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# Supporting Information

## Organocatalysed one-pot three component Synthesis of 3,3′-disubstituted Oxindoles Featuring an all-Carbon Quaternary center and Spiro[2H-pyran-3,4′-indoline]

Chandrakant B. Nichinde,[ab]‡ Baliram R. Patil ,[ab]‡ Suryakant S. Chaudhari, [ab] Bhupendra P. Mali,[bc] Rajesh G. Gonnade*[bc] and Anil K. Kinage*[ab]

# Supporting Information

1. General information---------- S2
2. Single crystal X-ray diffraction study---------- S3
3. Synthesis of N-protected isatin derivatives ---------- S5
4. Synthesis of isatylidine malononitrile---------- S6
5. One pot Synthesis of 3,3′-disubstituted oxindoles featuring an all-carbon quaternary center---------- S6
6. One pot Synthesis of Spiro[2H-pyran-3,4′-indoline]---------- S7
7. Characterization data for products---------- S8
8. References ---------- S23
9. NMR Spectra of Compounds---------- S24

***General information***

The one pot reactions were carried out with anhydrous solvents in reaction tube. All solvents were purchased anhydrous. The reactions were monitored by analytical thin layer chromatography (TLC) visualizing under UV light (254 nm) or $I_2$ staining. Flash chromatography was performed using silica gel (Merck and Spectrochem, 230-400 mesh), eluting with solvents as indicated. Flash column was performed using Sebo aquarium air pump (SB-548A). $^{1}H$, $^{13}C$, 135 DEPT and $^{19}F$ spectrum were acquired in deuterated solvents at room temperature on Bruker: Ultrashield 400 MHz, Ultrashield 500 MHz and JEOL 400 spectrometer. Chemical shifts (δ) are reported for $^{1}HNMR$ in ppm from TMS as internal standard and $^{13}C$ from the residual solvent peak. $^{1}H$ NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for 13C NMR spectra are reported in terms of chemical shift (δ ppm). High resolution (HRMS) mass spectral analyses were recorded by High- resolution mass spectrometry using ESI TOF mass analyzer.

## SINGLE CRYSTAL X-RAY DIFFRACTION STUDIES

The good quality single crystals of each compound suitable for single-crystal X-ray diffraction analysis were selected using Leica polarizing microscope (S8APO). The X-ray intensity data for all compounds were measured on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics with X-ray generator power setting at 50 kV and 1.4 mA. The intensity measurements were carried out with both Cu and Mo micro-focus sealed tube diffraction source (CuKα = 1.54178 Å; Mo Kα = 0.71073 Å) at 100(2) K temperature. A preliminary set of cell constants and an orientation matrix were calculated from 36 and 40 frames for Mo and Cu radiations, respectively. The complete intensity data were collected using an optimized strategy that consisted of different sets of $\omega$, $\varphi$ and $2\theta$ with 0.5° width keeping the sample-to-detector distance fixed at 5.00 cm with varying exposure time (10-20 sec) depending on the diffraction power of the crystals. The whole process of X-ray data acquisition (unit–cell measurements and data collection) was controlled and monitored by the APEX3 program suite of Bruker-AXS (Bruker, 2016).[1] The complete data sets were corrected for Lorentz-polarization and absorption effects (multi-scan method) using SAINT and SADABS programs with the transmission coefficients. Using the APEX3 (Bruker, 2016) program suite,[1] the structure was solved using direct methods with the ShelXS-97 (Sheldrick, 2008) structure solution program.[2] The model was refined with ShelXL-2013 (Sheldrick, 2015) using Least Squares minimization based on $F^2$.[3] All non-hydrogen atoms were refined anisotropically. Conversely, hydrogen atoms were refined isotropically by placing them in a geometrically idealized position (C-H = 0.95 Å for sp2 hybridized C-atoms including H atoms in phenyl and ethyne groups, C-H = 0.98 Å for the methyl H-atoms) and constrained to ride on their parent atoms [Uiso(H) = 1.2 Ueq(C) or 1.5 Ueq(methyl C)]. ORTEPs for all the compounds were plotted at the 50% probability displacement ellipsoids, and H atoms are

shown as small spheres of arbitrary radii.[4] The molecular packing diagrams were generated using the Mercury program.[5] Geometrical calculations were performed using SHELXTL (Bruker, 2016)[1] and PLATON.[6] Experiment details of the single crystal X-ray diffraction analysis, including crystal data, data collection and structure refinement for all the compounds, are summarized in Table 1.

CRYSTALLOGRAPHIC DATA FOR POLYMORPHS

Table 1. Single crystal X-ray diffraction data for polymorphs, Form I and Form II of **1.**

| Crystal Data | 4Ae | 4Ah | 5Aa | 5Bb |
|---|---|---|---|---|
| Formula | C14 H10 Cl N3 O2 | C14 H10 F N3 O2 | C14 H13 N3 O2 | C17 H19 N3 O2 |
| $M_r$ | 287.70 | 271.25 | 255.27 | 297.35 |
| Crystal Size, mm | 0.150 × 0.13 × 0.120 | 0.120 × 0.100 × 0.100 | 0.140 × 0.110 × 0.090 | 0.180 × 0.140 × 0.110 |
| Temp. (K) | 100(2) | 100(2) | 100(2) | 100(2) |
| Crystal Syst. | Triclinic | monoclinic | Orthorhombic | monoclinic |
| Space Group | P-1 | $P2_1/c$ | $P2_12_12_1$ | $P2_1/n$ |
| *a*/Å | 6.9044(6) | 10.0790(8) | 8.7768(9) | 9.9716(3) |
| *b*/Å | 6.9108(5) | 7.1417(5) | 8.9125(9) | 13.6586(4) |
| *c*/Å | 13.8175(11) | 17.9545(13) | 15.809(16) | 11.3692(3) |
| $\alpha$/$^0$ | 91.301(3) | 90 | 90 | 90 |
| $\beta$/$^0$ | 100.548(3) | 91.403(3) | 90 | 93.5400(10) |
| $\gamma$/$^0$ | 103.119(3) | 90 | 90 | 90 |
| *V*/Å$^3$ | 629.82(9) | 1292.00(17) | 1236.7(2) | 1545.51(8) |
| Z | 2 | 4 | 4 | 4 |
| Radiation type | MoKα | MoKα | CuKα | CuKα |
| Wavelength (Å) | 0.71073 | 0.71073 | 1.54178 | 1.54178 |
| $D_{calc}$/g cm$^{-3}$ | 1.517 | 1.394 | 1.371 | 1.278 |
| *m*/mm$^{-1}$ | 0.308 | 0.106 | 0.774 | 0.690 |
| *F*(000) | 296 | 560 | 536 | 632 |
| *Ab. Correct.* | multi-scan | multi-scan | multi-scan | multi-scan |
| $T_{min}$/ $T_{max}$ | 0.955/0.964 | 0.987/0.989 | 0.899/0.934 | 0.886/0.928 |
| $2\theta_{max}$ | 70.48 | 69.79 | 145.07 | 158.64 |
| Total reflns. | 44763 | 88591 | 18194 | 55739 |
| unique reflns. | 5247 | 5486 | 2428 | 3326 |
| Obs. reflns. | 4508 | 4545 | 2389 | 2782 |
| *h, k, l* (min, max) | (-11,10), (-11, 11), (-21, 21) | (-16, 16), (-11, 11), (-28, 27) | (-10,10), (-11, 9), (-19, 18) | (-12,12), (-17, 16), (-14, 14) |
| $R_{int}$ | 0.0572 | 0.0626 | 0.0413 | 0.0702 |
| No. of para | 186 | 186 | 182 | 201 |
| *R*1 [$I > 2\sigma(I)$] | 0.0337 | 0.0398 | 0.0292 | 0.0455 |

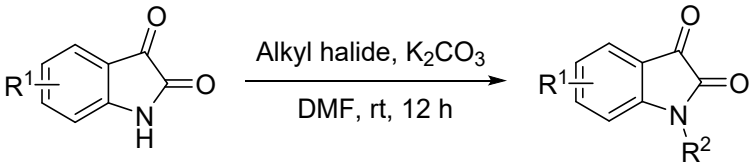
| | | | | |
|---|---|---|---|---|
| *wR*2[*I*> 2$\sigma$(*I*)] | 0.0836 | 0.1019 | 0.0758 | 0.1049 |
| *R1* [all data] | 0.0433 | 0.0534 | 0.0295 | 0.0572 |
| *wR2* [all data] | 0.0891 | 0.1090 | 0.0762 | 0.1171 |
| Goodness-of-fit (*S*) | 1.031 | 1.041 | 1.069 | 1.060 |
| Absolute structure parameter | | | **0.02(6)** | |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$($eÅ^{-3}$) | +0.545, -0.350 | +0.509, -0.294 | +0.211,-0.154 | +0.298,-0.379 |
| CCDC nos. | **2224164** | **2224165** | **2224166** | **2224167** |

**Experimental Procedures:**

1. **Synthesis of N-protected isatin derivatives:**

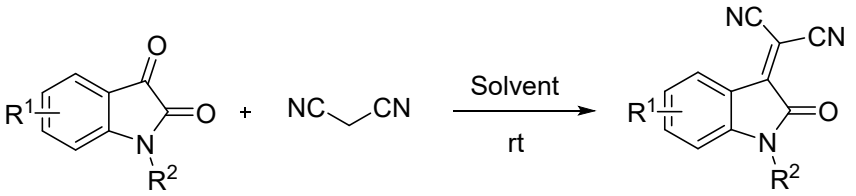
N-Protected isatin derivatives were synthesized from commercially available isatins and alkyl or aryl halides in the presence of potassium carbonate as base in DMF solution. Alkyl halides (12 mmol, 1.2 equiv) was added to a stirred solution of isatin (10 mmol, 1.0 equiv) and $K_2CO_3$ (12 mmol, 1.2 equiv) in DMF and stirred for 12 h at room temperature. Reactions were monitored by TLC until completion. The reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic phases were washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuum. The crude residue was then purified by column chromatography on silica gel with ethyl acetate-pet ether (10/90 to 20/80) to provide N-protected isatin derivatives.[1,2]

**Scheme A:**



**2. Synthesis of isatylidine malononitrile:**

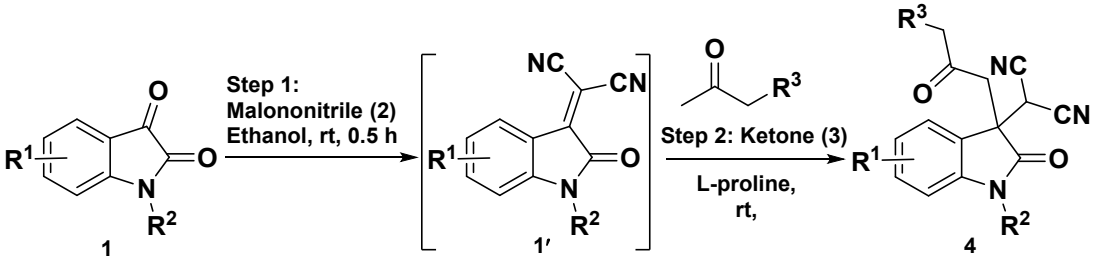
A mixture of isatin (0.5 mmol, 1 equiv.), malononitrile (0.55 mmol, 1.1 equiv.) in solvent (1 mL) was stirred at room temperature until isatin was total conversion of starting material to product (monitored by TLC). After completion of reaction solvent removed under low pressure. Obtained residue wash with cold methanol to get pure product.




| Entry | Solvent | Time | Isolated yield % |
|---|---|---|---|
| 1. | - | 2 h | 94 |
| 3. | EtOAc | 12 h | 95 |
| 4. | Ethanol | 10 min | 98 |
| 5. | Acetonitrile | 14 | 90 |
| 6. | Methanol | 10 min | 96 |
| 7. | DMF | 6 h | 94 |
| 8. | DMSO | 6 h | 92 |

**3. One pot Synthesis of 3,3′-disubstituted oxindoles featuring an all-carbon quaternary center:**

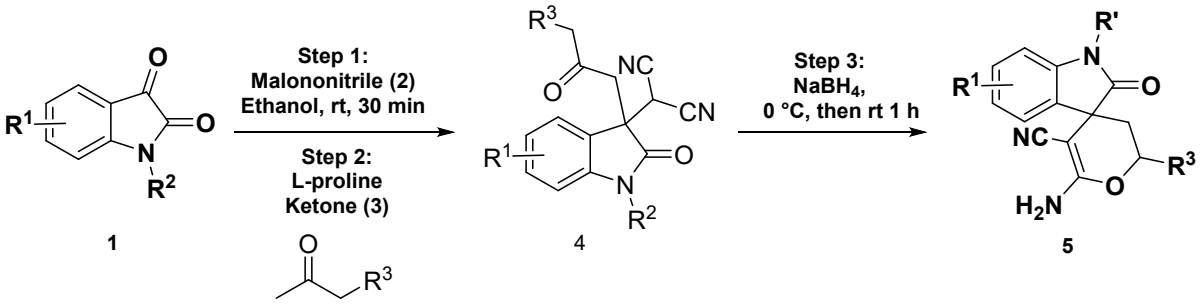
A mixture of isatin derivative (0.5 mmol, 1 equiv.), malononitrile (0.55 mmol, 1.1 equiv.) in Ethanol (1 mL) was stirred at room temperature for 30 minutes, followed by addition of Ketone (2.5 mmol, 5.0 equiv.) and L-proline (0.1 mmol, 20 mol%), stirred continuously for next 30 min at rt (In case of ketones except acetone reaction took time up to 24 h for complete conversion).



**4. One pot Synthesis of Spiro[2H-pyran-3,4′-indoline]:**

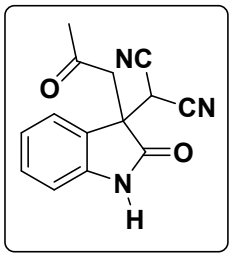
A mixture of isatin derivative (0.5 mmol, 1 equiv.), malononitrile (0.55 mmol, 1.1 equiv.) in Ethanol (1 mL) was stirred at room temperature for 30 minutes, followed by addition of ketone (2.5 mmol, 5.0 equiv.) and L-proline (0.1 mmol, 20 mol%), stirred continuously, reaction was monitored by TLC until completion. After complete formation of 4, added NaBH4 (1 mmol) at 0 °C then stirred reaction mixture for 10 min then at rt for 1-2 h.

Mentioned dr are calculated by $^1$H NMR of crude product. Yields shown above are the combine yield of two diastereomers. We separate two diastereomer by silica gel column chromatography and characterisations provided are for major diastereomer only. The relative stereochemistry of the major diastereoisomers are different for different compounds as in single crystal x-ray structure for 5Aa is verified as R,R and for 5Bb as S,S configuration. As both compound having different configuration it is difficult to assign relative stereochemistry for other major diastereomer from the obtained crystal structure of two compounds. In conclusion this desired reaction is not stereocontrol so the formed diastereomeric product may be R,R or S, S.



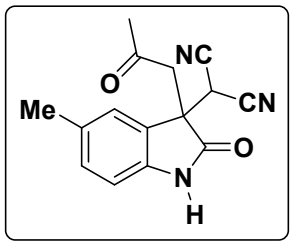
**Characterization data for products:**

**2-(2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Aa):**



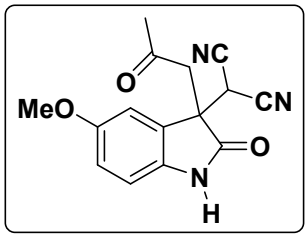
The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (122.7 mg, 97% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.6;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.99 (s, 1H), 7.38 (d, *J*=7.50 Hz, 1H), 7.31 (td, *J*=7.72, 1.19 Hz, 1H), 7.03 (td, *J*=7.60, 0.94 Hz, 1H), 6.94 (d, *J*=7.75 Hz, 1H), 5.53 (s, 1H), 3.61 (d, *J*=18.01 Hz, 1H), 3.29 (d, *J*=18.01 Hz, 1H), 2.05 (s, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.6, 175.4, 143.0, 129.9, 126.5, 123.4, 122.0, 111.6, 111.2, 110.1, 48.2, 45.7, 30.1, 29.9; **HRMS** (ESI) m/z Calculated for $C_{14}H_{11}N_3O_2$ [Na]+ : 276.0749, found: 276.0743; **mp**: 199-200 °C.

**2-(5-methyl-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Ab):**



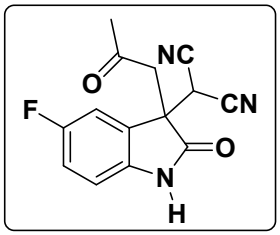
The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (126.82 mg, 95% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.5;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.88 (s, 1H), 7.19 (s, 1H), 7.05 - 7.14 (m, 1H), 6.83 (d, *J*=7.88 Hz, 1H), 5.50 (s, 1H), 3.57 (d, *J*=18.01 Hz, 1H), 3.26 (d, *J*=18.01 Hz, 1H), 2.26 (s, 3H), 2.05 (s, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.5, 175.3, 140.6, 130.8, 130.2, 126.6, 123.9, 111.6, 111.3, 109.9, 48.3, 45.7, 30.1, 29.9, 20.8. **HRMS** (ESI) m/z Calculated for $C_{15}H_{13}N_3O_2$ [H]+: 268.1086, found: 268.1081; **mp**: 205-206 °C.

**2-(5-methoxy-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Ac):**



The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (133 mg, 94% yield).
$R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.55;
**$^1$H NMR (500 MHz, *DMSO-d$_6$*)** δ 10.81 (s, 1H), 7.03 (s, 1H), 6.77 - 6.94 (m, 2H), 5.51 (s, 1H), 3.71 (s, 3H), 3.60 (d, *J*=18.0 Hz, 1H), 3.26 (d, *J*=18.01 Hz, 1H), 2.06 (s, 3H); **$^{13}$C NMR (126 MHz, *DMSO-d$_6$*)** δ 203.5, 175.2, 154.9, 136.2, 127.8, 114.0, 111.6, 111.2, 110.8, 110.5, 55.4, 48.6, 45.6, 30.1, 29.8. **HRMS** (ESI) m/z Calculated for $C_{15}H_{13}N_3O_3$ [Na]+: 306.0855, found: 306.0849; **mp**: 202-204 °C.

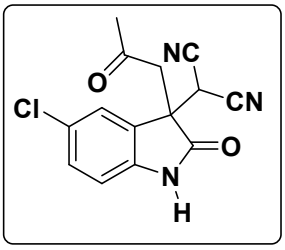
**2-(5-fluoro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Ad):**



The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (138 mg, 96% yield).
$R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.6;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 11.02 (s, 1H), 7.28 (d, *J*=7.63 Hz, 1H), 7.15 (t, *J*=8.38 Hz, 1H), 6.94 (dd, *J*=7.75, 4.00 Hz, 1H), 5.55 (s, 1H), 3.65 (d, *J*=18.14 Hz, 1H), 3.31 (d, *J*=18.26 Hz, 1H), 2.06 (m, 3H)**; $^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.7, 175.4, 157.5 (d, $J_{C-F}$=242.2 Hz), 139.4 (d, $J_{C-F}$=1.4 Hz), 128.2 (d, $J_{C-F}$=8.4 Hz), 116.3

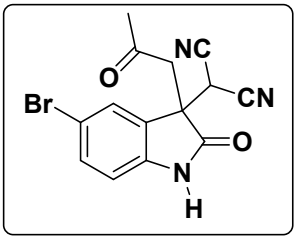
(d, $J_{C-F}$=23.4 Hz), 111.6 (d, $J_{C-F}$=24.8 Hz), 111.4, 111.1(d, $J_{C-F}$=8.3 Hz), 48.6, 45.7, 29.9, 29.7; **$^{19}$F NMR (376 MHz, *DMSO-d$_6$*)** δ -120.98; **HRMS** (ESI) m/z Calculated for $C_{14}H_{10}FN_3O_2$ [H]+: 272.0835, found: 272.0830; **mp**: 204-206 °C.

**2-(5-chloro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Ae):**



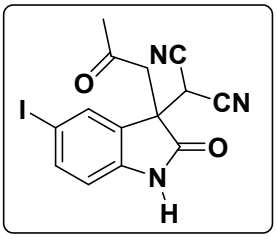

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (157 mg, 94% yield).
***R$_f$*** (Ethyl acetate/Pet. ether; 30:70) = 0.6;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 11.15 (s, 1H), 7.48 (d, *J*=2.25 Hz, 1H), 7.37 (dd, *J*=8.32, 2.19 Hz, 1H), 6.97 (d, *J*=8.38 Hz, 1H), 5.57 (s, 1H), 3.70 (d, *J*=18.39 Hz, 1H), 3.33 (d, *J*=18.13 Hz, 1H), 2.07 (s, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.7, 175.1, 142.1, 129.8, 128.6, 125.9, 123.8, 111.6, 111.3, 111.0, 48.4, 45.7, 29.9, 29.6; **HRMS** (ESI) m/z Calculated for $C_{14}H_{10}ClN_3O_2$ [Na]+: 310.0359, found: 310.0354; **mp**: 208-210 °C.

**2-(5-bromo-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Af):**



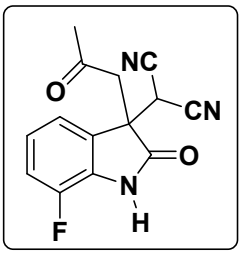

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (180 mg, 95% yield).
***R$_f$*** (Ethyl acetate/Pet. ether; 30:70) = 0.6;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 11.15 (s, 1H), 7.59 (d, *J*=2.00 Hz, 1H), 7.50 (dd, *J*=8.32, 2.06 Hz, 1H), 6.92 (d, *J*=8.38 Hz, 1H), 5.57 (s, 1H), 3.71 (d, *J*=18.26 Hz, 1H), 3.33 (d, *J*=18.26 Hz, 1H), 2.07 (s, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.7, 175.0, 142.5, 132.6, 129.0, 126.5, 113.5, 112.0, 111.3, 111.0, 48.3, 45.7, 29.9, 29.6; **HRMS** (ESI) m/z Calculated for $C_{14}H_{10}BrN_3O_2$ [Na]+: 353.9849, found: 353.9849; **mp**: 225-226 °C.

**2-(5-iodo-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Ag):**



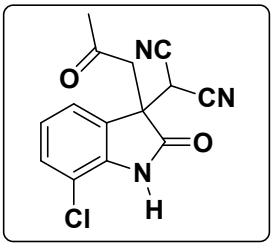

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (180 mg, 95% yield).
***R$_f$*** (Ethyl acetate/Pet. ether; 30:70) = 0.62;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 11.14 (s, 1H), 7.71 (s, 1H), 7.66 (d, *J*=8.13 Hz, 1H), 6.80 (d, *J*=8.13 Hz, 1H), 5.55 (s, 1H), 3.68 (d, *J*=18.26 Hz, 1H), 3.31 (d, *J*=18.26 Hz, 1H), 2.07 (t, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.8, 174.9, 143.0, 138.5, 131.9, 129.3, 112.6, 111.4, 111.1, 84.7, 48.1, 45.7, 29.9, 29.7; **HRMS** (ESI) m/z Calculated for $C_{14}H_{10}IN_3O_2$ [Na]+: 401.9710, found: 401.9715; **mp**: 228-230 °C.

**2-(7-fluoro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Ah):**



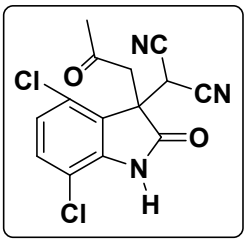
The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (129 mg, 95% yield).
$R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.6;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 11.54 (s, 1H), 7.18 - 7.30 (m, 2H), 7.06 (td, *J*=7.94, 4.75 Hz, 1H), 5.58 (s, 1H), 3.67 (d, *J*=18.14 Hz, 1H), 3.35 (d, *J*=18.14 Hz, 1H), 2.06 (s, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.7, 175.2, 146.4 (d, $J_{C\text{-}F}$=243.2 Hz), 130.2 (d, $J_{C\text{-}F}$=12.3 Hz), 129.5 (d, $J_{C\text{-}F}$=4.2 Hz), 123.1 (d, $J_{C\text{-}F}$=5.6 Hz), 119.5 (d, $J_{C\text{-}F}$=3.4 Hz), 117.1 (d, $J_{C\text{-}F}$=17.1 Hz), 111.4, 111.0, 48.5, 48.5, 45.9, 30.0, 29.7; **$^{19}$F NMR (376 MHz, *DMSO-d$_6$*)** δ -132.11; **HRMS** (ESI) m/z Calculated for $C_{14}H_{10}FN_3O_2$ [Na]+:294.0655, found: 294.0649; **mp**: 218-220 °C.

**2-(7-chloro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Ai):**



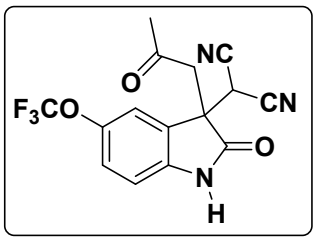
The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (136 mg, 95% yield).
$R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.6;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 11.46 (s, 1H), 7.39 (dd, *J*=8.19, 0.81 Hz, 1H), 7.36 (d, *J*=7.38 Hz, 1H), 7.07 (t, *J*=7.88 Hz, 1H), 5.60 (s, 1H), 3.68 (d, *J*=18.14 Hz, 1H), 3.36 (d, *J*=18.14 Hz, 1H), 2.06 (s, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.7, 175.3, 140.8, 130.0, 128.4, 123.3, 122.1, 114.3, 111.3, 111.0, 48.9, 45.8, 29.9, 29.7; **HRMS** (ESI) m/z Calculated for $C_{14}H_{10}ClN_3O_2$ [Na]+: 310.0359, found: 310.0354; **mp**: 198-200 °C.

**2-(4,7-dichloro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Aj):**



The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (150 mg, 93% yield).
$R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.65;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 11.81 (s, 1H), 7.47 (d, *J*=8.88 Hz, 1H), 7.10 (d, *J*=8.75 Hz, 1H), 5.63 (s, 1H), 3.91 (d, *J*=18.39 Hz, 1H), 3.40 (d, *J*=18.39 Hz, 1H), 2.12 (s, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.7, 174.3, 143.0, 131.8, 128.0, 124.1, 123.8, 113.6, 110.8, 110.4, 50.3, 44.5, 29.4, 28.4; **HRMS** (ESI) m/z Calculated for $C_{14}H_9Cl_2N_3O_2$ [Na]+: 343.9970, found: 343.9964; **mp**: 214-216 °C.

