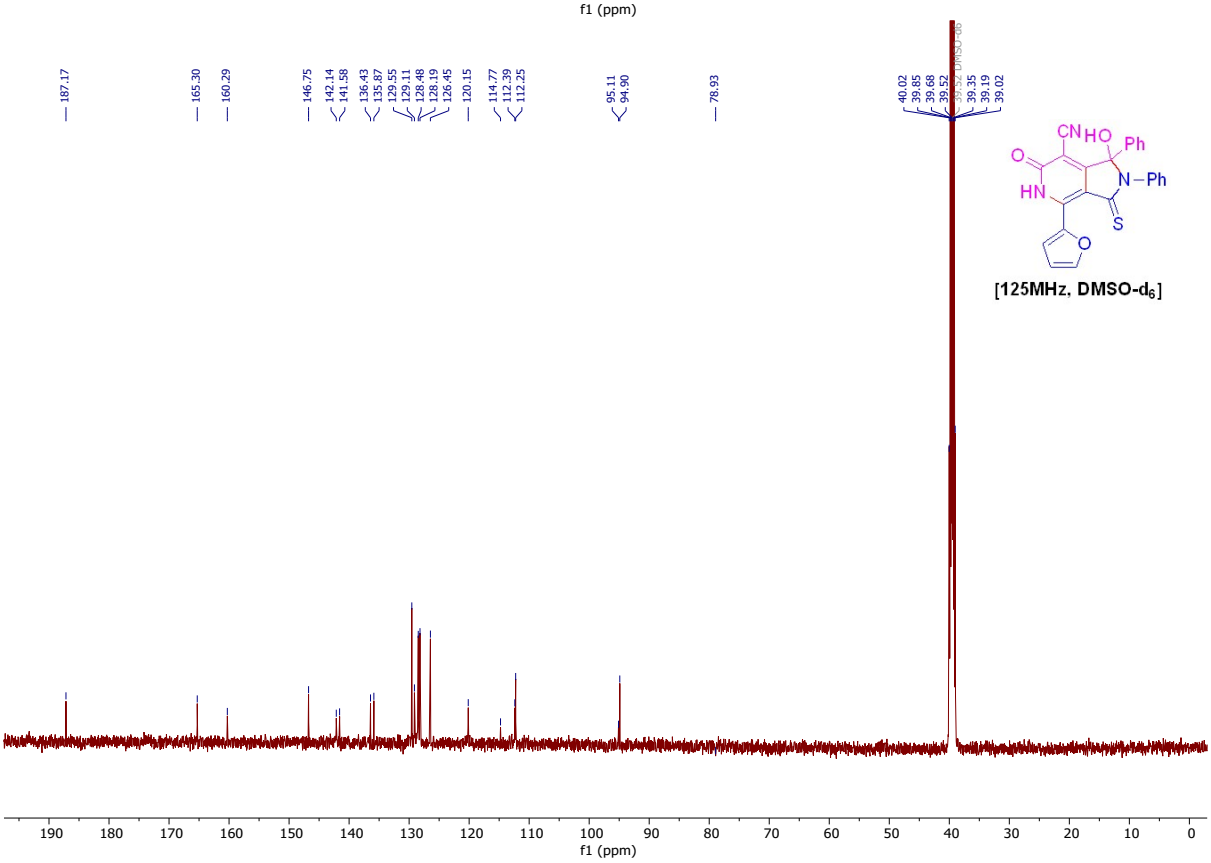
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3p



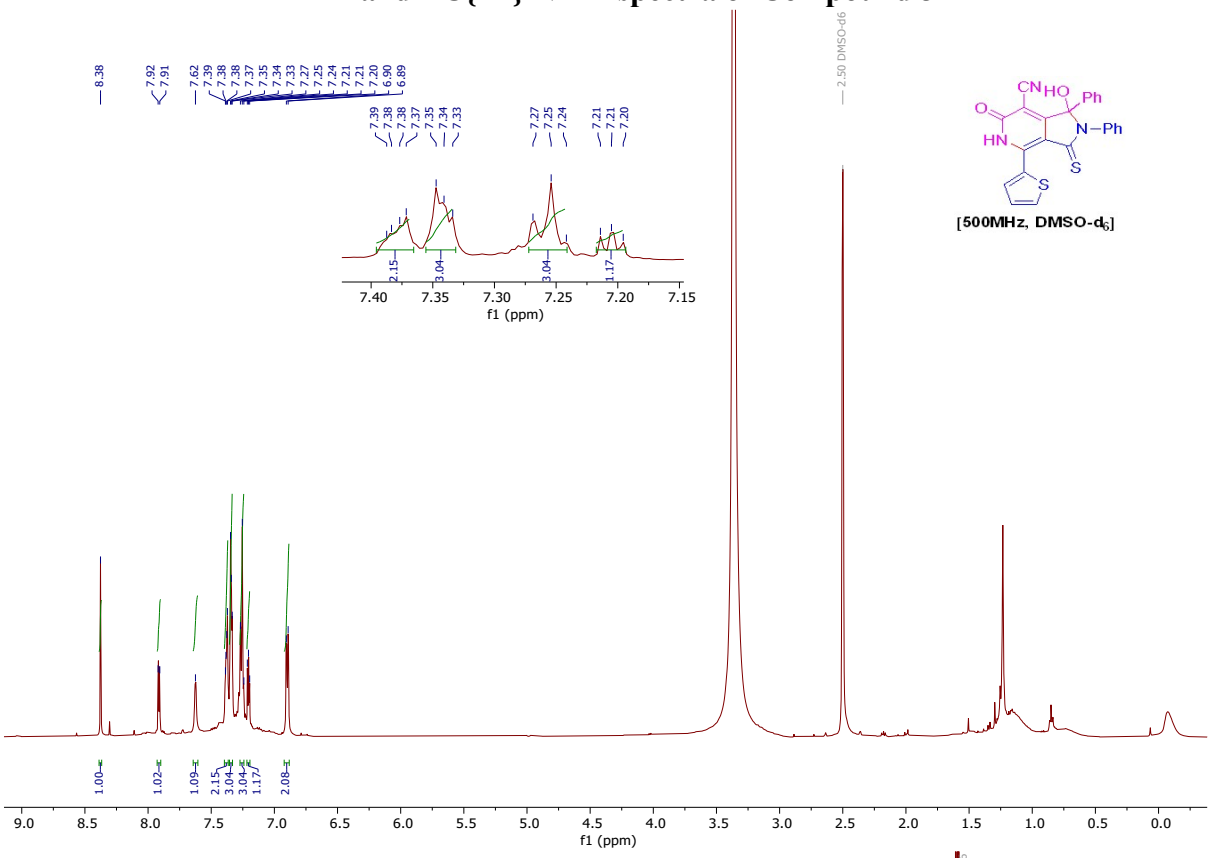


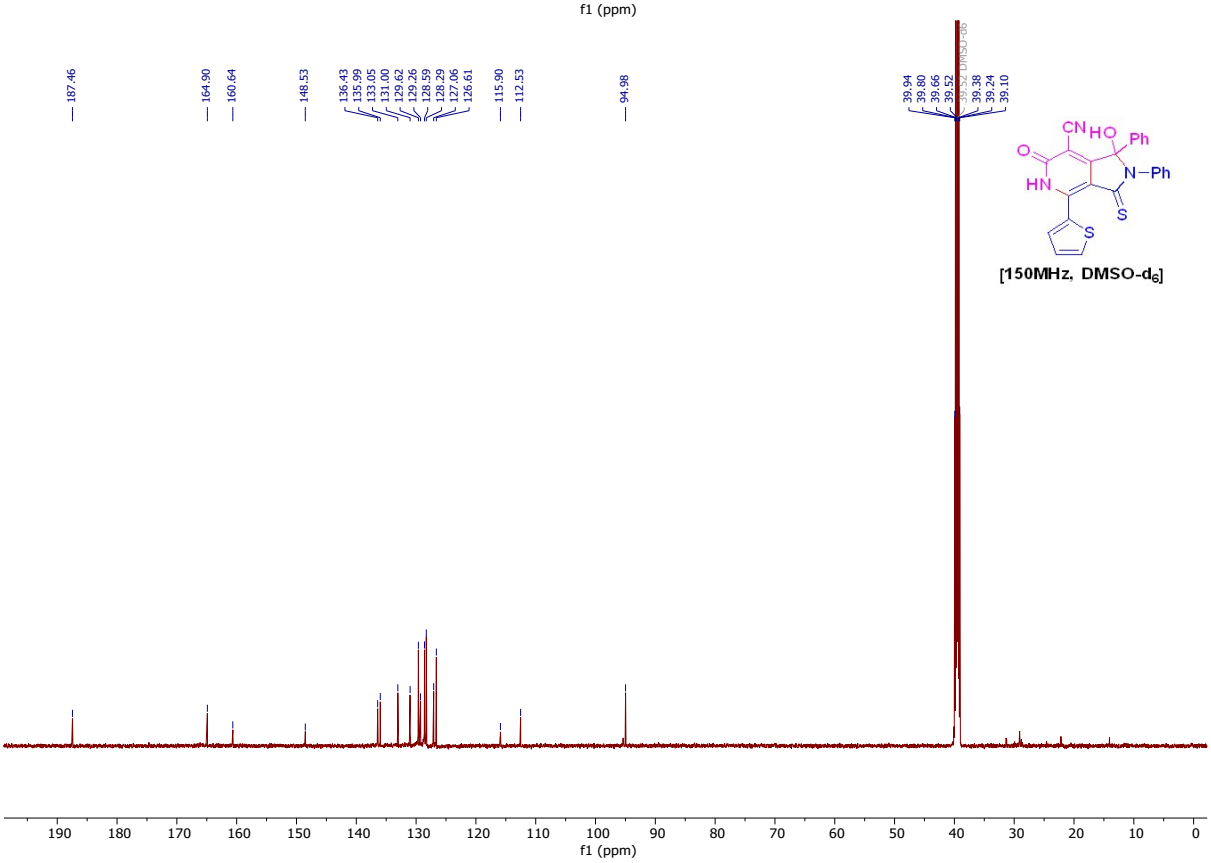
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3q



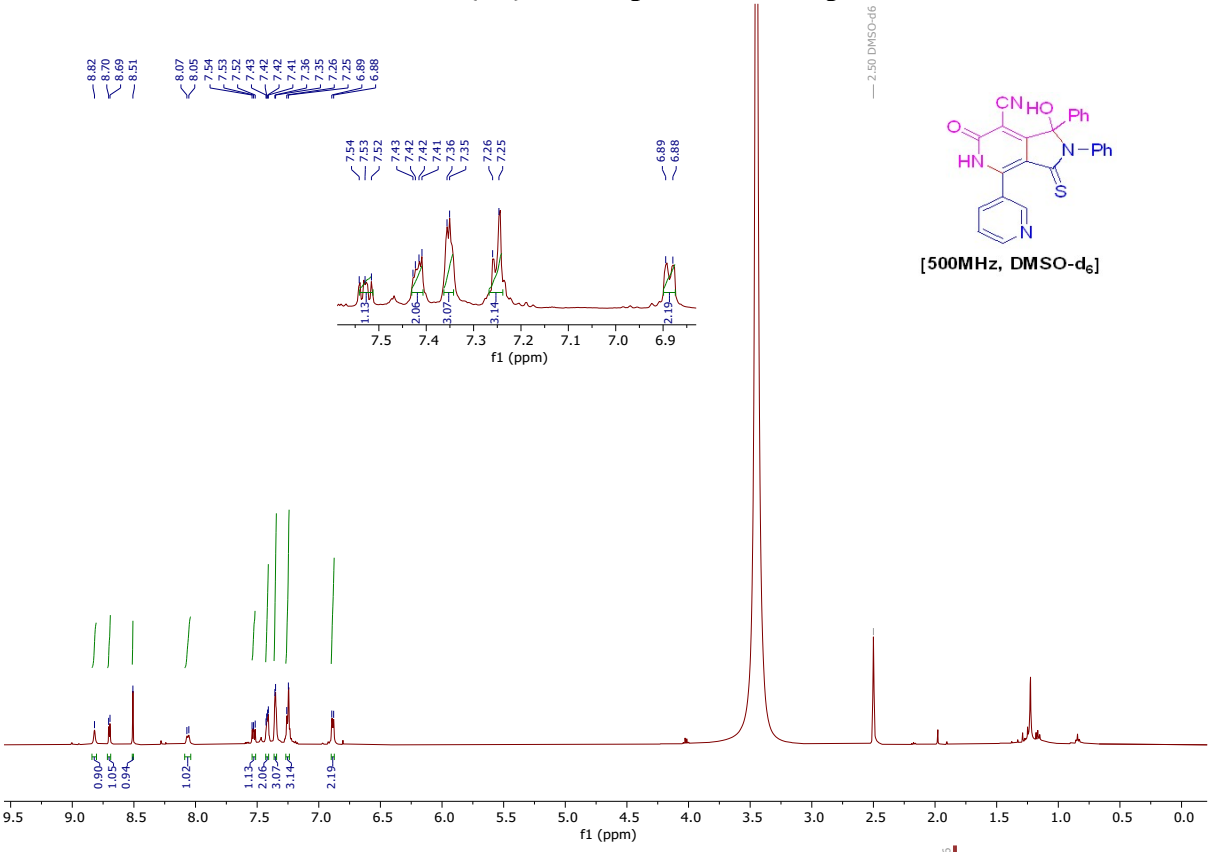


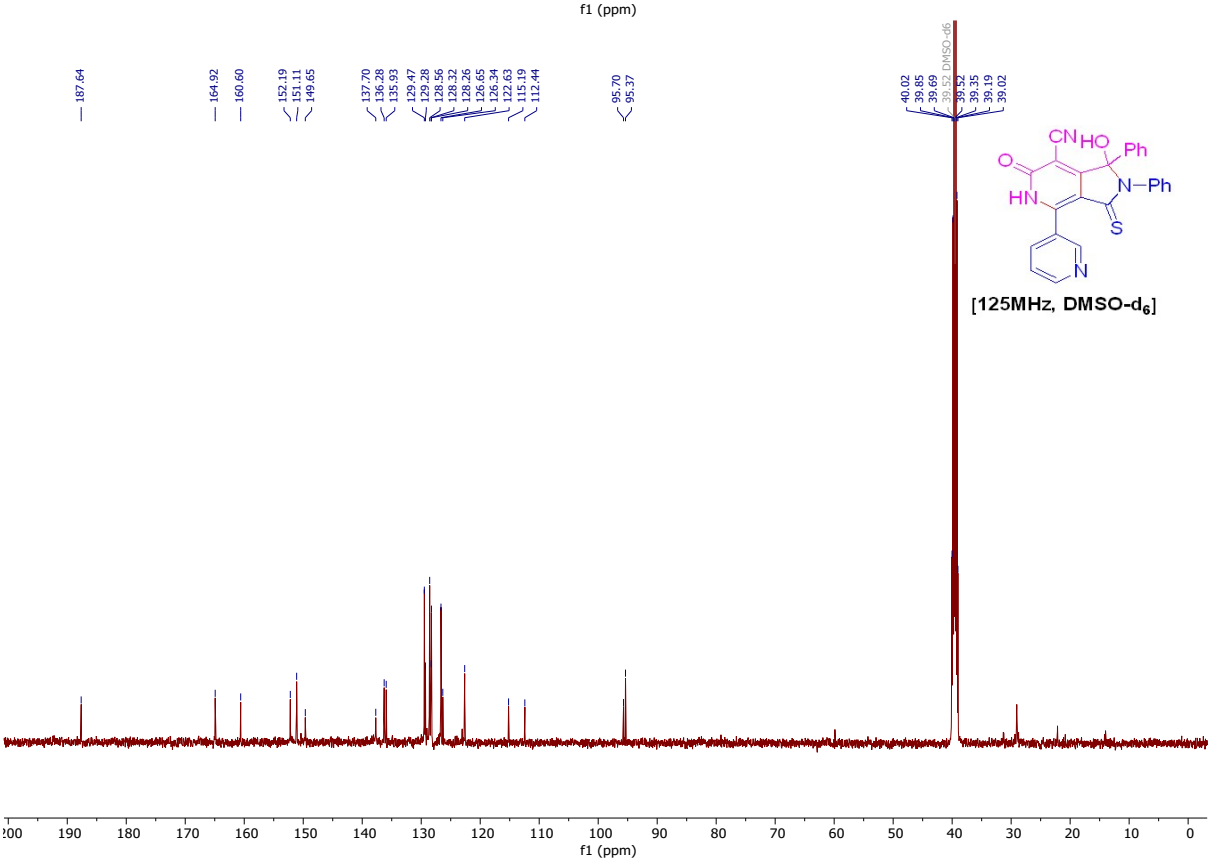
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3r



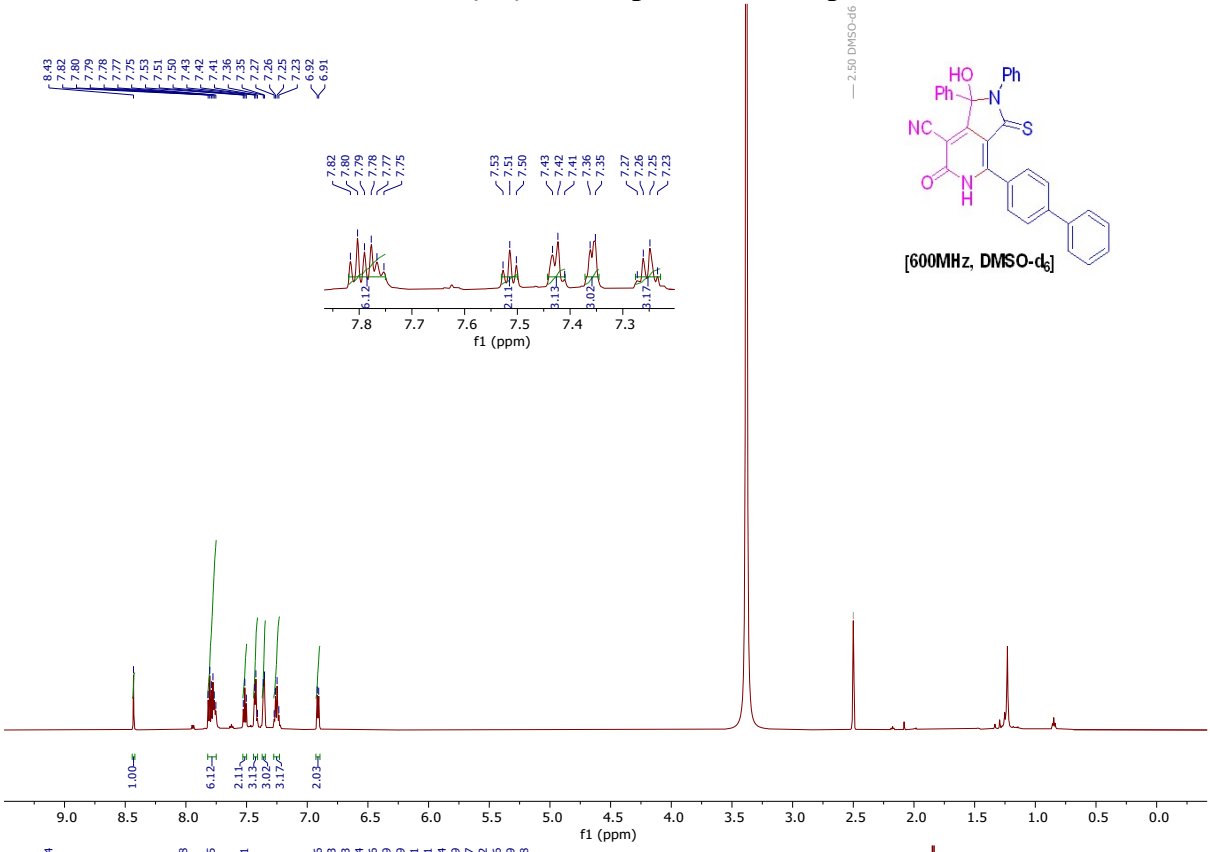


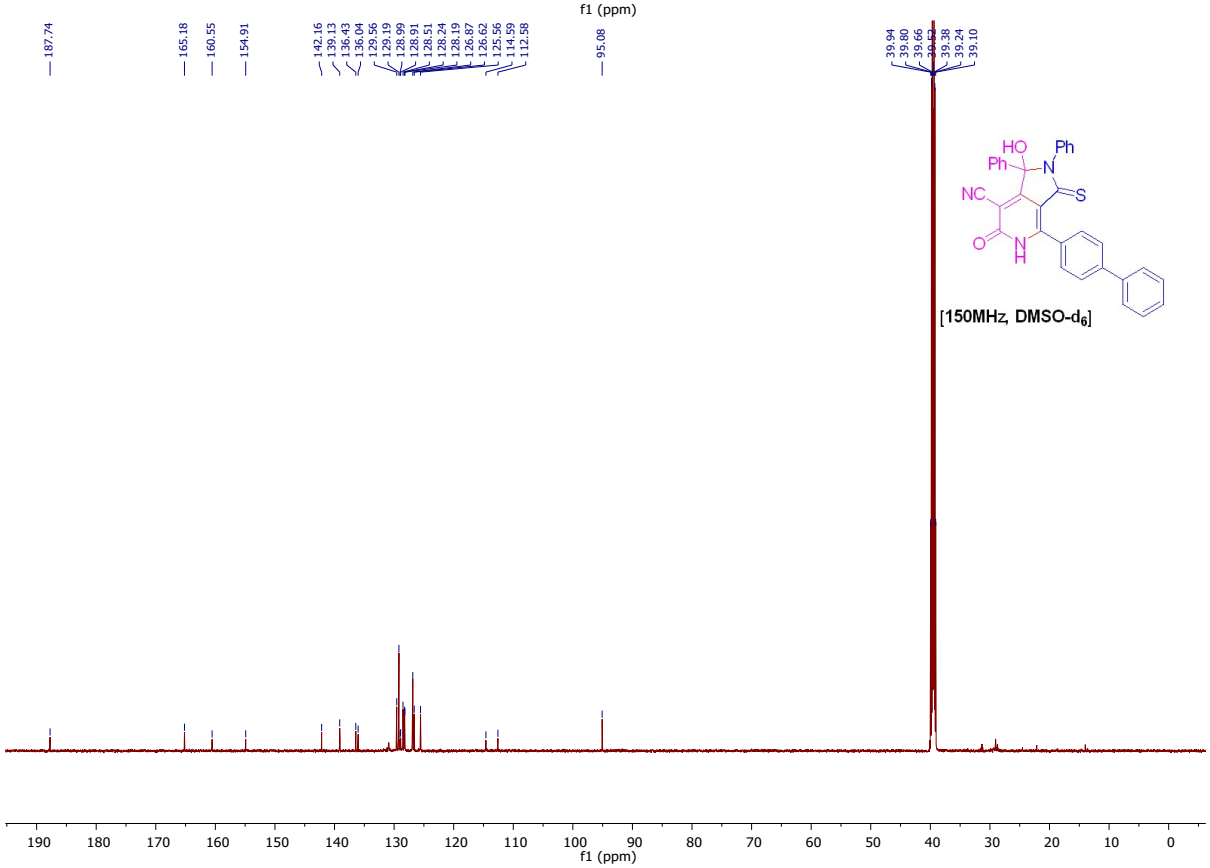
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3s