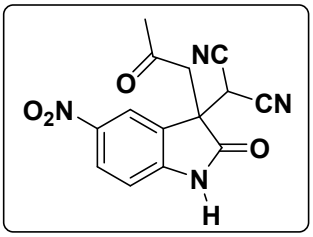
**2-(2-oxo-3-(2-oxopropyl)-5-(trifluoromethoxy)indolin-3-yl)malononitrile (4Ak):**



The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (162 mg, 96% yield).
$R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.4;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 11.20 (s, 1H), 7.39 - 7.52 (m, 1H), 7.27 - 7.37 (m, 1H), 7.03 (d, *J*=8.50 Hz, 1H), 5.59 (s, 1H), 3.73 (d, *J*=18.14 Hz, 1H), 3.34 (d, *J*=18.14 Hz, 1H), 2.06 (s, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.8, 175.4, 143.0, 142.3, 128.2, 123.2, 117.6, 111.2, 111.0, 111.0, 48.5, 45.5, 29.8, 29.7;

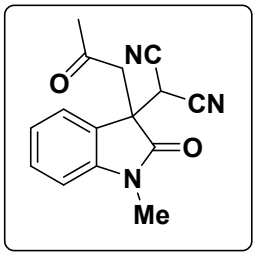
**$^{19}$F NMR (376 MHz, *DMSO-d$_6$*)** δ -57.41 (s); **HRMS** (ESI) m/z Calculated for $C_{15}H_{10}F_3N_3O_3$ [H]+: 337.0674, found: 337.0668; **mp**: 182-184 °C.

**2-(5-nitro-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Al):**



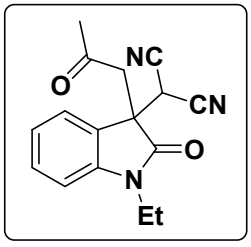

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (145 mg, 97% yield). ***R$_f$*** (Ethyl acetate/Pet. ether; 30:70) = 0.3;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 11.75 (s, 1H), 8.39 (d, *J*=2.38 Hz, 1H), 8.30 (dd, *J*=8.63, 2.38 Hz, 1H), 7.18 (d, *J*=8.63 Hz, 1H), 5.74 (s, 1H), 3.89 (d, *J*=18.39 Hz, 1H), 3.43 (d, *J*=18.39 Hz, 1H), 2.09 (s, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 204.1, 176.0, 149.7, 142.3, 127.7, 127.3, 119.9, 111.2, 110.9, 110.3, 48.2, 46.0, 29.7, 29.5; **HRMS** (ESI) m/z Calculated for $C_{14}H_{10}N_4O_4$ [Na]+: 321.0600, found: 321.0594; **mp**: 234-236 °C.

**2-(1-methyl-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Ba):**




The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (125 mg, 93% yield). ***R$_f$*** (Ethyl acetate/Pet. ether; 30:70) = 0.4;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 7.37 - 7.48 (m, 2H), 7.06 - 7.20 (m, 2H), 5.57 (s, 1H), 3.65 (s, 4H), 3.67 (d, *J*=18.01 Hz, 1H), 3.35 (d, *J*=18.01 Hz, 1H), 3.21 (s, 3H), 2.03 (s, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.5, 173.8, 144.5, 130.1, 125.8, 123.1, 122.7, 111.5, 111.1, 109.1, 47.8, 45.8, 30.0, 29.7, 26.5; **HRMS** (ESI) m/z Calculated for $C_{15}H_{13}N_3O_2$ [M]+ : 268.1086, found: 268.1081; **mp**: 168-170 °C.

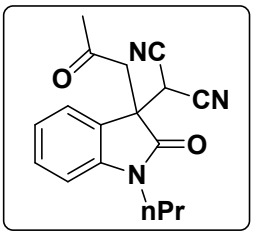
**2-(1-ethyl-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Bb):**




The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (132 mg, 94% yield). ***R$_f$*** (Ethyl acetate/Pet. ether; 30:70) = 0.4;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 7.34 - 7.52 (m, 2H), 7.18 (d, *J*=7.88 Hz, 1H), 7.10 (td, *J*=7.54, 0.81 Hz, 1H), 5.56 (s, 1H), 3.78 (m, 2H), 3.66 (d, *J*=18.01 Hz, 1H), 3.3 (d, *J*=18.01 Hz, 1H), 2.03 (s, 3H), 1.20 (t, *J*=7.13 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.4, 173.3, 143.5, 130.0, 125.9, 123.2, 122.5, 111.4, 111.0, 109.2, 47.6, 45.8, 34.5,

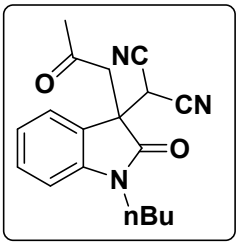
30.1, 29.7, 11.9; **HRMS** (ESI) m/z Calculated for $C_{16}H_{15}N_3O_2$ [H]+:282.1243, found: 282.1237; **mp**: 155-157 °C.

**2-(2-oxo-3-(2-oxopropyl)-1-propylindolin-3-yl)malononitrile (4Bc):**



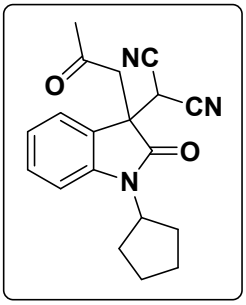

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (136 mg, 92% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.4;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 7.43 (d, *J*=7.25 Hz, 1H), 7.35 - 7.41 (m, 1H), 7.18 (d, *J*=7.75 Hz, 1H), 7.09 (t, *J*=7.50 Hz, 1H), 5.57 (s, 1H), 3.62 - 3.74 (m, 3H), 3.34 (d, *J*=18.14 Hz, 1H), 2.03 (s, 3H), 1.59 - 1.72 (m, 2H), 0.95 (t, *J*=7.44 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.5, 173.8, 144.1, 130.1, 125.9, 123.2, 122.5, 111.5, 111.2, 109.4, 48.6, 47.8, 45.9, 41.5, 30.2, 29.8, 20.3, 11.3; **HRMS** (ESI) m/z Calculated for $C_{17}H_{17}N_3O_2$ [M]+: 296.1399, found: 296.1394; **mp**: 132-134 °C.

**2-(1-butyl-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Bd):**




The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (141 mg, 91% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.4;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 7.37 - 7.47 (m, 2H), 7.17 (d, *J*=7.88 Hz, 1H), 7.07 - 7.13 (m, 1H), 5.57 (s, 1H), 3.64 - 3.79 (m, 3 H), 3.33 (t, *J*=18.14 Hz, 3H), 2.03 (s, 3H), 1.57 - 1.66 (m, 2H), 1.39 (m, 2H), 0.90 (t, *J*=7.38 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.6, 173.8, 144.1, 130.2, 126.0, 123.3, 122.6, 111.6, 111.2, 109.4, 48.7, 47.8, 46.0, 30.2, 29.9, 29.1, 19.7, 13.8; **HRMS** (ESI) m/z Calculated for $C_{18}H_{19}N_3O_2$ [H]+: 310.1556, found: 310.1550; **mp**: 126-128 °C.

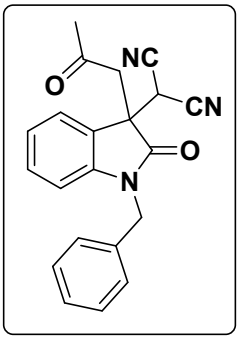
**2-(1-cyclopentyl-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Be):**




The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (149 mg, 93% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.4;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 7.41 - 7.46 (m, 1H), 7.34 - 7.41 (m, 1H), 7.18 (d, *J*=7.88 Hz, 1H), 7.09 (t, *J*=7.57 Hz, 1H), 5.48 - 5.59 (m, 1H), 4.57 - 4.78 (m, 1H), 3.65 (d, *J*=7.88 Hz, 1H), 3.31 (d, *J*=7.88 Hz, 1H), 1.95 - 2.15 (m, 5H), 1.78 - 1.95 (m, 4H), 1.53 - 1.71 (m, 2H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 203.5, 173.6, 143.6, 130.0, 126.0, 123.3, 122.3, 111.5, 111.1, 110.0, 52.6, 47.7, 46.0, 30.3, 29.7, 27.5, 27.4, 24.9; **HRMS** (ESI) m/z Calculated for $C_{19}H_{19}N_3O_2$ [H]+:

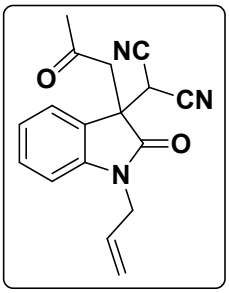
322.1556, found: 322.1550; **mp**: 158-160 °C.

**2-(1-benzyl-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Bf):**



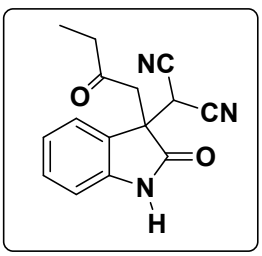
The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (158 mg, 92% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.2;
**$^1$H NMR (400 MHz, *DMSO-d*$_6$)** δ 7.45 - 7.53 (m, 3H), 7.27 - 7.36 (m, 4H), 7.07 - 7.13 (m, 1H), 6.91 (d, *J*=7.88 Hz, 1H), 5.66 (s, 1H), 4.87 - 5.07 (m, 2H), 3.76 (d, *J*=18.13 Hz, 1H), 3.43 (d, *J*=18.13 Hz, 1H), 2.08 (s, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d*$_6$)** δ 203.8, 174.1, 143.7, 135.7, 130.0, 128.5, 127.5, 127.5, 127.4, 125.9, 123.3, 122.9, 111.6, 111.3, 109.9, 48.0, 46.0, 43.6, 30.3, 29.8; **HRMS** (ESI) m/z Calculated for $C_{21}H_{17}N_3O_2$ [M]+: 344.1399, found: 344.1394; **mp**: 246-248 °C.

**2-(1-allyl-2-oxo-3-(2-oxopropyl)indolin-3-yl)malononitrile (4Bg):**



The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (135 mg, 93% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.25;
**$^1$H NMR (400 MHz, *DMSO-d*$_6$)** δ 7.42 - 7.49 (m, 1H), 7.34 - 7.42 (m, 1H), 7.08 - 7.17 (m, 1H), 7.05 (d, *J*=7.75 Hz, 1H), 5.85 (m, 1H), 5.60 (s, 1H), 5.38 - 5.50 (m, 1H), 4.32 - 4.45 (m, 2H), 3.70 (d, *J*=18.13 Hz, 1H), 3.38 (d, *J*=18.13 Hz, 1H), 2.04 (s, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d*$_6$)** δ 203.6, 173.6, 143.6, 131.4, 129.9, 125.8, 123.2, 122.7, 117.3, 111.5, 111.1, 109.8, 47.8, 45.9, 42.2, 30.1, 29.7; **HRMS** (ESI) m/z Calculated for $C_{17}H_{15}N_3O_2$ [H]+: 294.1243, found: 294.1237; **mp**: 134-136 °C.

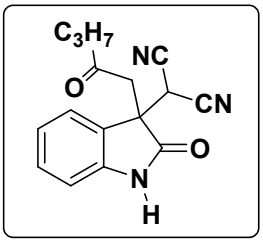
**2-(2-oxo-3-(2-oxobutyl)indolin-3-yl)malononitrile (4Ca):**



The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (126 mg, 94% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.6;
**$^1$H NMR (400 MHz, *DMSO-d*$_6$)** δ 10.99 (s, 1H), 7.37 (d, *J*=7.38 Hz, 1H), 7.30 (td, *J*=7.69, 1.00 Hz, 1H), 7.00 - 7.08 (m, 1H), 6.94 (d, *J*=7.75 Hz, 1H), 5.53 (s, 1H), 3.57 (d, *J*=17.76 Hz, 1H), 3.25 (d, *J*=17.76 Hz, 1H), 2.27 - 2.49 (m, 2H), 0.77 (t, *J*=7.25 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d*$_6$)** δ 206.0, 175.4, 143.0, 129.9, 126.6, 123.3, 122.0, 111.6, 111.2, 110.1, 48.3, 44.6, 35.0, 30.1, 7.1; **HRMS**

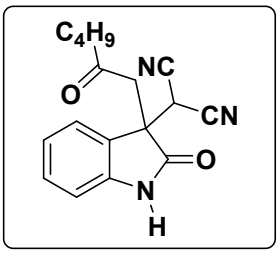
(ESI) m/z Calculated for $C_{15}H_{13}N_3O_2$ [Na]+: 290.0905, found: 290.0900; **mp**: 167-168 °C.

**2-(2-oxo-3-(2-oxopentyl)indolin-3-yl)malononitrile (4Cb):**



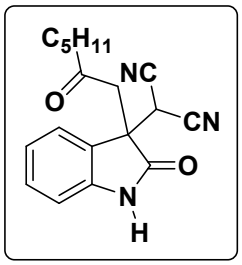

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (128 mg, 91% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.6;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.98 (s, 1H), 7.36 (d, *J*=7.50 Hz, 1H), 7.30 (td, *J*=7.75, 1.13 Hz, 1H), 6.98 - 7.06 (m, 1H), 6.93 (d, *J*=7.75 Hz, 1H), 5.53 (s, 1H), 3.56 (d, *J*=17.76 Hz, 1H), 3.23 (d, *J*=17.76 Hz, 1H), 2.27 - 2.45 (m, 2H), 1.33 (m, 2H), 0.70 (t, *J*=7.44 Hz, 3 H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 205.9, 175.5, 143.1, 130.1, 126.6, 123.5, 122.2, 111.7, 111.3, 110.3, 48.4, 45.1, 43.8, 30.2, 16.5, 13.3; **HRMS** (ESI) m/z Calculated for $C_{16}H_{15}N_3O_2$ [Na]+: 304.1062, found: 304.1056; **mp**: 124-126 °C.

**2-(2-oxo-3-(2-oxohexyl)indolin-3-yl)malononitrile (4Cc):**




The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (130 mg, 88% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.6;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.98 (s, 1H), 7.37 (d, *J*=7.38 Hz, 1H), 7.30 (td, *J*=7.75, 1.13 Hz, 1H), 7.02 (td, *J*=7.60, 0.81 Hz, 1H), 6.94 (d, *J*=7.63 Hz, 1H), 5.53 (s, 1H), 3.57 (d, *J*=17.76 Hz, 1H), 3.24 (d, *J*=17.76 Hz, 1H), 2.28 - 2.49 (m, 2H), 1.22 - 1.34 (m, 2H), 1.04 - 1.17 (m, 2H), 0.77 (t, *J*=7.25 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 205.7, 175.4, 143.0, 129.9, 126.5, 123.3, 122.0, 111.6, 111.2, 110.2, 48.3, 44.9, 41.5, 30.0, 25.0, 21.4, 13.6; **HRMS** (ESI) m/z Calculated for $C_{17}H_{17}N_3O_2$ [Na]+: 318.1218, found: 318.1213; **mp**: 126-128 °C.

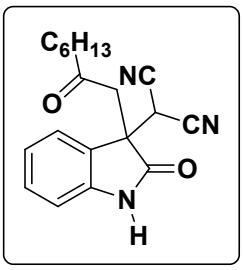
**2-(2-oxo-3-(2-oxoheptyl)indolin-3-yl)malononitrile (4Cd):**




The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (133 mg, 86% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.6;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.98 (s, 1H), 7.37 (d, *J*=7.50 Hz, 1H), 7.30 (td, *J*=7.75, 1.13 Hz, 1H), 7.02 (td, *J*=7.57, 0.88 Hz, 1H), 6.94 (d, *J*=7.75 Hz, 1H), 5.54 (s, 1H), 3.57 (d, *J*=17.64 Hz, 1H), 3.24 (d, *J*=17.76 Hz, 1H), 2.28 - 2.46 (m, 2H), 1.31 (m, 2H), 1.13 - 1.22 (m, 2H), 1.01 - 1.10 (m, 2H), 0.79 (t, *J*=7.25 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 205.7, 175.4, 143.0, 129.9, 126.5, 123.3, 121.9, 111.6, 111.2, 110.1, 48.3, 44.9, 41.7, 30.4, 30.0, 22.5, 21.8, 13.7; **HRMS**

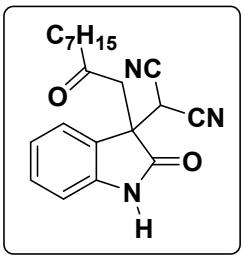
(ESI) m/z Calculated for $C_{18}H_{19}N_3O_2$ [H]+: 310.1556, found: 310.1550; **mp**: 88-90 °C.

**2-(2-oxo-3-(2-oxooctyl)indolin-3-yl)malononitrile (4Ce):**



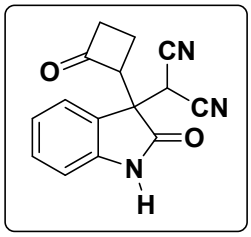

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (136 mg, 84% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.6;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.98 (s, 1H), 7.36 (d, *J*=7.50 Hz, 1H), 7.30 (td, *J*=7.69, 1.13 Hz, 1H), 7.02 (td, *J*=7.57, 0.88 Hz, 1H), 6.94 (d, *J*=7.75 Hz, 1H), 5.54 (s, 1H), 3.56 (d, *J*=17.76 Hz, 1H), 3.24 (d, *J*=17.76 Hz, 1H), 2.28 - 2.46 (m, 2H), 1.30 (m, 2H), 1.06 - 1.22 (m, 4H), 0.82 (t, *J*=7.07 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 205.7, 175.3, 143.0, 129.9, 126.5, 123.3, 121.9, 111.6, 111.2, 110.1, 48.3, 44.9, 41.7, 30.9, 30.4, 30.0, 27.9, 22.8, 21.9, 13.8, 13.7; **HRMS** (ESI) m/z Calculated for $C_{19}H_{21}N_3O_2$ [H]+: 324.1712, found: 324.1707; **mp**: 86-88 °C.

**2-(2-oxo-3-(2-oxononyl)indolin-3-yl)malononitrile (4Cf):**




The titled compound was prepared by following the optimized migration procedure B, obtained as a sticky solid (144 mg, 83% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.6;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 11.01 (s, 1H), 7.39 (dt, *J*=7.54, 0.67 Hz, 1H), 7.27 - 7.33 (m, 1H), 6.99 - 7.06 (m, 1H), 6.96 (dd, *J*=7.69, 0.81 Hz, 1H), 5.54 (s, 1H), 3.57 (d, *J*=17.64 Hz, 1H), 3.26 (d, *J*=17.76 Hz, 1H), 2.29 - 2.46 (m, 2H), 1.28 - 1.36 (m, 2H), 1.19 - 1.25 (m, 2H), 1.14 - 1.19 (m, 4H), 1.03 - 1.12 (m, 2H), 0.84 (t, *J*=7.07 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 205.7, 175.4, 143.1, 129.9, 126.6, 123.4, 122.0, 111.6, 111.2, 110.2, 48.4, 45.0, 41.9, 31.1, 30.1, 28.4, 28.3, 22.9, 22.1, 13.9; **HRMS** (ESI) m/z Calculated for $C_{20}H_{23}N_3O_2$ [Na]+: 360.1688, found: 360.1682.

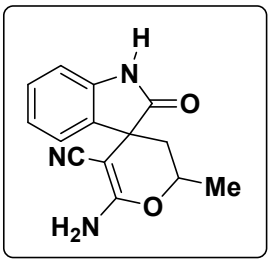
**2-(2-oxo-3-(2-oxocyclobutyl)indolin-3-yl)malononitrile (4E):**




The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (115 mg, 87% yield). $R_f$ (Ethyl acetate/Pet. ether; 30:70) = 0.45;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 11.22 (s, 1H), 11.17 (s, 1H), 7.53 (d, *J*=7.50 Hz, 1H), 7.39 (m, 2H), 7.25 (d, *J*=7.50 Hz, 1H), 7.13 (m, 2H), 6.99 (dd, *J*=7.69, 4.57 Hz, 2H), 5.77 (s, 1H), 5.64 (s, 1H), 4.21 (m, 1H), 4.12 (m, 1H), 3.04 - 3.24 (m, 1 H), 2.73 (m, 1H), 2.57 - 2.67 (m, 1H), 2.18 (m, 1H), 2.04 - 2.13 (m, 1H), 1.92 - 2.03 (m, 1H), 1.56 - 1.69 (m, 1H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 205.8, 205.3, 173.9, 173.9, 142.5, 142.4, 130.6, 130.6, 124.7, 124.5, 124.0, 124.0, 122.7, 111.7, 111.6, 111.2, 111.1, 110.7, 110.6, 60.4, 60.1, 51.5, 50.2, 44.9,

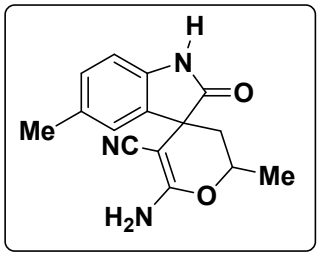
44.7, 28.3, 28.1, 13.2, 12.3; **HRMS** (ESI) m/z Calculated for $C_{15}H_{11}N_3O_2$ [H]+: 266.0930, found: 266.0924; **mp**: 150-152 °C.

**6'-amino-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Aa):**



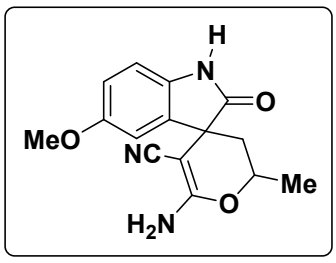

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (121 mg, 95% yield, 9:1 dr), $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.4;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.49 (s, 1H), 7.33 - 7.45 (m, 1H), 7.13 - 7.27 (m, 1H), 6.94 - 7.03 (m, 1H), 6.83 - 6.90 (m, 1H), 6.59 (s, 2H), 4.48 - 4.61 (m, 1H), 1.69 - 1.81 (m, 2H), 1.32 (d, *J*=6.13 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.5, 165.6, 141.0, 135.0, 128.2, 124.1, 121.8, 120.0, 109.6, 70.4, 53.4, 47.7, 38.7, 20.4; **HRMS** (ESI) m/z Calculated for $C_{14}H_{13}N_3O_2$ [H]+: 256.1086, found: 256.1081; **mp**: 284-286 °C.

**6'-amino-2',5-dimethyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Ab):**



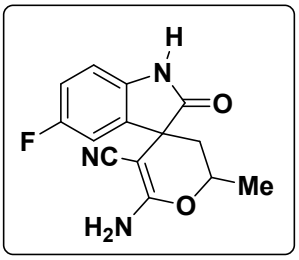

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (125 mg, 93% yield, 7:1 dr). $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.4;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.41 (s, 1H), 7.18 - 7.26 (m, 1H), 6.99 - 7.04 (m, 1H), 6.75 (d, *J*=7.88 Hz, 1H), 6.61 (s, 2H), 4.48 - 4.61 (m, 1H), 2.27 (s, 3H), 1.68 - 1.81 (m, 2H), 1.32 (d, *J*=6.25 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.6, 165.6, 138.6, 135.0, 130.8, 128.5, 124.8, 120.2, 109.4, 70.5, 53.6, 48.7, 47.8, 38.7, 20.8, 20.5; **HRMS** (ESI) m/z Calculated for $C_{15}H_{15}N_3O_2$ [H]+: 270.1243, found: 270.1237; **mp**: 274-276 °C.

**6'-amino-5-methoxy-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Ac):**



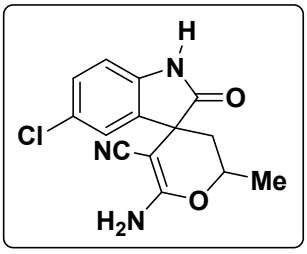

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (131 mg, 92% yield, 5.3:1 dr). $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.41;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.35 (s, 1H), 6.94 - 7.03 (m, 1H), 6.73 - 6.83 (m, 2H), 6.63 (s, 2H), 4.48 - 4.65 (m, 1H), 3.73 (s, 3H), 1.68 - 1.82 (m, 2H), 1.31 (d, *J*=6.25 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.5, 165.8, 155.2, 136.3, 134.3, 120.3, 112.9, 111.2, 110.1, 70.4, 55.6, 53.5, 48.3, 38.7, 20.5; **HRMS** (ESI) m/z Calculated for $C_{15}H_{15}N_3O_3$ [M]+: 286.1192, found: 286.1186; **mp**: 240-242 °C.

**6'-amino-5-fluoro-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Ad):**



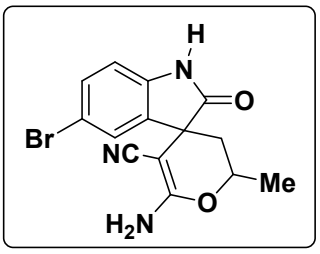

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (129 mg, 94% yield, 8:1 dr). $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.35;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.51 (s, 1H), 7.37 (dd, *J*=8.57, 2.56 Hz, 1H), 6.97 - 7.11 (m, 1H), 6.85 (dd, *J*=8.44, 4.44 Hz, 1H), 6.65 (s, 2H), 4.57 (m, 1H), 1.71 - 1.82 (m, 2H), 1.31 (d, *J*=6.13 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.5, 165.8, 158.3 (d, $J_{C-F}$=236.7 Hz), 137.2 (d, $J_{C-F}$=1.5 Hz) , 136.6 (d, $J_{C-F}$=7.9 Hz), 120.0, 114.5 (d, $J_{C-F}$= 23.6 Hz), 112.2 (d, $J_{C-F}$=26.0 Hz), 110.3 (d, $J_{C-F}$=7.7 Hz), 70.3, 53.1, 48.3, 38.3, 20.3; **$^{19}$F NMR (376 MHz, *DMSO-d$_6$*)** δ -121.42; **HRMS** (ESI) m/z Calculated for $C_{14}H_{12}FN_3O_2$ [H]+: 274.0992, found: 274.0986; **mp**: 286-288 °C.