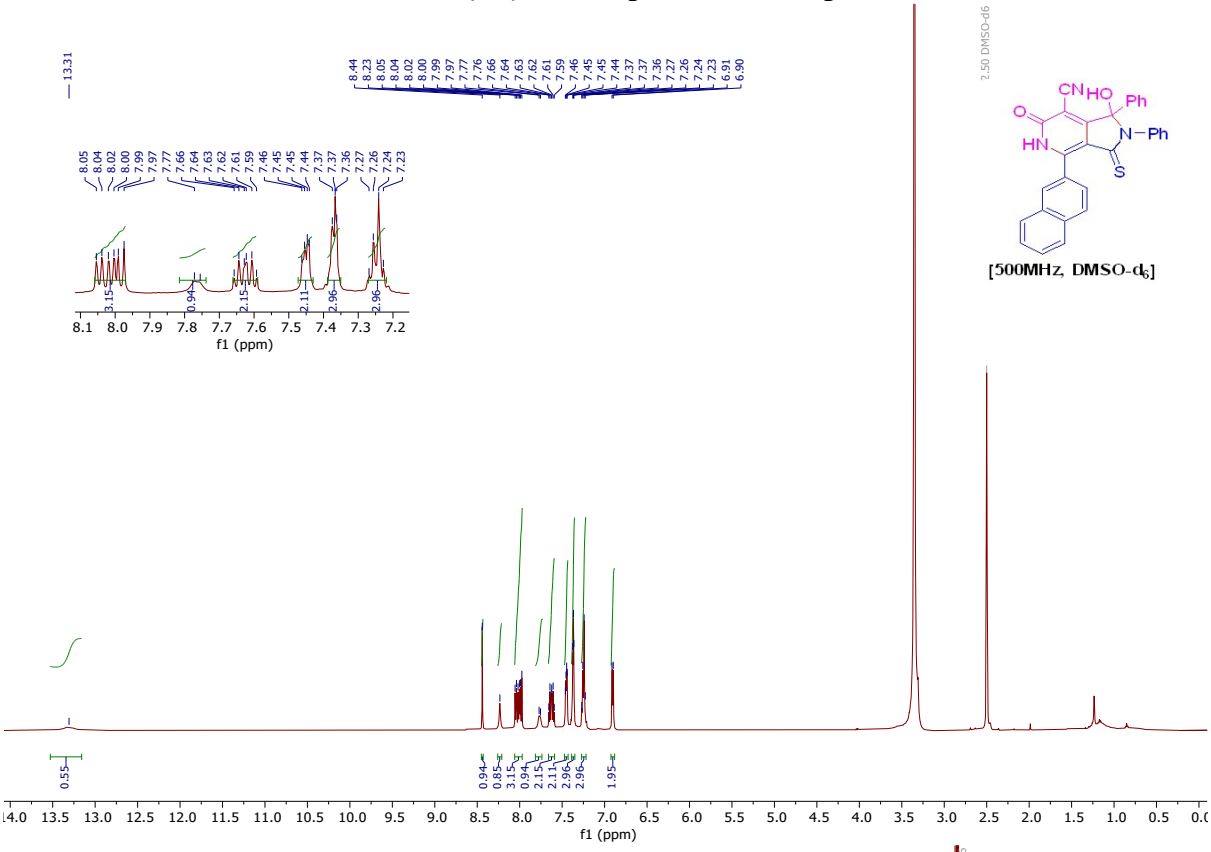


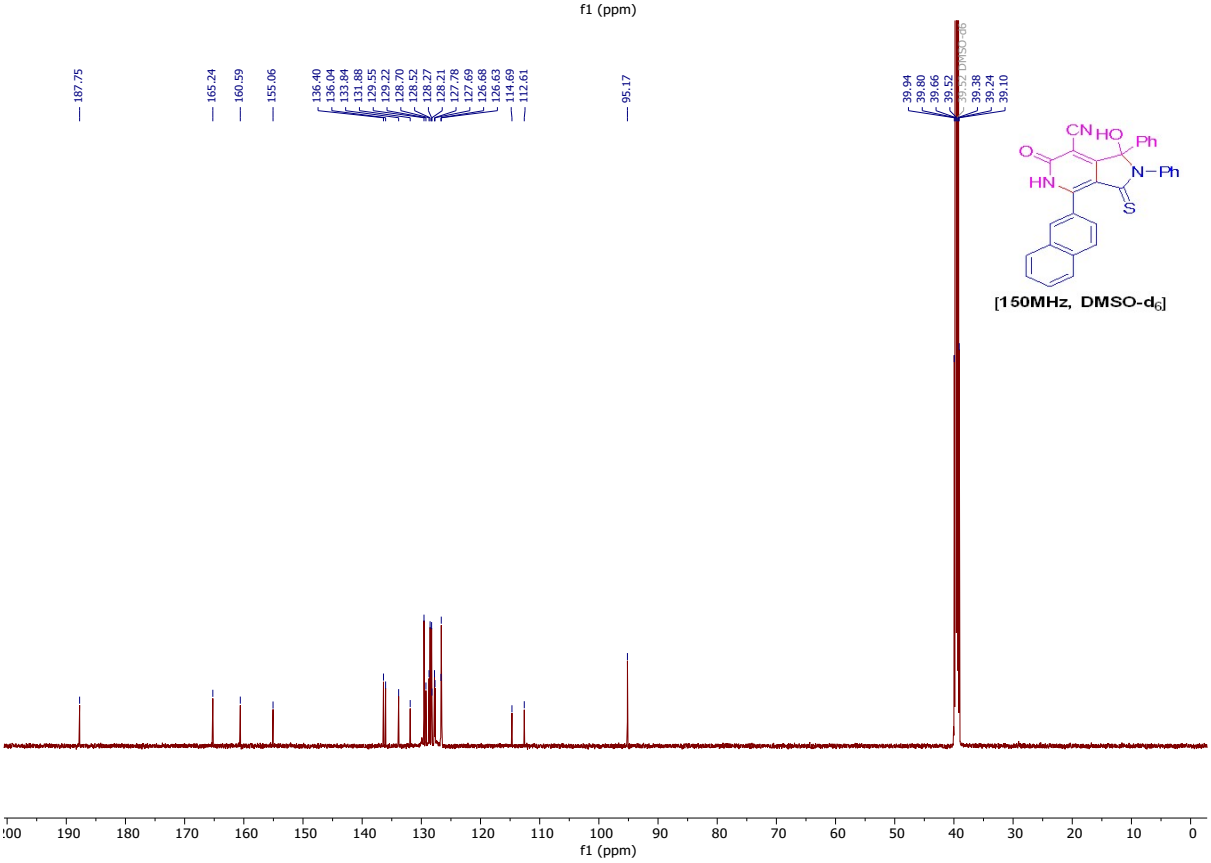
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3t



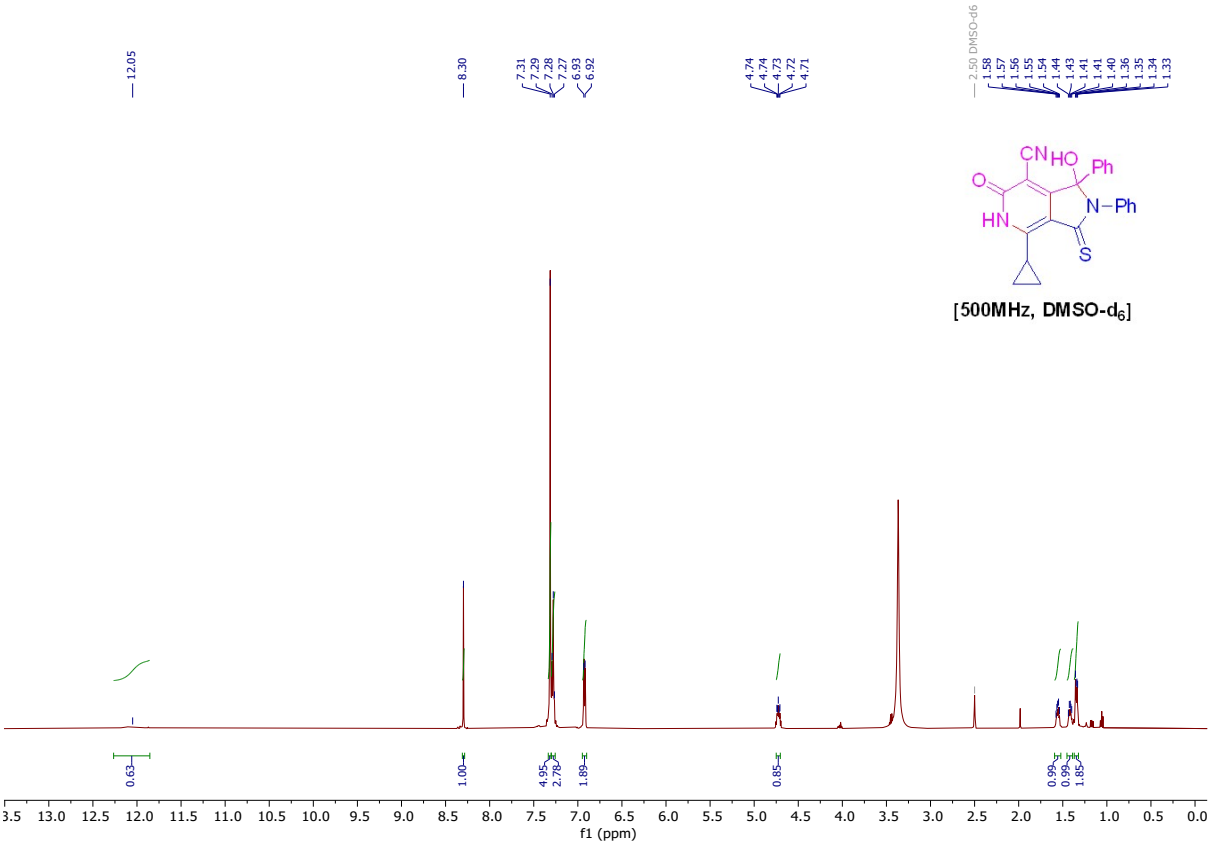


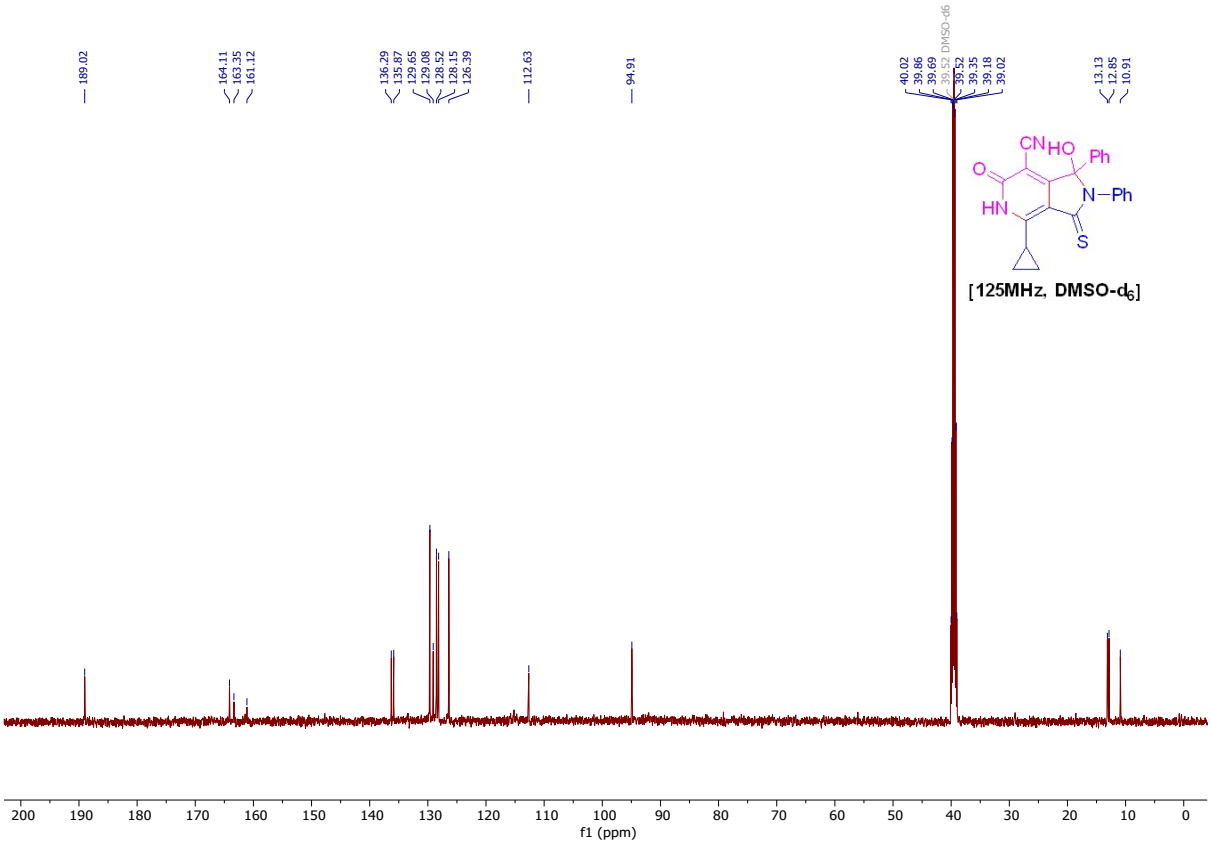
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3u



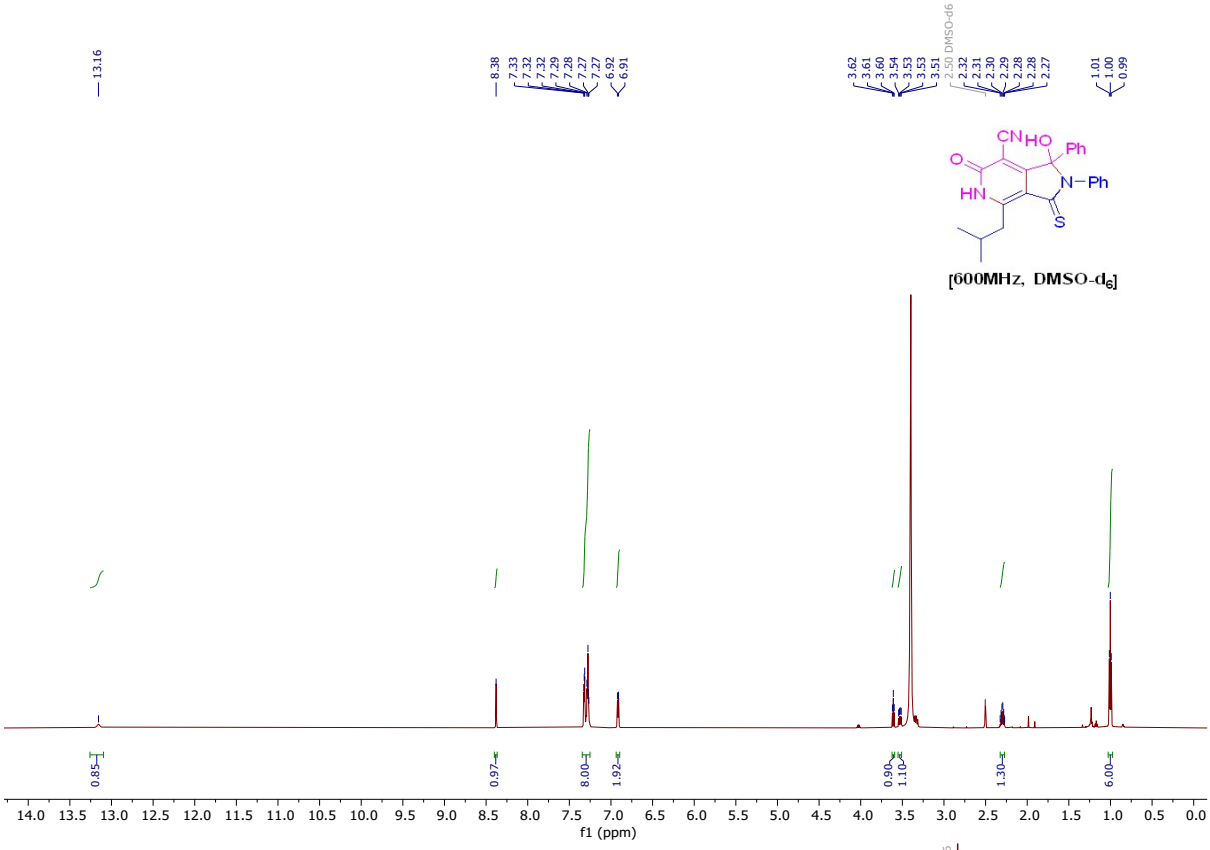


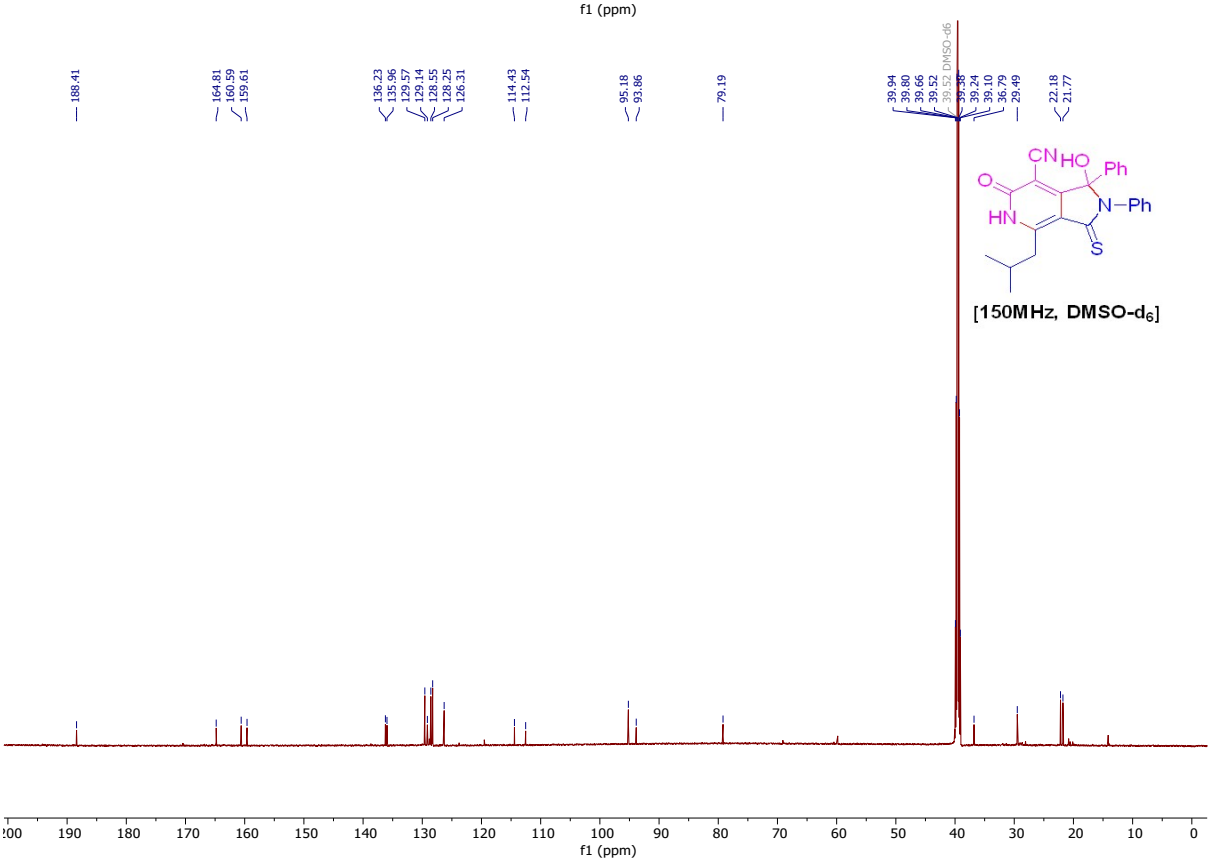
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3v



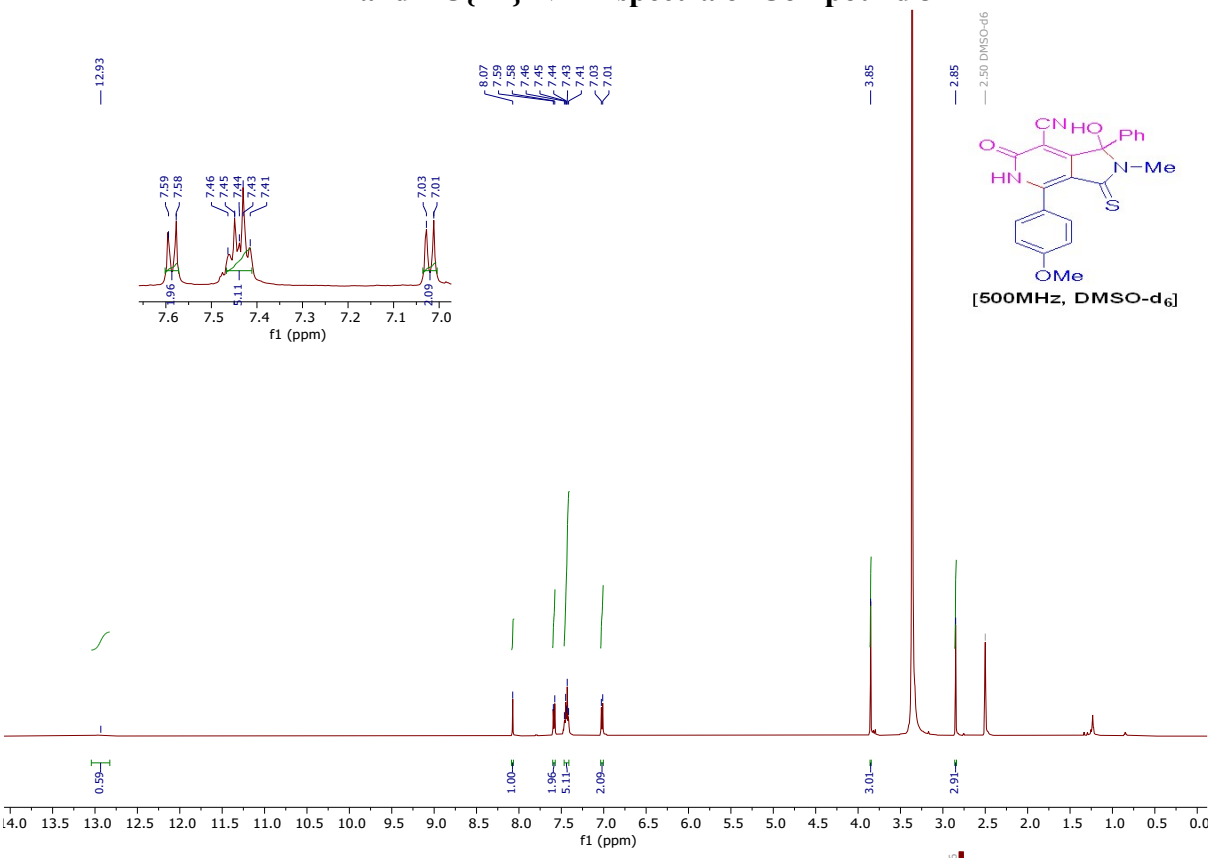


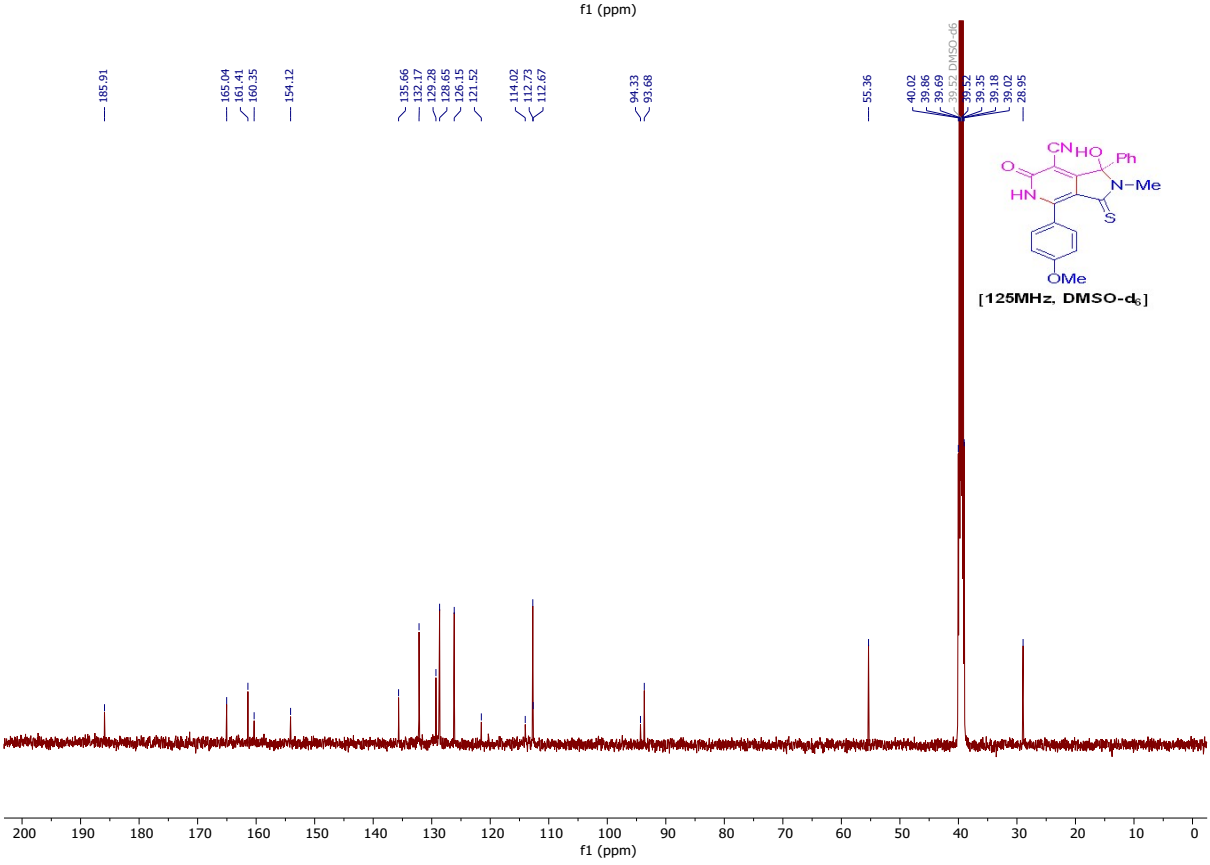
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3w



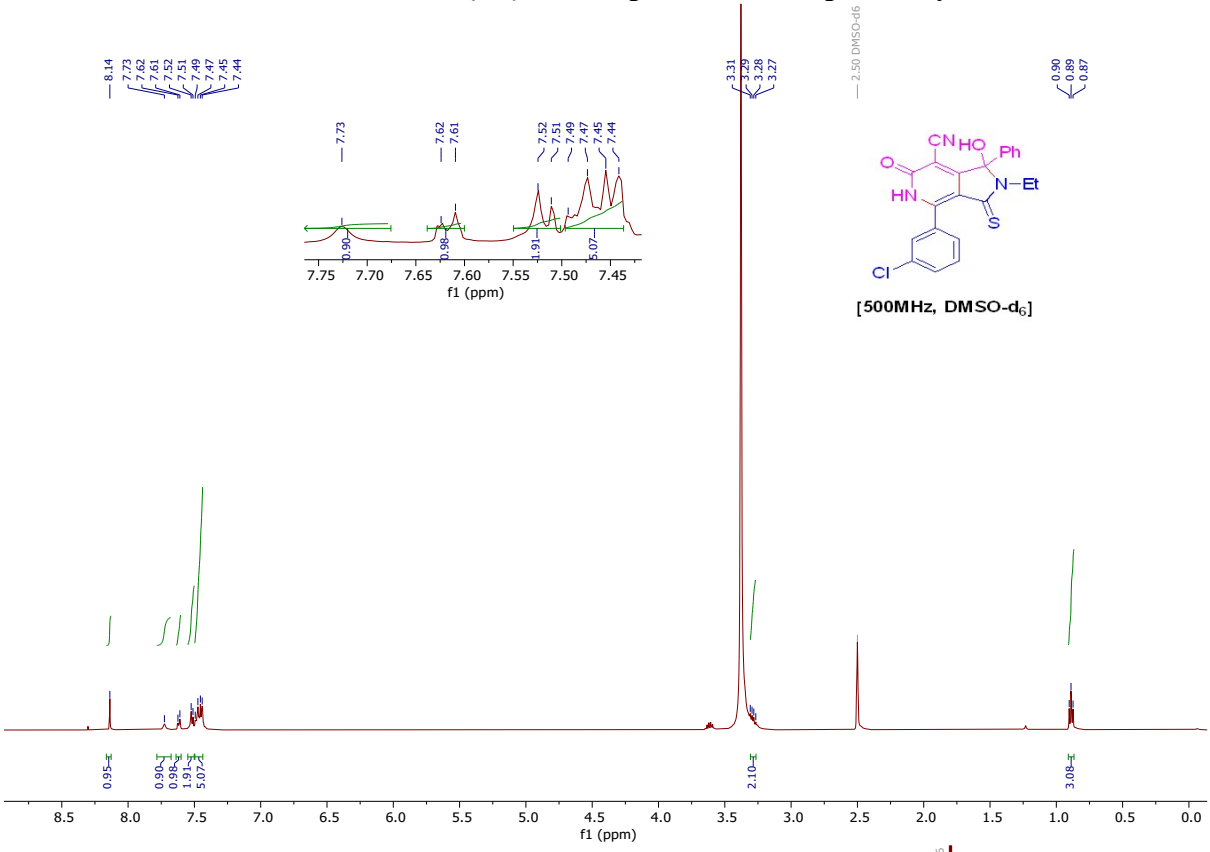


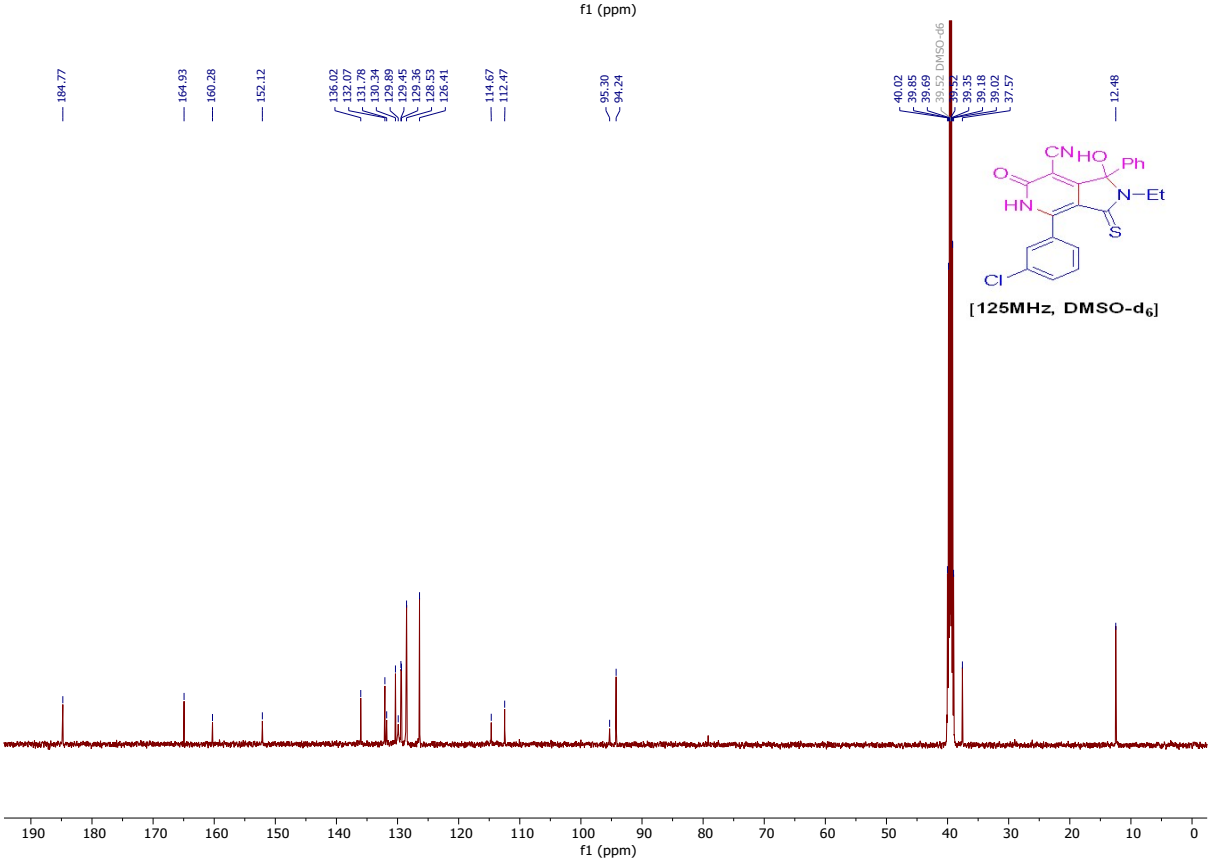
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3x



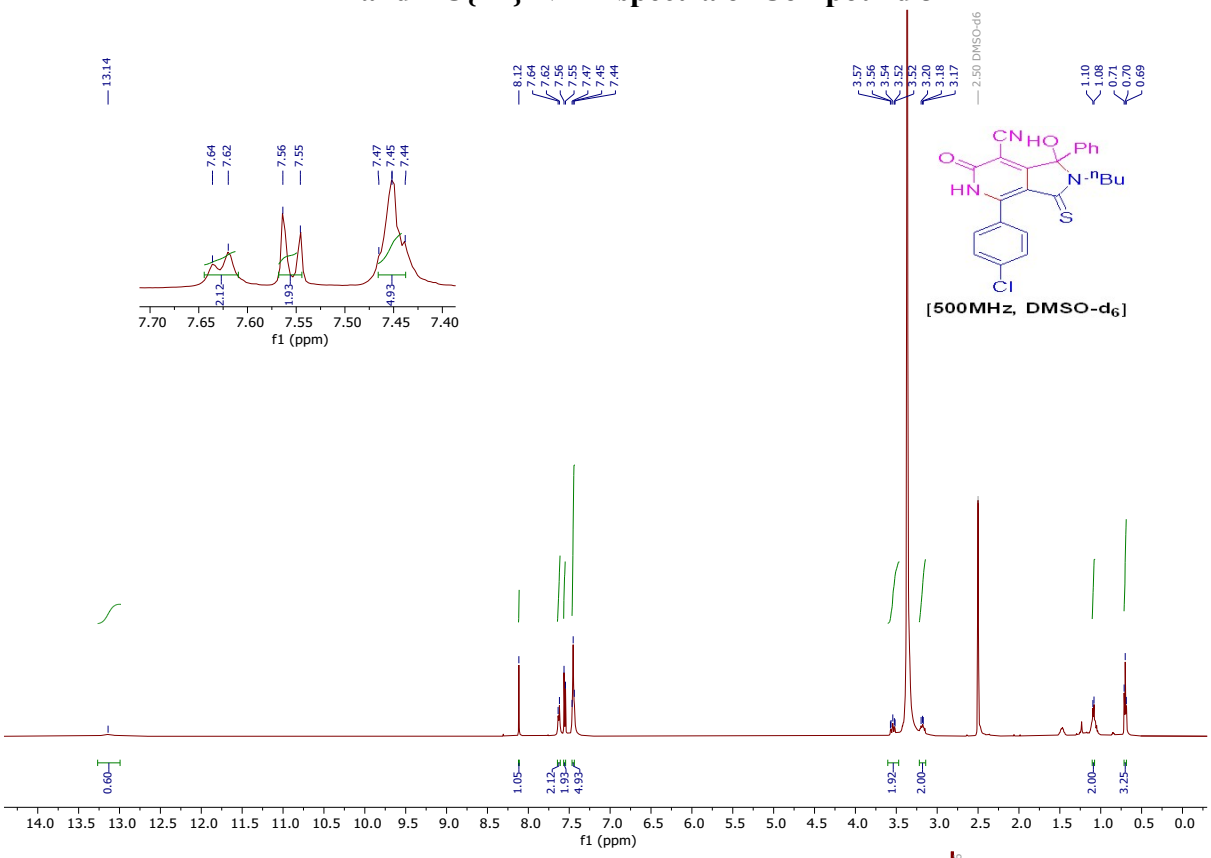


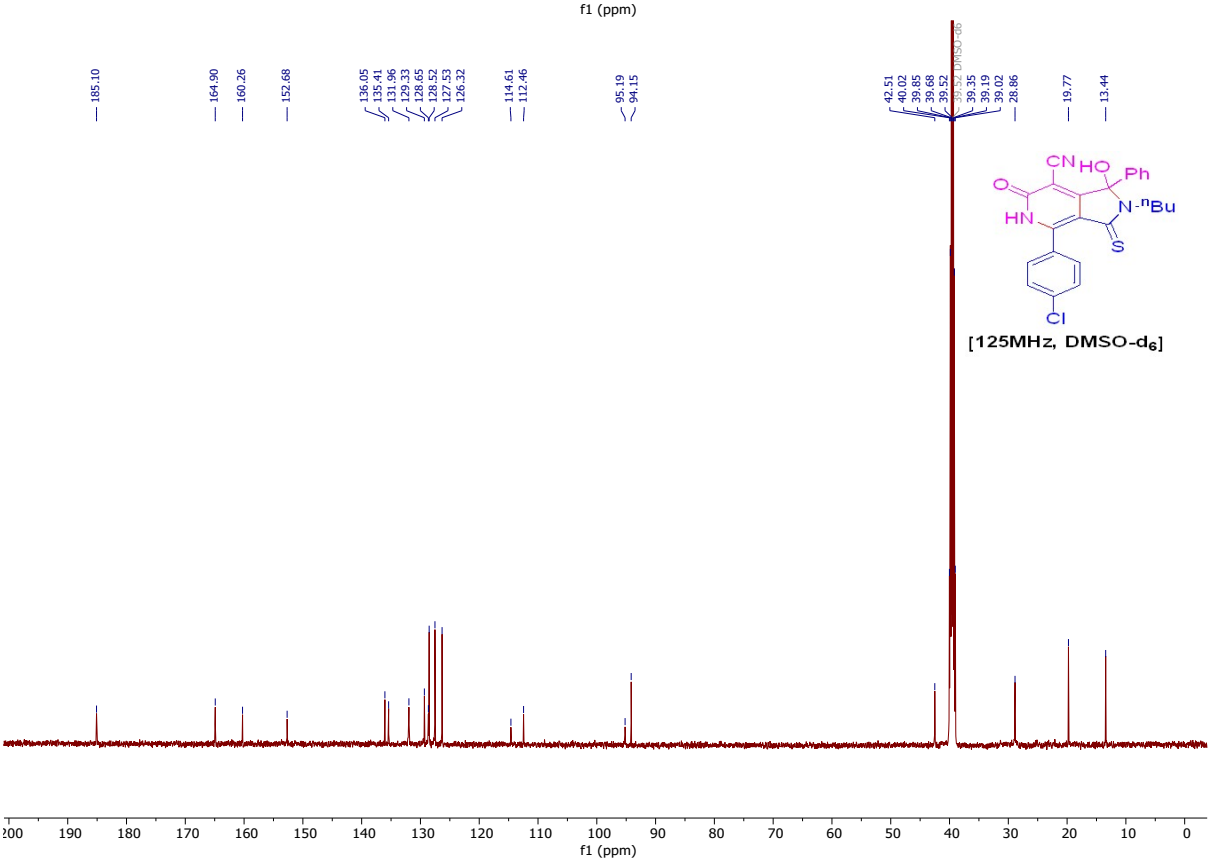
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3y



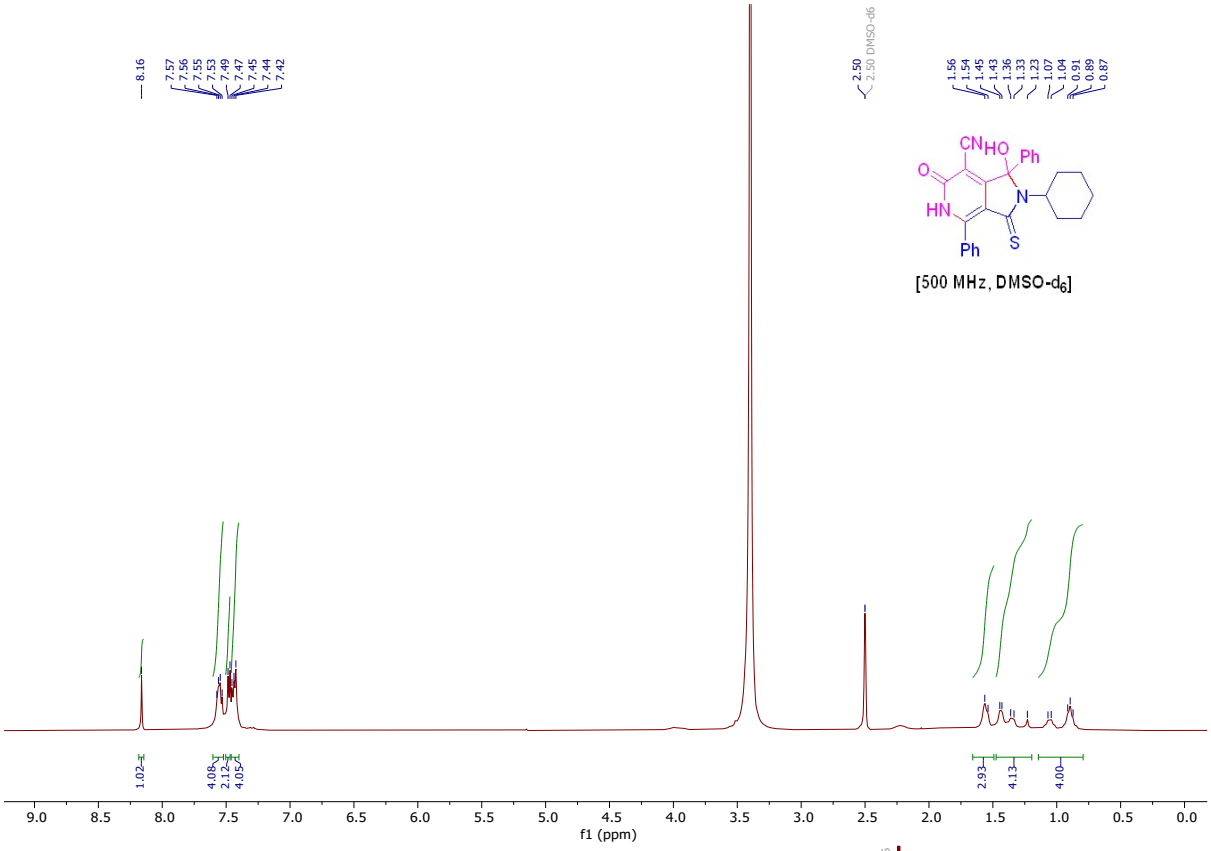


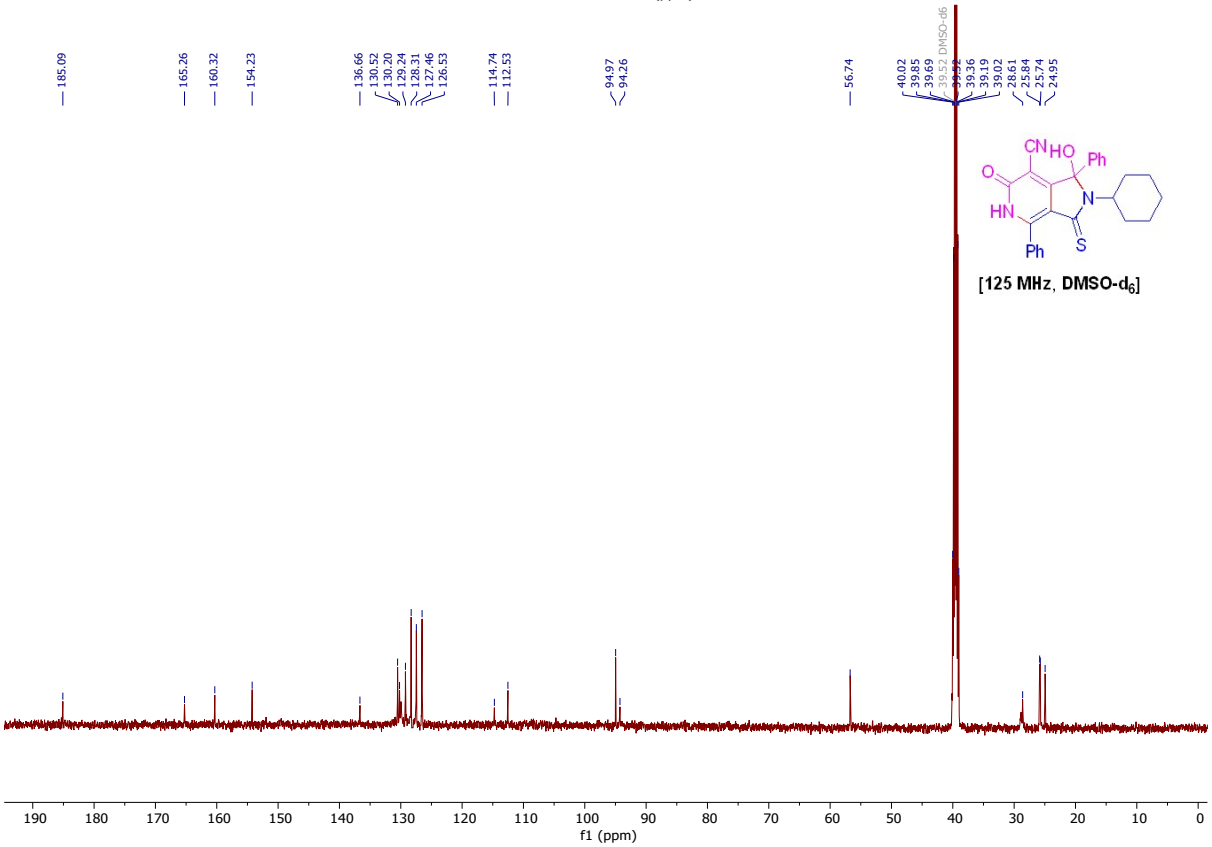
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3z



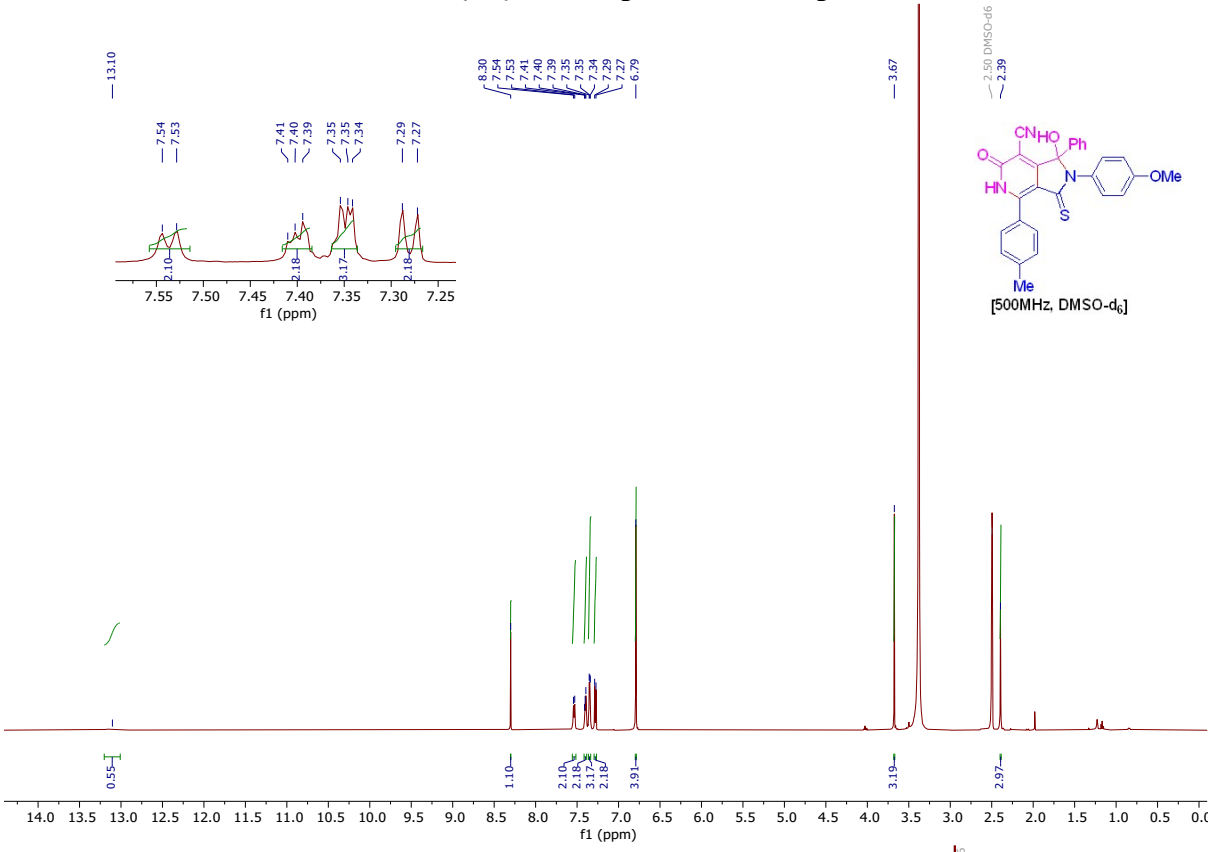


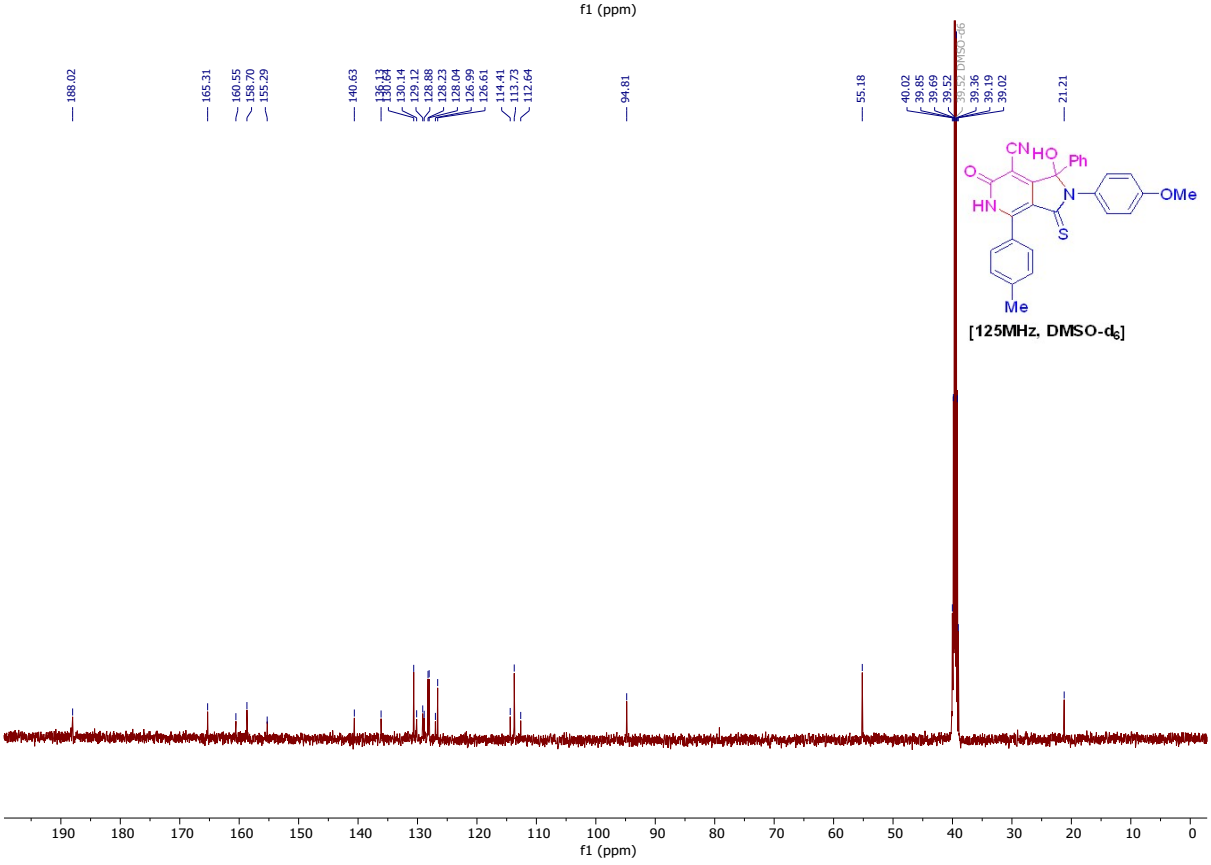
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3za