**6'-amino-5-chloro-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Ae):**



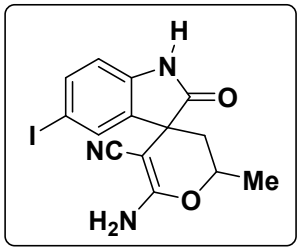

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (137 mg, 95% yield, 7:1 dr). $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.35;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.65 (s, 1H), 7.52 (d, *J*=2.25 Hz, 1H), 7.27 (dd, *J*=8.25, 2.13 Hz, 1H), 6.87 (d, *J*=8.25 Hz, 1H), 6.70 (s, 2H), 4.53 - 4.63 (m, 1H), 1.64 - 1.89 (m, 2H), 1.31 (d, *J*=6.25 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.3, 165.9, 140.0, 136.9, 128.2, 126.1, 124.4, 120.0, 111.1, 70.4, 52.9, 48.2, 38.2, 20.4; **HRMS** (ESI) m/z Calculated for $C_{14}H_{12}ClN_3O_2$ [H]+: 290.0696, found: 290.0694; **mp**: 290-292 °C.

**6'-amino-5-bromo-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Af):**



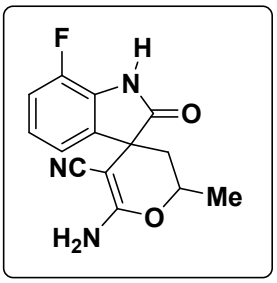

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (156 mg, 93% yield, 7.3:1 dr). $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.35;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.66 (s, 1H), 7.61 (d, *J*=2.13 Hz, 1H), 7.40 (dd, *J*=8.19, 2.06 Hz, 1H), 6.83 (d, *J*=8.25 Hz, 1H), 6.71 (s, 2H), 4.48 - 4.66 (m, 1H), 1.67 - 1.87 (m, 2H), 1.31 (d, *J*=6.13 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.2, 165.9, 140.4, 137.3, 131.1, 127.0, 120.0, 113.8, 111.6, 70.4, 52.9, 48.1, 38.2, 20.4; **HRMS** (ESI) m/z Calculated for $C_{14}H_{12}BrN_3O_2$ [H]+: 334.0191, found: 334.0186; **mp**: 286-288 °C.

**6'-amino-5-iodo-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Ag):**



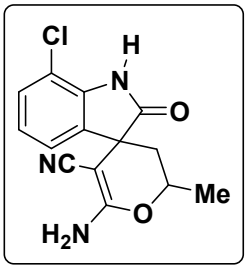

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (177 mg, 93% yield, 7.6:1 dr). $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.35;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.61 (s, 1H), 7.64 - 7.76 (m, 1H), 7.56 (dd, *J*=8.13, 1.75 Hz, 1H), 6.71 (d, *J*=8.13 Hz, 1H), 6.66 (s, 2H), 4.48 - 4.63 (m, 1H), 1.68 - 1.84 (m, 2H), 1.31 (d, *J*=6.25 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 178.9, 165.8, 140.8, 137.5, 136.9, 132.2, 119.9, 112.1, 85.0, 70.4, 52.9, 47.9, 38.2, 20.3; **HRMS** (ESI) m/z Calculated for $C_{14}H_{12}IN_3O_2$ [H]+: 382.0052, found: 382.0047; **mp**: 270-272 °C.

**6'-amino-7-fluoro-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Ah):**



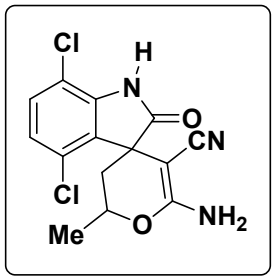

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (126 mg, 92% yield, 5:1 dr). $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.3;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.94 (s, 1H), 7.35 - 7.42 (m, 1H), 7.27 - 7.32 (m, 1H), 6.98 - 7.04 (m, 1H), 6.68 (s, 2H), 4.45 - 4.61 (m, 1H), 1.72 - 1.85 (m, 2H), 1.32 (d, *J*=6.25 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 180.4, 166.6, 147.1 (d, $J_{C\text{-}F}$=245.3 Hz), 138.3 (d, $J_{C\text{-}F}$=2.9 Hz), 128.4 (d, $J_{C\text{-}F}$=12.5 Hz), 123.9 (d, $J_{C\text{-}F}$=5.8 Hz), 120.8, 120.8, 116.2 (d, $J_{C\text{-}F}$=19.8 Hz), 71.4, 53.6, 48.9, 48.9, 21.0; **$^{19}$F NMR (376 MHz, *DMSO-d$_6$*)** δ -132.66; **HRMS** (ESI) m/z Calculated for $C_{14}H_{12}FN_3O_2$ [H]+: 274.0992, found: 274.0986; **mp**: 276-278 °C.

**6'-amino-7-chloro-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Ai):**



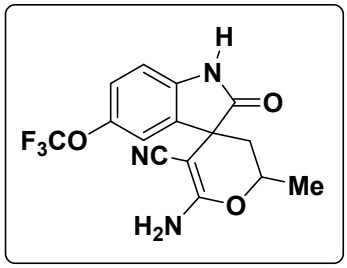

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (51.1 mg, 87% yield, 8:1 dr). $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.3;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.94 (s, 1H), 7.39 (d, *J*=7.25 Hz, 1H), 7.27 - 7.32 (m, 1H), 6.98 - 7.04 (m, 1H), 6.68 (s, 2H), 4.47 - 4.59 (m, 1H), 1.73 - 1.85 (m, 2H), 1.32 (d, *J*=6.13 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.5, 165.7, 138.7, 136.7, 128.3, 123.1, 122.8, 119.9, 113.9, 70.3, 52.9, 48.7, 38.5, 20.3; **HRMS** (ESI) m/z Calculated for $C_{14}H_{12}ClN_3O_2$ [H]+: 290.0696, found: 290.0691; **mp**: 280-282 °C.

**6'-amino-4,7-dichloro-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Aj):**



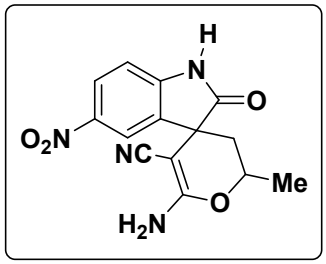

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (151mg, 93% yield, 4:1 dr), $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.25;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 11.20 (s, 1H), 7.32 - 7.38 (m, 1H), 7.01 - 7.07 (m, 1H), 6.82 (s, 2H), 4.76 - 4.86 (m, 1H), 2.12 - 2.20 (m, 1H), 1.81 - 1.91 (m, 1H), 1.30 (d, *J*=6.13 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.6, 166.7, 141.2, 131.3, 130.0, 128.4, 124.3, 119.8, 113.3, 72.0, 50.5, 50.2, 20.5; **HRMS** (ESI) m/z Calculated for $C_{14}H_{11}Cl_2N_3O_2$ [H]+: 324.0307, found: 324.0301; **mp**: 220-222 °C.

**6'-amino-2'-methyl-2-oxo-5-(trifluoromethoxy)-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Ak):**



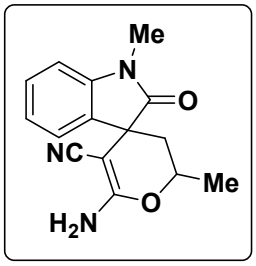

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (158 mg, 93% yield, 8:1 dr), $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.3;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.70 (s, 1H), 7.43 - 7.53 (m, 1H), 7.19 - 7.28 (m, 1H), 6.95 (d, *J*=8.50 Hz, 1H), 6.69 (s, 2H), 4.49 - 4.68 (m, 1H), 1.69 - 1.88 (m, 2H), 1.32 (d, *J*=6.13 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.6, 165.9, 143.5, 140.3, 136.6, 121.4, 119.9, 118.2, 110.4, 70.3, 52.8, 48.3, 38.3, 20.4; **$^{19}$F NMR (376 MHz, *DMSO-d$_6$*)** δ -57.15; **HRMS** (ESI) m/z Calculated for $C_{15}H_{12}F_3N_3O_3$ [H]+: 340.0909, found: 340.0904; **mp**: 228-230 °C.

**6'-amino-2'-methyl-5-nitro-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Al):**



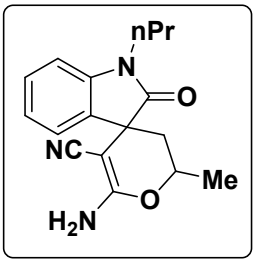

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (143 mg, 95% yield, 8:1 dr), $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.21;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.38 (s, 1H), 7.17 - 7.22 (m, 1H), 6.97 - 7.02 (m, 1H), 6.75 (d, *J*=7.88 Hz, 1H), 6.56 (s, 2H), 4.49 - 4.58 (m, 1H), 1.68 - 1.80 (m, 2H), 1.31 (d, *J*=6.25 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.5, 165.6, 138.5, 135.0, 130.8, 128.5, 124.8, 120.2, 109.4, 70.4, 53.6, 48.7, 47.7, 29.6, 20.7, 20.5; **HRMS** (ESI) m/z Calculated for $C_{14}H_{12}N_4O_4$ [H]+: 301.0937, found: 301.0943; **mp**: 282-284 °C.

**6'-amino-1,2'-dimethyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Ba):**



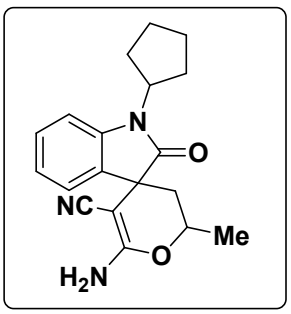

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (122 mg, 91% yield, 9.5:1 dr), $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.4;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 7.42 - 7.48 (m, 1H), 7.29 - 7.35 (m, 1H), 7.03 - 7.09 (m, 2H), 6.63 (s, 2H), 4.51 - 4.62 (m, 1H), 3.16 (s, 3H), 1.70 - 1.84 (m, 2H), 1.32 (d, *J*=6.13 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 177.7, 165.7, 142.5, 134.1, 128.4, 123.8, 122.5, 119.9, 108.6, 70.5, 53.2, 47.4, 38.7, 26.4, 20.4; **HRMS** (ESI) m/z Calculated for $C_{15}H_{15}N_3O_2$ [H]+: 270.1243, found: 270.1237; **mp**: 218-220 °C.

**6'-amino-1-propyl-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Bb):**



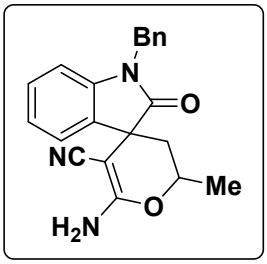

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (137 mg, 92% yield, 6:1 dr), $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.5;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 7.45 (d, *J*=7.00 Hz, 1H), 7.30 (td, *J*=7.72, 1.06 Hz, 1H), 6.97 - 7.12 (m, 2H), 6.62 (s, 2H), 4.49 - 4.64 (m, 1H), 3.60 - 3.73 (m, 2H), 1.69 - 1.84 (m, 2H), 1.61 (m, 2H), 1.32 (d, *J*=6.13 Hz, 3H), 0.87 (t, *J*=7.38 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 177.8, 165.7, 141.8, 134.2, 128.4, 123.9, 122.3, 119.8, 108.8, 70.4, 53.3, 47.3, 41.0, 38.8, 20.4, 20.2, 11.0; **HRMS** (ESI) m/z Calculated for $C_{17}H_{19}N_3O_2$ [H]+: 298.1556, found: 298.1550; **mp**: 198-200 °C.

**6'-amino-1-cyclopentyl-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Bc):**



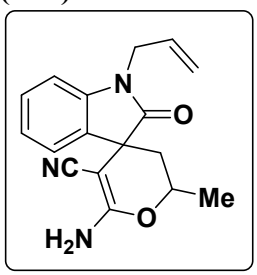

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (149 mg, 92% yield, 7:1 dr), $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.45;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 7.39 - 7.49 (m, 1H), 7.23 - 7.35 (m, 1H), 7.01 - 7.17 (m, 2H), 6.60 (br. s., 2H), 4.62 - 4.73 (m, 1H), 4.48 - 4.62 (m, 1H), 1.95 - 2.05 (m, 2H), 1.80 - 1.91 (m, 4H), 1.70 - 1.80 (m, 2H), 1.59 - 1.68 (m, 2H), 1.32 (d, *J*=6.25 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 178.5, 166.4, 142.1, 135.4, 129.1, 124.9, 123.0, 120.6, 110.4, 71.3, 54.5, 53.2, 48.0, 28.5, 28.4, 25.7, 25.6, 21.3; **HRMS** (ESI) m/z Calculated for $C_{19}H_{21}N_3O_2$ [H]+: 324.1712, found: 324.1707; **mp**: 222-224 °C.

**6'-amino-1-benzyl-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Bd):**



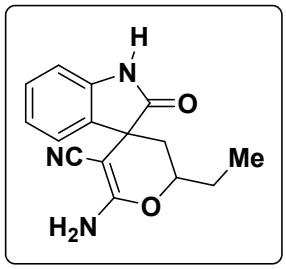

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (157 mg, 91% yield, 16:1), $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.24;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 7.44 - 7.52 (m, 1H), 7.27 - 7.34 (m, 4H), 7.23 - 7.27 (m, 1H), 7.18 - 7.23 (m, 1H), 7.01 - 7.07 (m, 1H), 6.83 - 6.88 (m, 1H), 6.69 (s, 2H), 4.99 (d, *J*=16.01 Hz, 1H), 4.89 (d, *J*=16.01 Hz, 1H), 4.53 - 4.65 (m, 1H), 1.76 - 1.95 (m, 2H), 1.34 (d, *J*=6.13 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** d 178.1, 165.8, 141.3, 136.0, 134.2, 128.6, 128.3, 127.3, 127.0, 124.0, 122.6, 120.1, 109.3, 70.5, 53.1, 47.5, 42.9, 20.4; **HRMS** (ESI) m/z Calculated for $C_{21}H_{19}N_3O_2$ [H]+: 346.1556, found: 346.1550; **mp**: 208-210 °C.

**1-allyl-6'-amino-2'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Be):**




The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (137 mg, 93% yield, 5.5:1 dr), $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.25;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 7.42 - 7.51 (m, 1H), 7.23 - 7.33 (m, 1H), 7.02 - 7.10 (m, 1H), 6.90 - 7.00 (m, 1H), 6.66 (s, 2H), 5.75 - 5.90 (m, 1H), 5.13 - 5.19 (m, 1H), 5.08 - 5.13 (m, 1H), 4.51 - 4.65 (m, 1H), 4.33 - 4.42 (m, 1H), 4.23 - 4.33 (m, 1H), 1.73 - 1.89 (m, 2H), 1.33 (d, *J*=6.25 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** d 177.6, 165.7, 141.4, 134.1, 131.5, 128.3, 123.9, 122.5, 119.9, 116.3, 109.2, 70.5, 53.2, 47.4, 41.6, 38.8, 20.4; **HRMS** (ESI) m/z Calculated for $C_{17}H_{17}N_3O_2$ [H]+: 296.1399, found: 296.1394; **mp**: 200-202 °C.

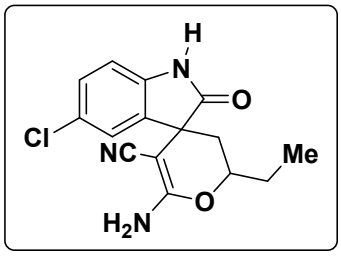
**6'-amino-2'-ethyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Ca):**




The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (121 mg, 90% yield, 9:1), $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.4;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.52 (s, 1H), 7.39 (d, *J*=7.38 Hz, 1H), 7.21 (t, *J*=7.57 Hz, 1H), 6.93 - 7.07 (m, 1H), 6.87 (d, *J*=7.50 Hz, 1H), 6.63 (s, 2H), 4.33 (d, *J*=5.88 Hz, 1H), 1.70 - 1.82 (m, 2H), 1.64 (m, 2H), 0.93 (t, *J*=7.32 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.6, 165.7, 141.0, 135.0, 128.3, 124.1, 121.9, 120.1, 109.7, 74.9, 53.5, 47.6, 36.7, 27.2, 9.0; **HRMS** (ESI) m/z Calculated for $C_{15}H_{15}N_3O_2$ [H]+:

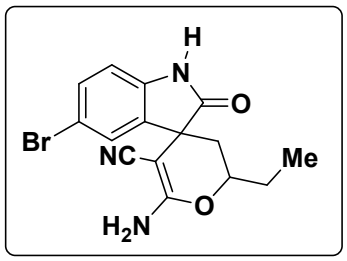
270.1243, found: 270.1237; **mp**: 248-250 °C.

**6'-amino-5-chloro-2'-ethyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Cb):**



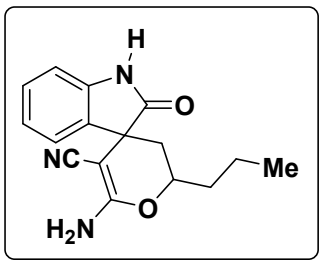

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (138 mg, 91% yield, 8:1 dr), $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.42;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.63 (s, 1H), 7.51 (d, *J*=2.25 Hz, 1H), 7.27 (dd, *J*=8.25, 2.13 Hz, 1H), 6.87 (d, *J*=8.25 Hz, 1H), 6.67 (s, 2H), 4.31 - 4.45 (m, 1H), 1.70 - 1.85 (m, 2H), 1.58 - 1.70 (m, 2H), 0.95 (t, *J*=7.44 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.4, 165.9, 140.0, 136.9, 128.2, 126.1, 124.3, 119.9, 111.0, 74.7, 53.0, 48.0, 36.2, 27.1, 8.9; **HRMS** (ESI) m/z Calculated for $C_{15}H_{14}ClN_3O_2$ [H]+: 304.0853, found: 304.0847; **mp**: 260-262 °C.

**6'-amino-5-bromo-2'-ethyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Cc):**



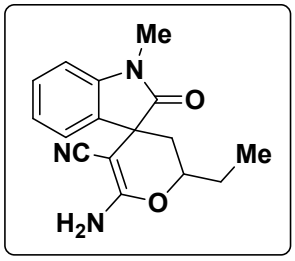

The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (157 mg, 90% yield, 8:1 dr). $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.42;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.64 (s, 1H), 7.60 (d, *J*=1.63 Hz, 1H), 7.40 (dd, *J*=8.25, 2.00 Hz, 1H), 6.83 (d, *J*=8.25 Hz, 1H), 6.67 (s, 2H), 4.29 - 4.43 (m, 1H), 1.69 - 1.85 (m, 2H), 1.64 (m, 2H), 0.95 (t, *J*=7.44 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** d 179.3, 165.9, 140.4, 137.3, 131.1, 126.9, 119.9, 113.8, 111.6, 74.7, 53.0, 48.0, 36.2, 27.1, 8.9; **HRMS** (ESI) m/z Calculated for $C_{15}H_{14}BrN_3O_2$ [H]+: 348.0348, found: 348.0342; **mp**: 274-276 °C.

**6'-amino-2-oxo-2'-propyl-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Cd):**




The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (124 mg, 87% yield, 9.5:1 dr). $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.45;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 10.49 (s, 1H), 7.33 - 7.44 (m, 1H), 7.15 - 7.27 (m, 1H), 6.94 - 7.04 (m, 1H), 6.86 (d, *J*=7.63 Hz, 1H), 6.49 - 6.64 (m, 2H), 4.31 - 4.46 (m, 1H), 1.67 - 1.82 (m, 2H), 1.58 - 1.67 (m, 1H), 1.50 - 1.58 (m, 1H), 1.32 - 1.50 (m, 2H), 0.89 (t, *J*=7.32 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.5, 165.6, 141.0, 134.9, 128.2, 124.0, 121.8, 120.0, 109.6, 73.6, 53.5, 47.6, 37.1, 36.1, 17.5, 13.7; **HRMS** (ESI) m/z Calculated for $C_{16}H_{17}N_3O_2$ [M]+: 284.1399, found: 284.1394; **mp**: 220-222 °C.

**6'-amino-2'-ethyl-1-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (5Ce):**




The titled compound was prepared by following the optimized migration procedure B, obtained as a solid (130 mg, 92% yield, 10:1 dr). $R_f$ (Ethyl acetate/Pet. ether; 40:60) = 0.4;
**$^1$H NMR (400 MHz, *DMSO-d$_6$*)** δ 7.45 (dt, *J*=7.38, 0.69 Hz, 1H), 7.29 - 7.35 (m, 1H), 7.03 - 7.09 (m, 2H), 6.63 (s, 2H), 4.27 - 4.43 (m, 1H), 3.16 (s, 3H), 1.69 - 1.83 (m, 2H), 1.58 - 1.69 (m, 2H), 0.93 (t, *J*=7.44 Hz, 3H); **$^{13}$C NMR (101 MHz, *DMSO-d$_6$*)** δ 177.8, 165.7, 142.5, 134.1, 128.4, 123.7, 122.5, 119.9, 108.6, 74.9, 53.3, 47.3, 36.7, 27.2, 26.4, 8.9; **HRMS** (ESI) m/z Calculated for $C_{16}H_{17}N_3O_2$ [H]+: 284.1399, found: 284.1394; **mp**: 200-202 °C.

## References: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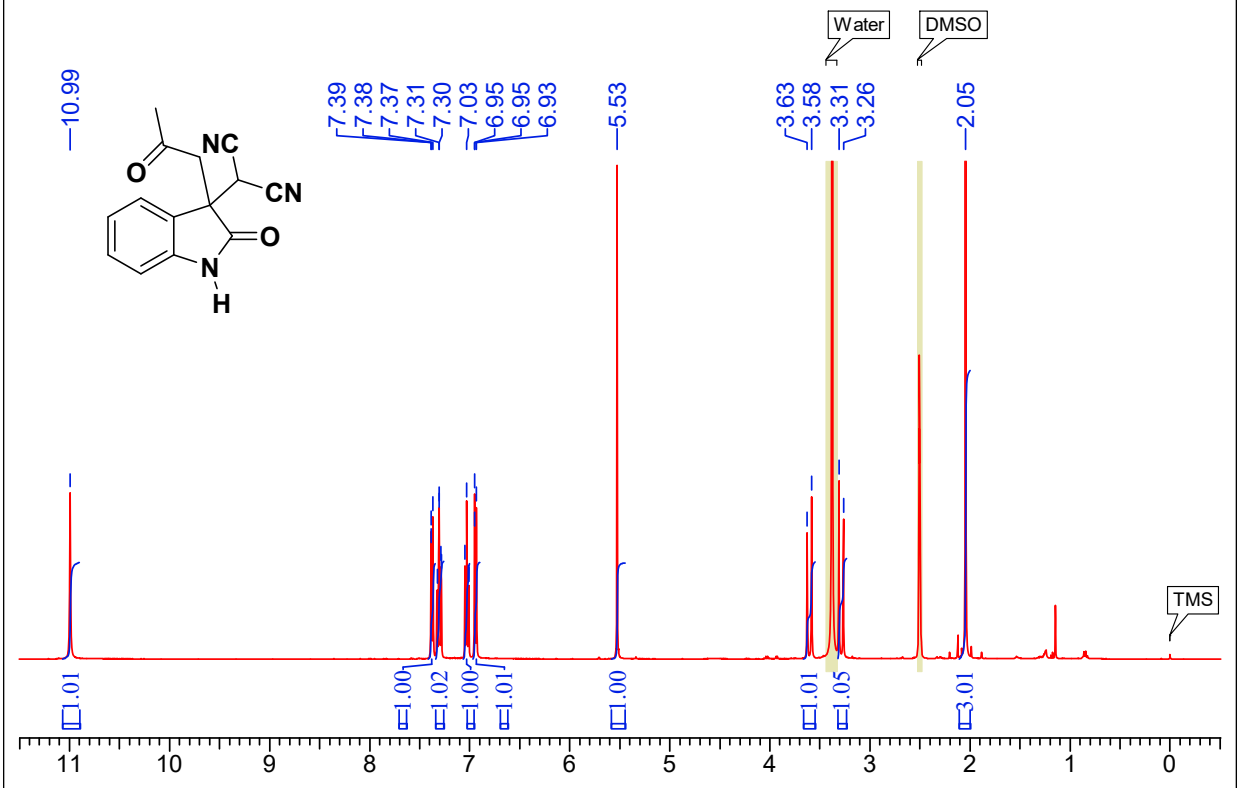
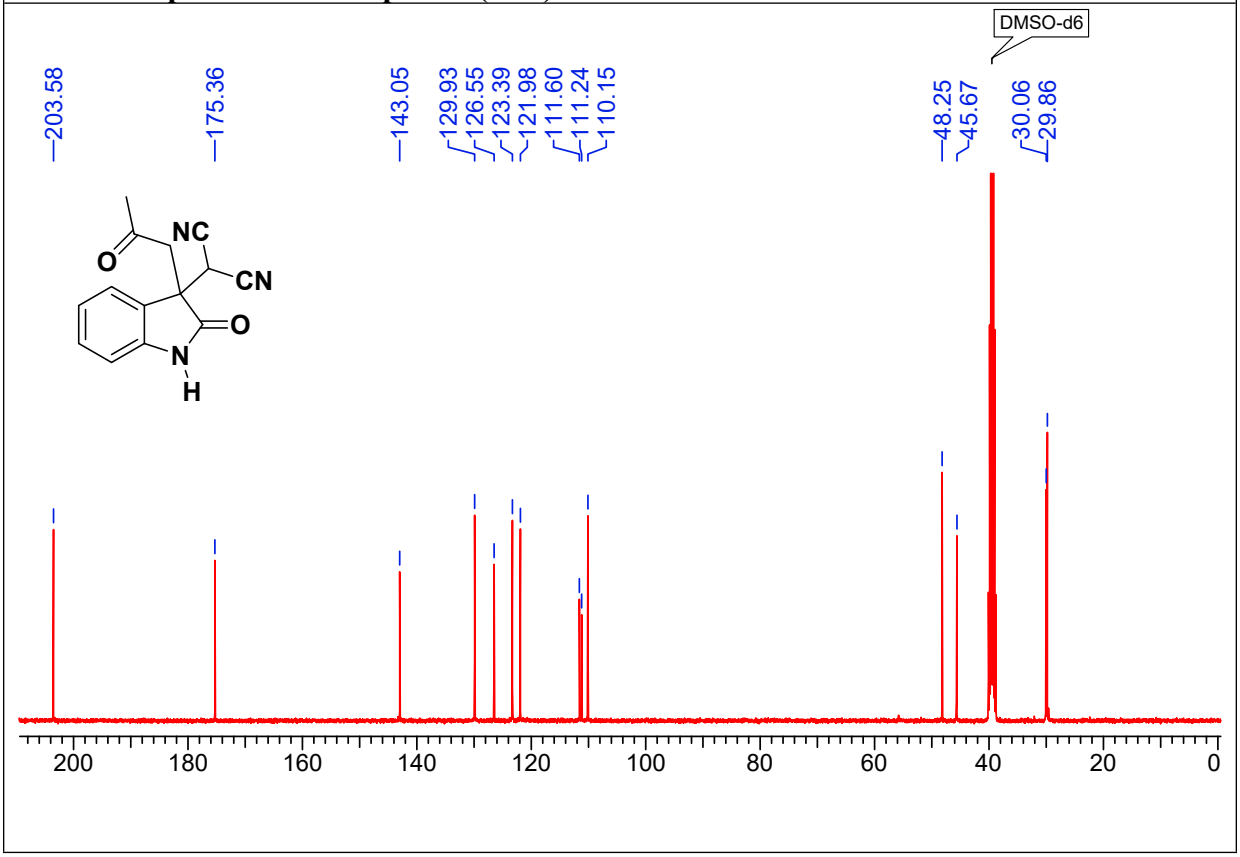
8. D. J. Vyas, R. Frohlich, M. Oestreich, *J. Org. Chem.,* 2010, **75**, 6720.