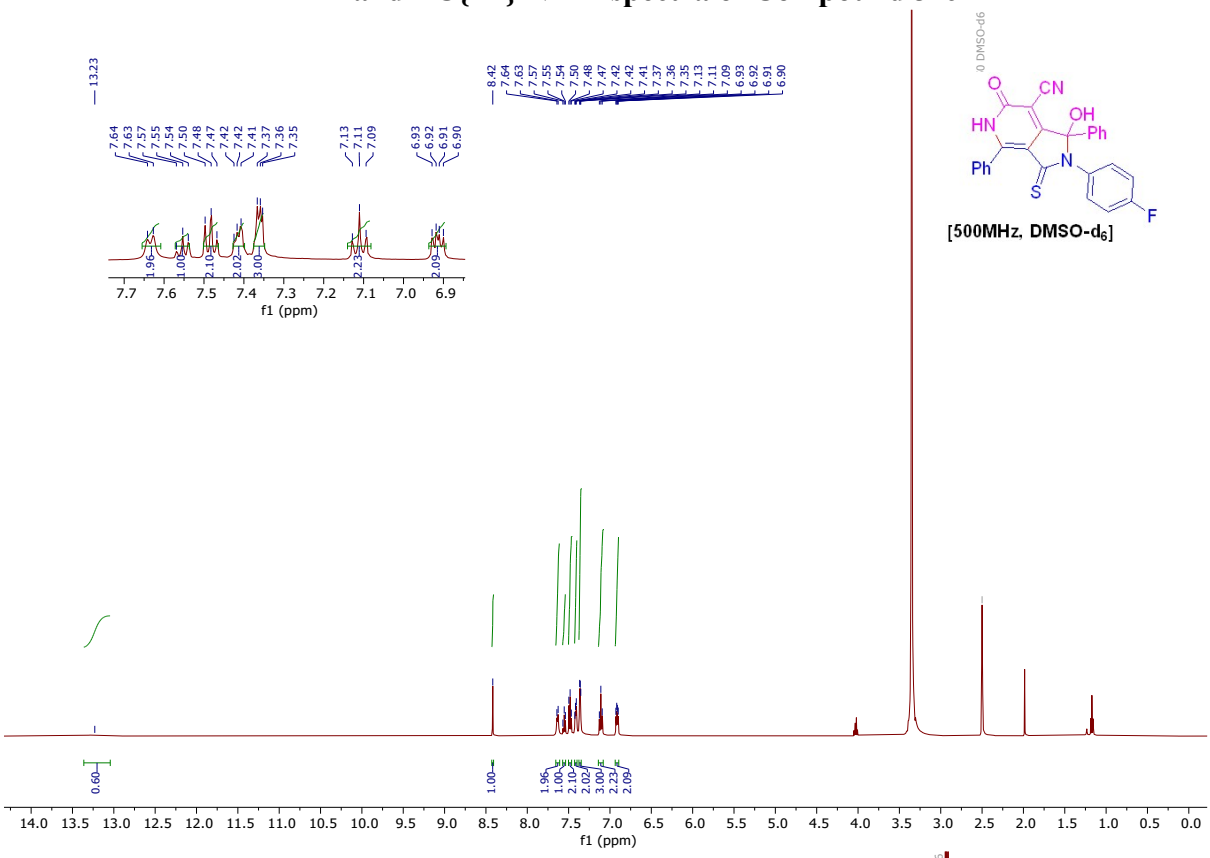


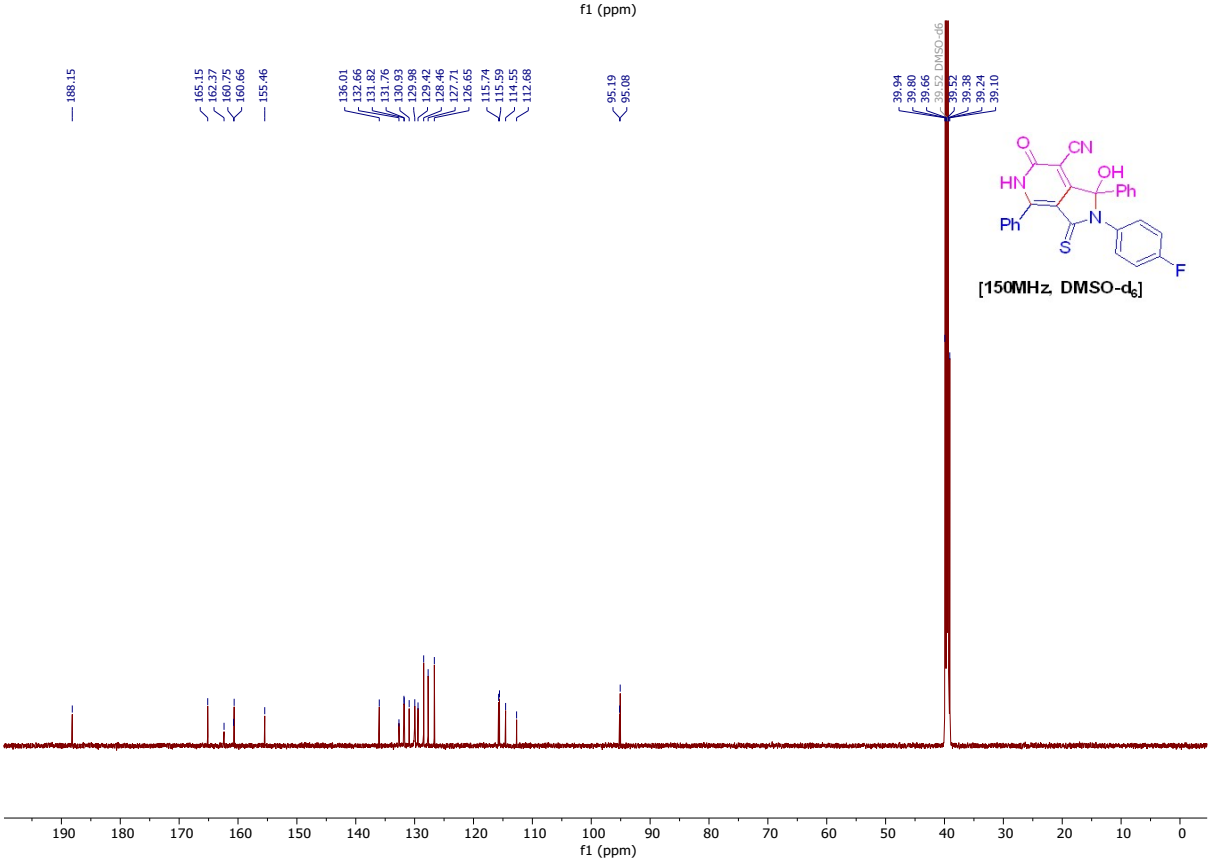
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zb



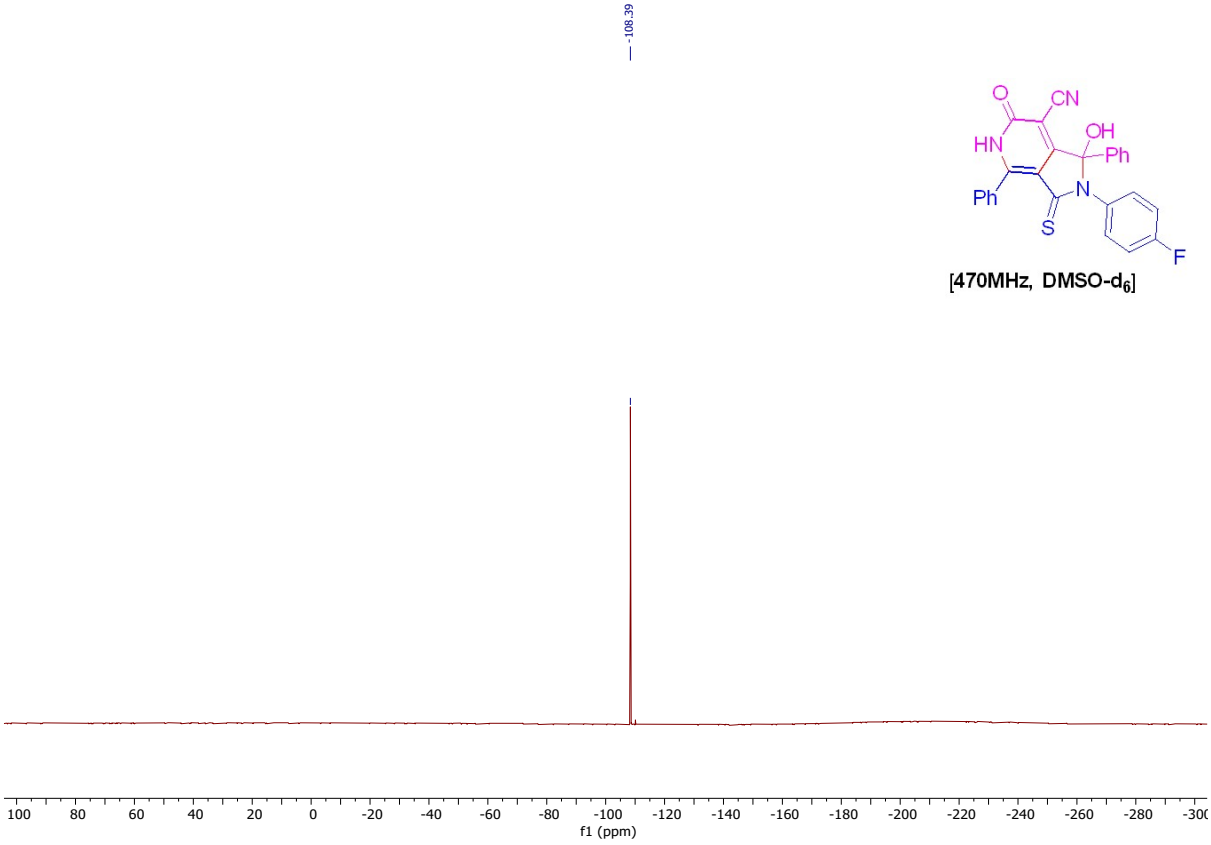


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zc

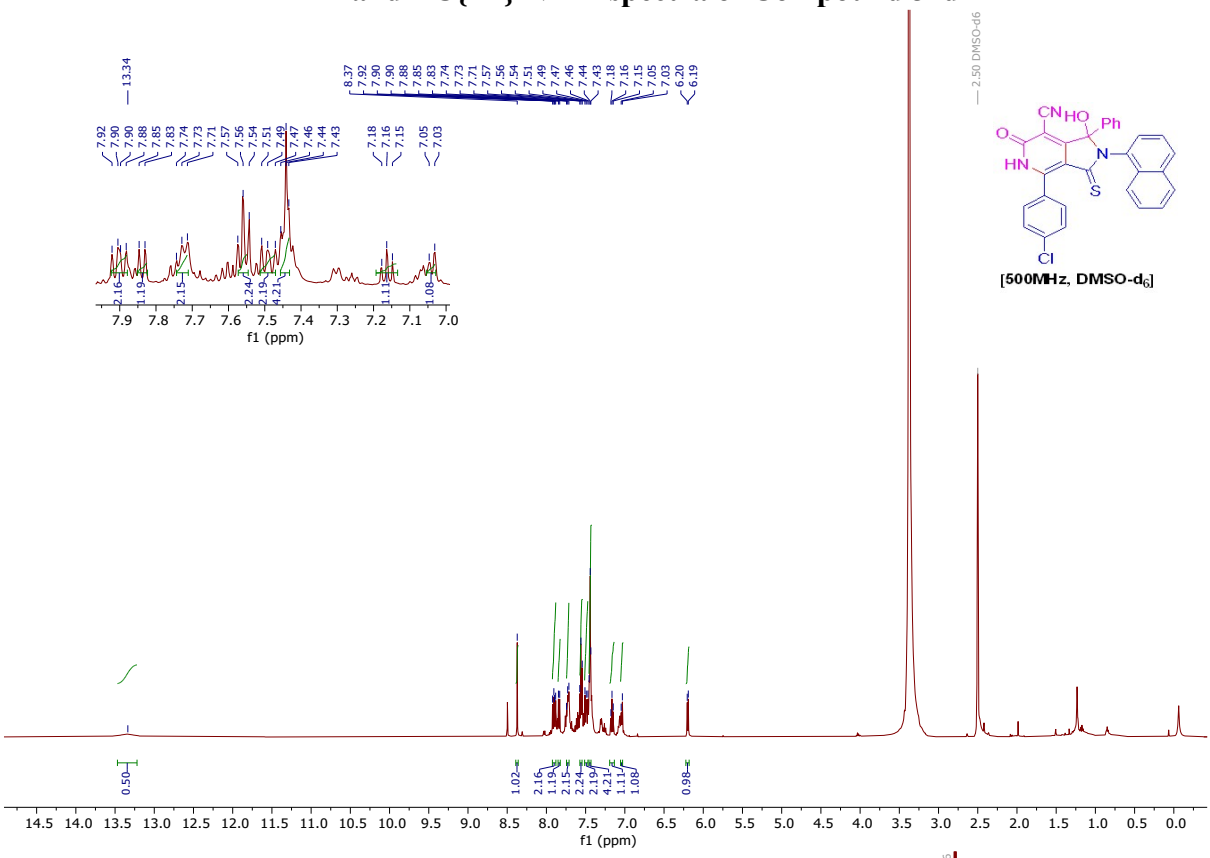


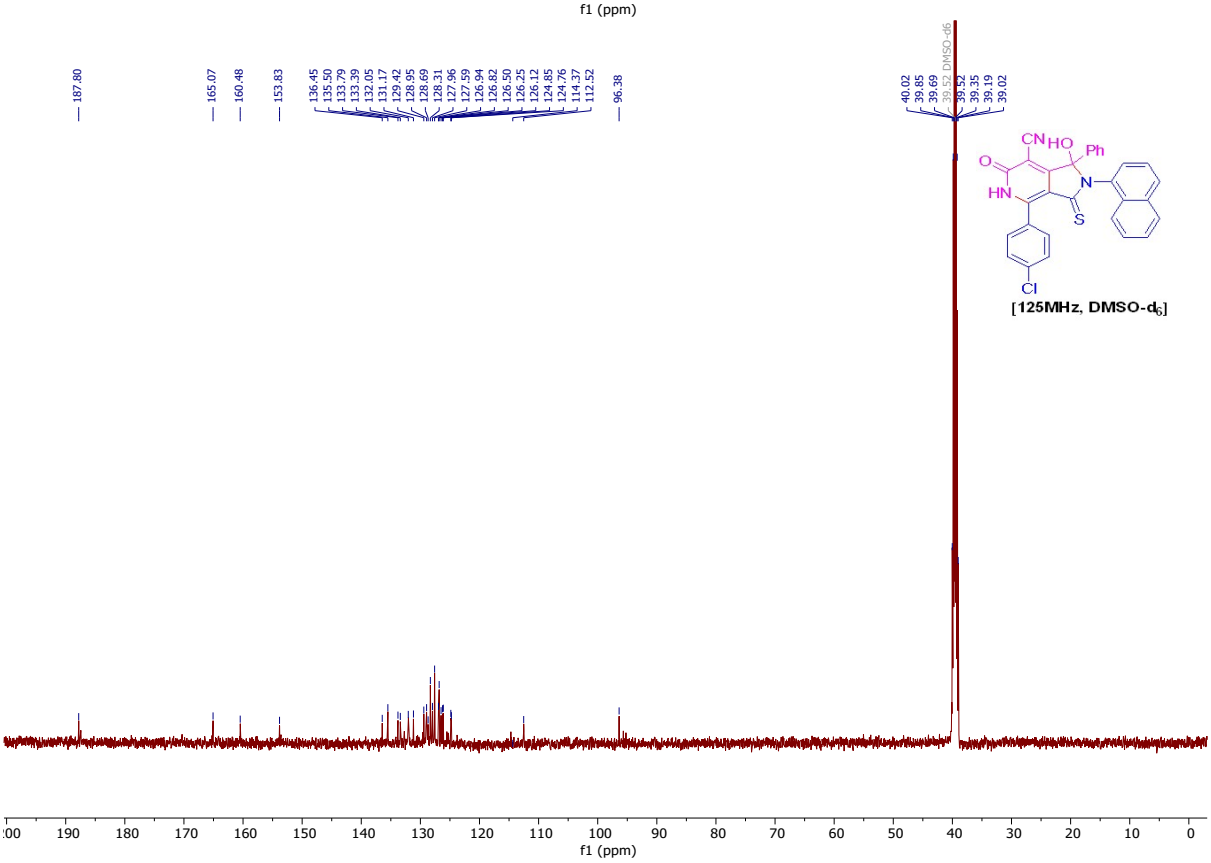


^{19}F NMR spectra of Compound 3zc

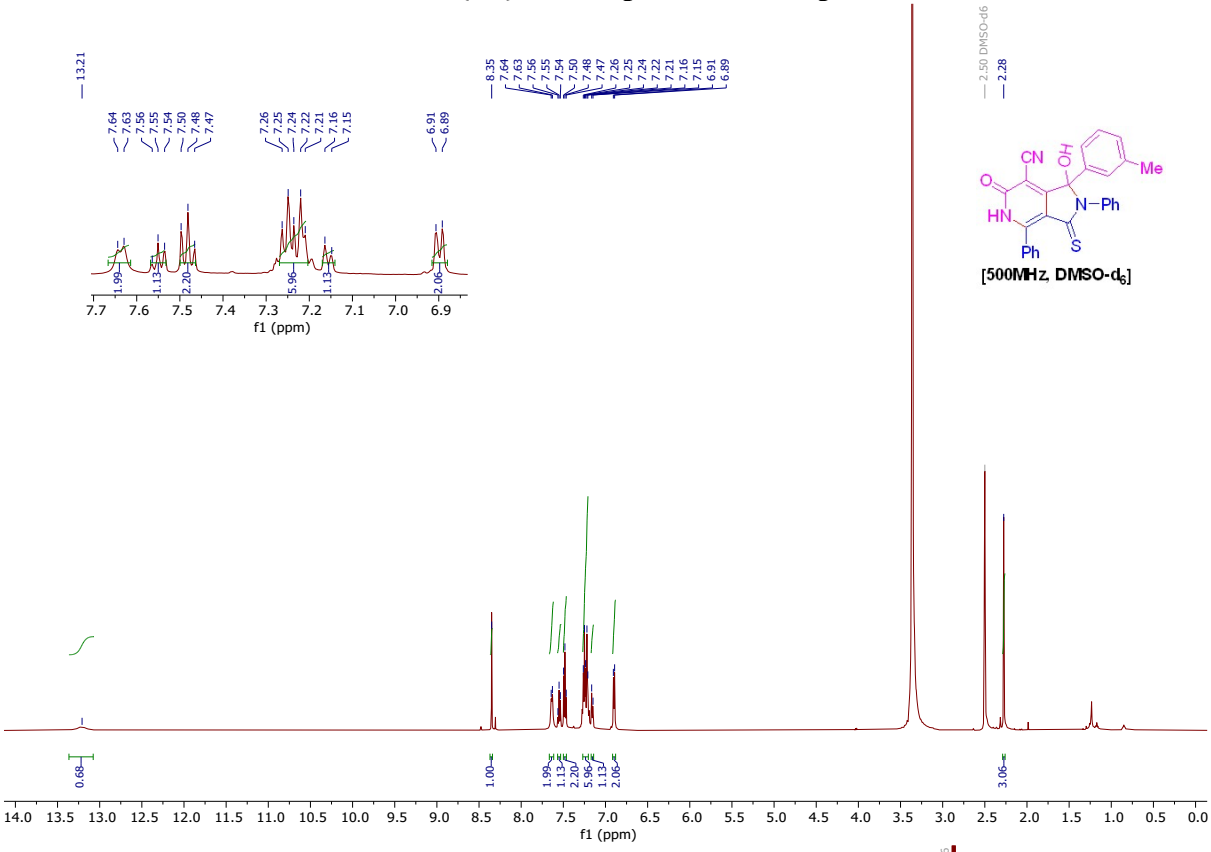


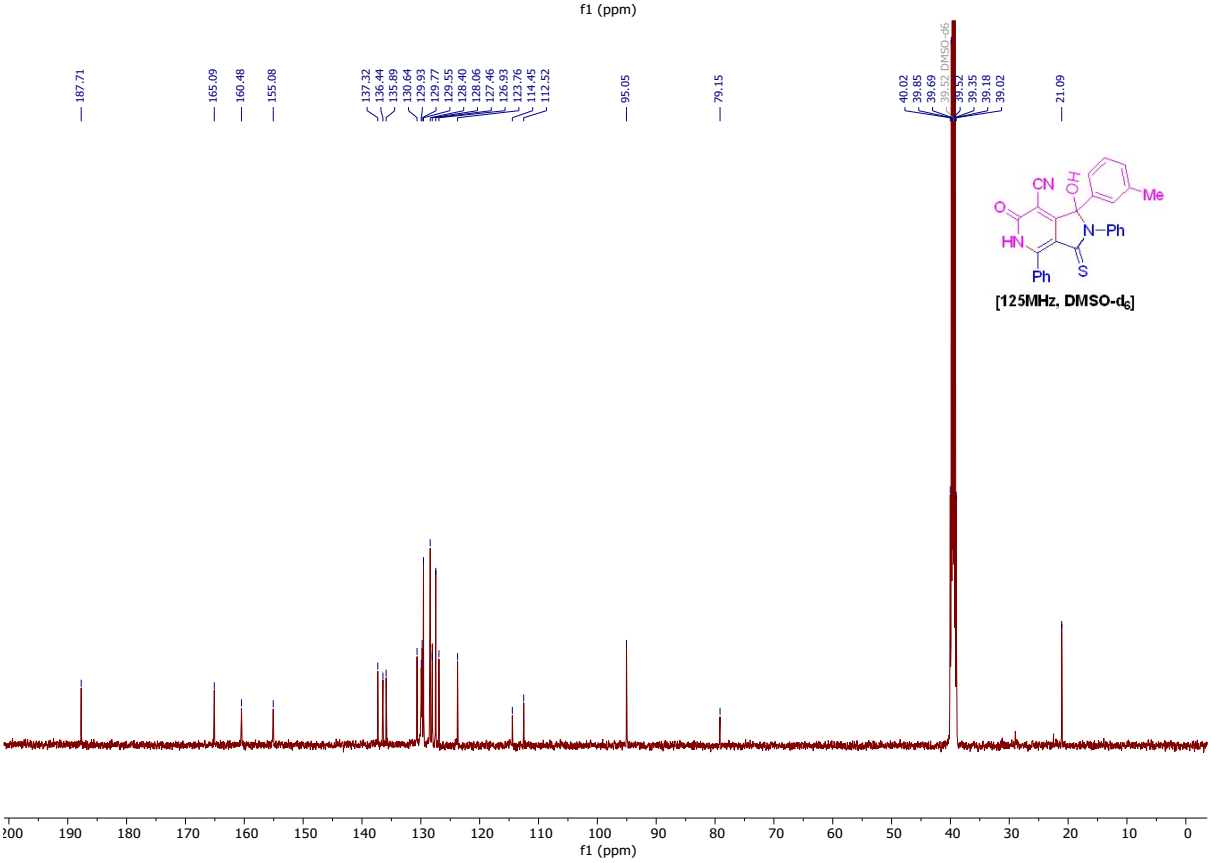
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zd



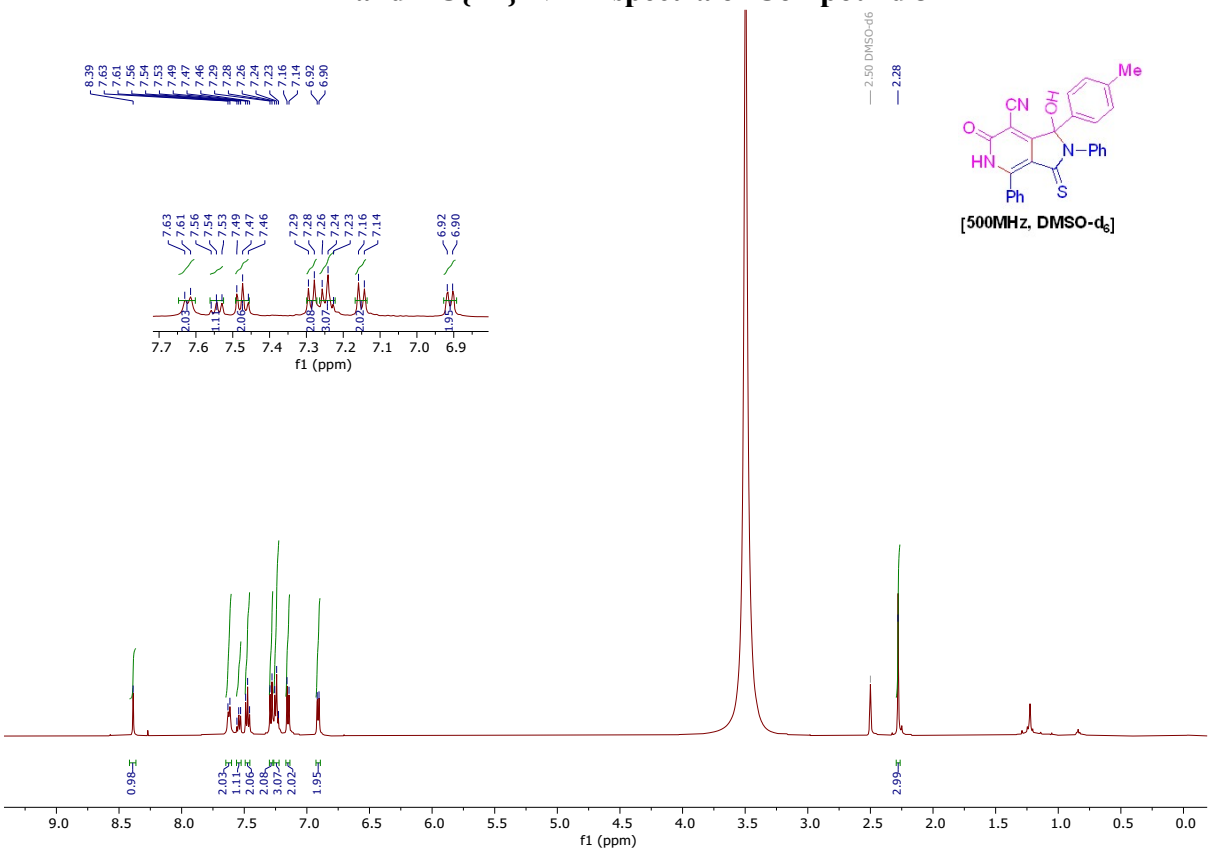


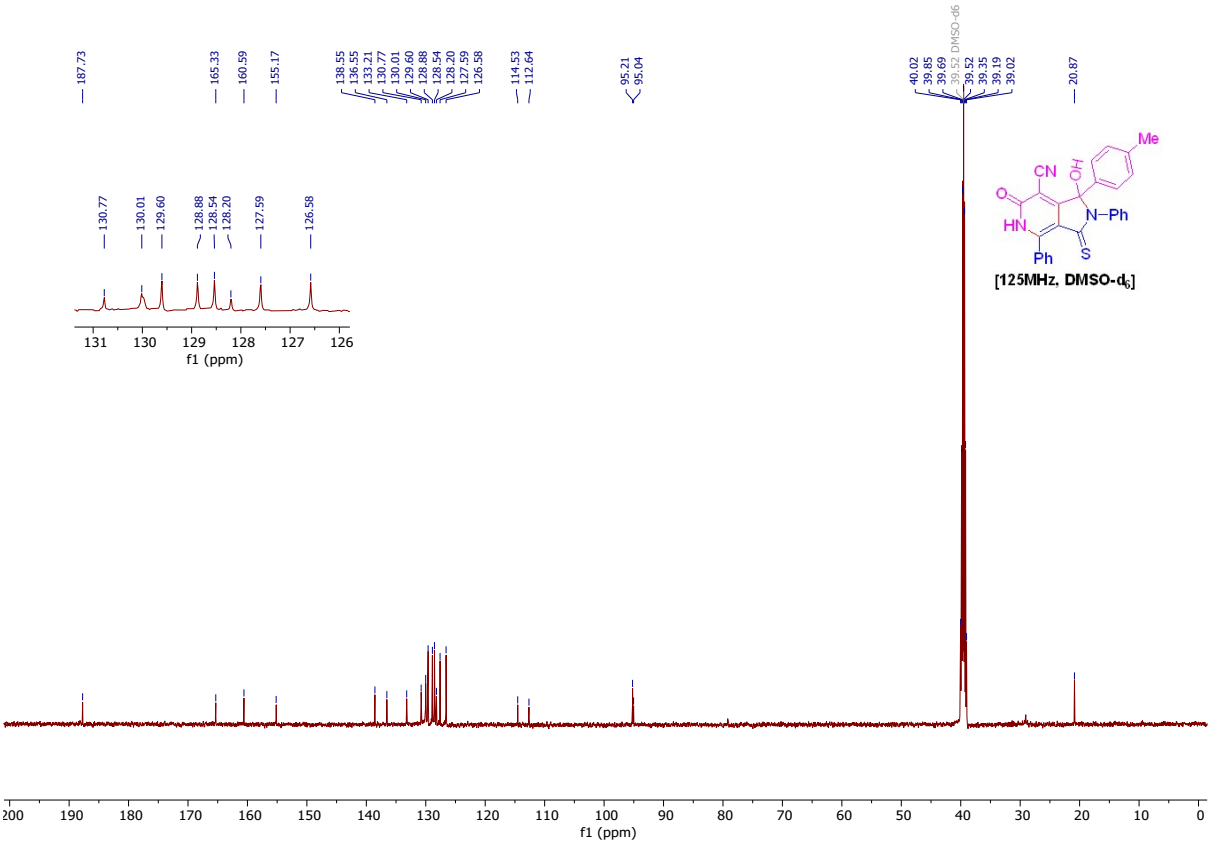
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3ze



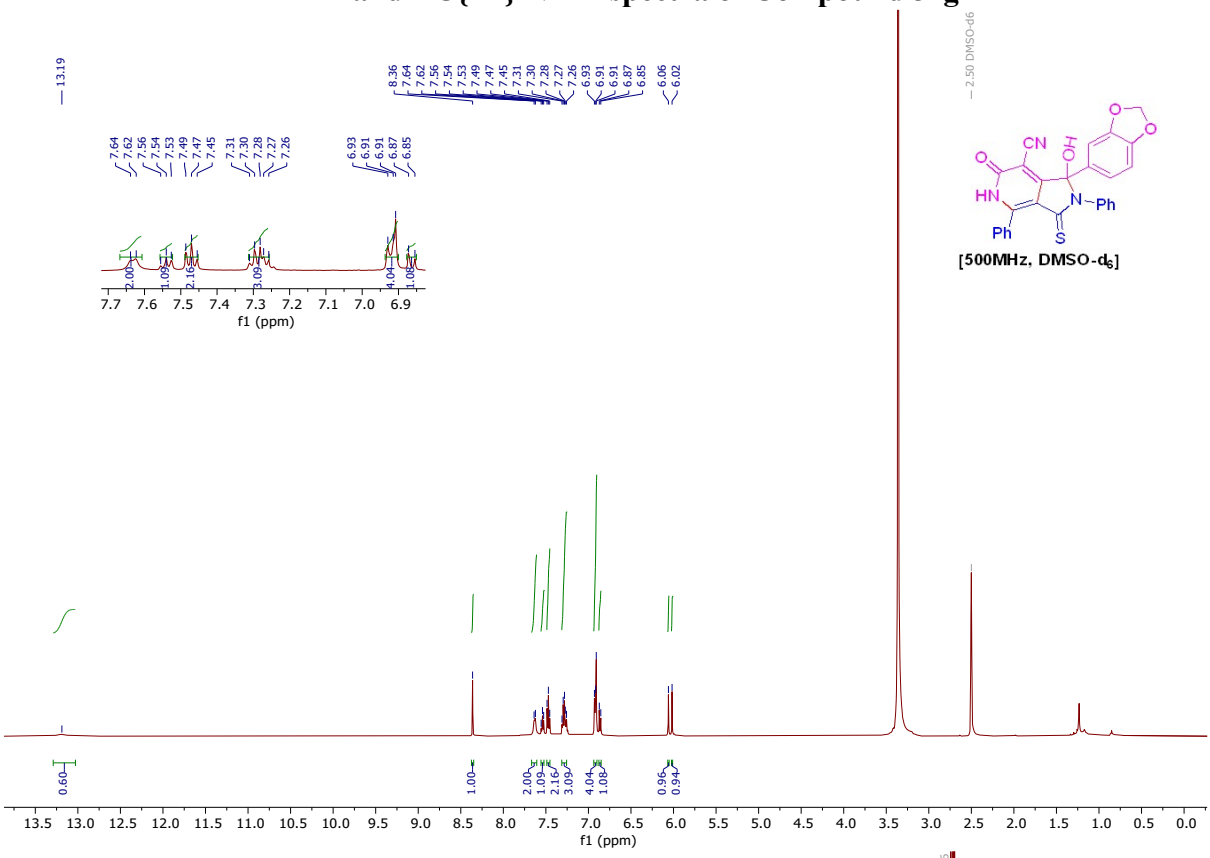


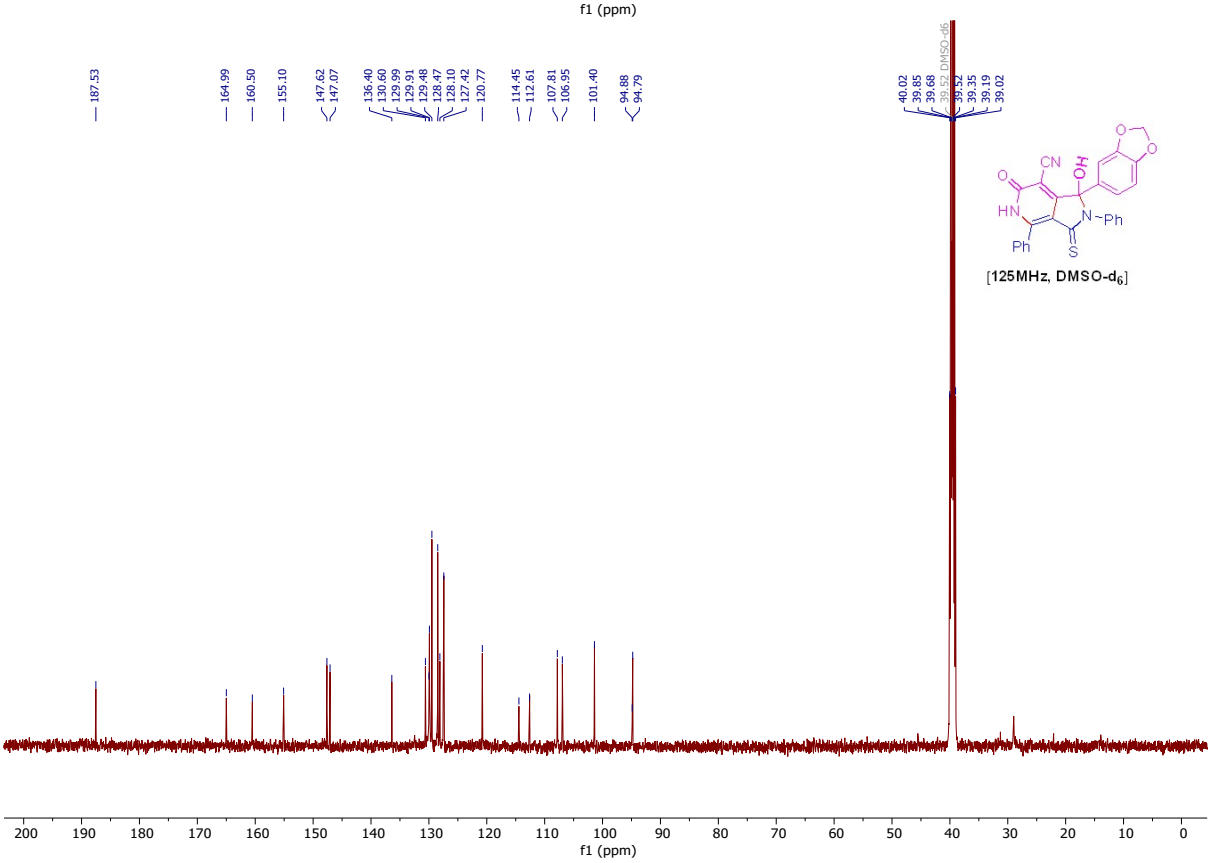
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zf



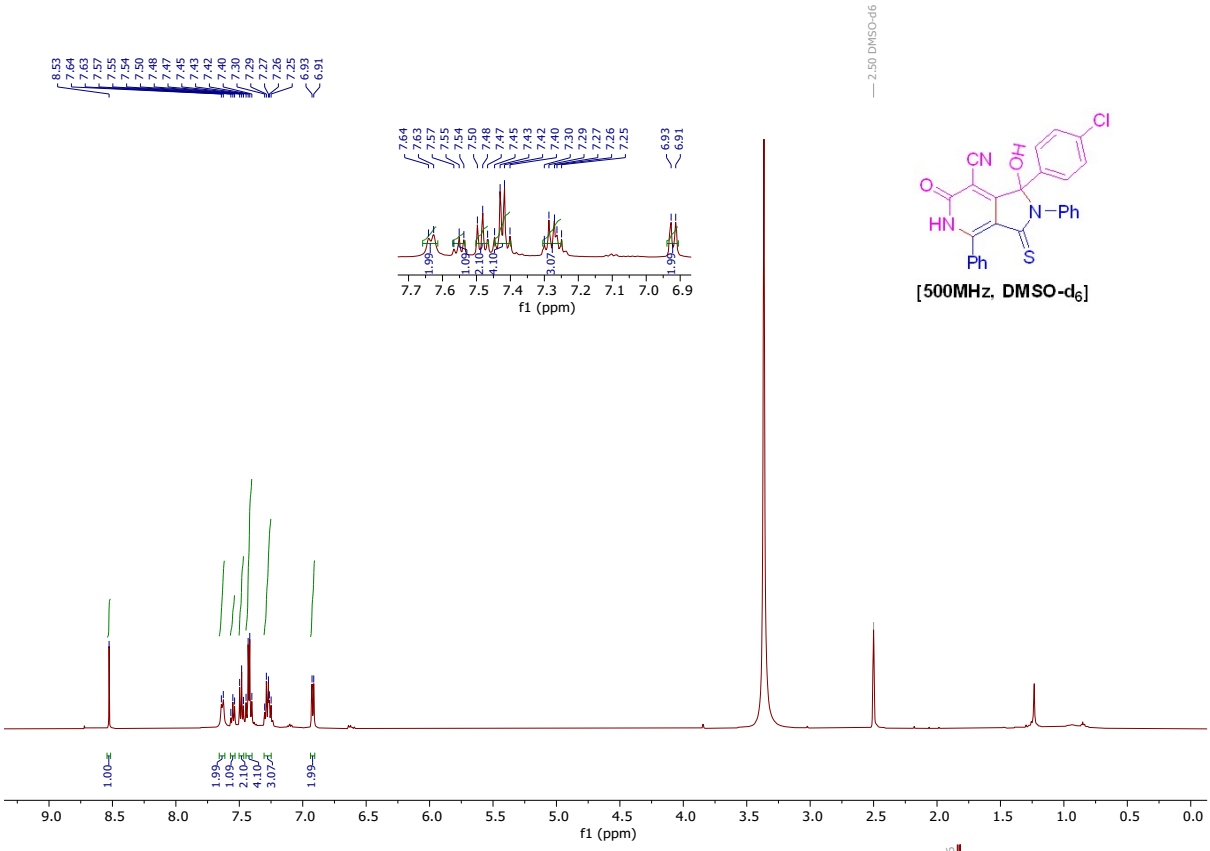


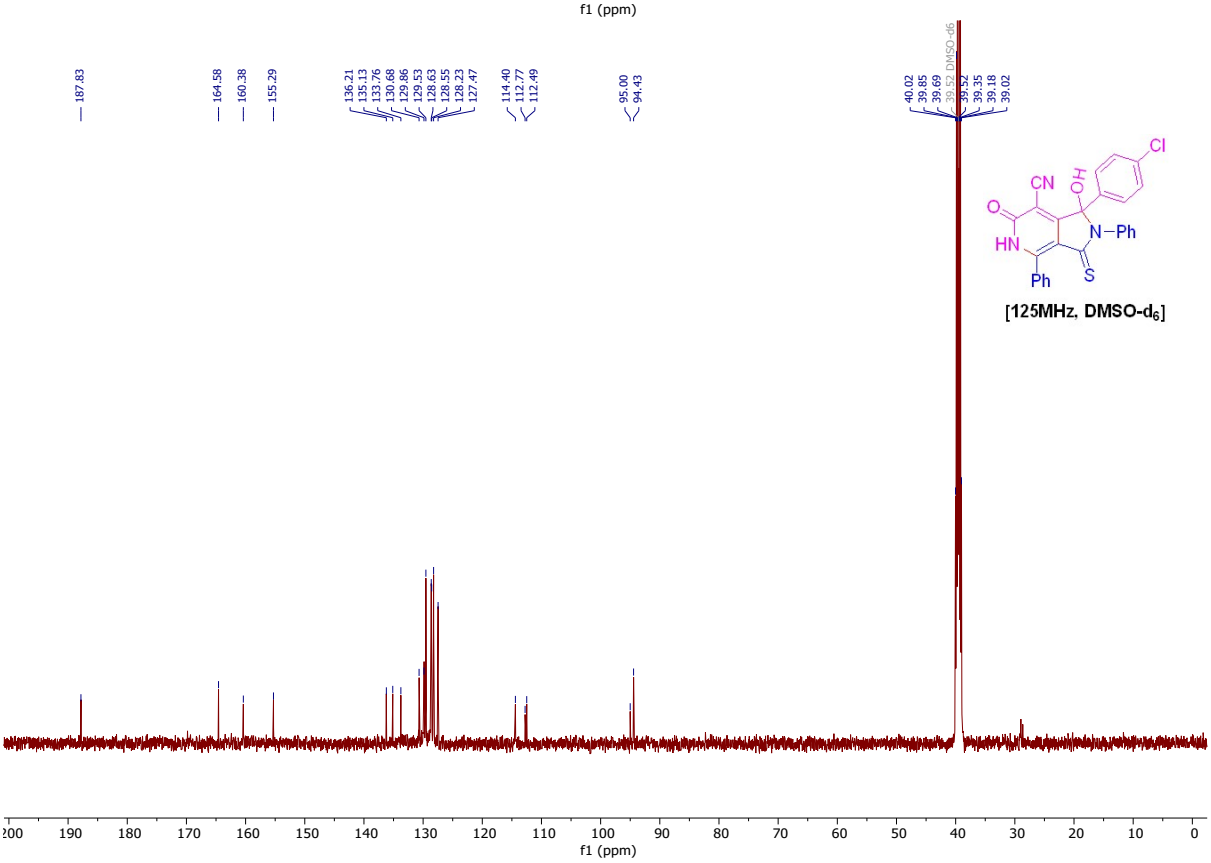
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zg



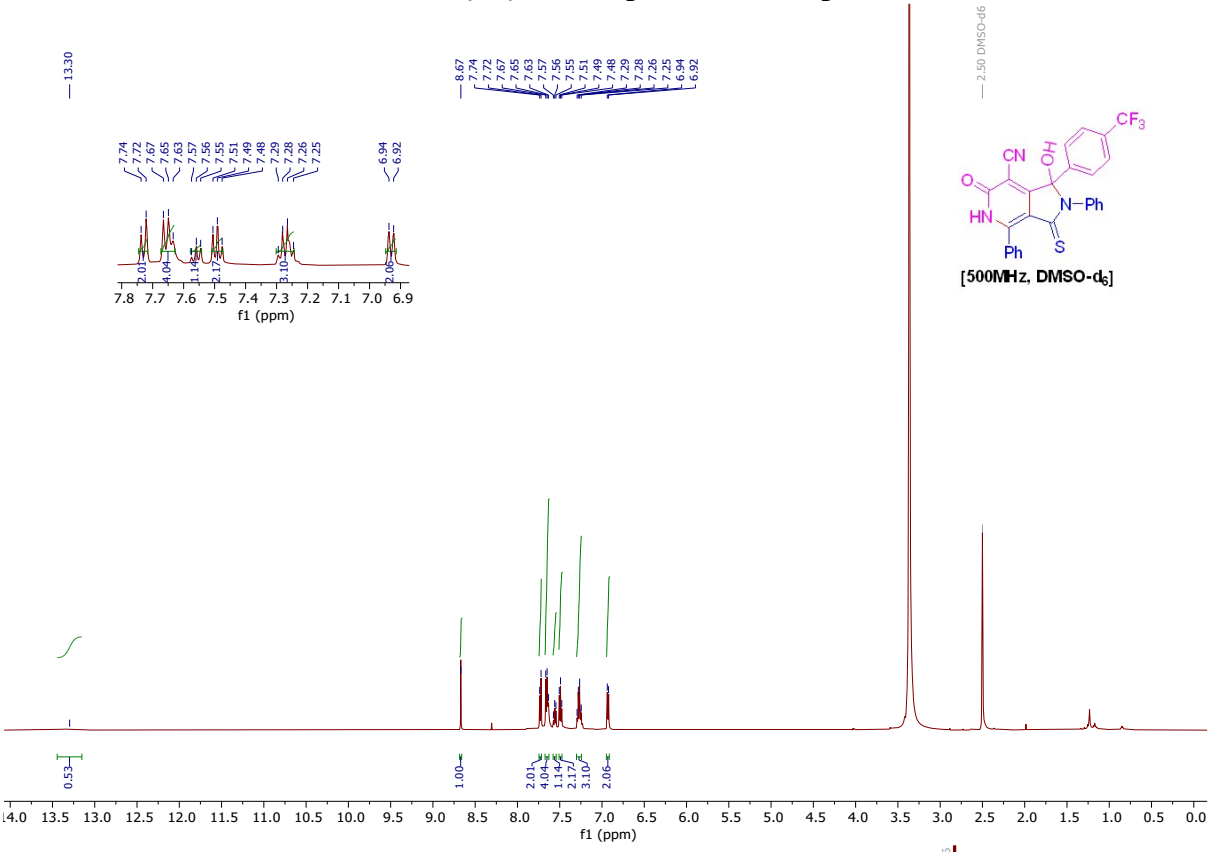


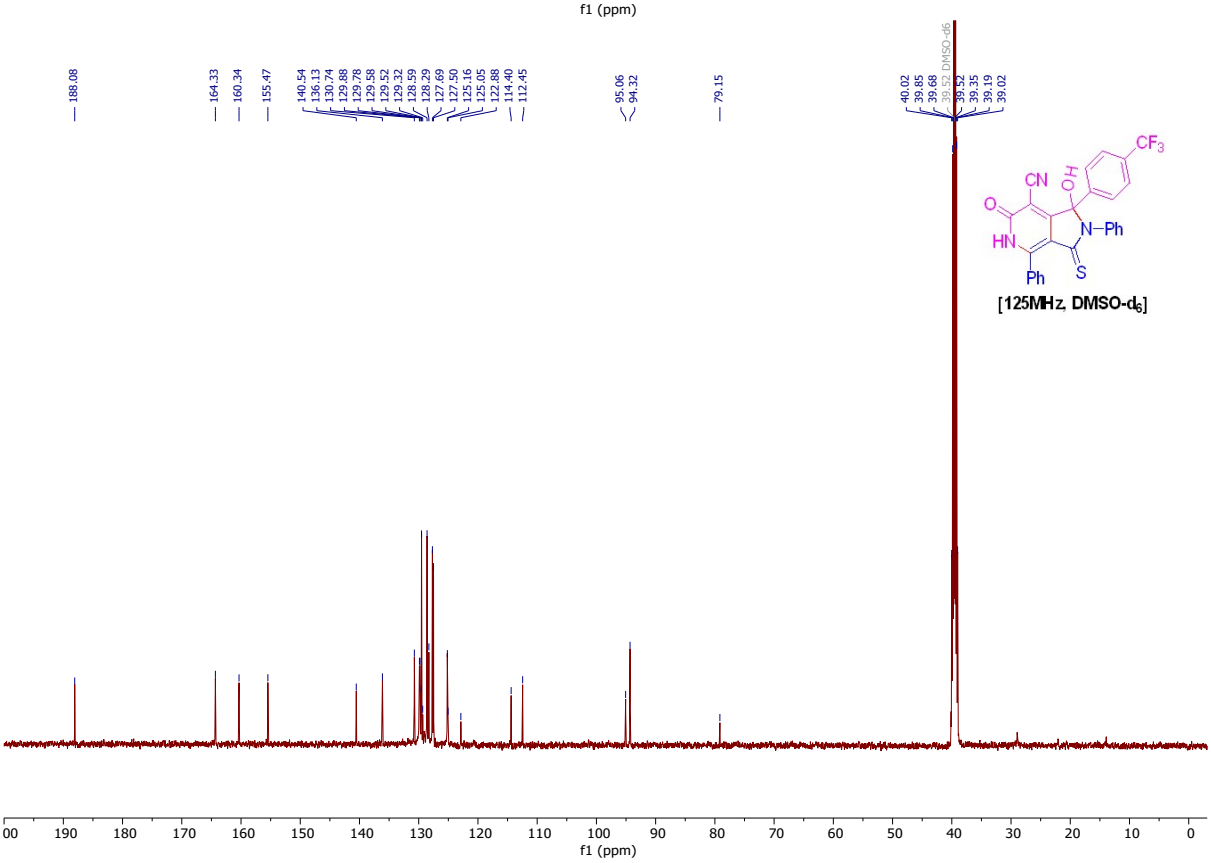
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zh