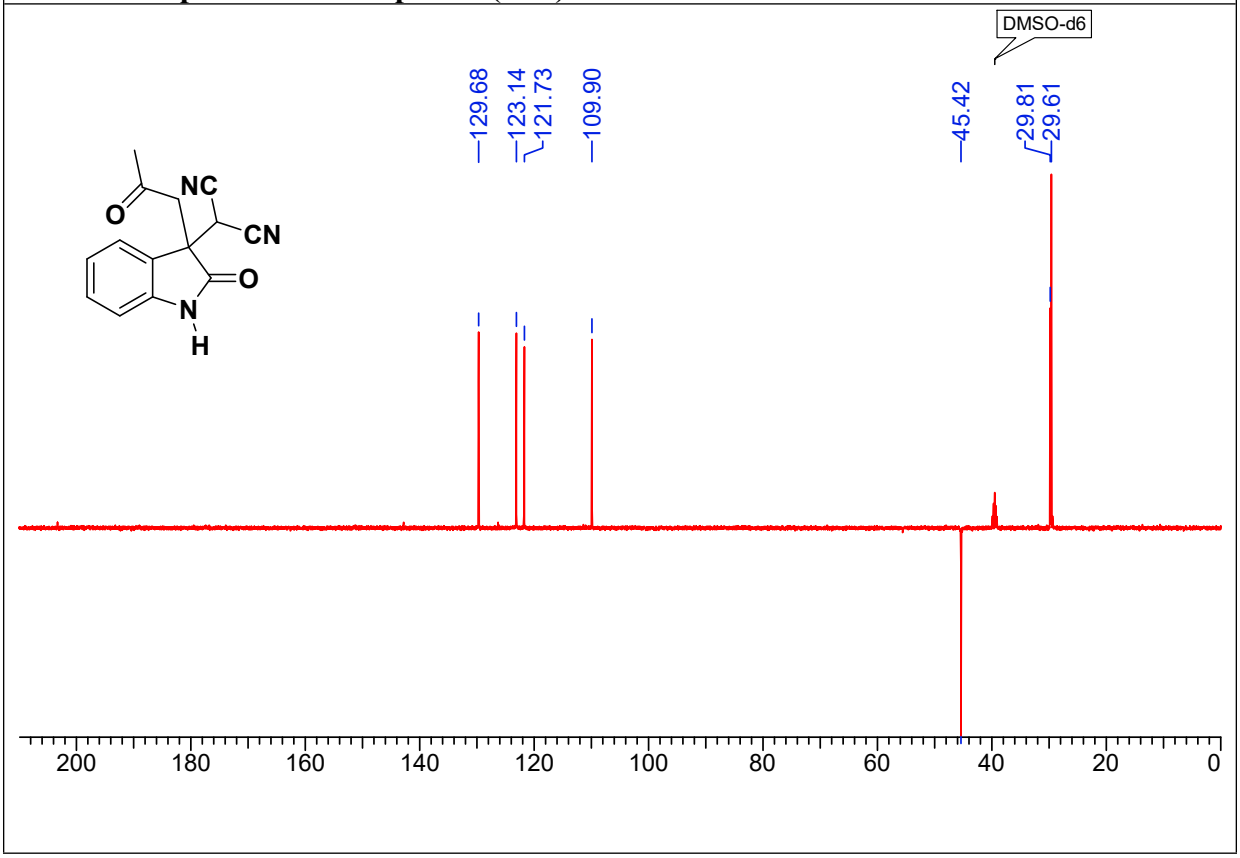
**$^{1}$H NMR spectrum of compound (4Aa):**



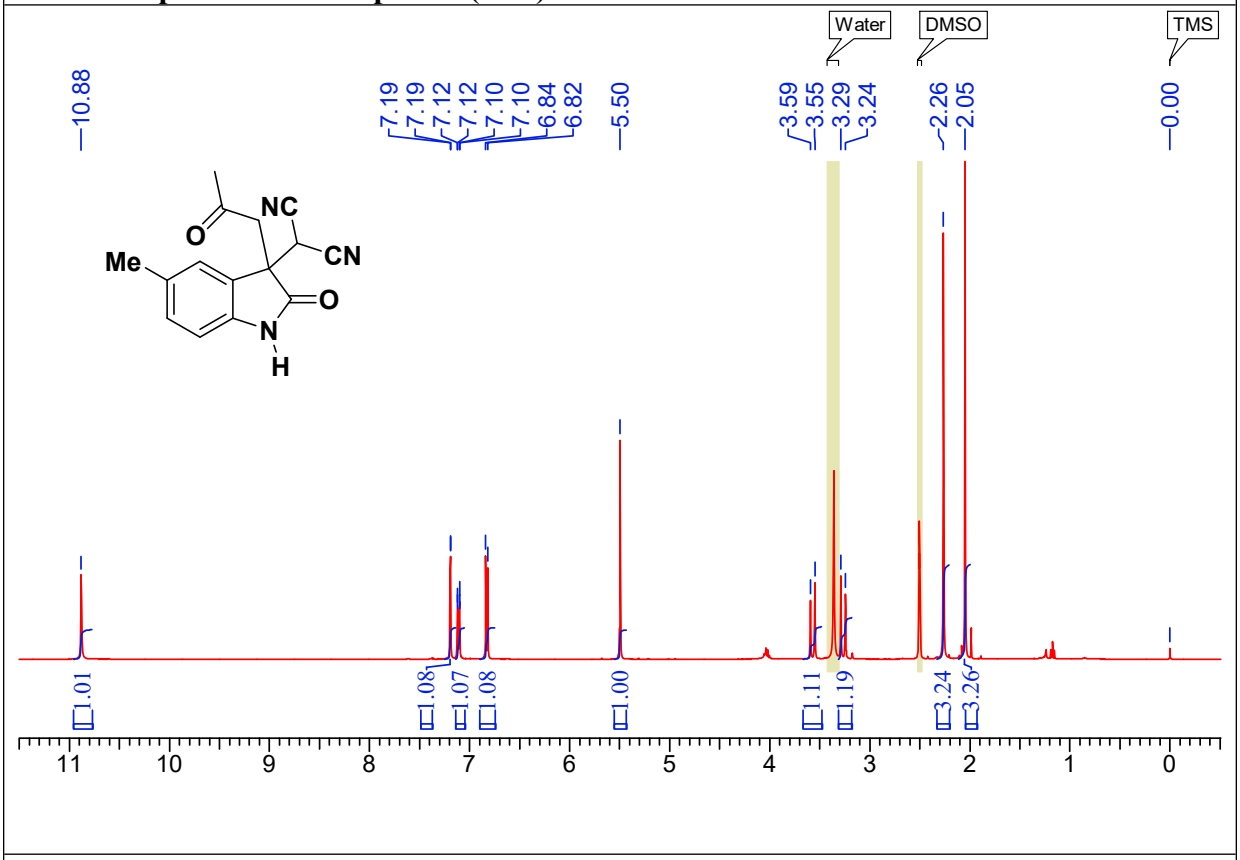

**$^{13}$C NMR spectrum of compound (4Aa)**



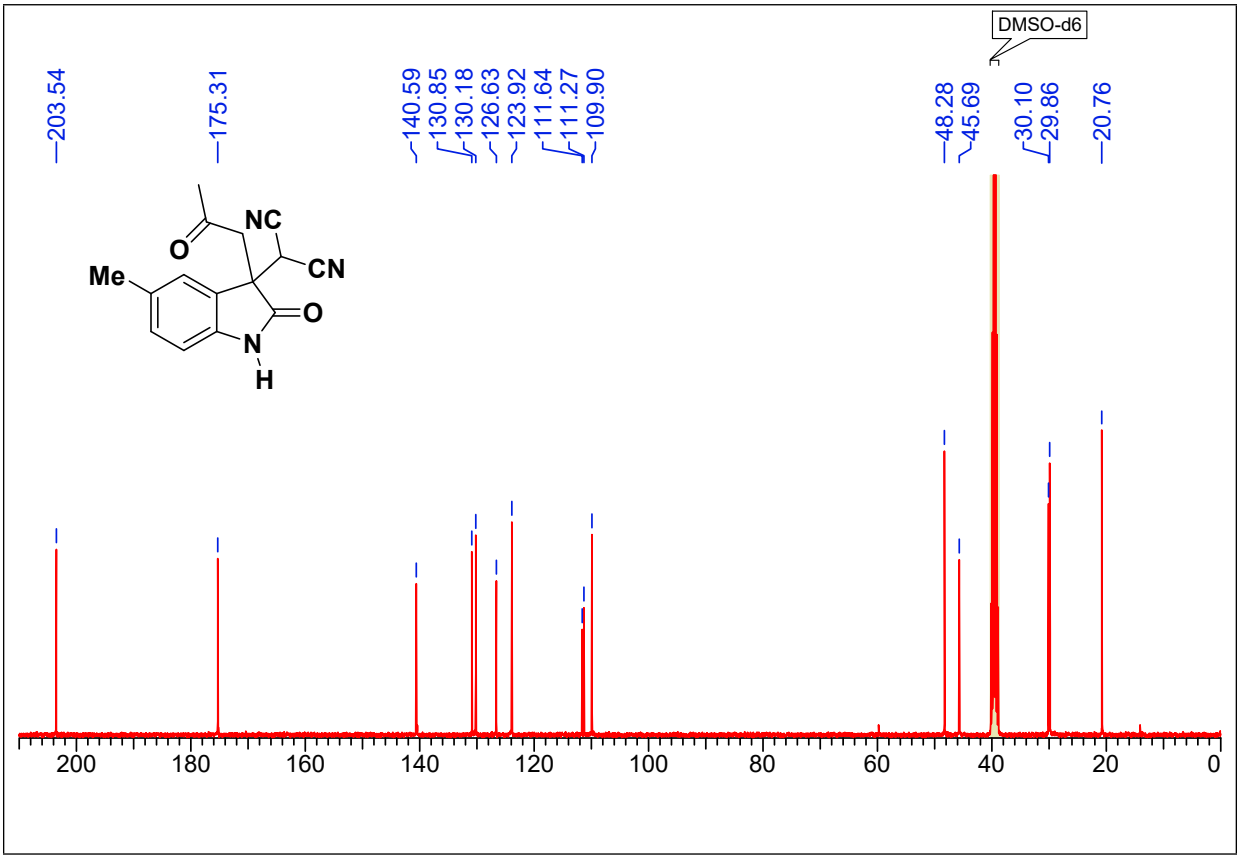
**135 DEPT spectrum of compound (4Aa)**



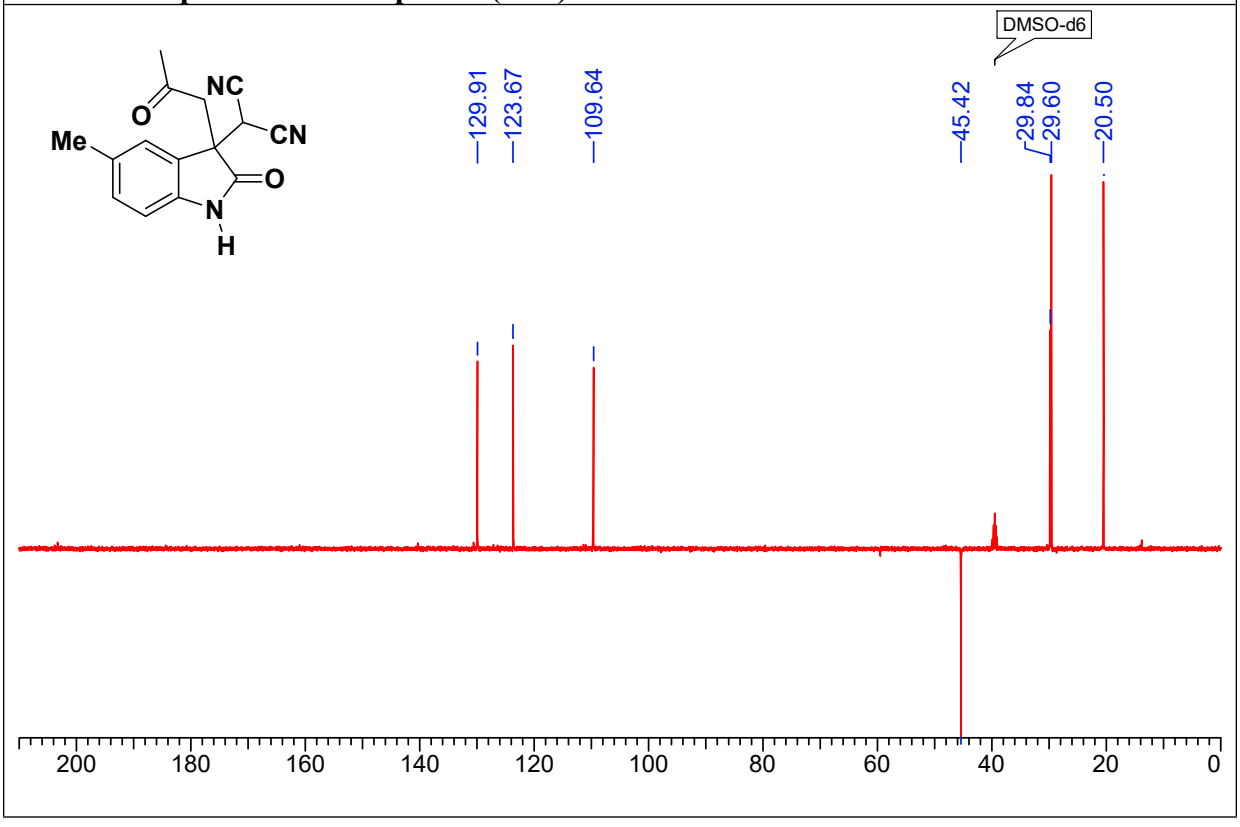
**$^{1}$H NMR spectrum of compound (4Ab)**



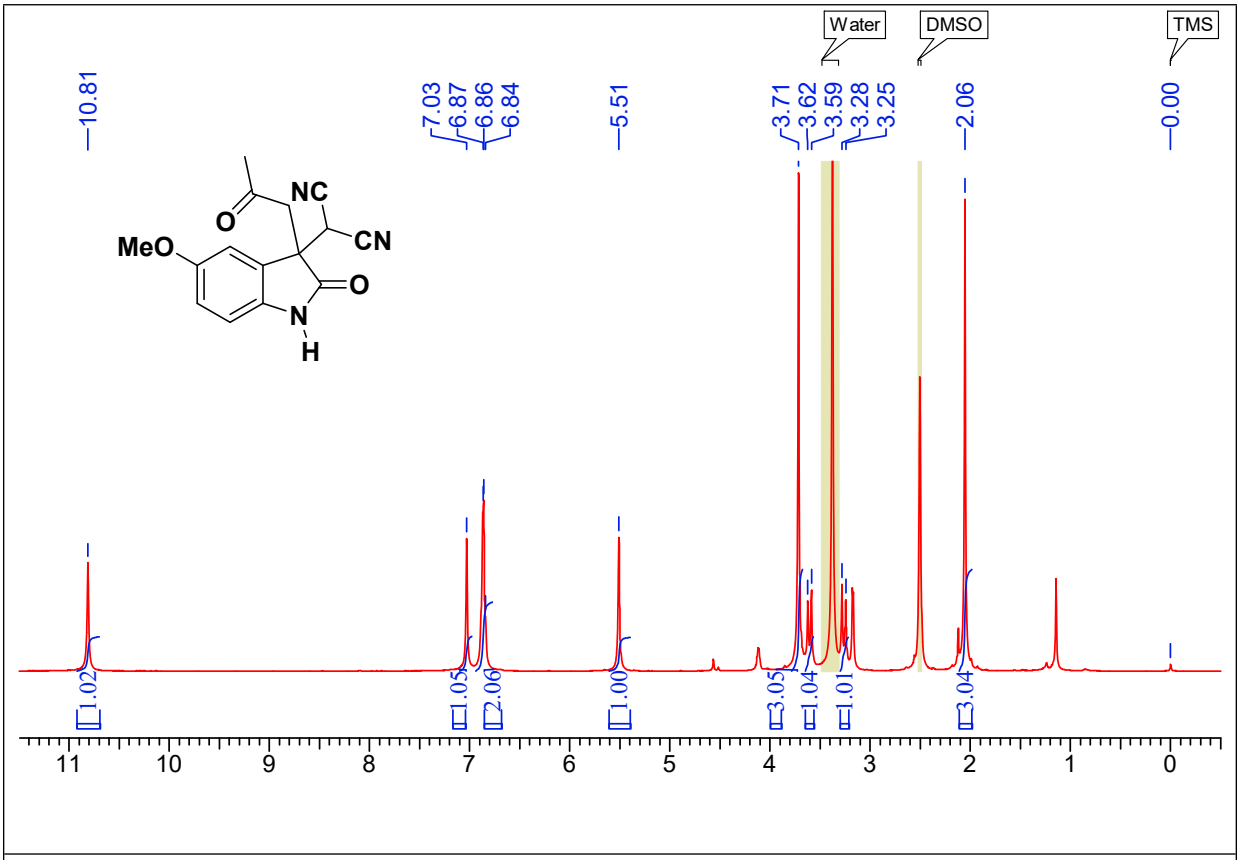

**$^{13}$C NMR spectrum of compound (4Ab)**



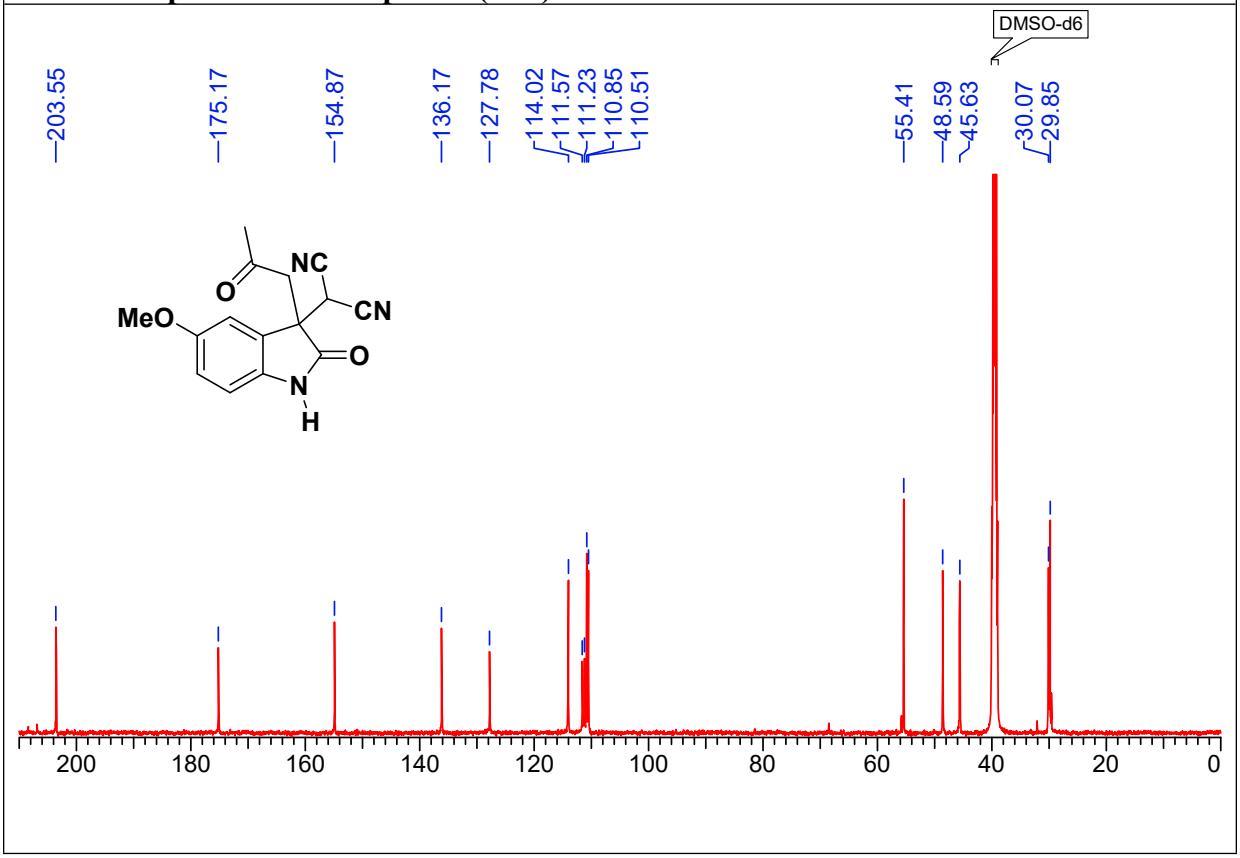

**135 DEPT spectrum of compound (4Ab)**



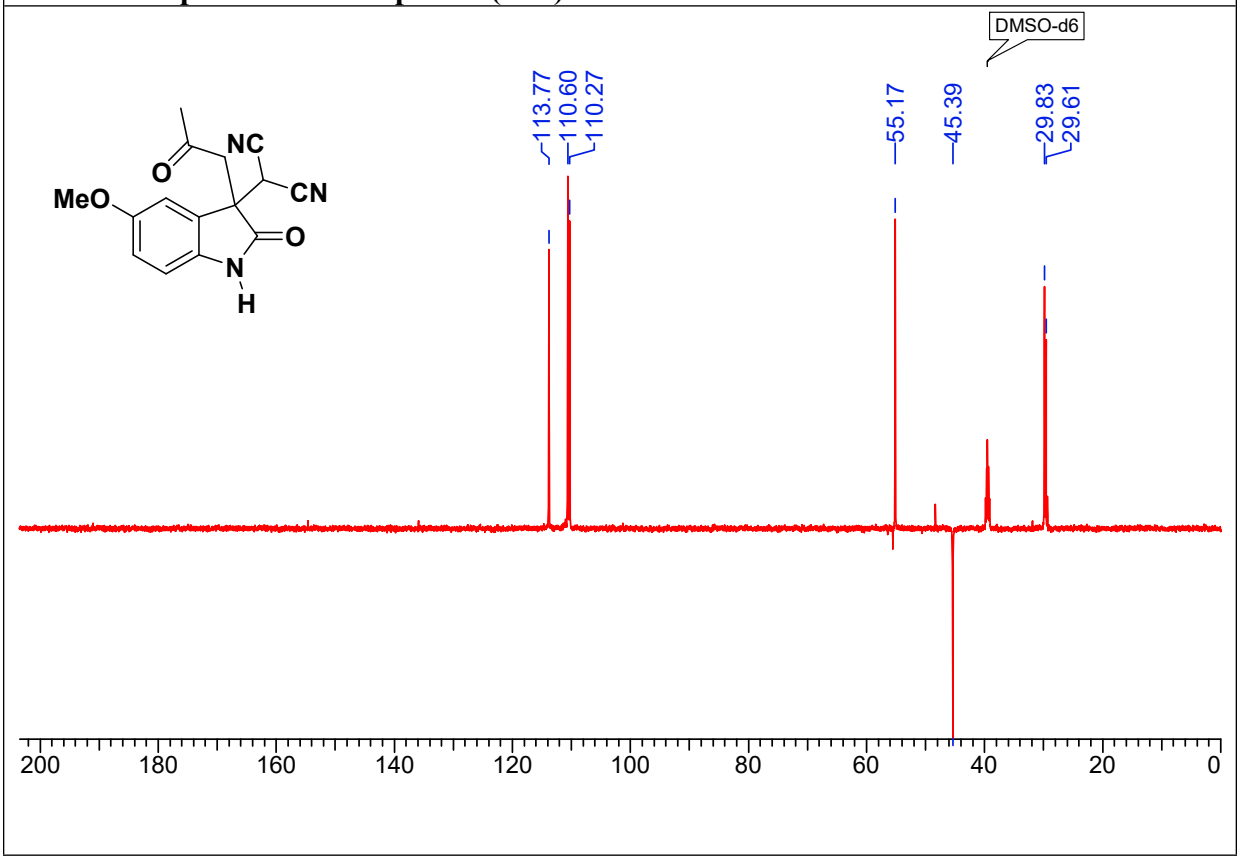
**$^{1}$H NMR spectrum of compound (4Ac)**



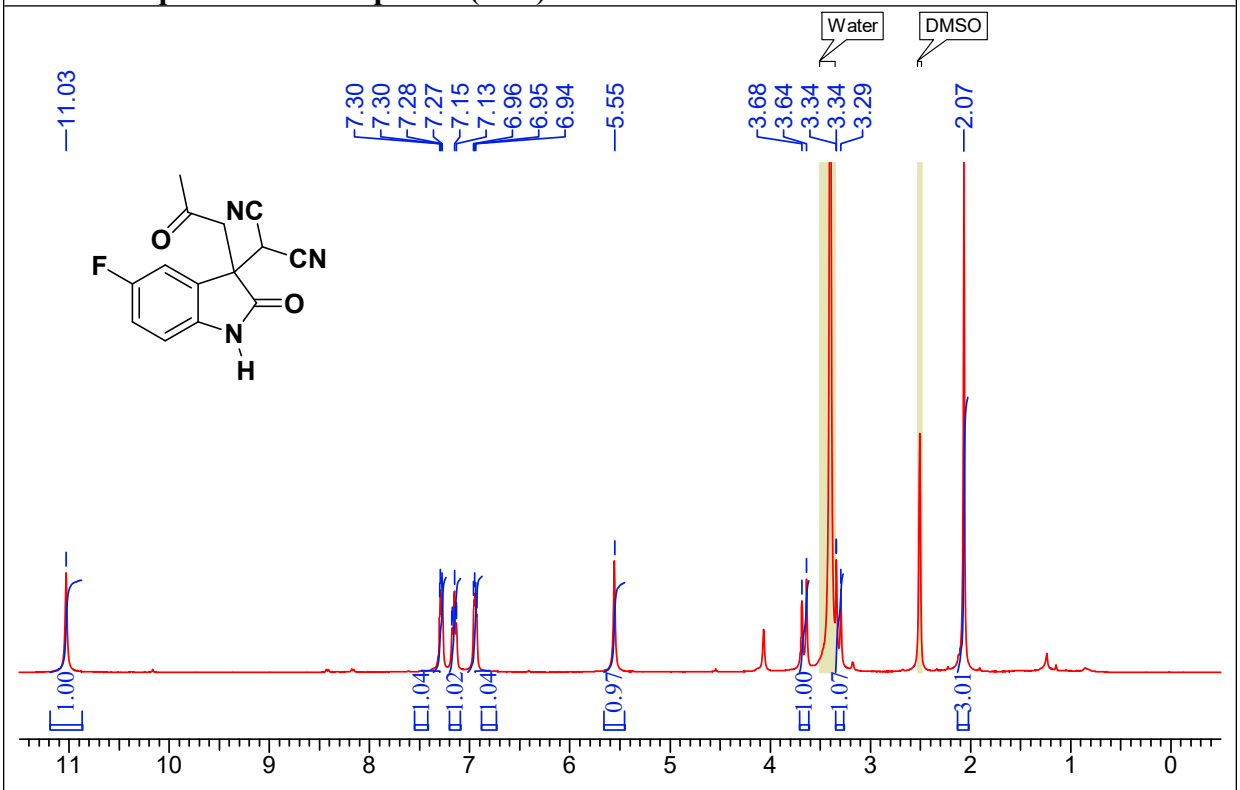

**$^{13}$C NMR spectrum of compound (4Ac)**



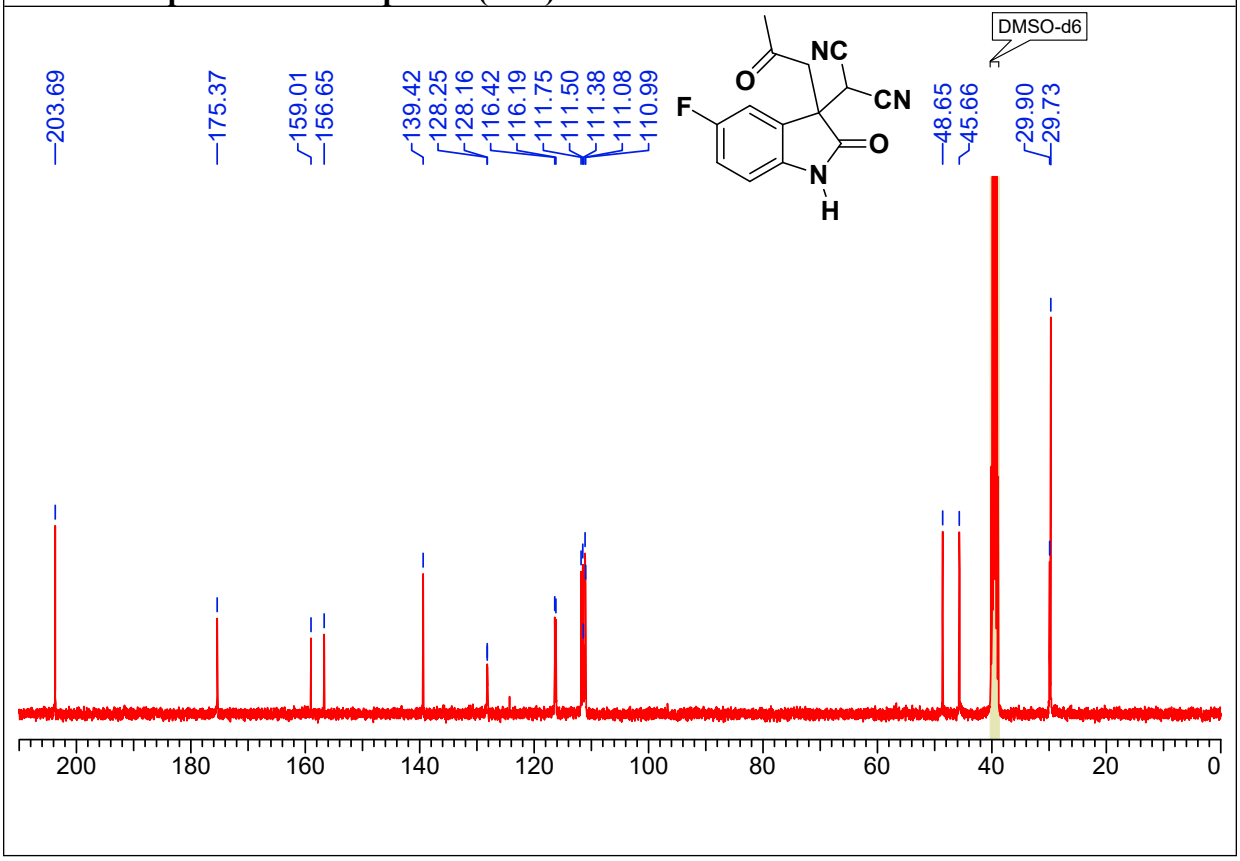
**135 DEPT spectrum of compound (4Ac)**



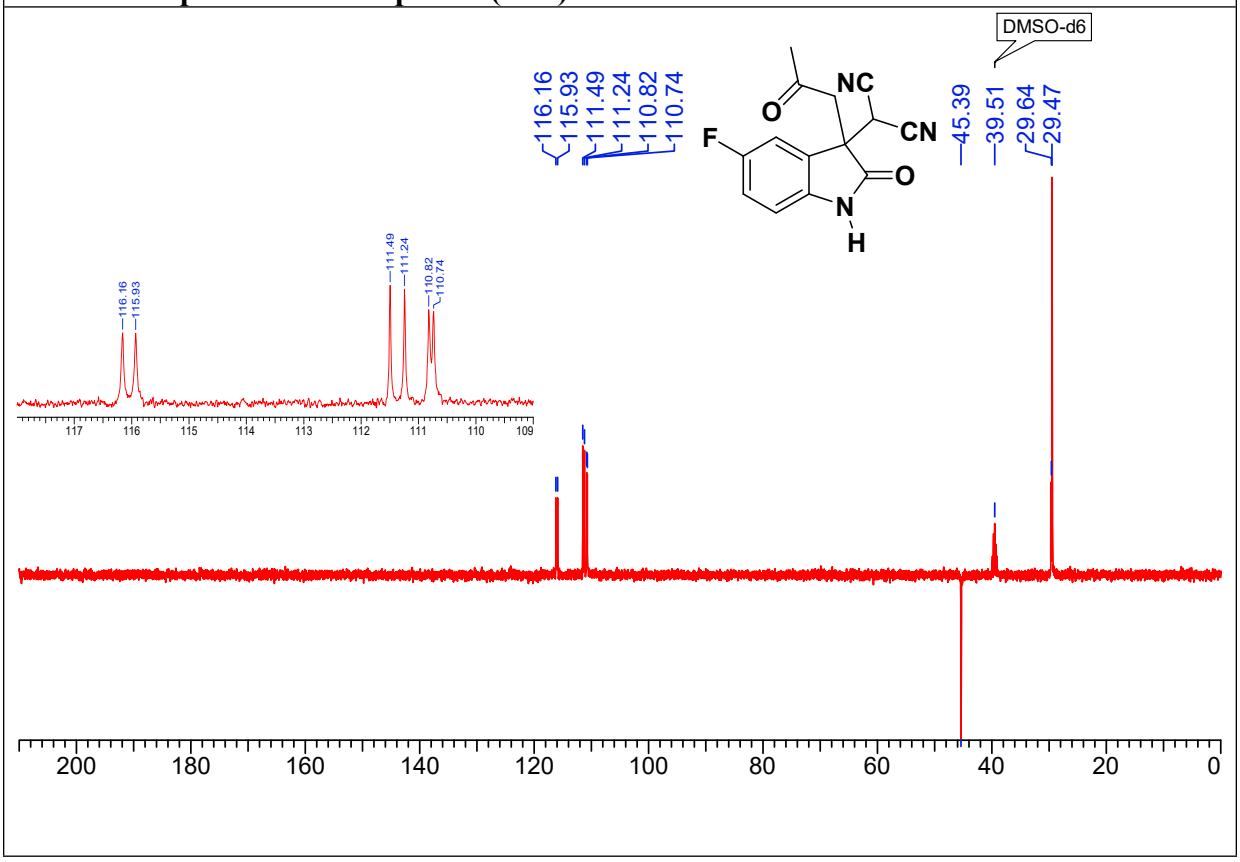
**$^{1}$H NMR spectrum of compound (4Ad)**