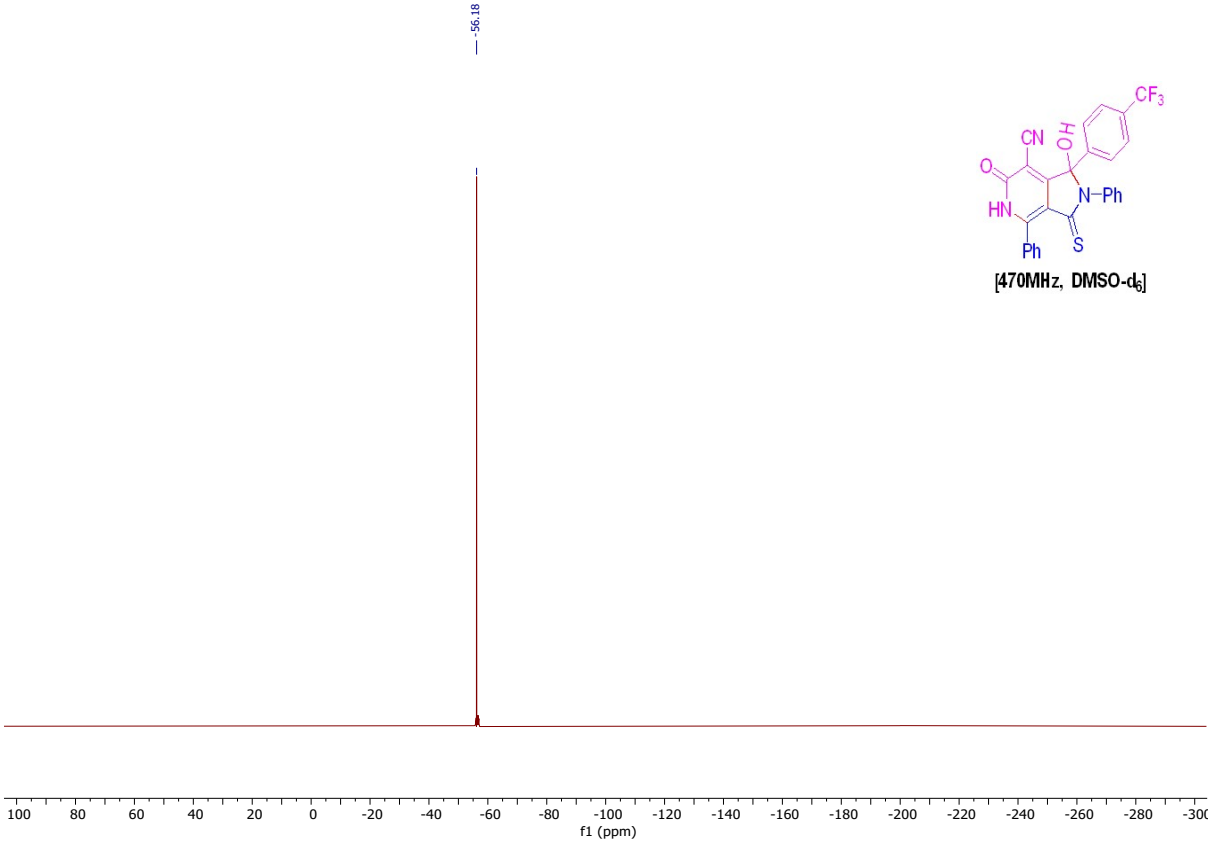


^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zi



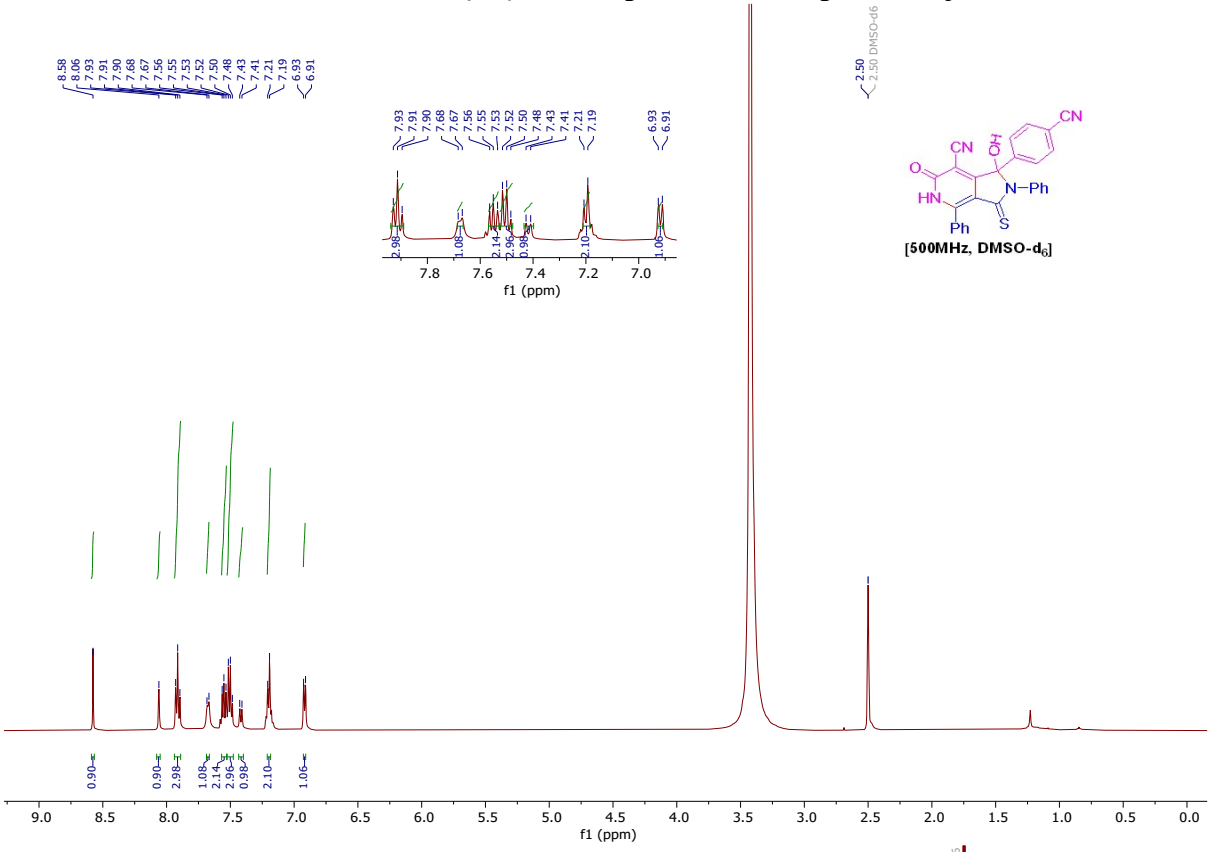


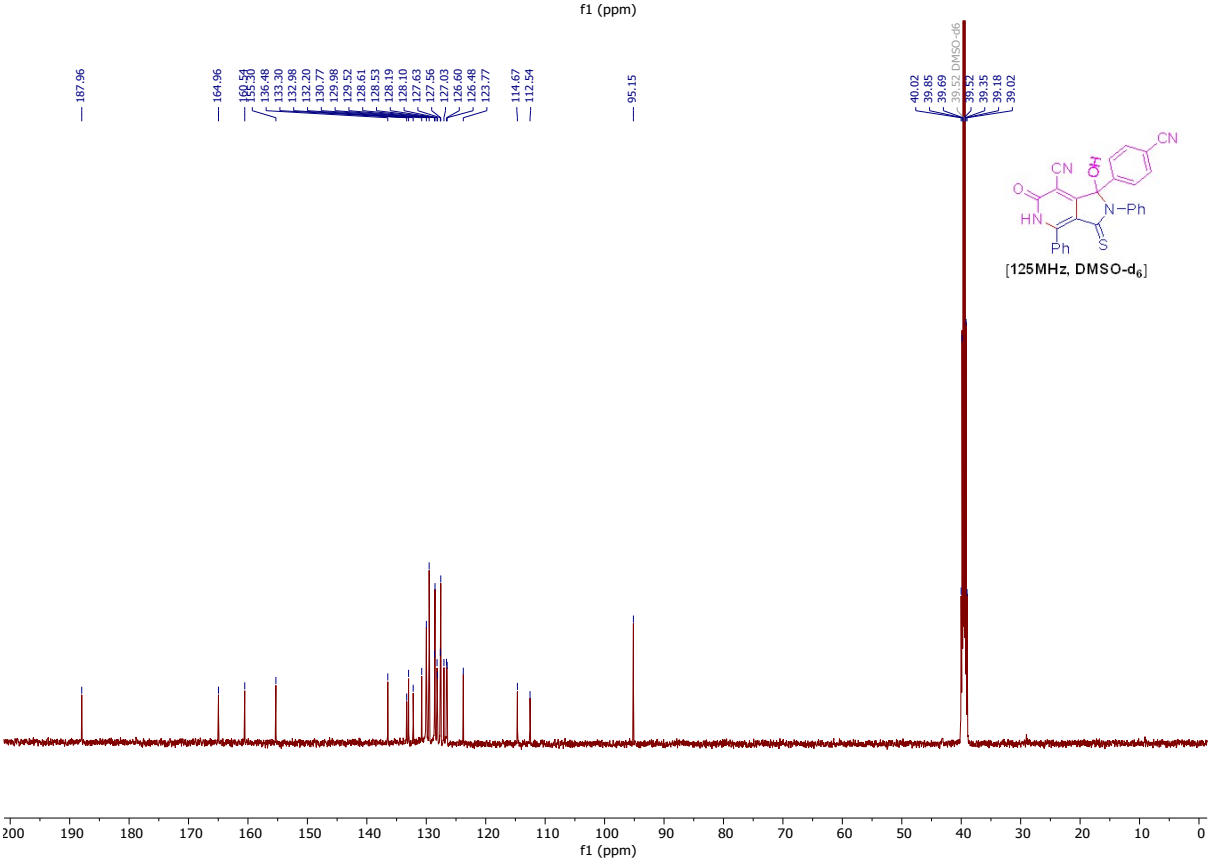
^{19}F NMR spectra of Compound 3zi



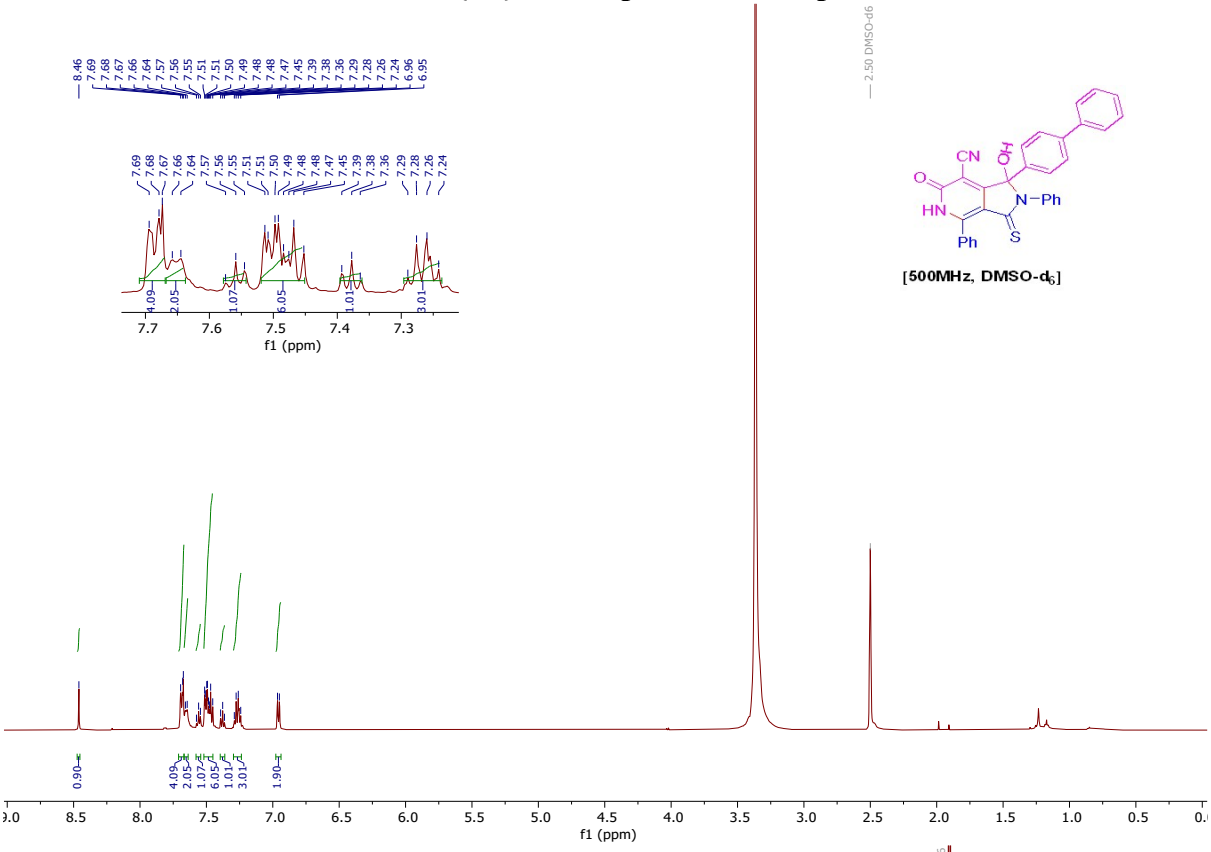
[470MHz, DMSO-d_6]

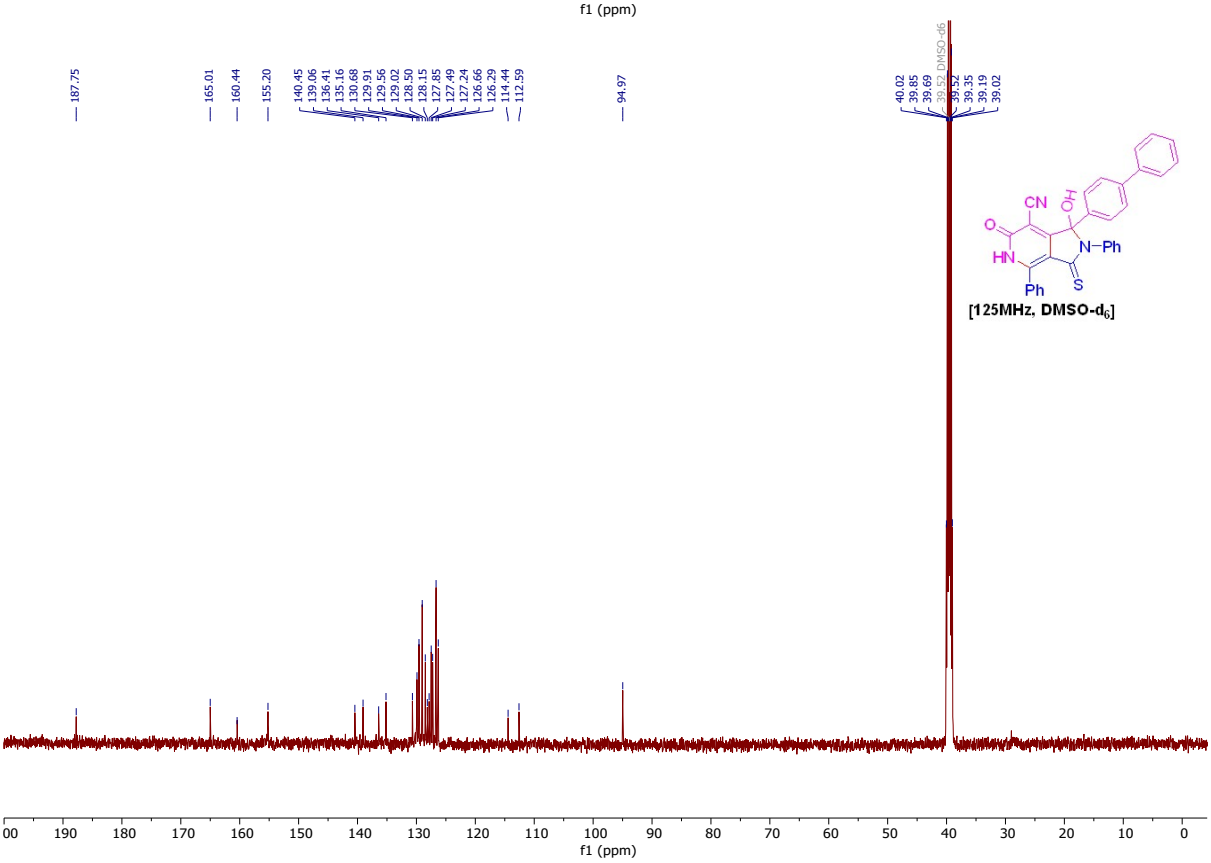
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zj



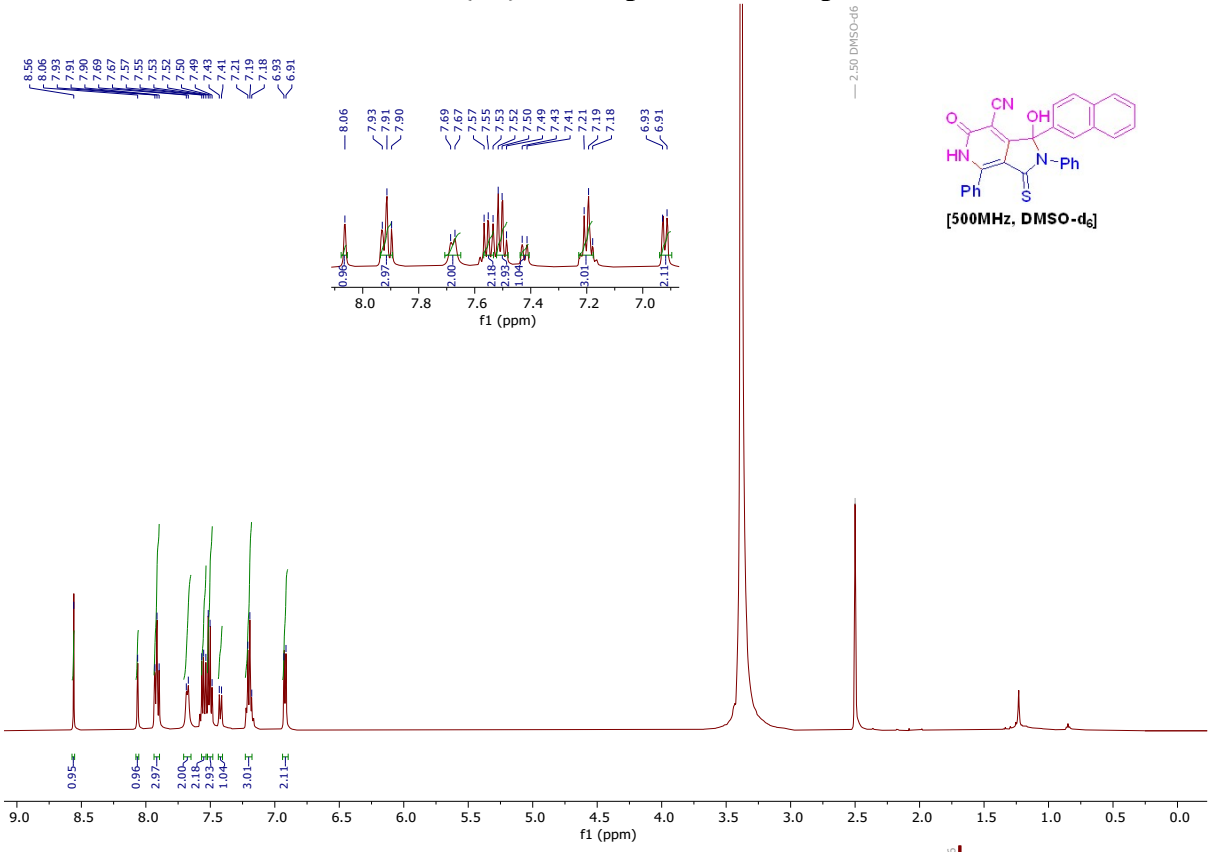


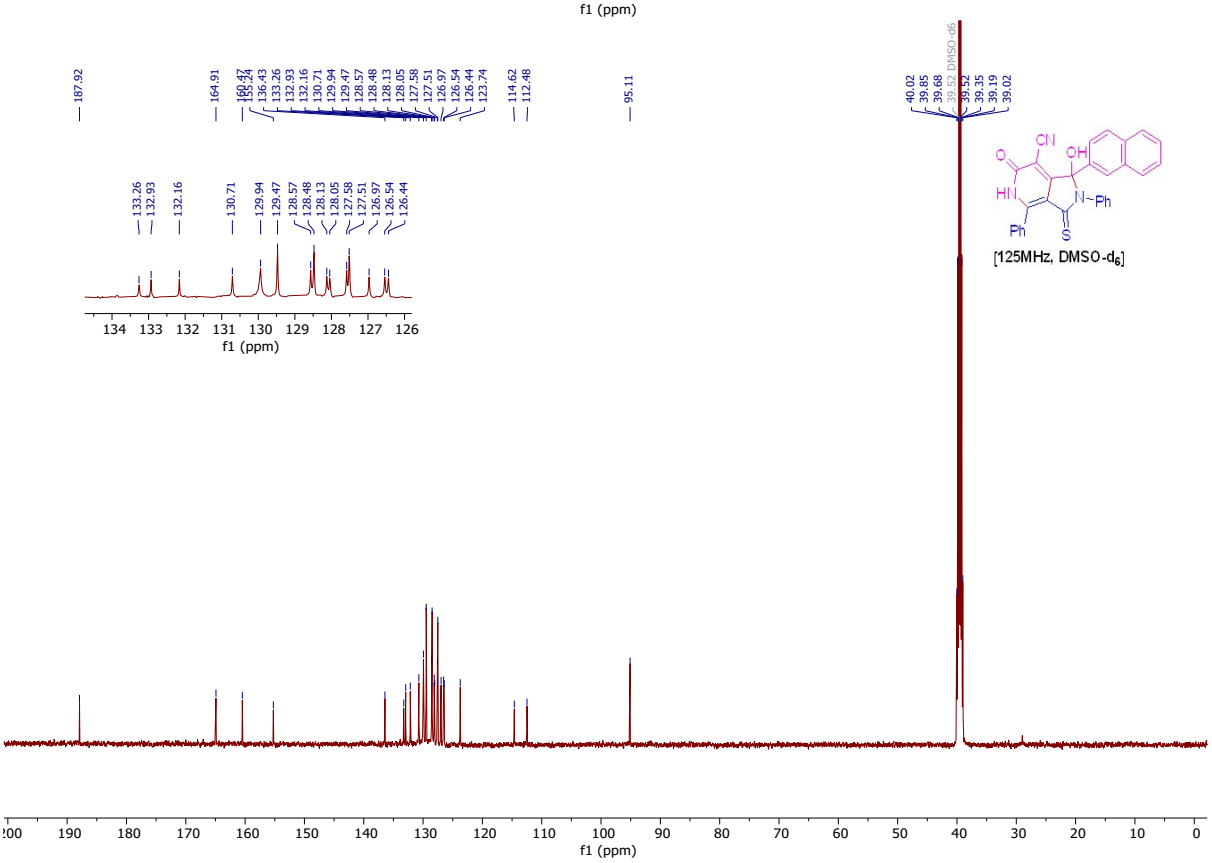
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zk