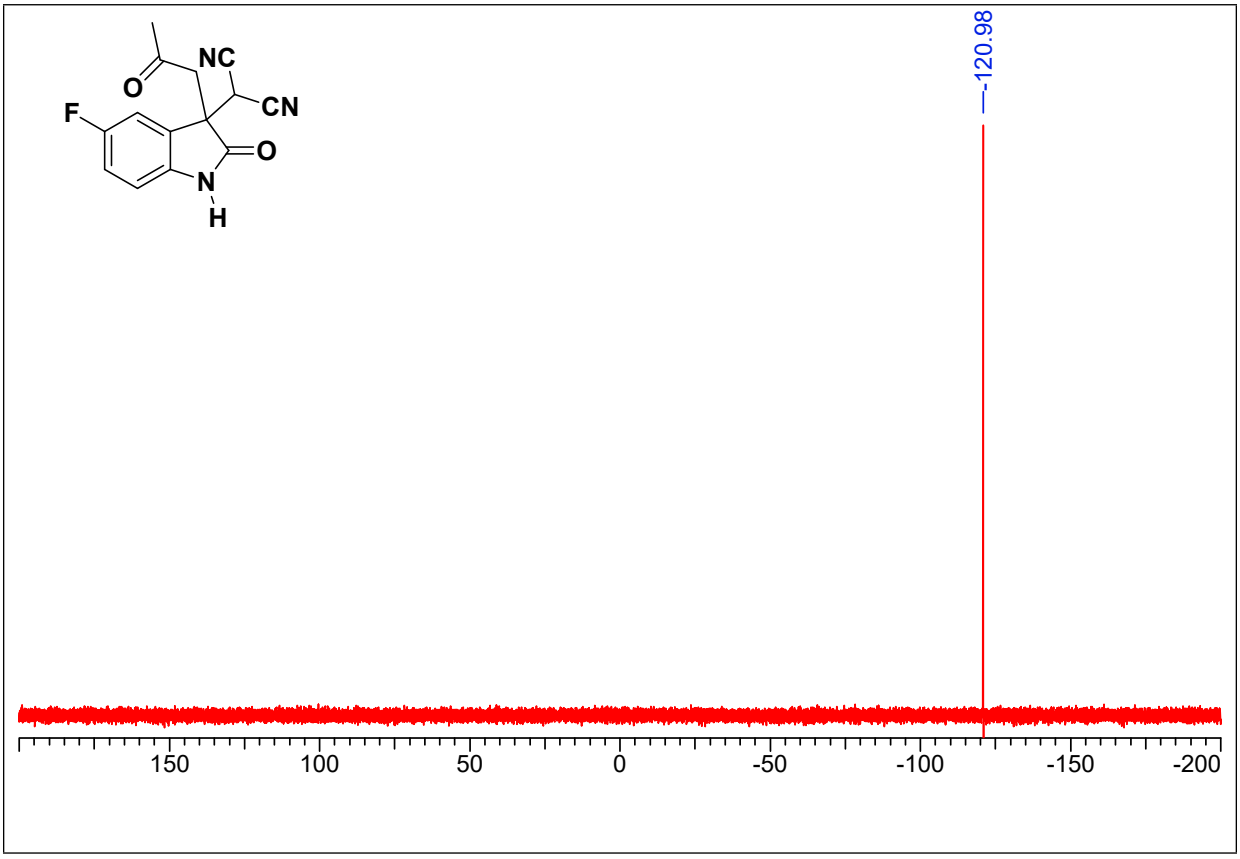

**$^{13}$C NMR spectrum of compound (4Ad)**



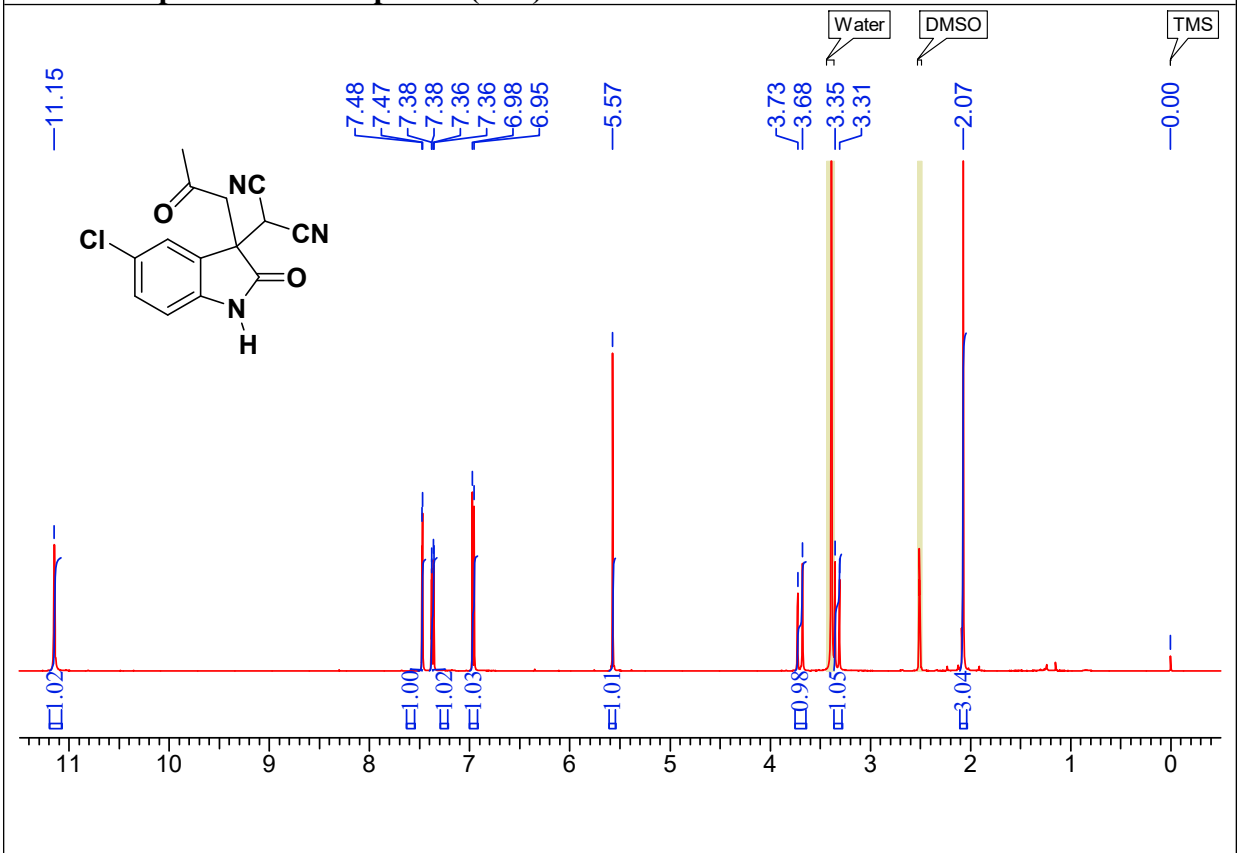
**135 DEPT spectrum of compound (4Ad)**



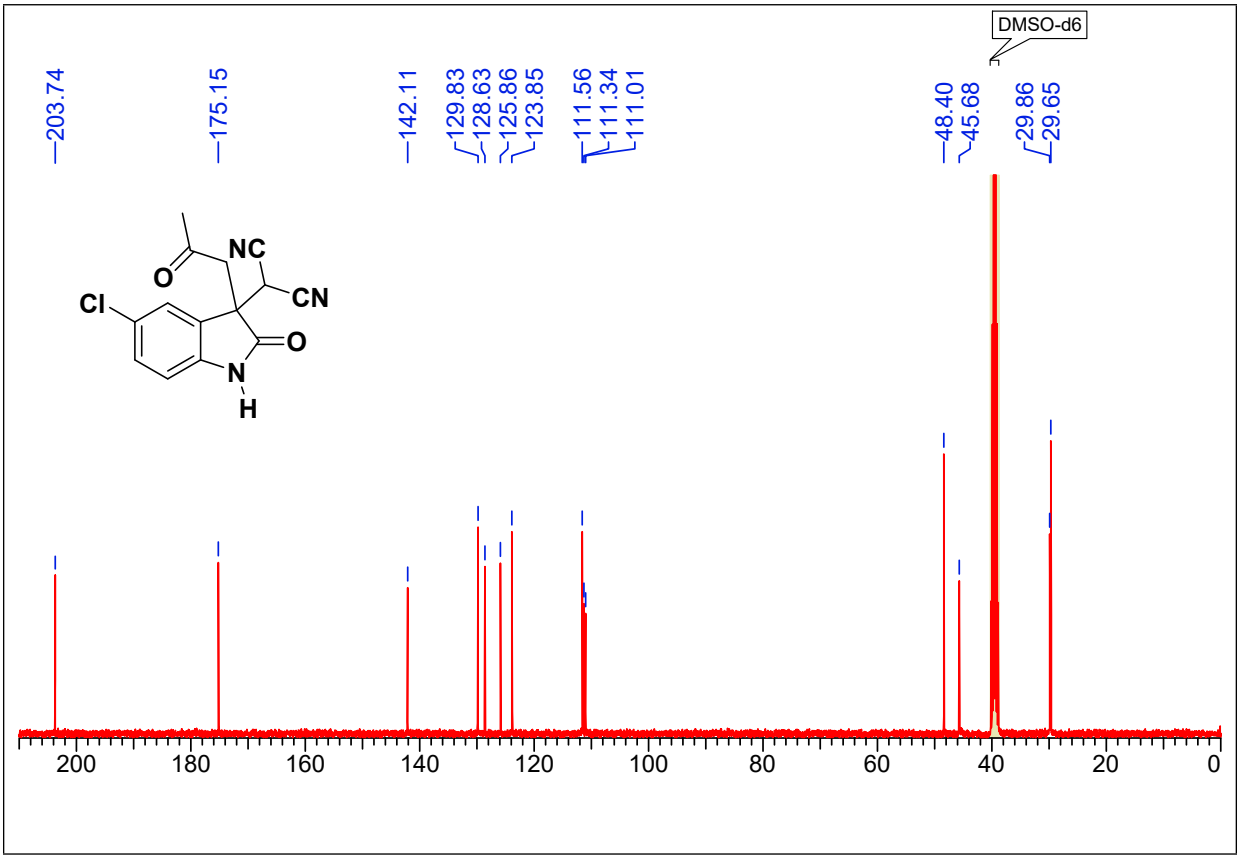

**$^{19}$F NMR spectrum of compound (4Ad)**



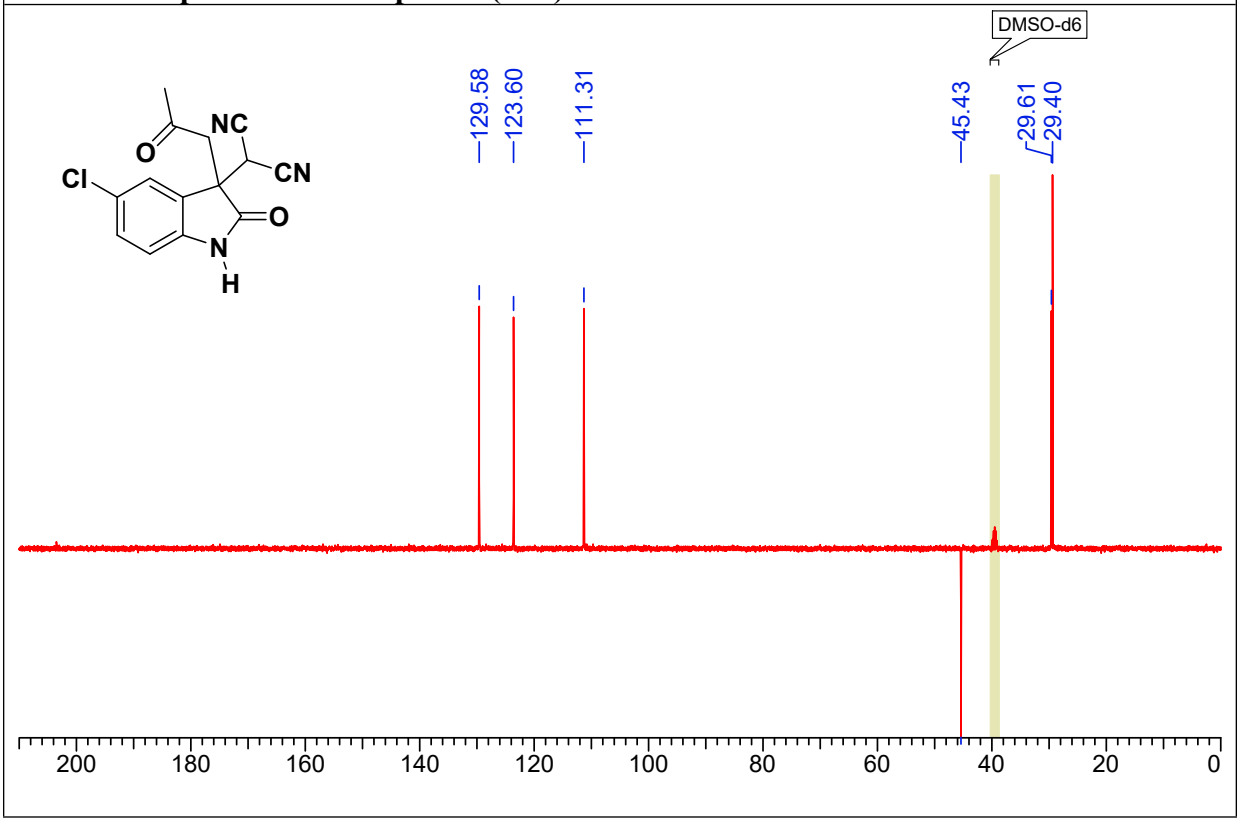

**$^{1}$H NMR spectrum of compound (4Ae)**



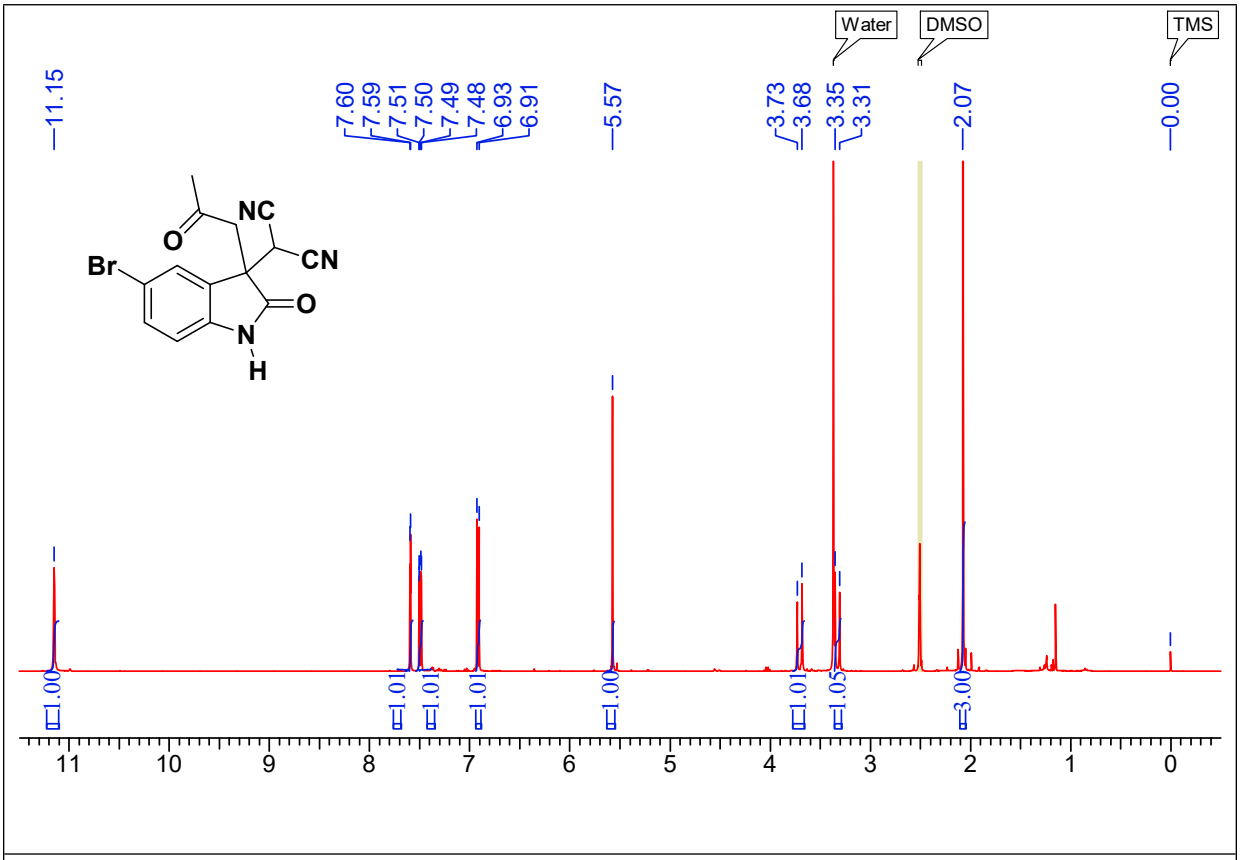

**$^{13}$C NMR spectrum of compound (4Ae)**



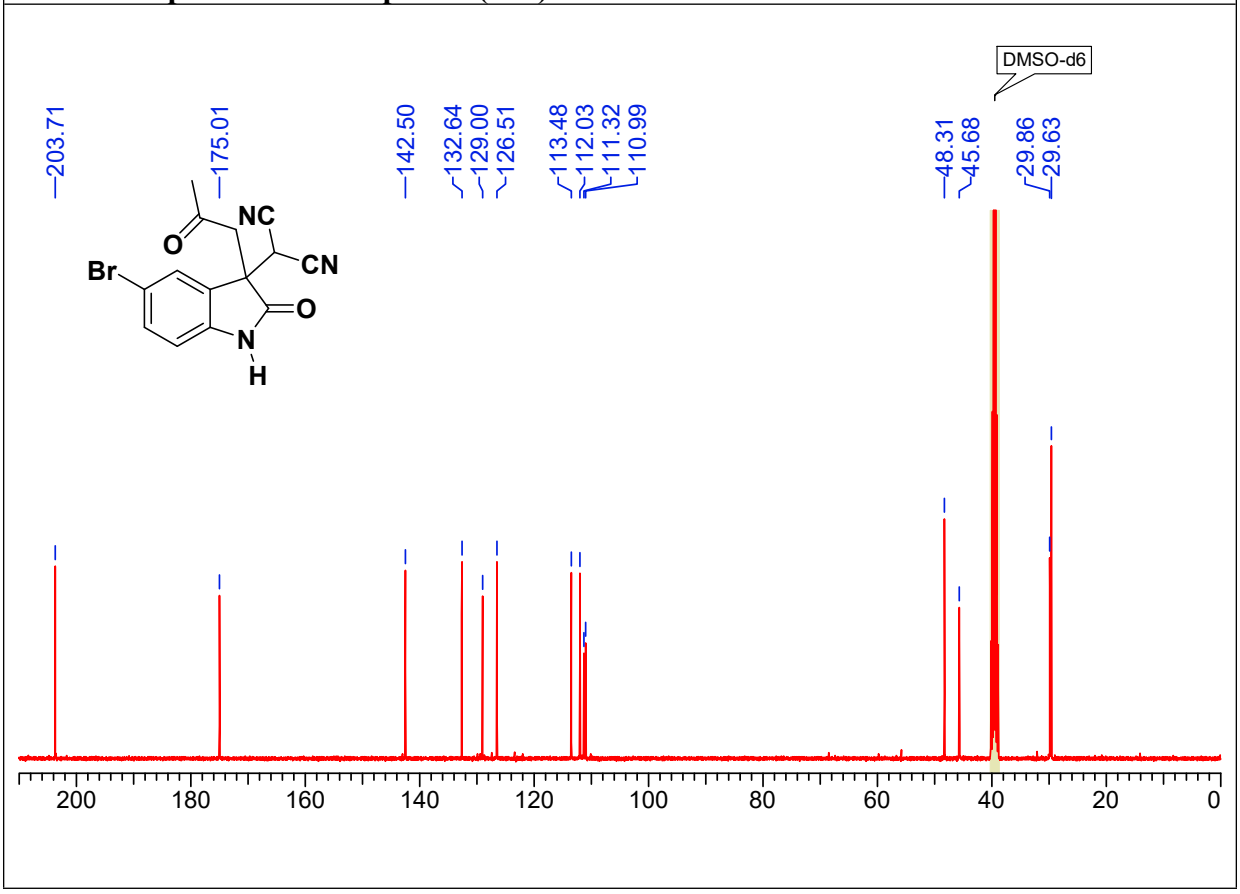

**135 DEPT spectrum of compound (4Ae)**



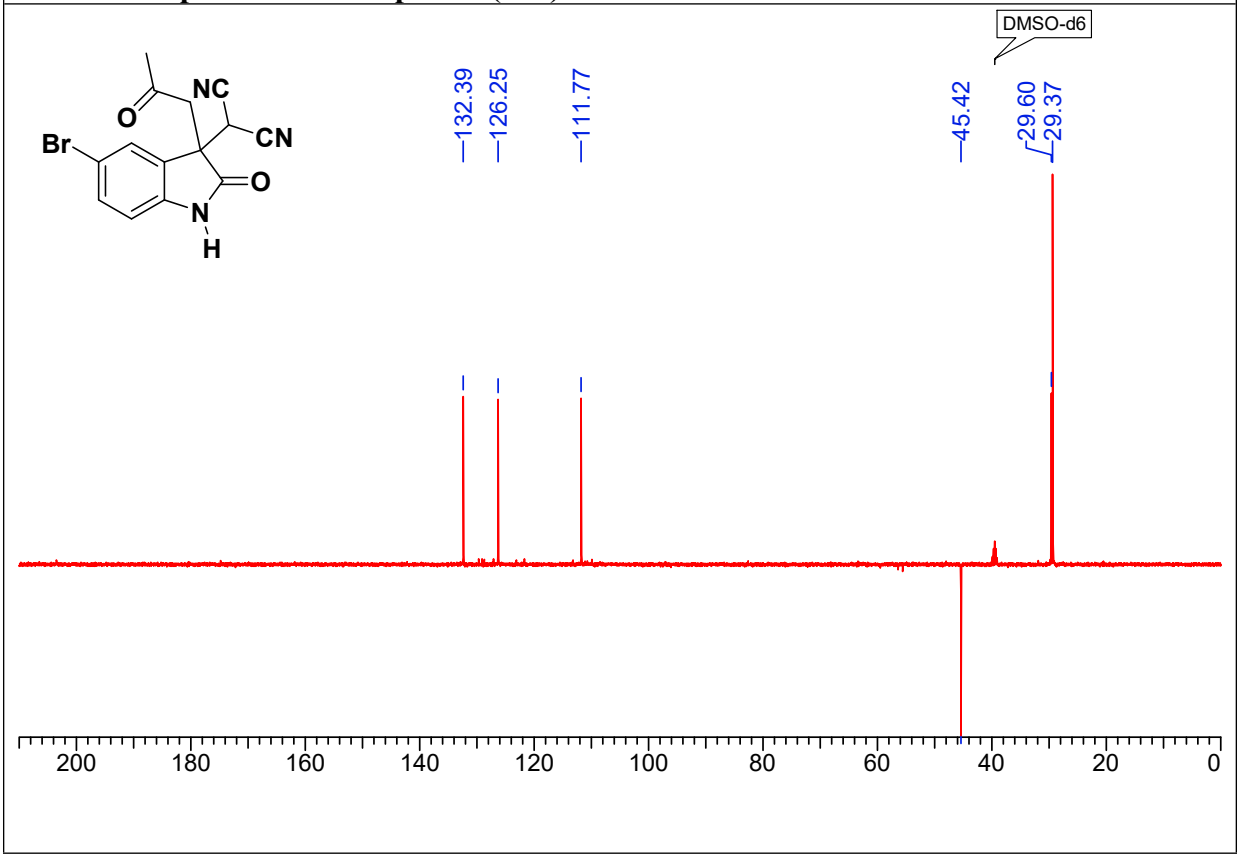
**$^1$H NMR spectrum of compound (4Af)**



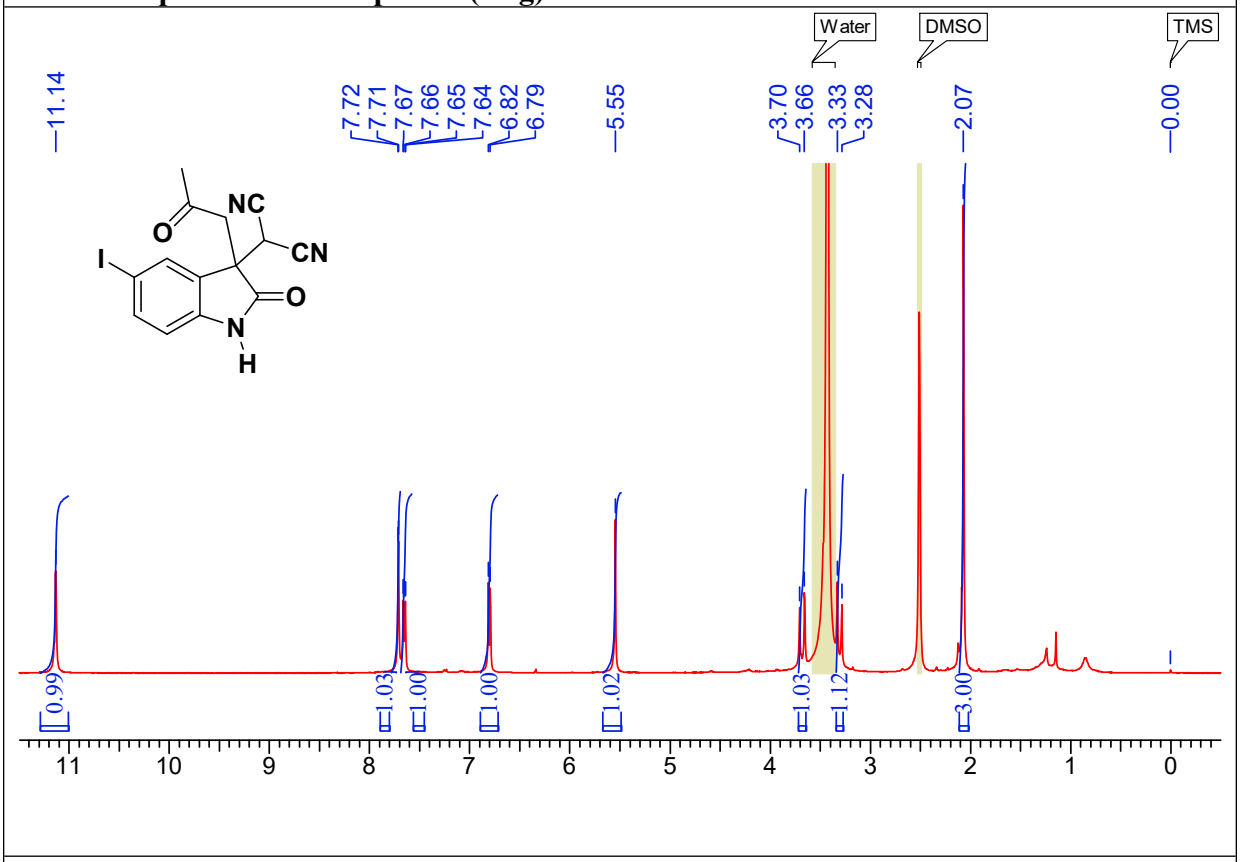

**$^{13}$C NMR spectrum of compound (4Af)**



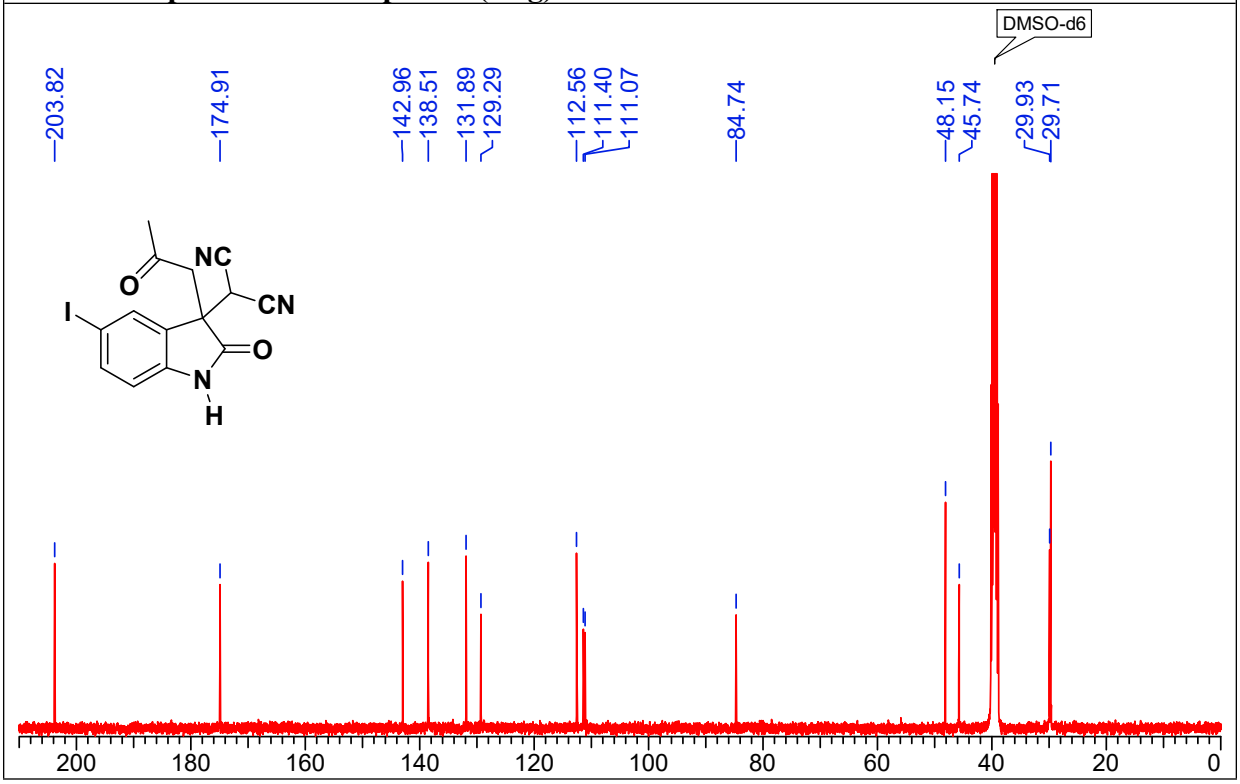
**135 DEPT spectrum of compound (4Af)**



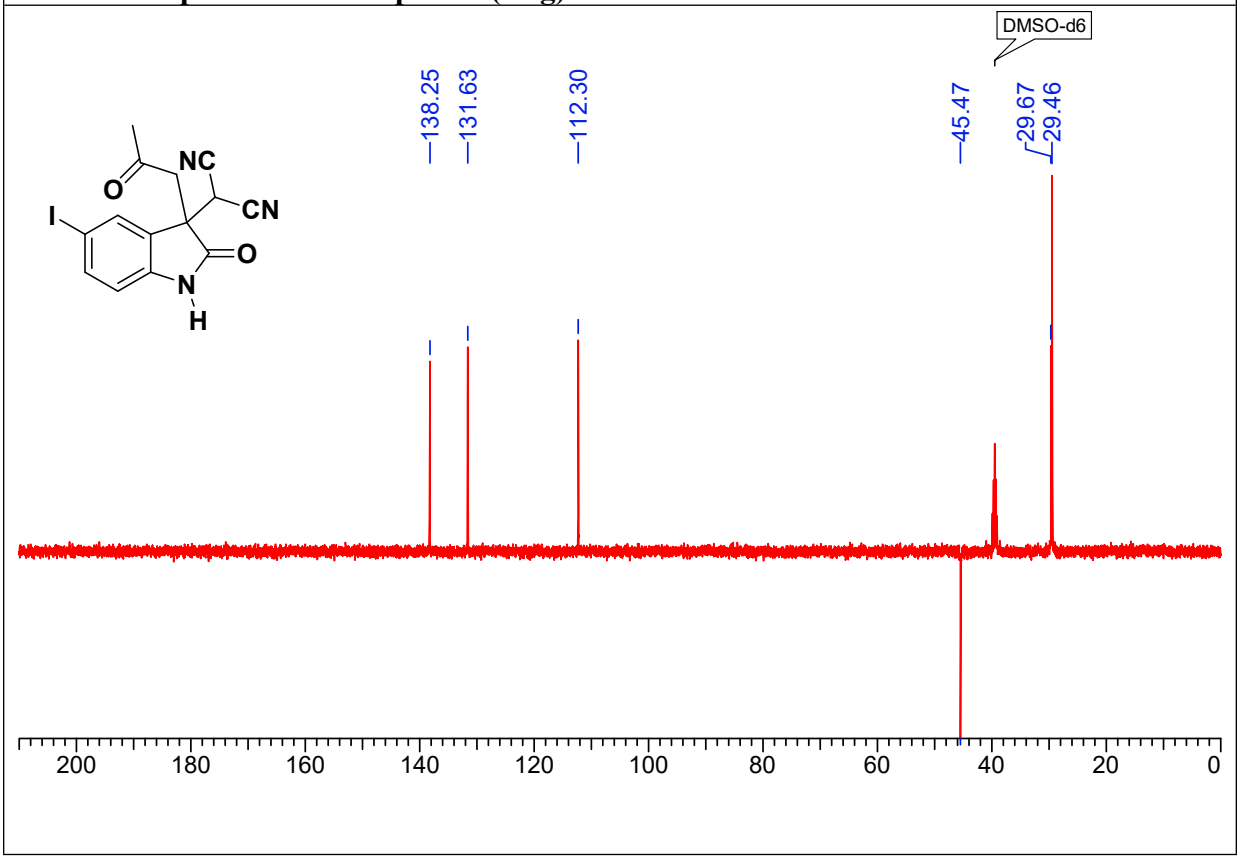
**$^{1}$H NMR spectrum of compound (4Ag)**



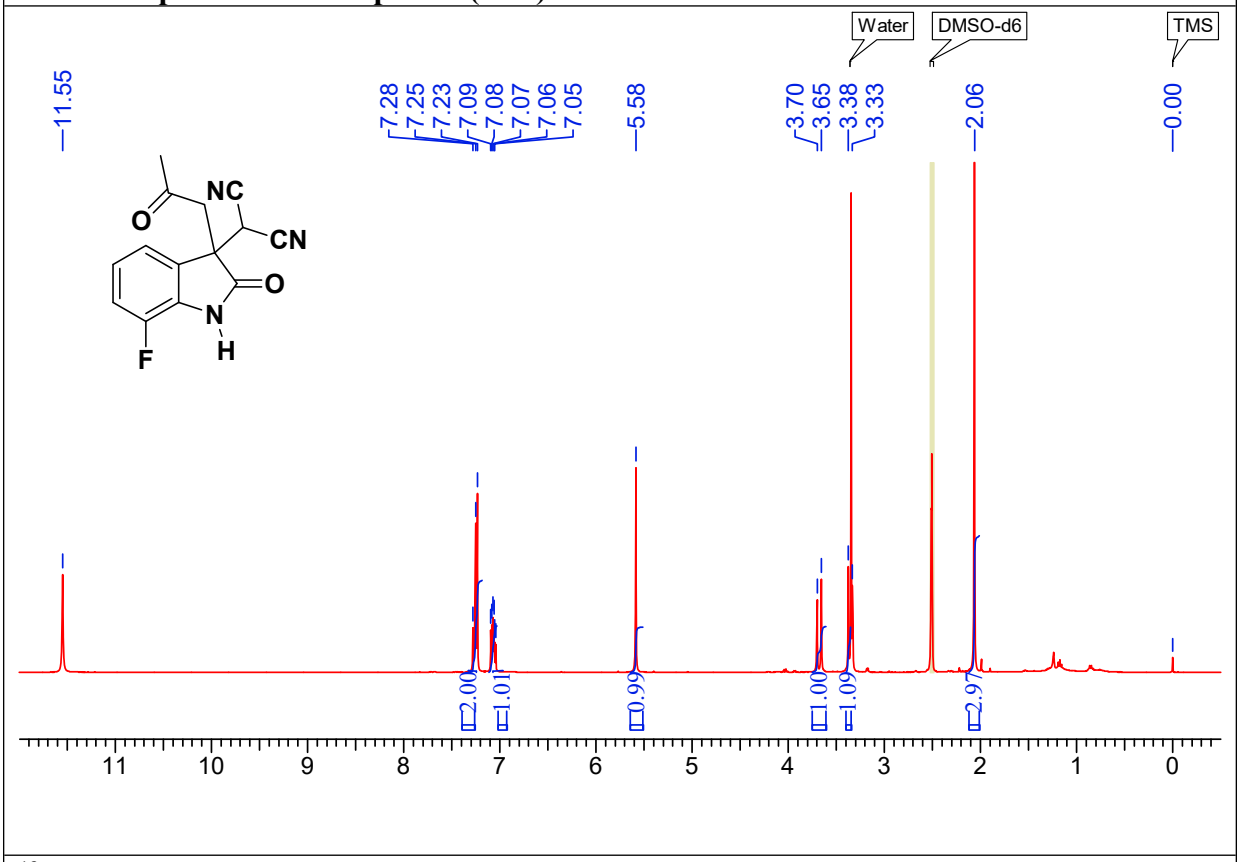

**$^{13}$C NMR spectrum of compound (4Ag)**



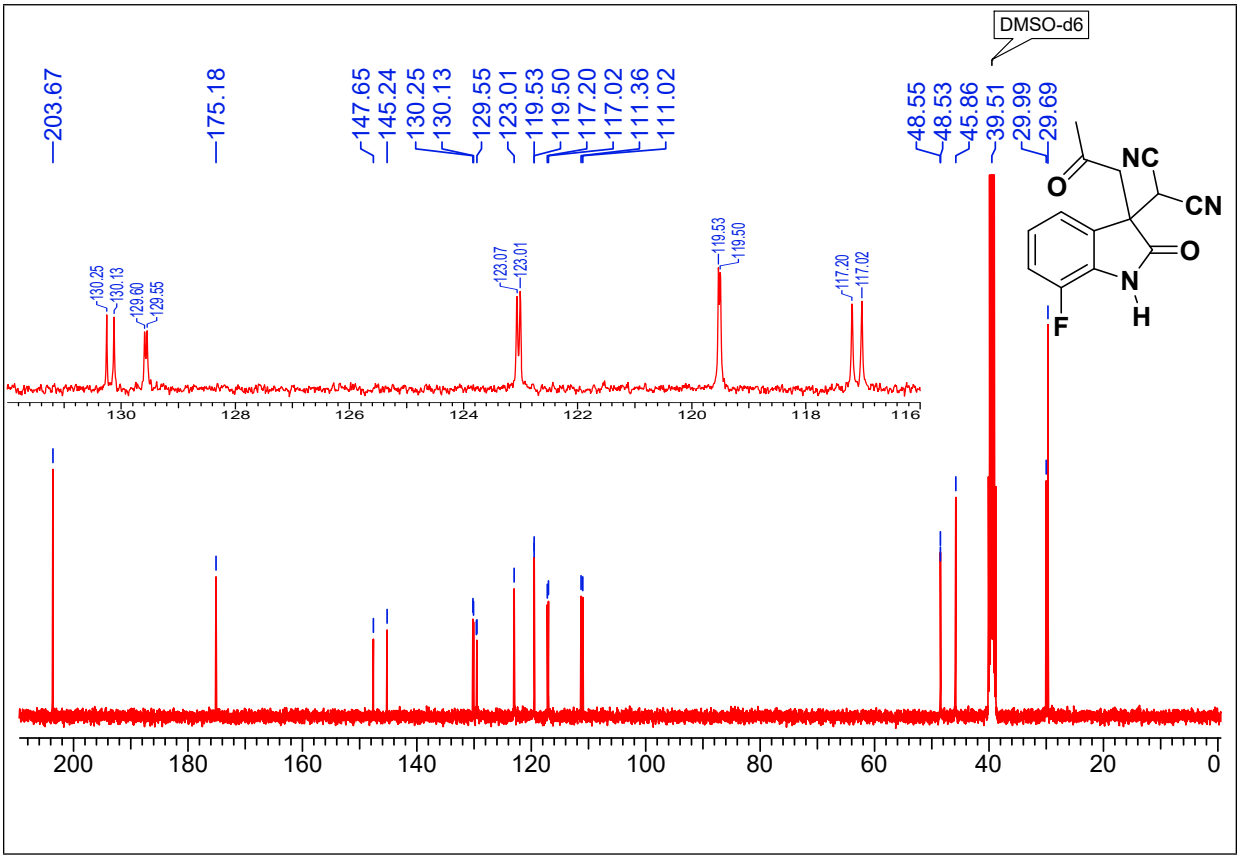
**135 DEPT spectrum of compound (4Ag)**



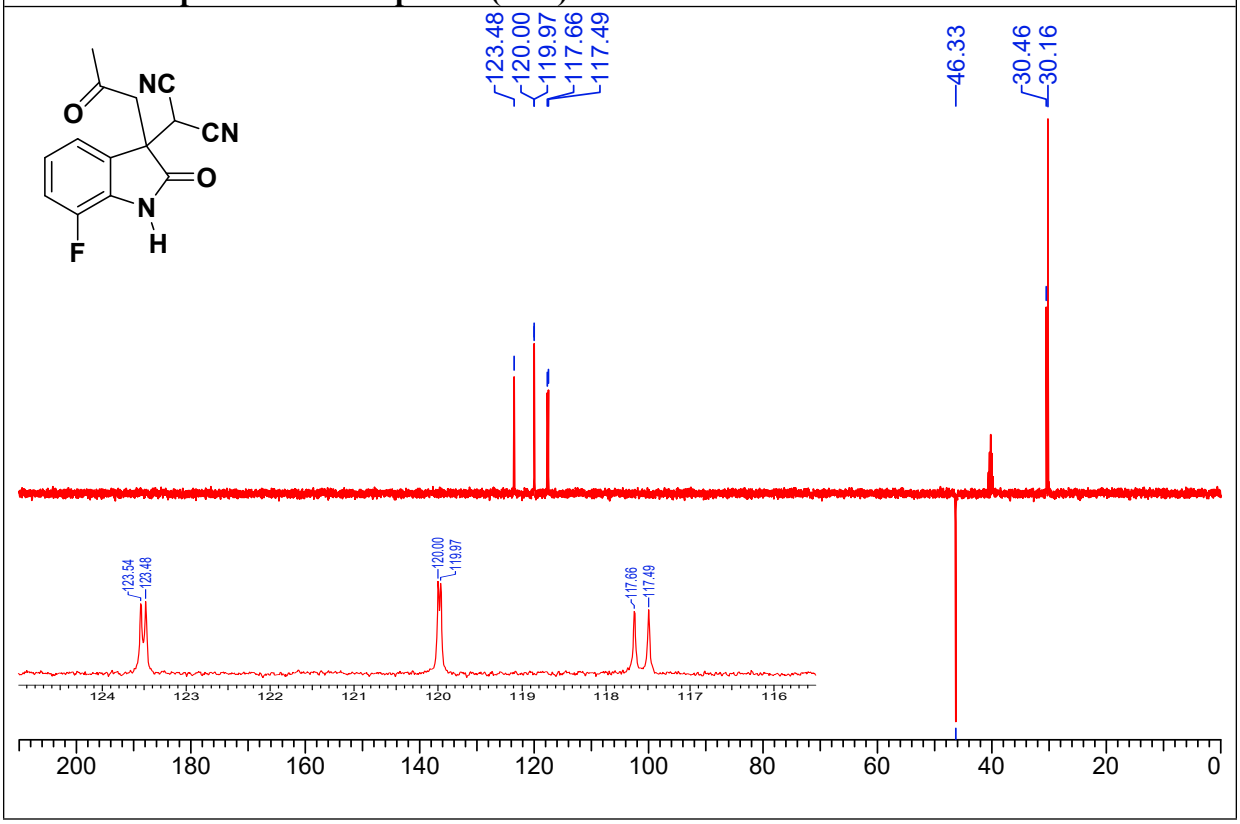
**$^{1}$H NMR spectrum of compound (4Ah)**



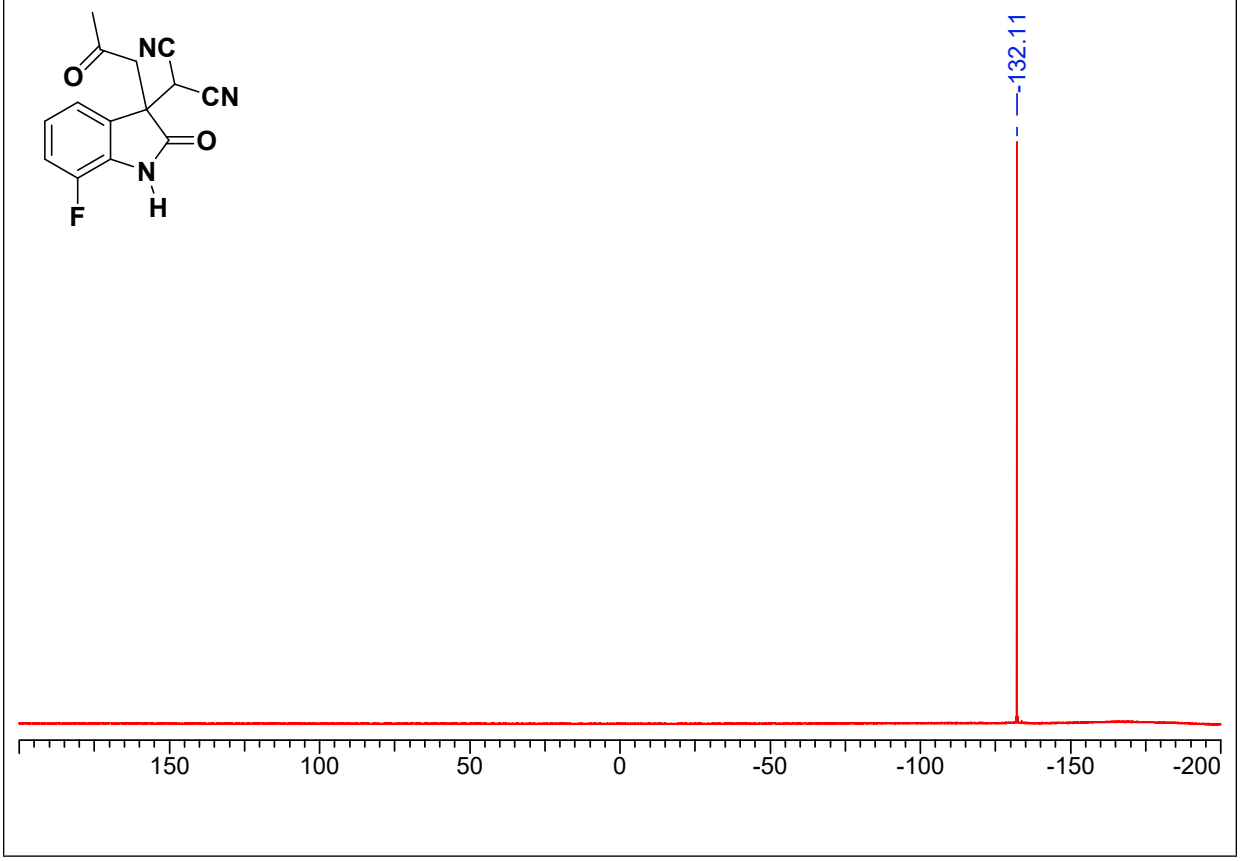

**$^{13}$C NMR spectrum of compound (4Ah)**



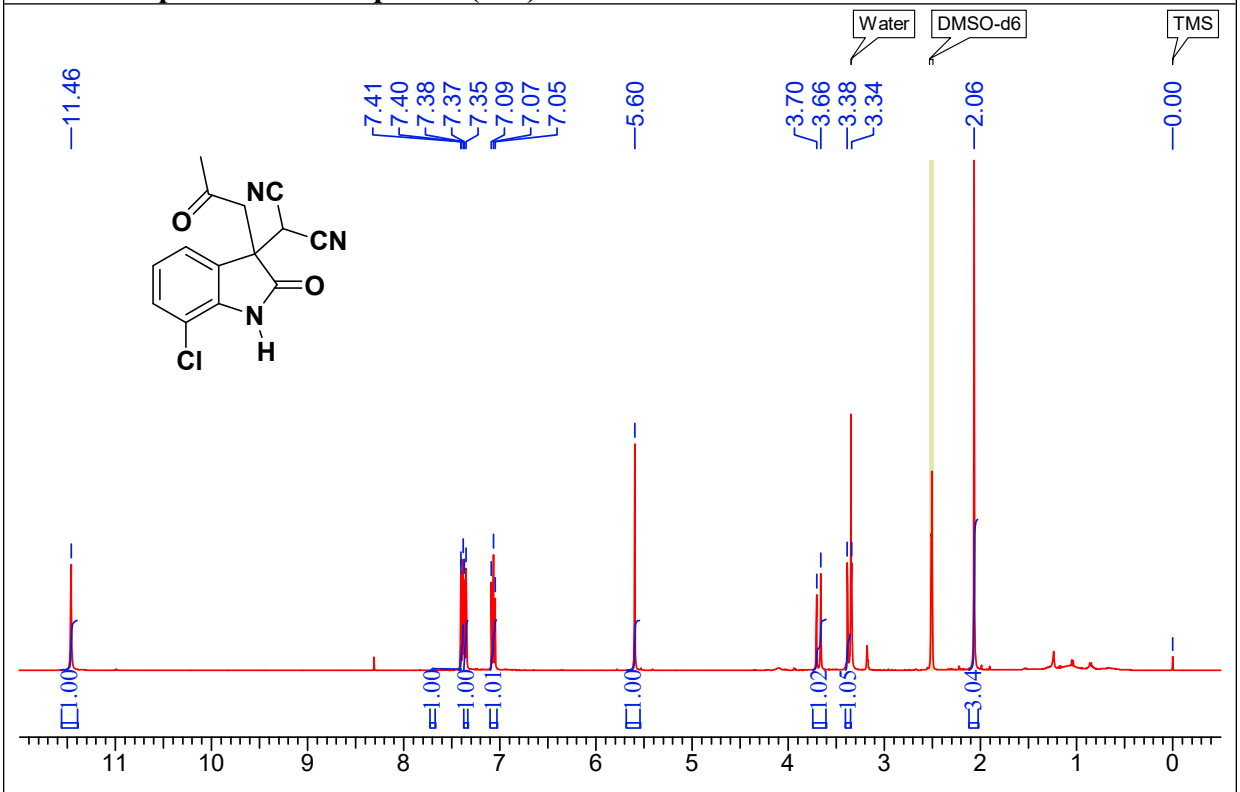

**135 DEPT spectrum of compound (4Ah)**



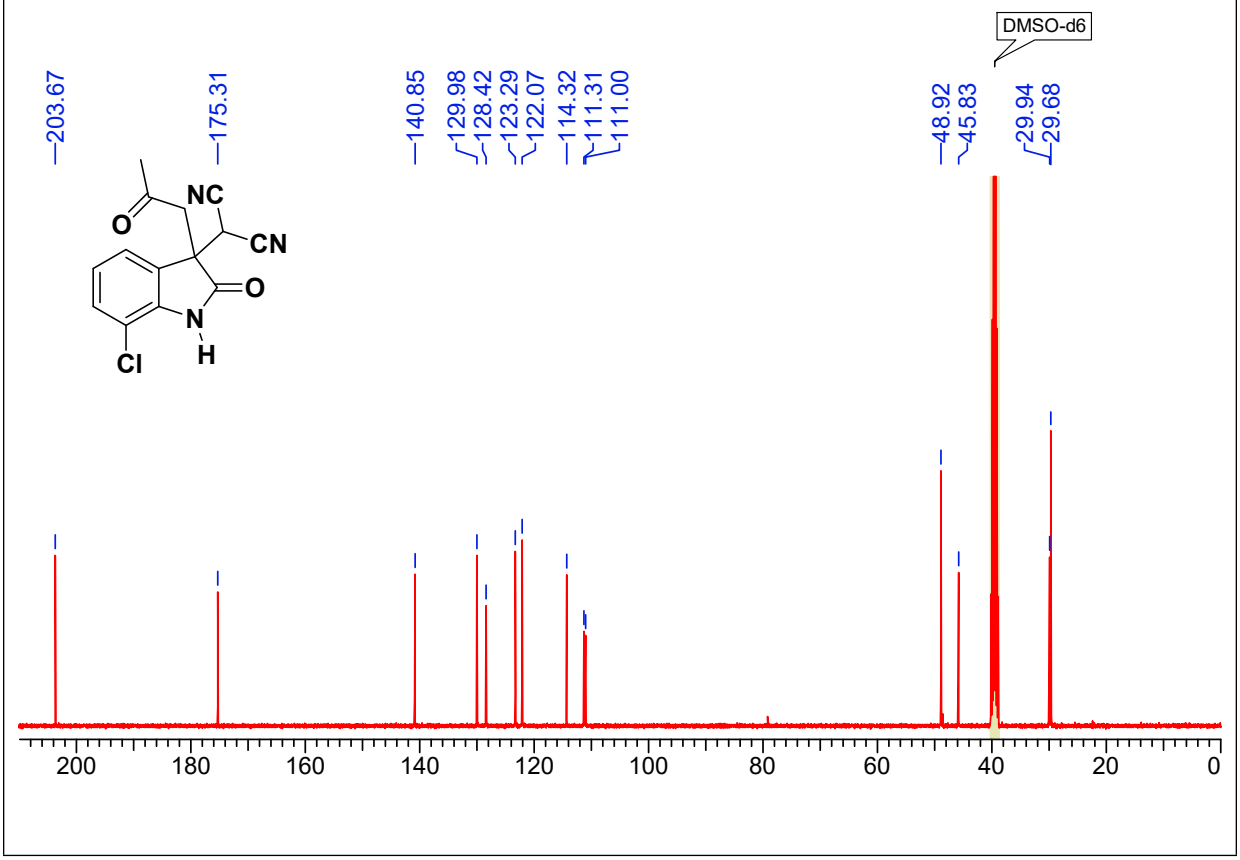
**$^{19}$F spectrum of compound (4Ah)**



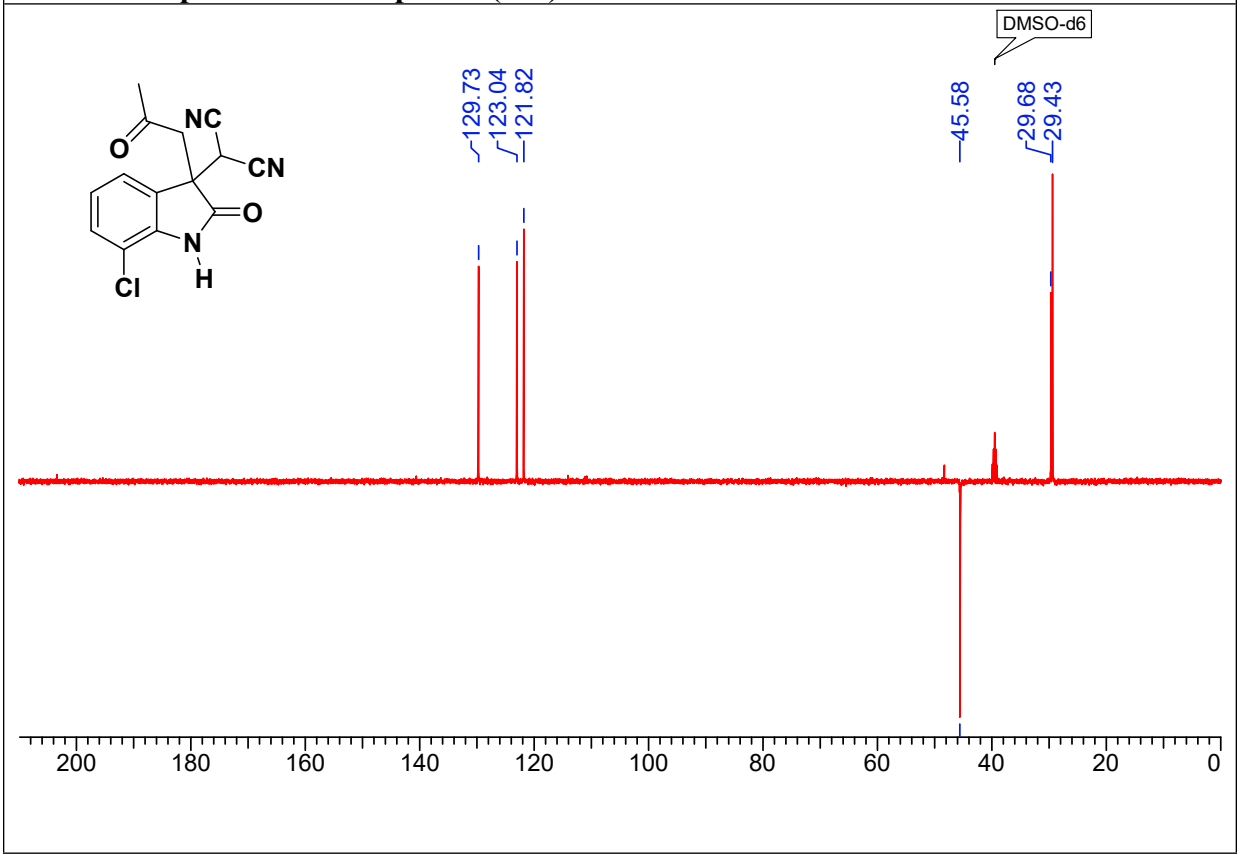
**$^{1}$H NMR spectrum of compound (4Ai)**



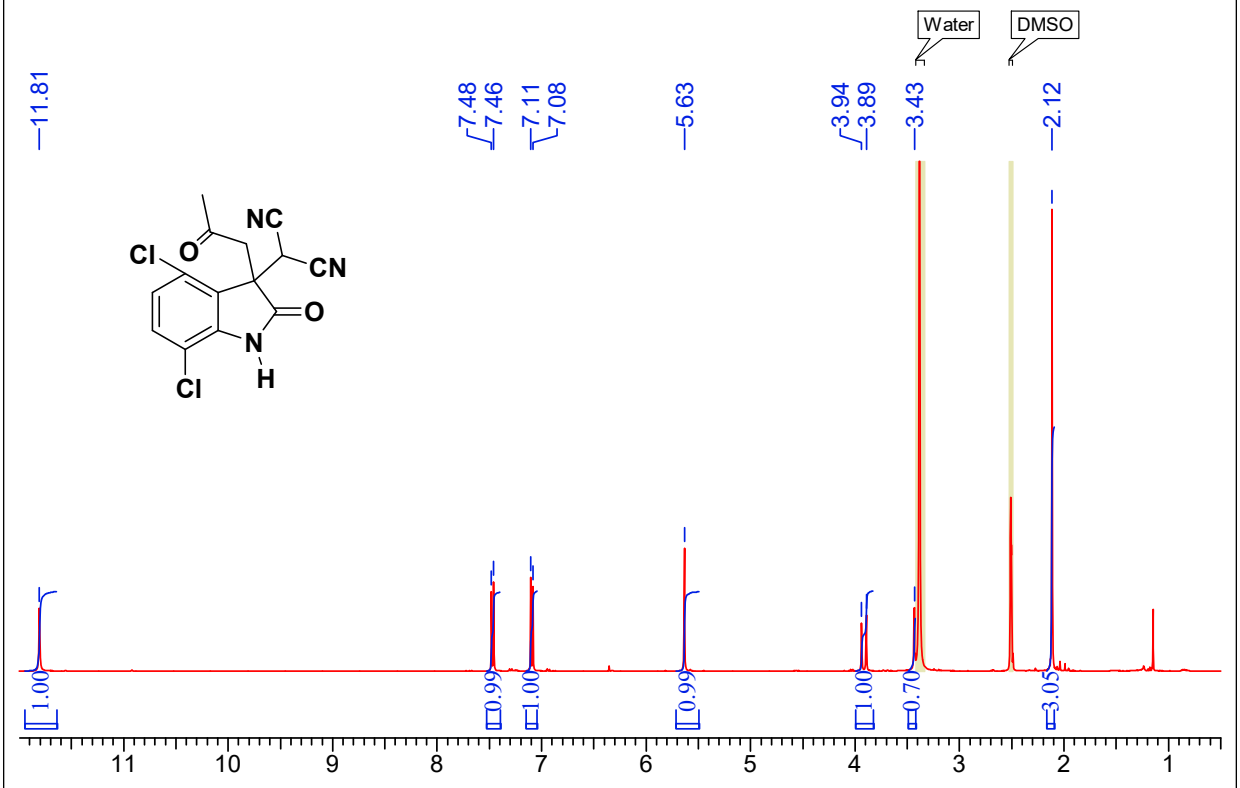

**$^{13}$C NMR spectrum of compound (4Ai)**



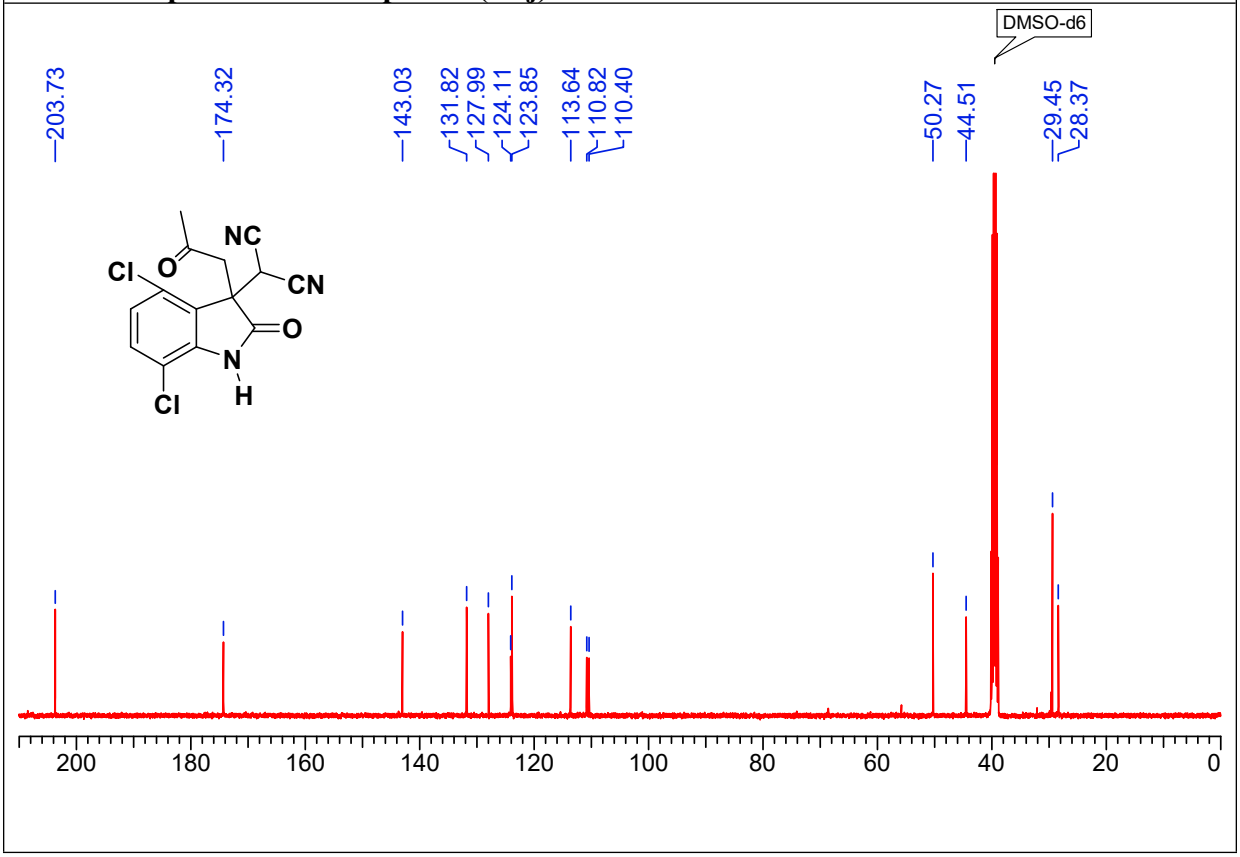
**135 DEPT spectrum of compound (4Ai)**



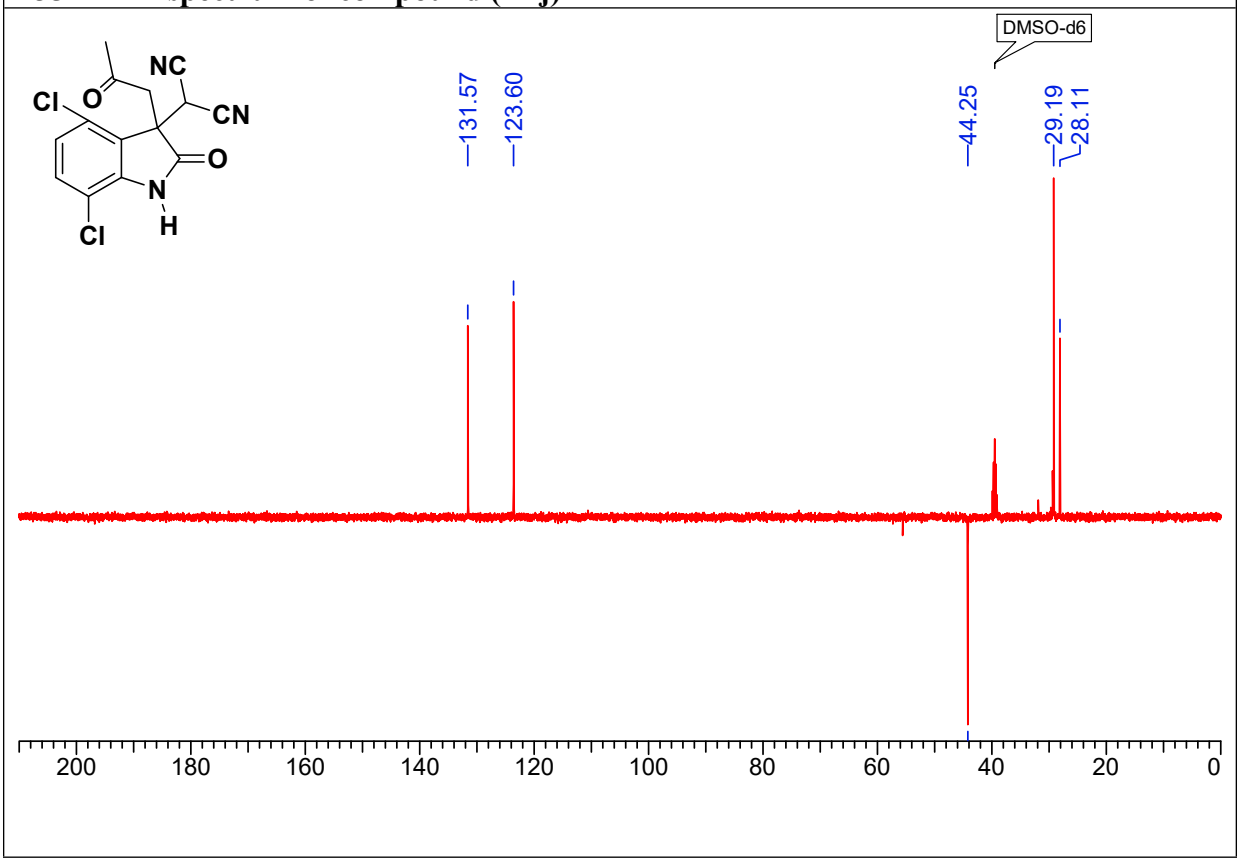
**$^{1}$H NMR spectrum of compound (4Aj)**