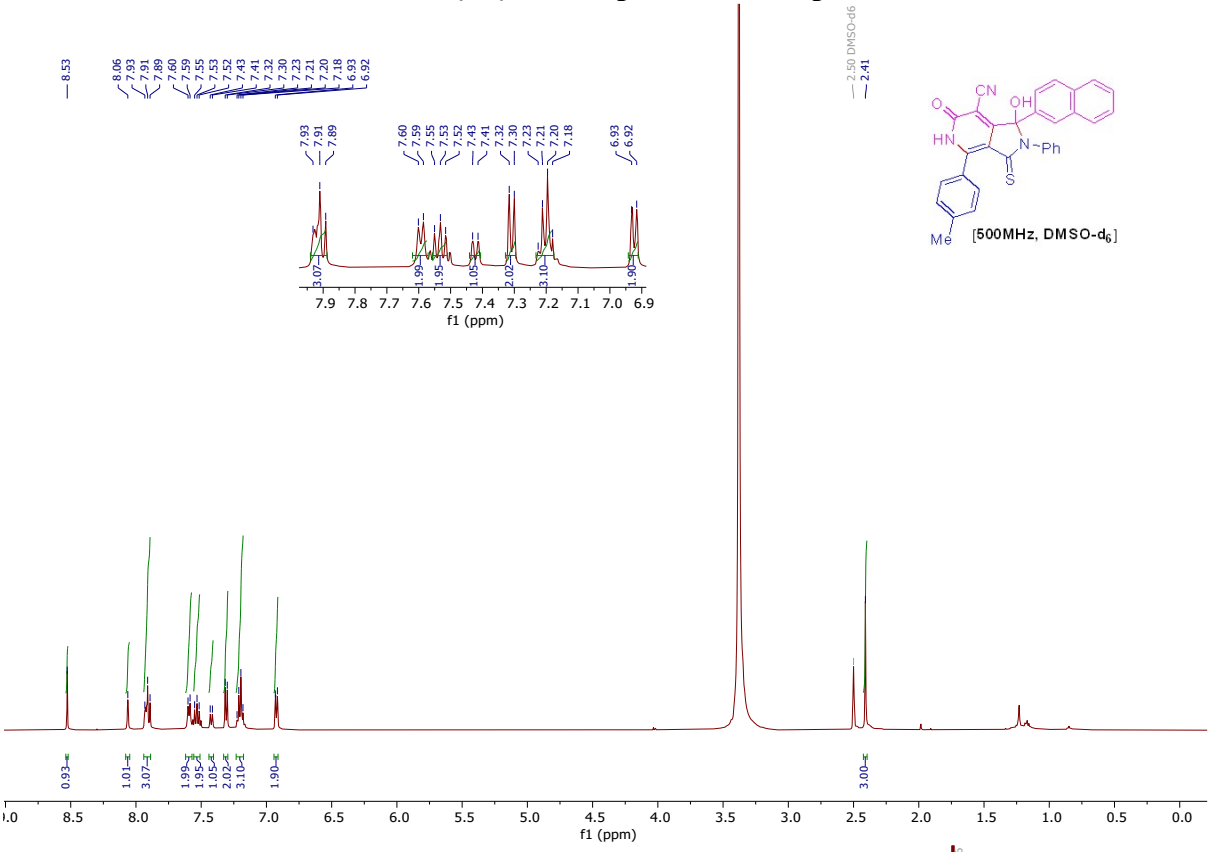


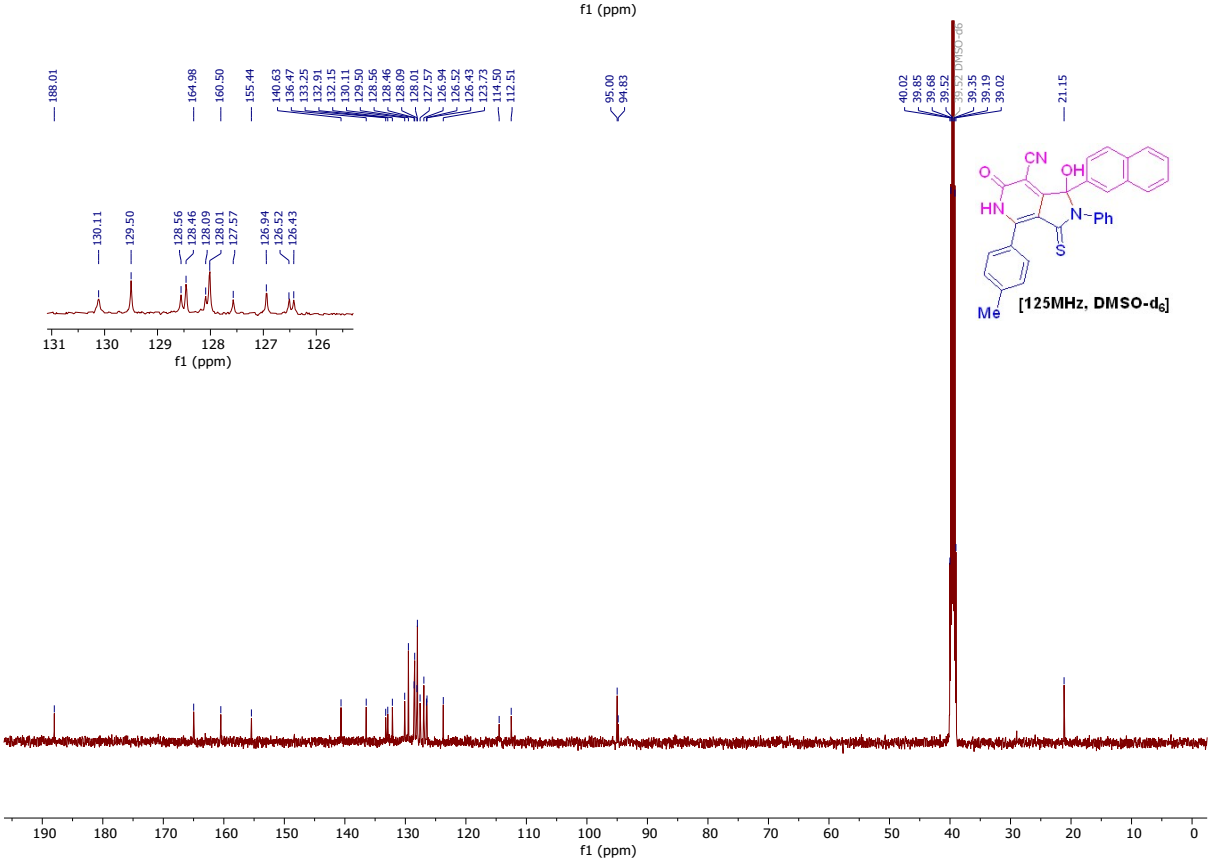
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zl



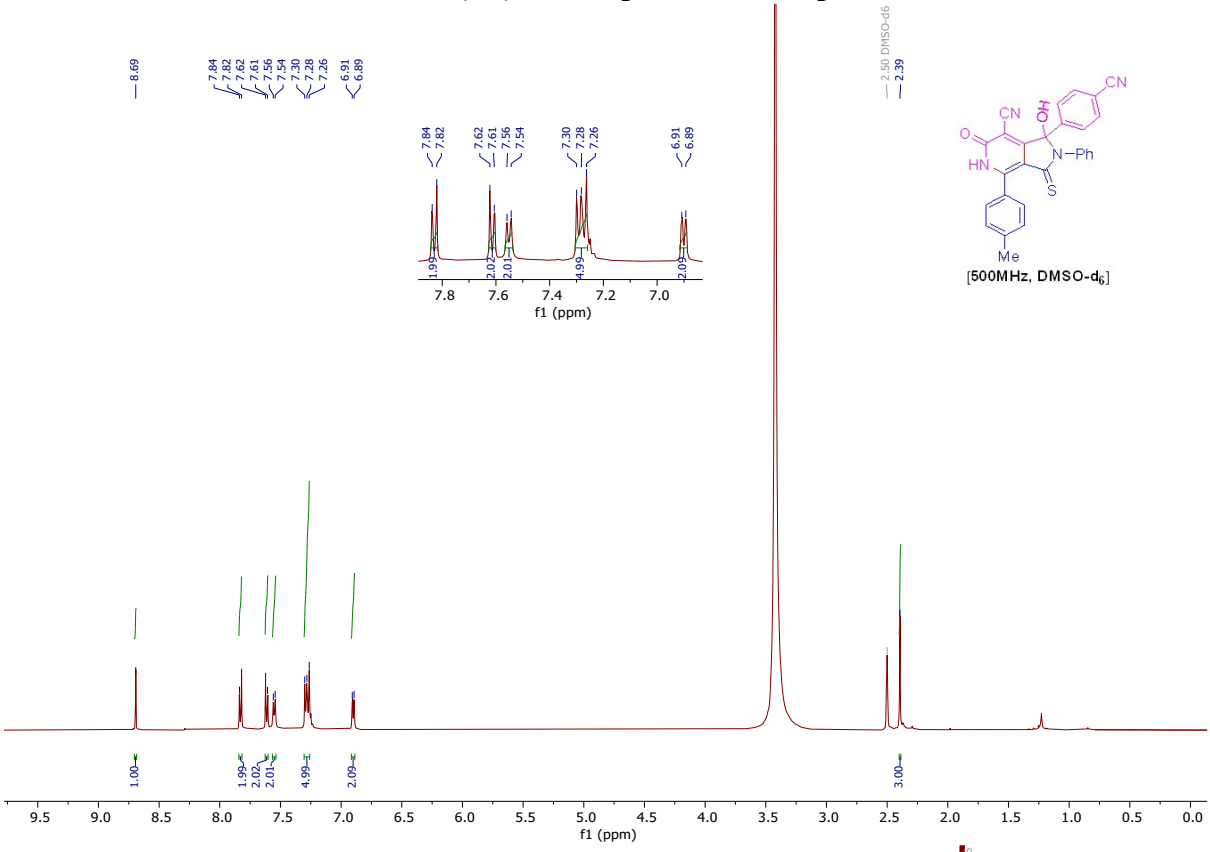


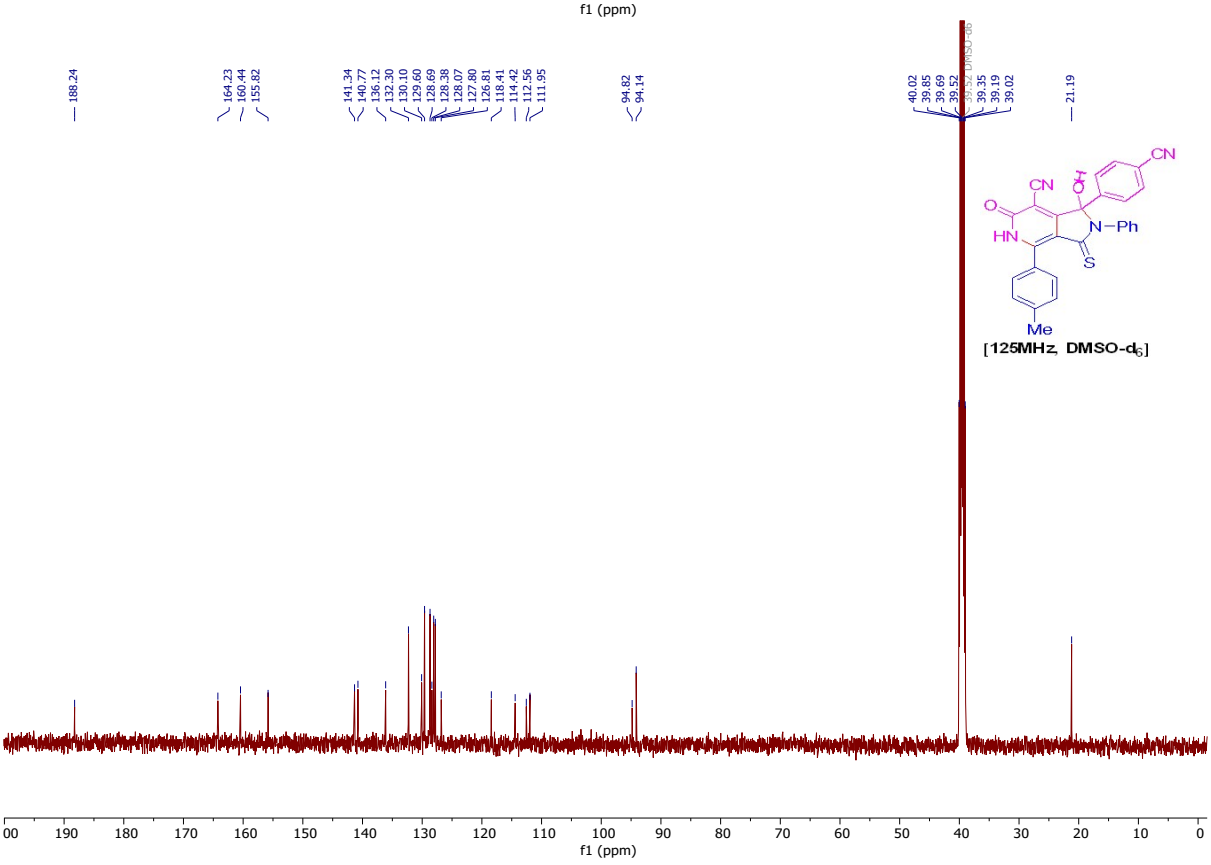
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zm



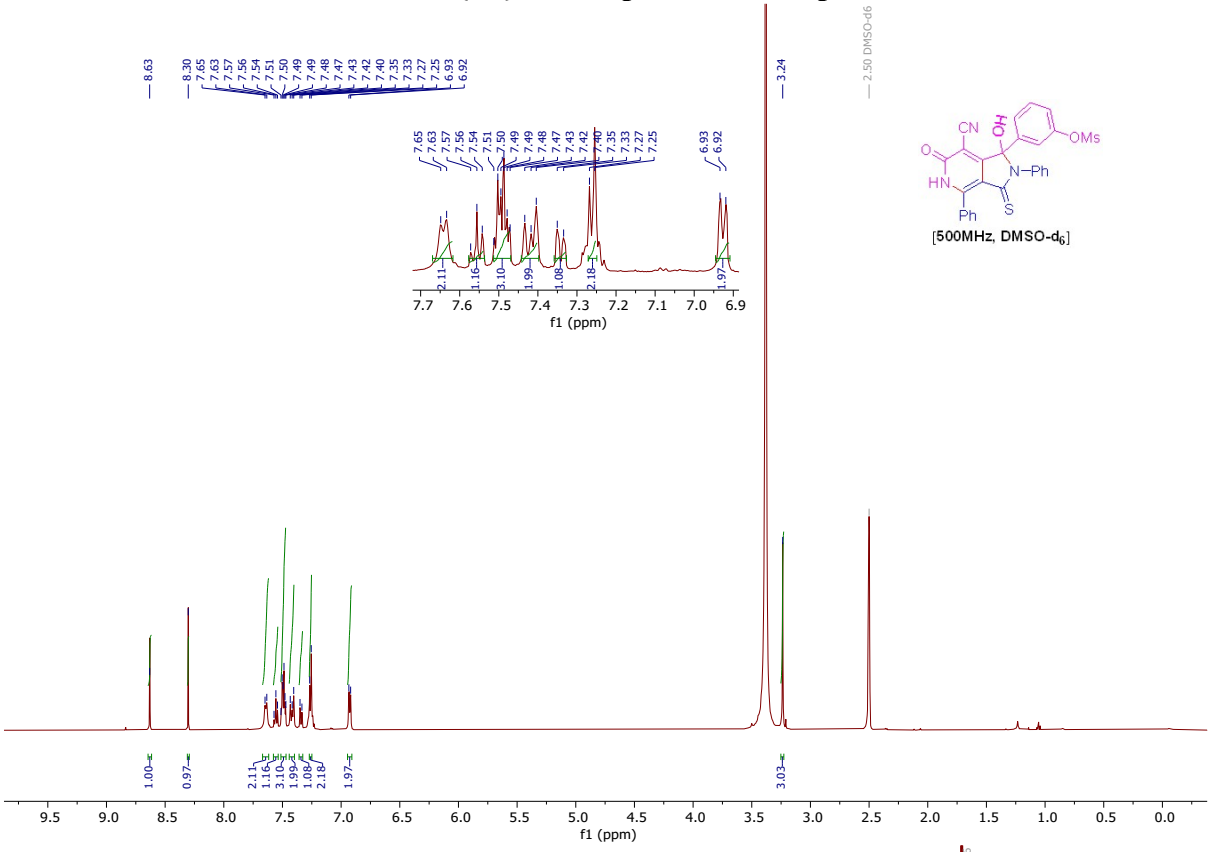


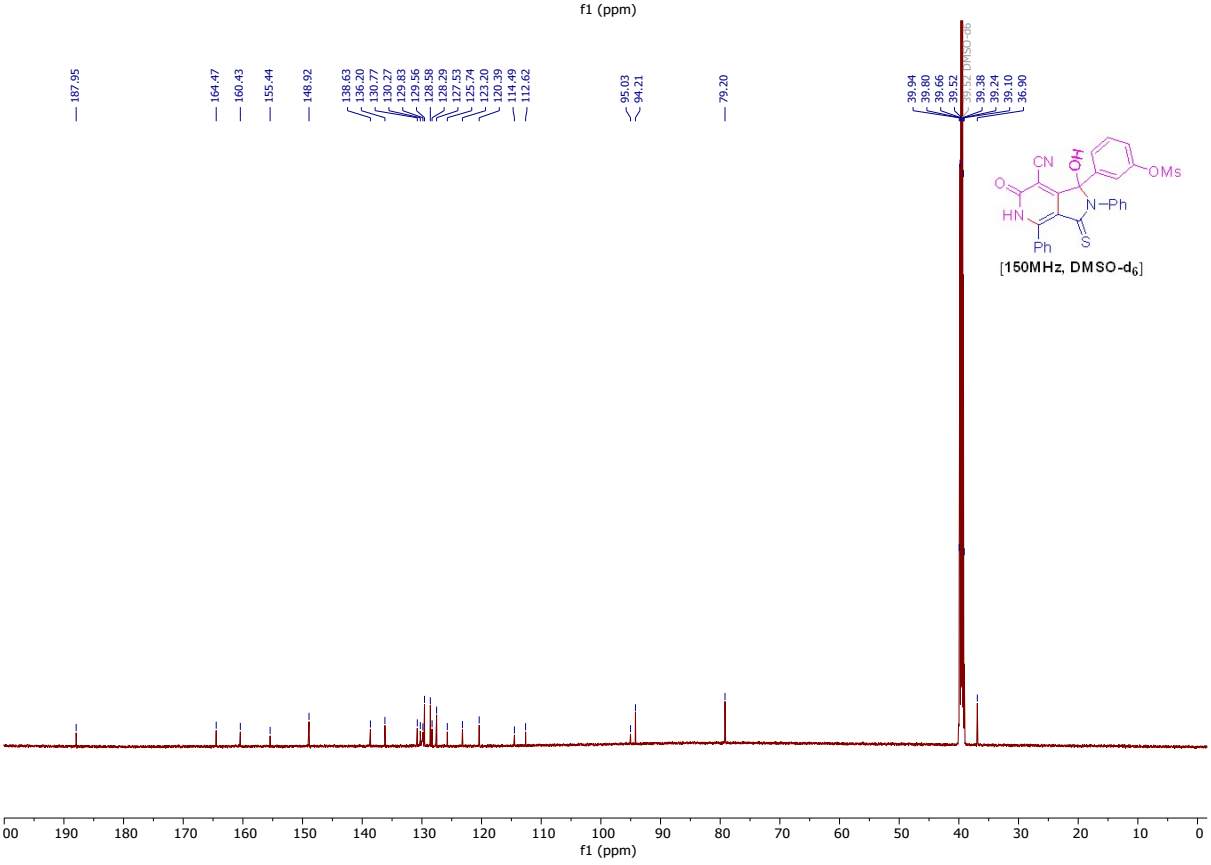
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zn



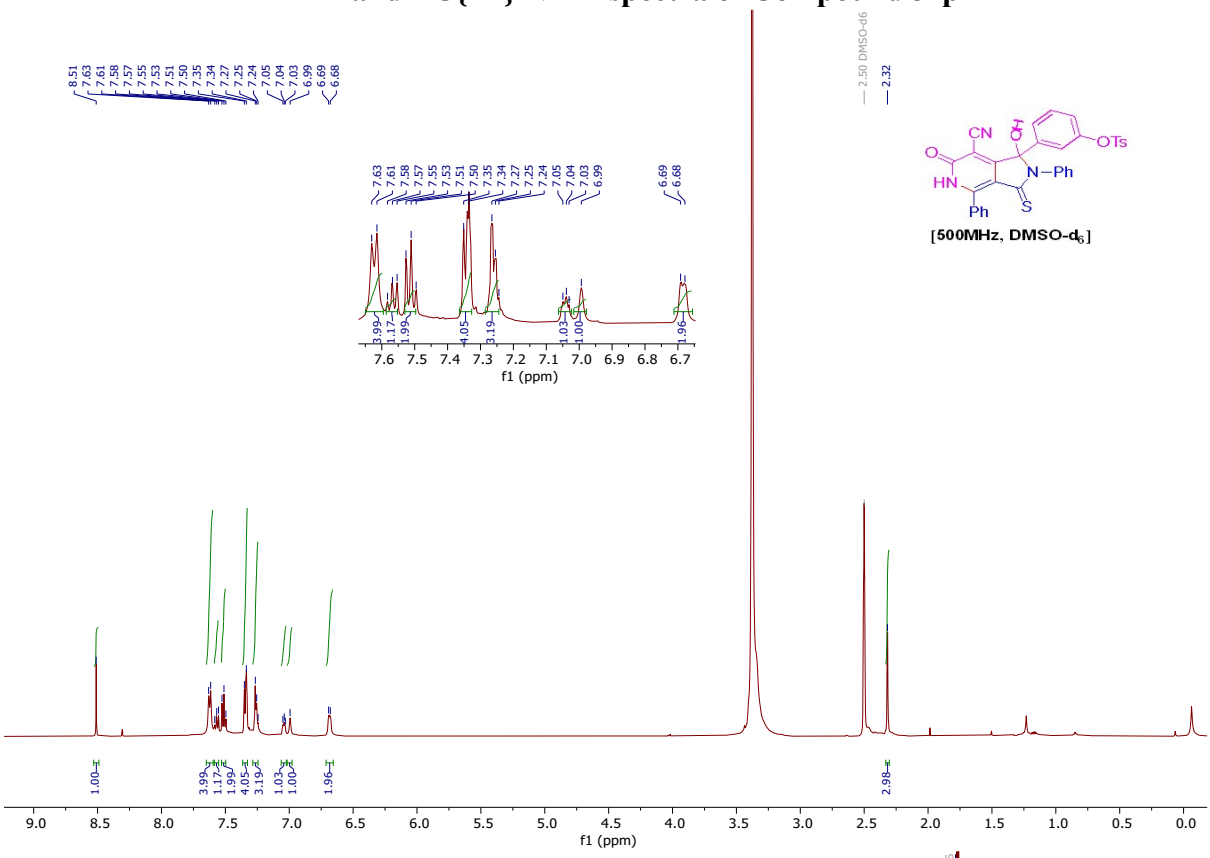


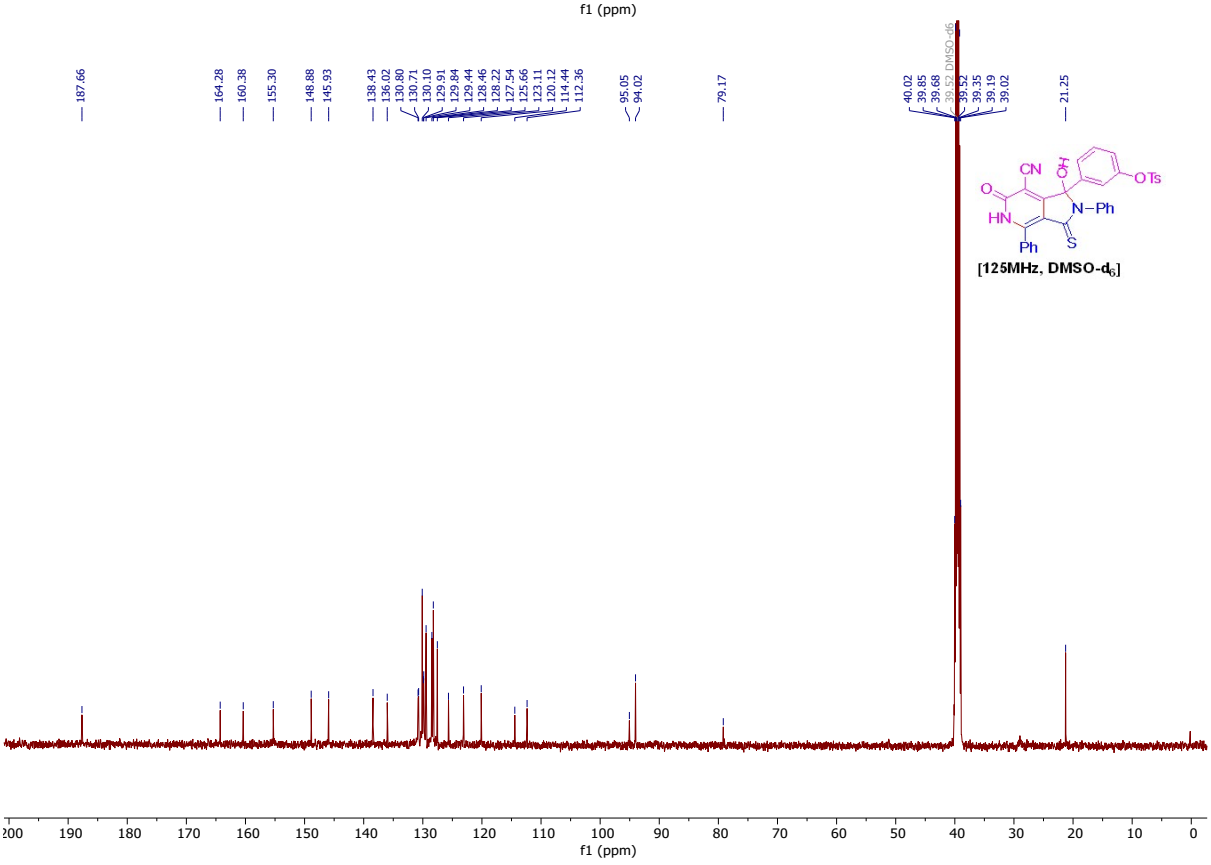
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zo



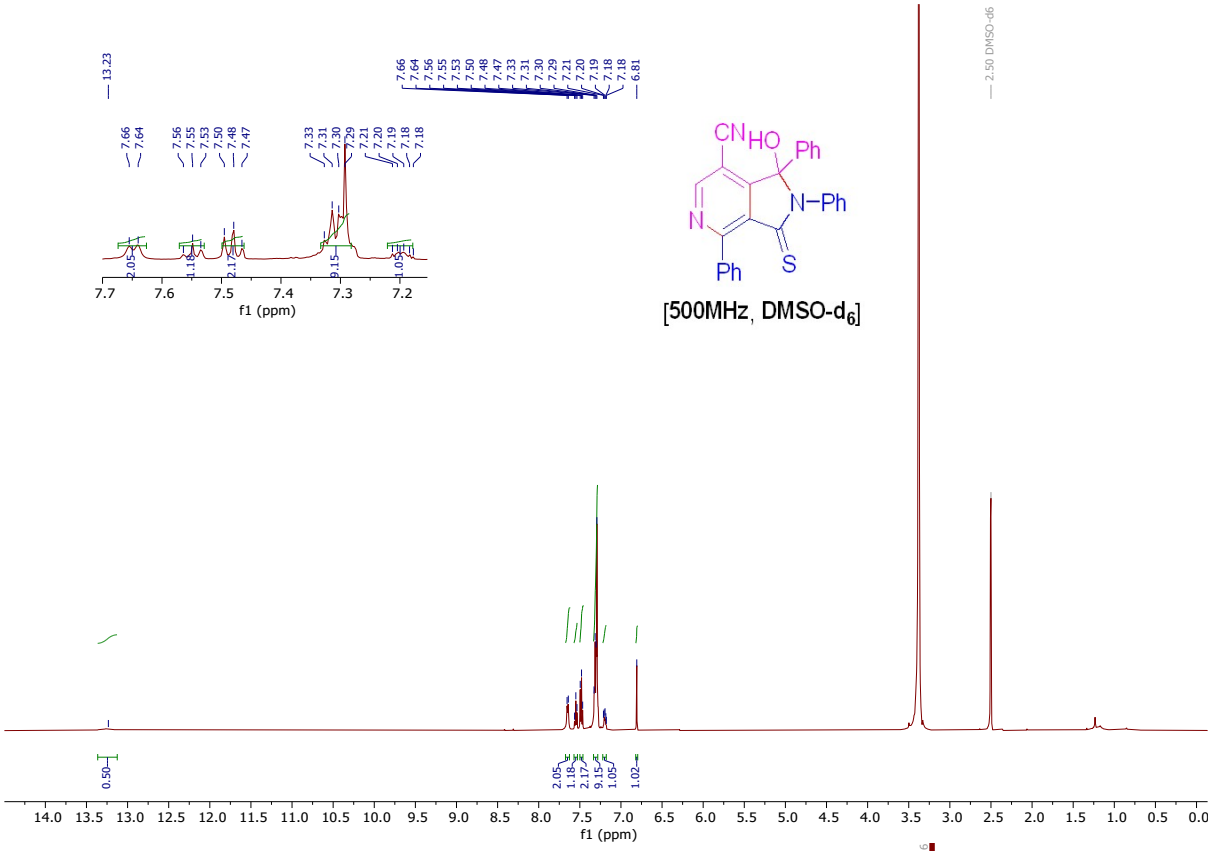


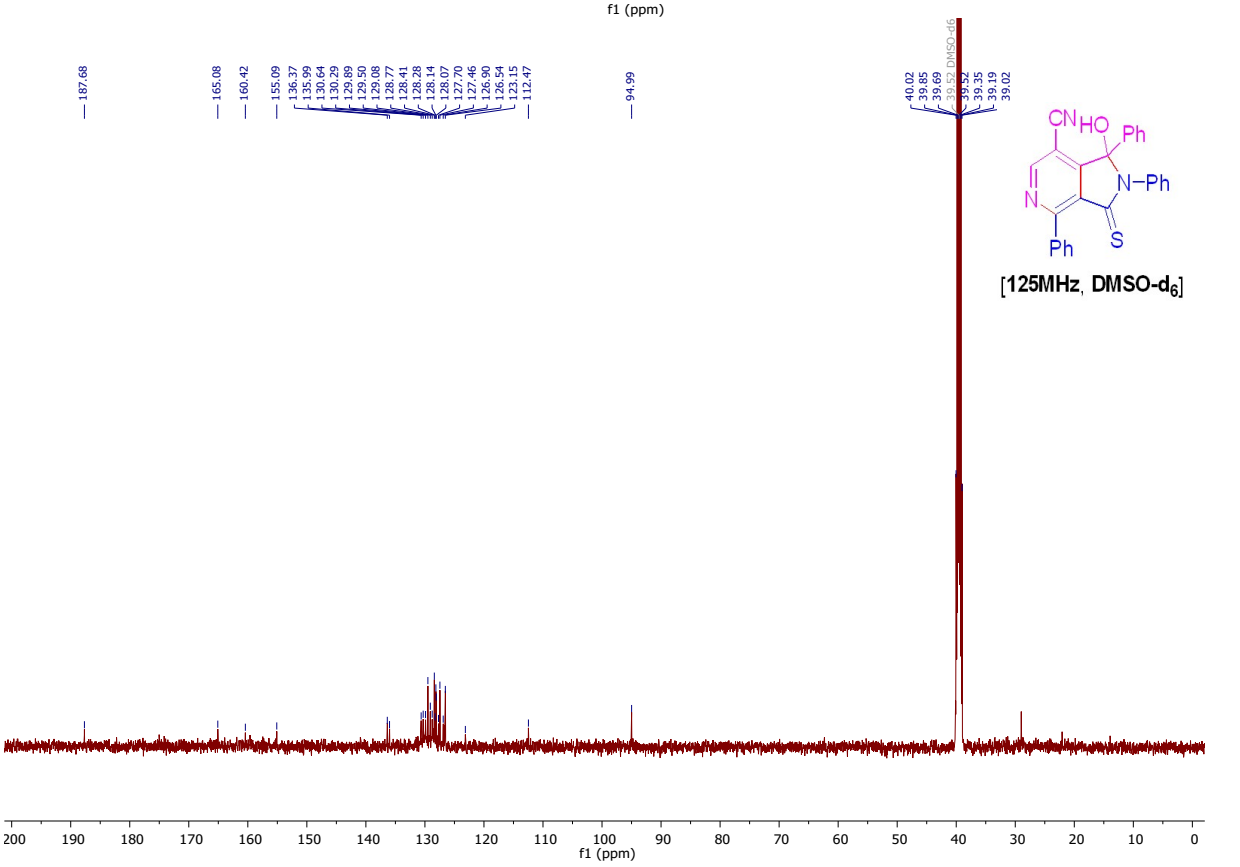
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 3zp



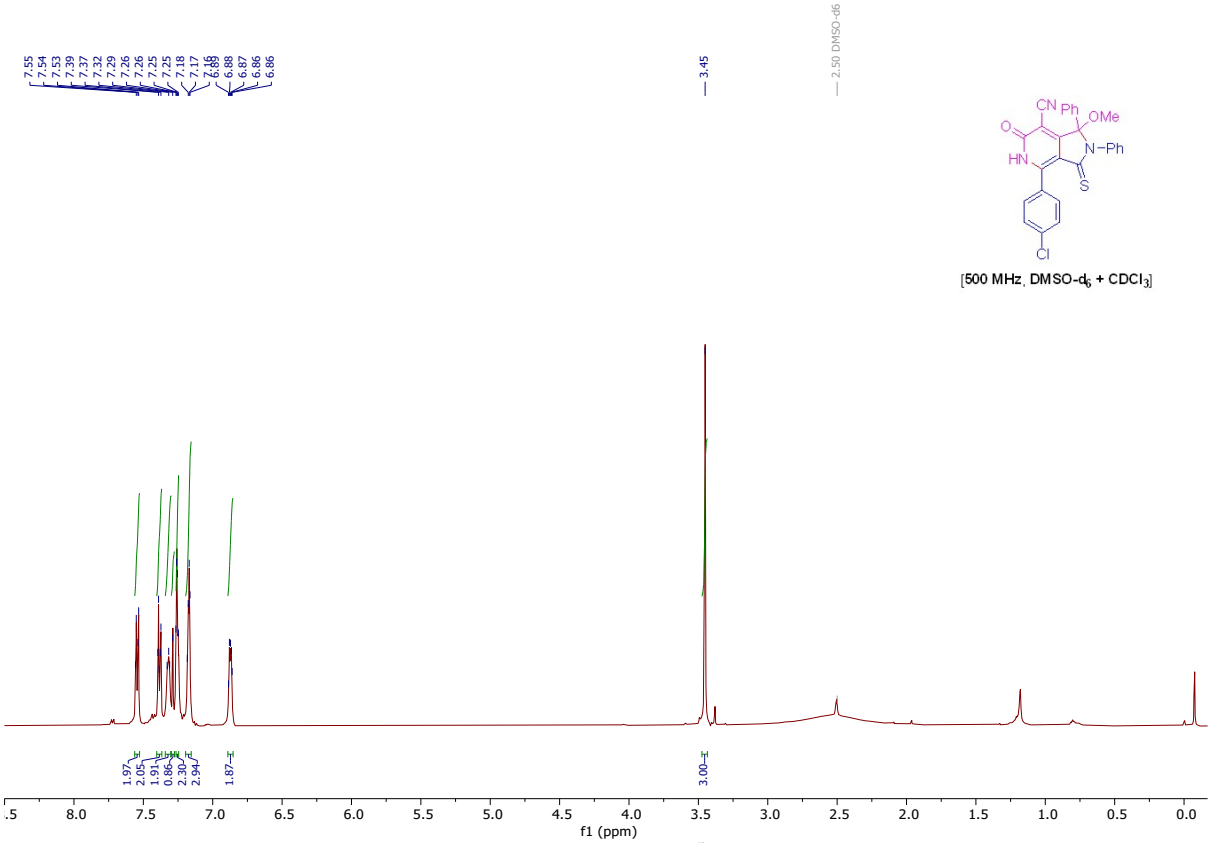


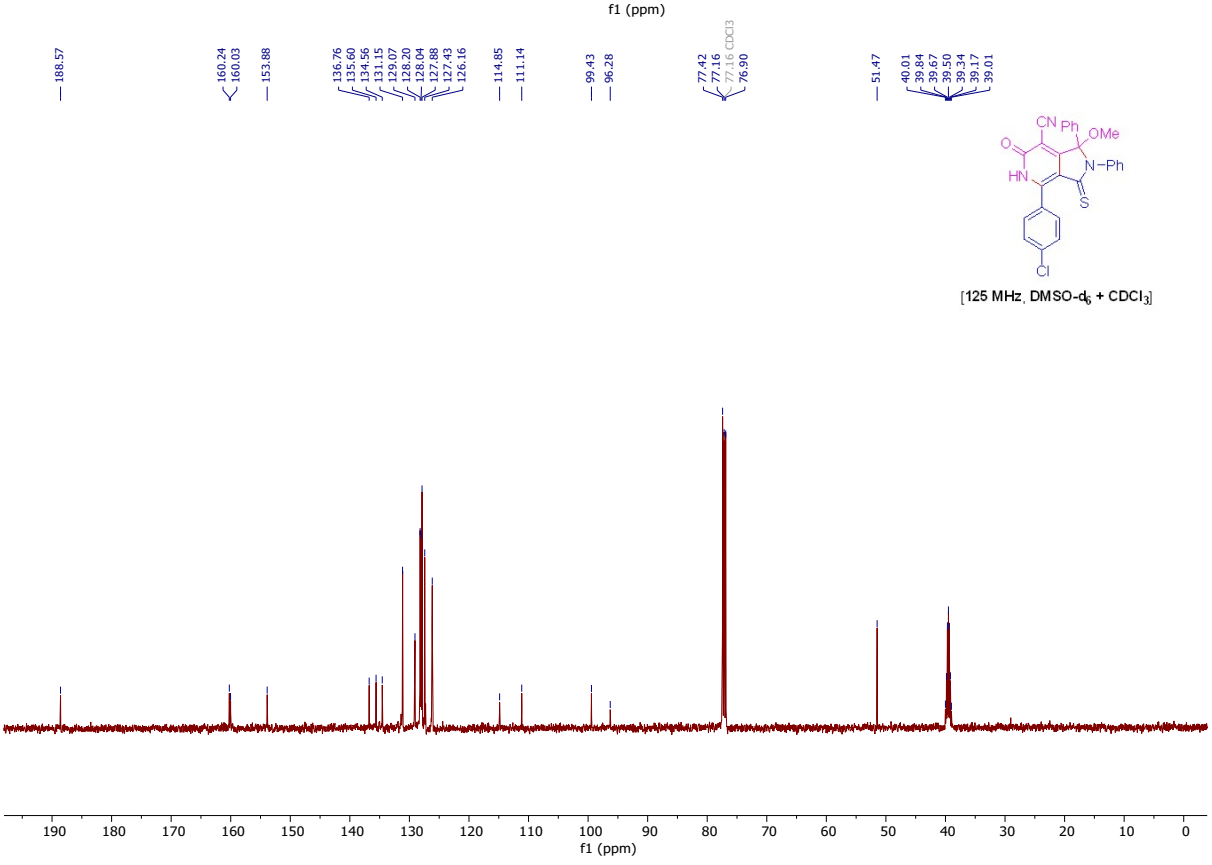
^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 4a





^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Compound 4b





8. Crystal data and structural refinement

Method for crystals growth of compounds 3d

For crystallization of the compound **3d** vacuum-dried pure samples were taken in separate vials and dissolved in 2.0 mL of acetonitrile. The vials were kept at room temperature in dark for slow evaporation. After 6 days, yellow solid coloured, cuboidal-shaped crystals were formed, which were further dried for 48 h under high vacuum to remove any solvent residues. The well-dried crystals were picked up and subjected to single crystal XRD study.

8.1 X-Ray Crystallographic Data & ORTEP diagram of 3d (CCDC No. **2373385**)

```
Bond precision:   C-C = 0.0033 A          Wavelength=1.54184

Cell:             a=21.6291(2)     b=8.6367(1)        c=30.4166(2)
                  alpha=90         beta=94.806(1)     gamma=90
Temperature:      100 K

                 Calculated                  Reported
Volume           5661.97(9)                  5661.97(9)
Space group      I 2/a                       I 1 2/a 1
Hall group       -I 2ya                      -I 2ya
Moiety formula   C27 H19 N3 O2 S, C2 H6 O S, C27 H19 N3 O2 S, C2 H6 O S,
                 H2 O                        H2 O
Sum formula      C29 H27 N3 O4 S2            C29 H27 N3 O4 S2
Mr               545.66                      545.65
Dx,g cm-3        1.280                       1.280
Z                8                           8
Mu (mm-1)        2.020                       2.020
F000             2288.0                      2288.0
F000'            2299.54
h,k,lmax         26,10,36                    26,10,36
Nref             5169                        5159
Tmin,Tmax        0.744,0.814                 0.696,1.000
Tmin'            0.730

Correction method= # Reported T Limits: Tmin=0.696 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 68.089

R(reflections)= 0.0471( 4394)                wR2(reflections)=
                                             0.1434( 5159)
S = 1.055                 Npar= 393
```

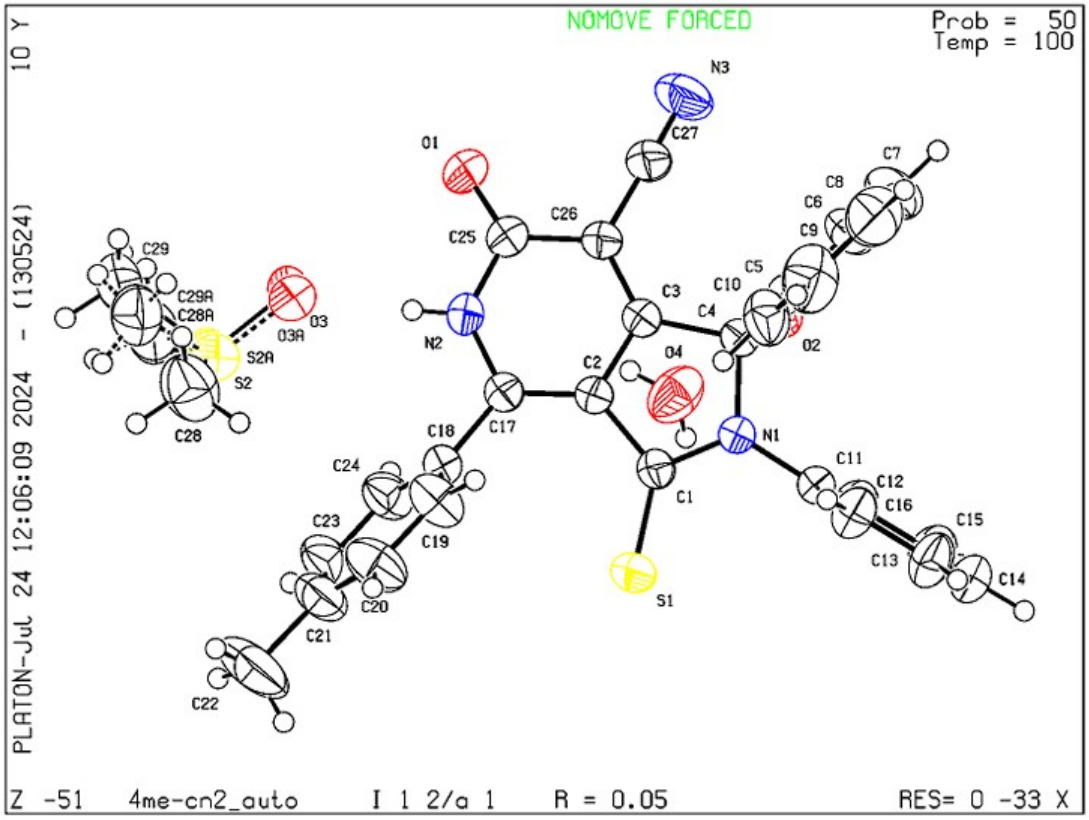


Fig: 1. ORTEP with 50% thermal ellipsoid probability level

9. HRMS spectra of reaction mixture

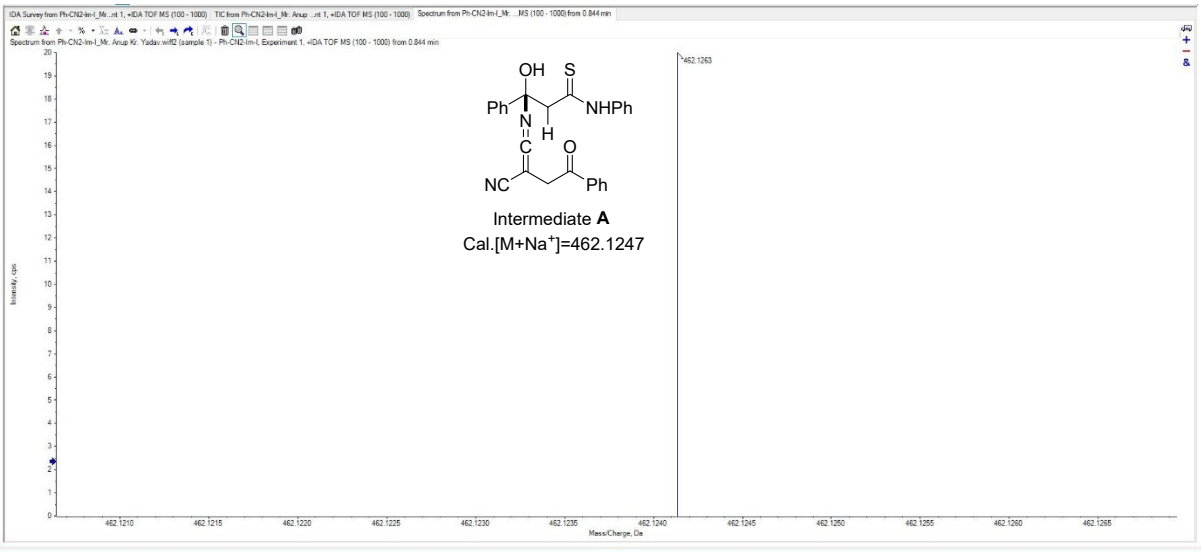


Fig: 2. HRMS spectra of reaction mixture containing intermediate **A** peak

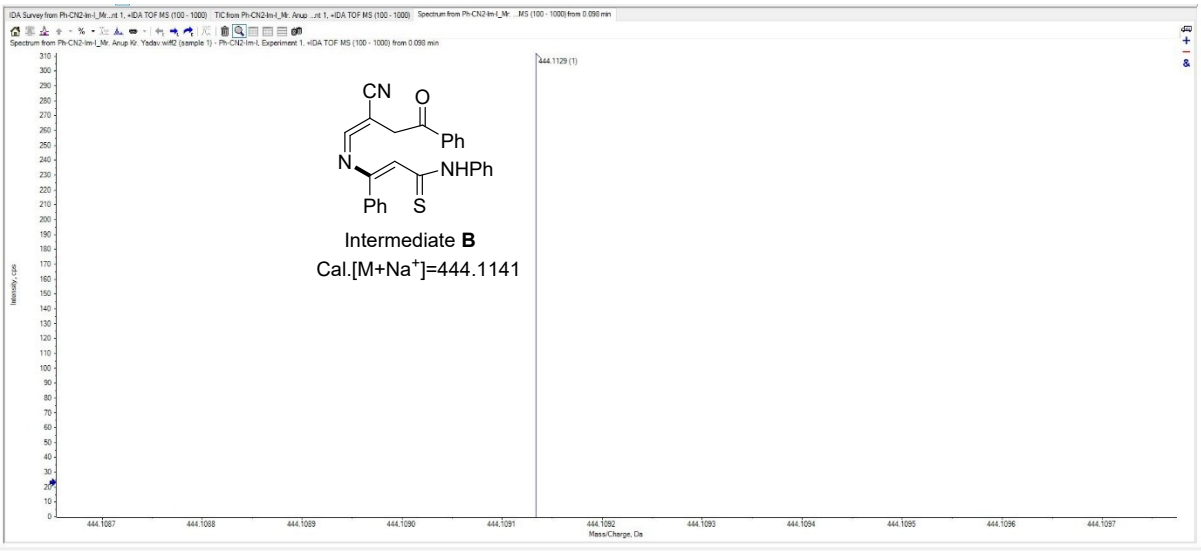


Fig: 3. HRMS spectra of reaction mixture containing intermediate **B** peak

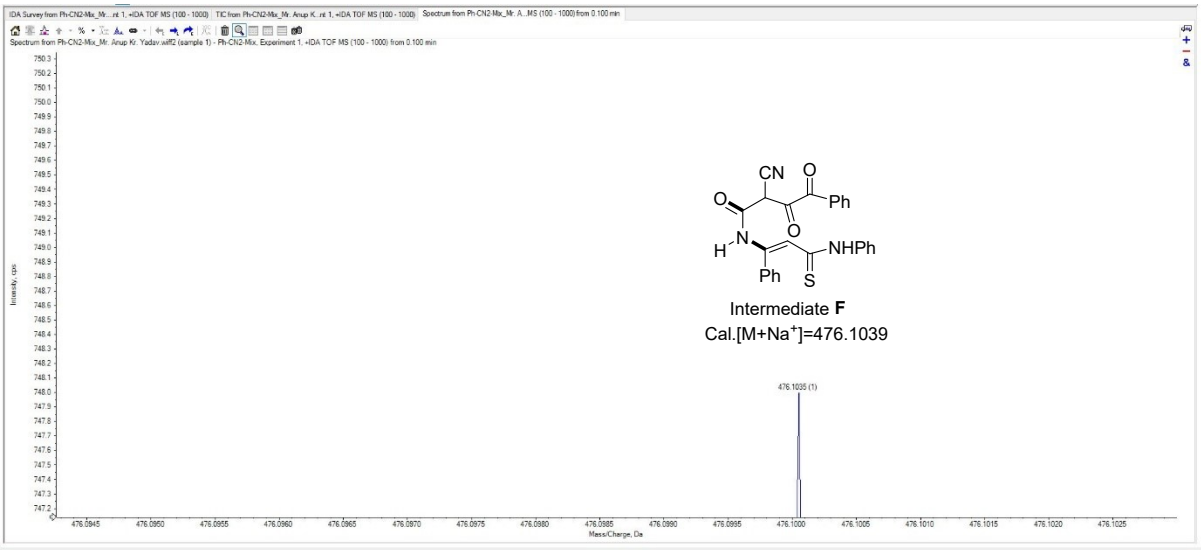


Fig: 4. HRMS spectra of reaction mixture containing intermediate **F** peak