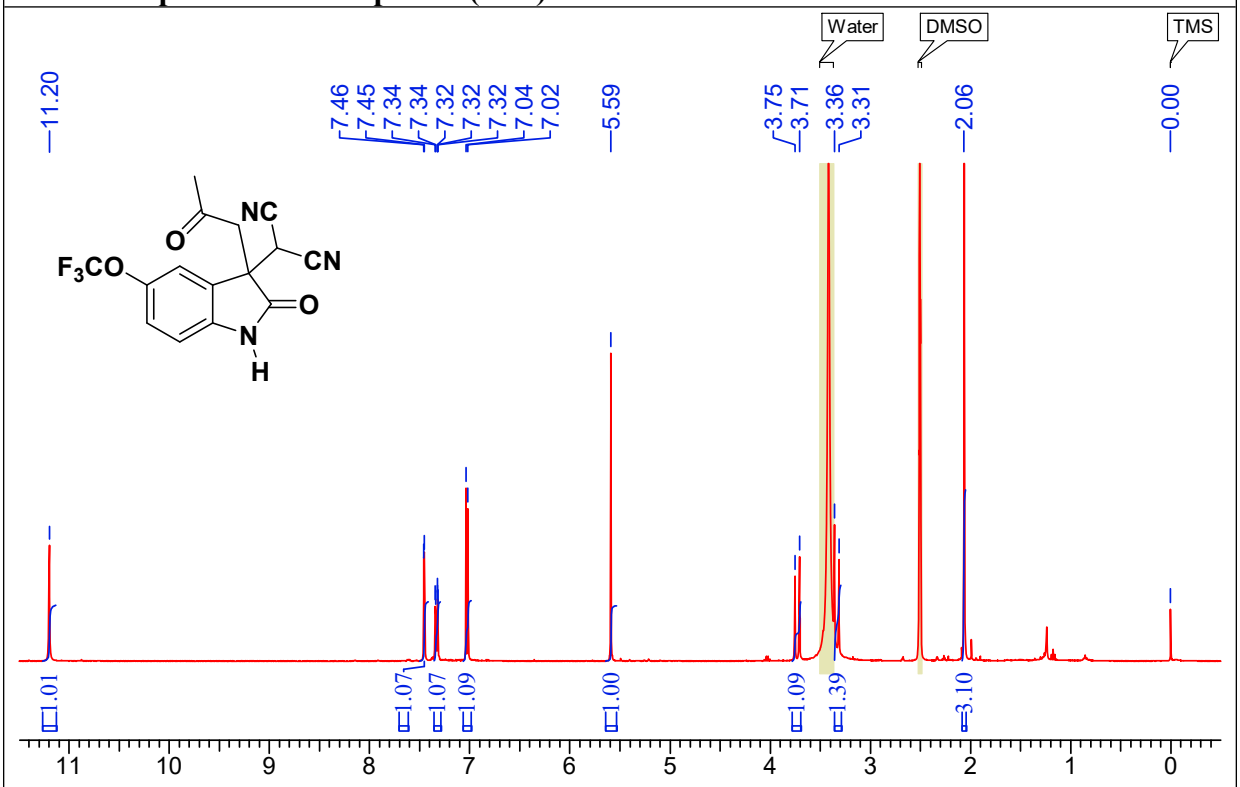

**$^{13}$C NMR spectrum of compound (4Aj)**



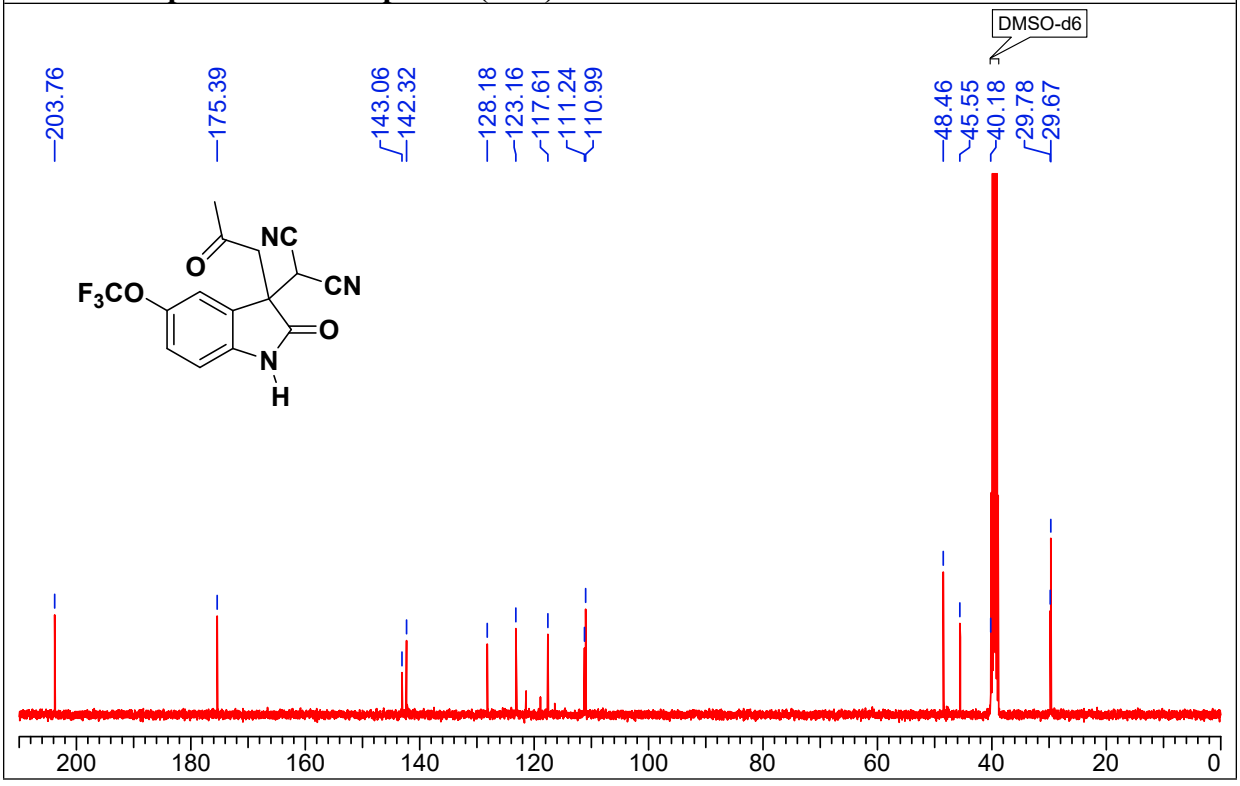
**135 DEPT spectrum of compound (4Aj)**



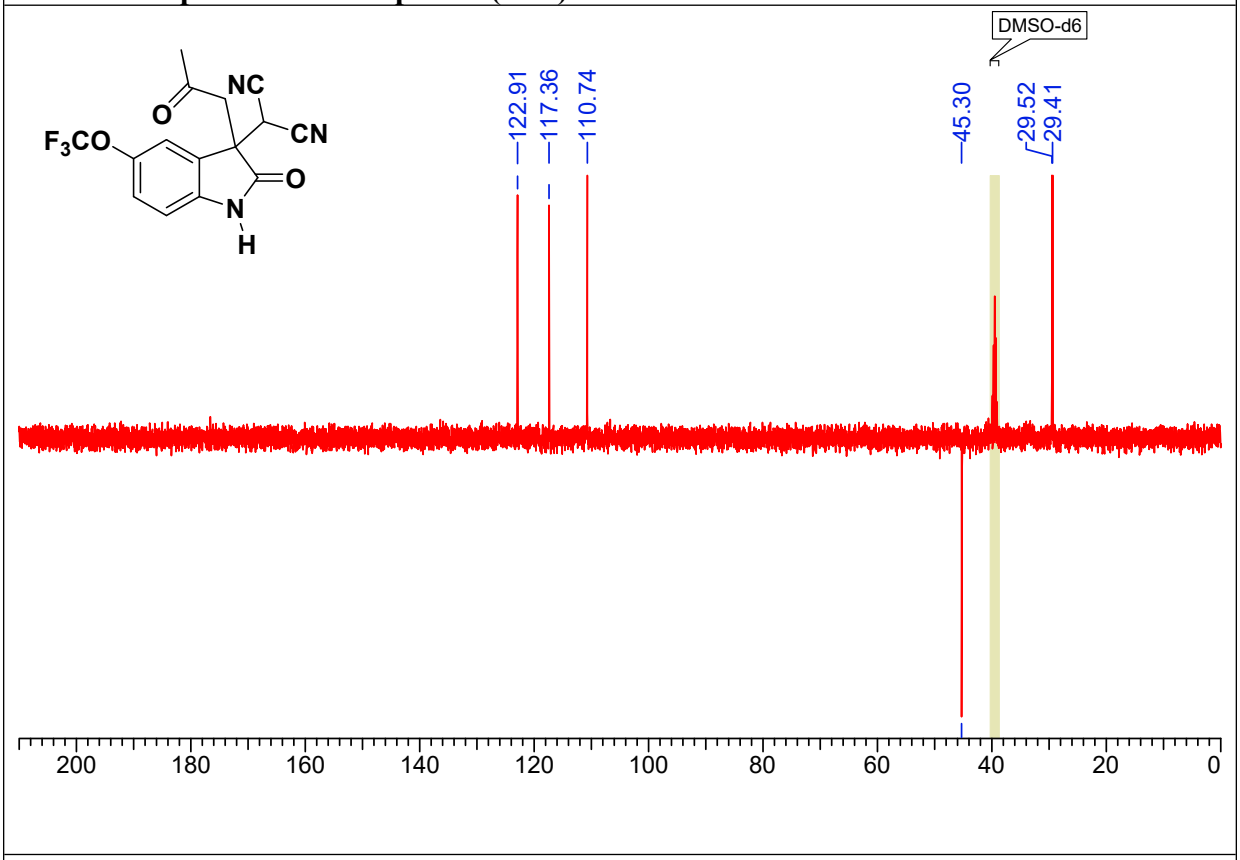
**$^{1}$H NMR spectrum of compound (4Ak)**



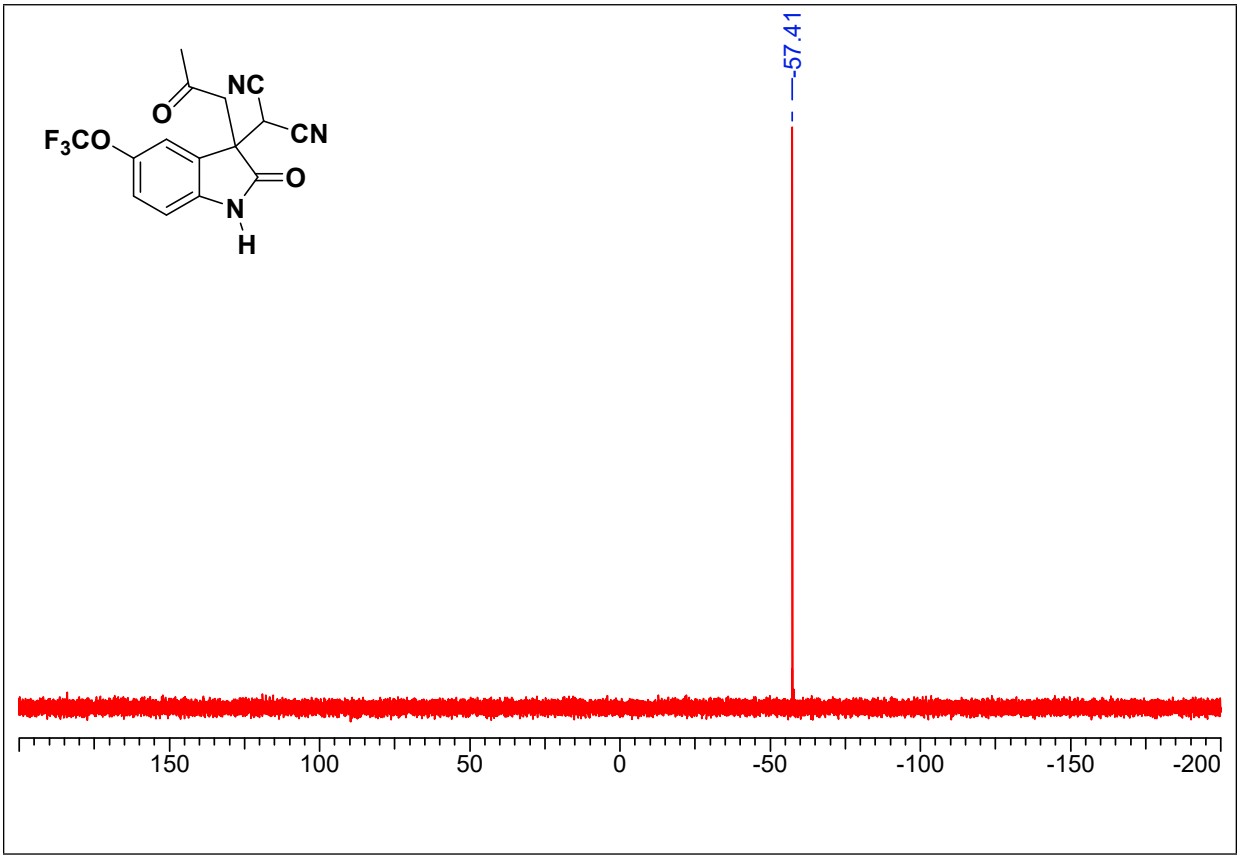

**$^{13}$C NMR spectrum of compound (4Ak)**



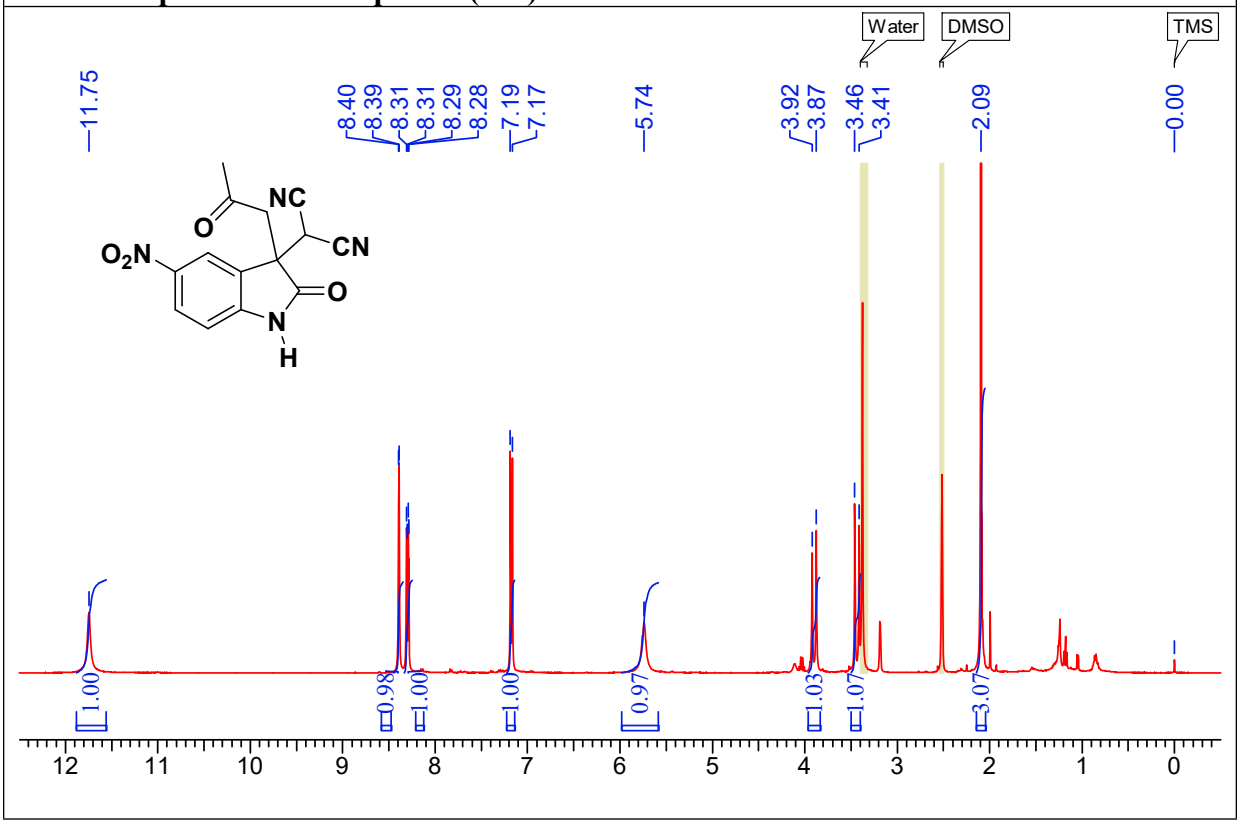
**135 DEPT spectrum of compound (4Ak)**



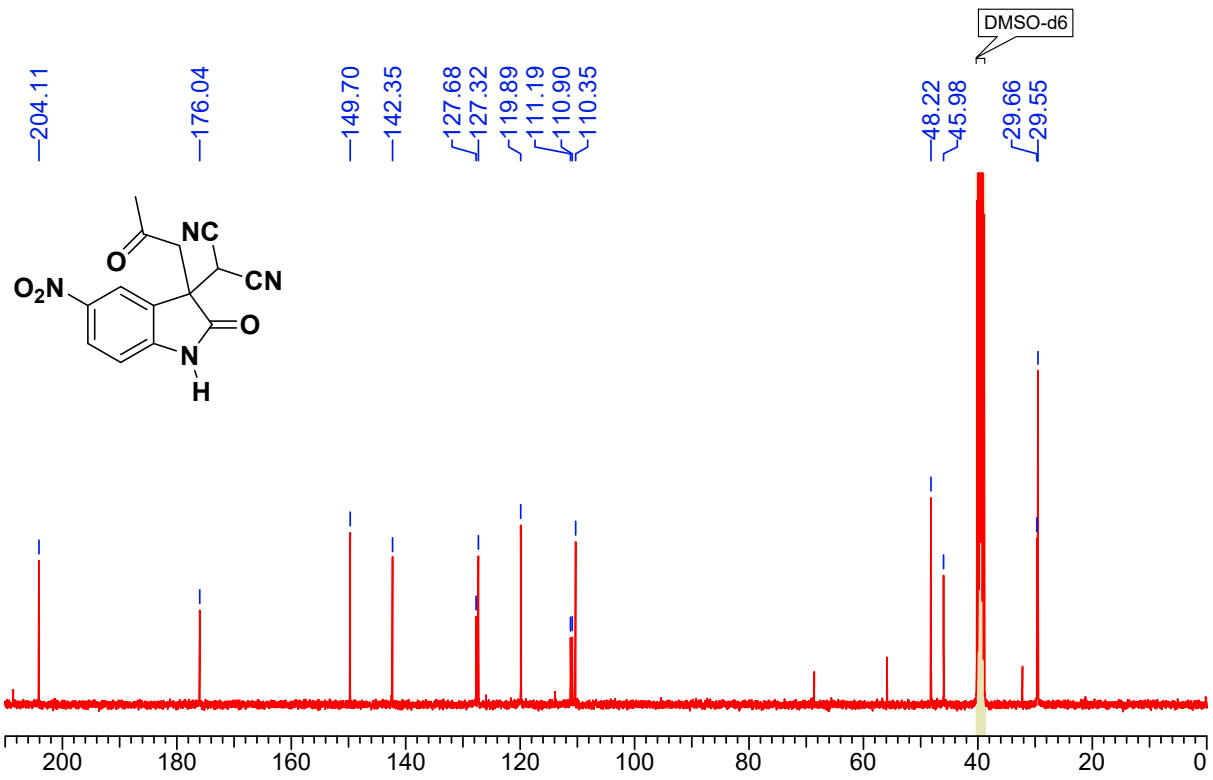

**$^{19}$F spectrum of compound (4Ak)**



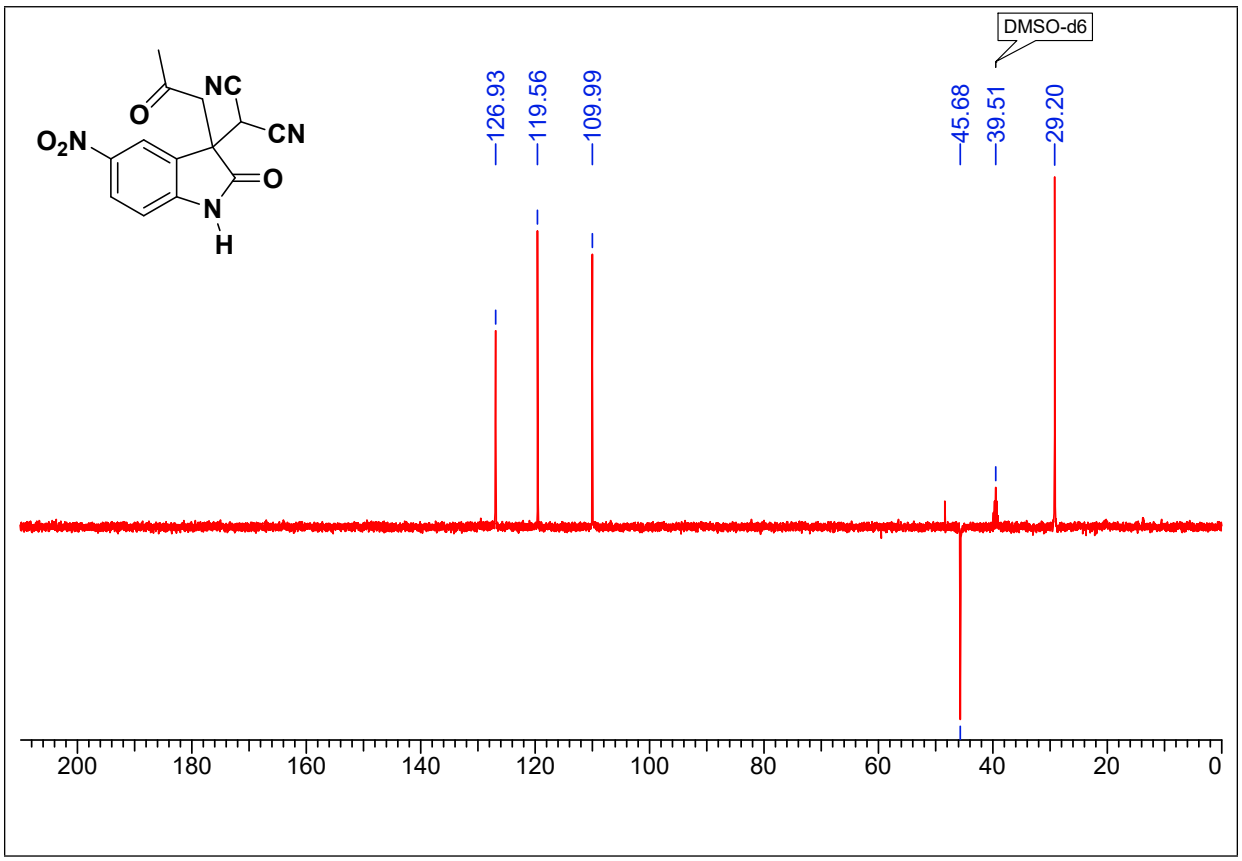

**$^{1}$H NMR spectrum of compound (4Al)**



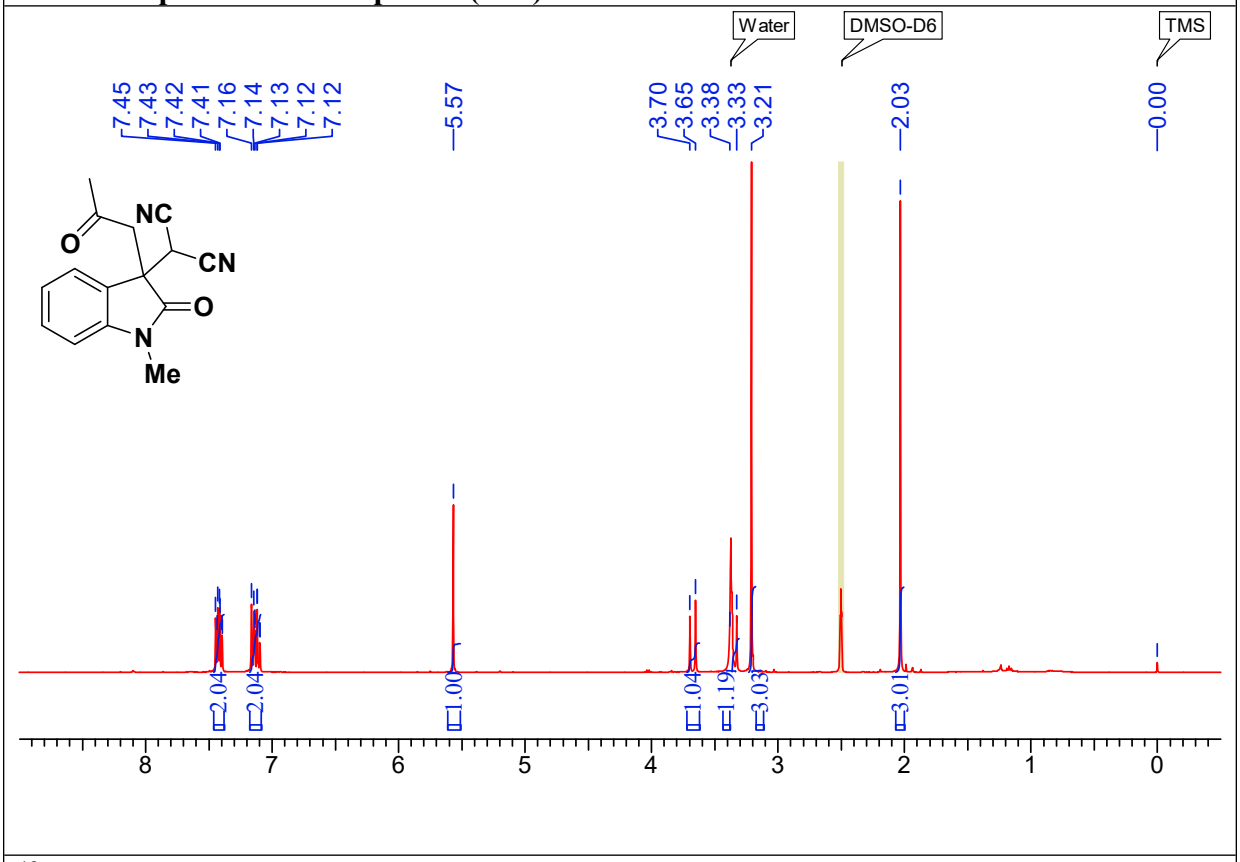
**$^{13}$C NMR spectrum of compound (4Al)**



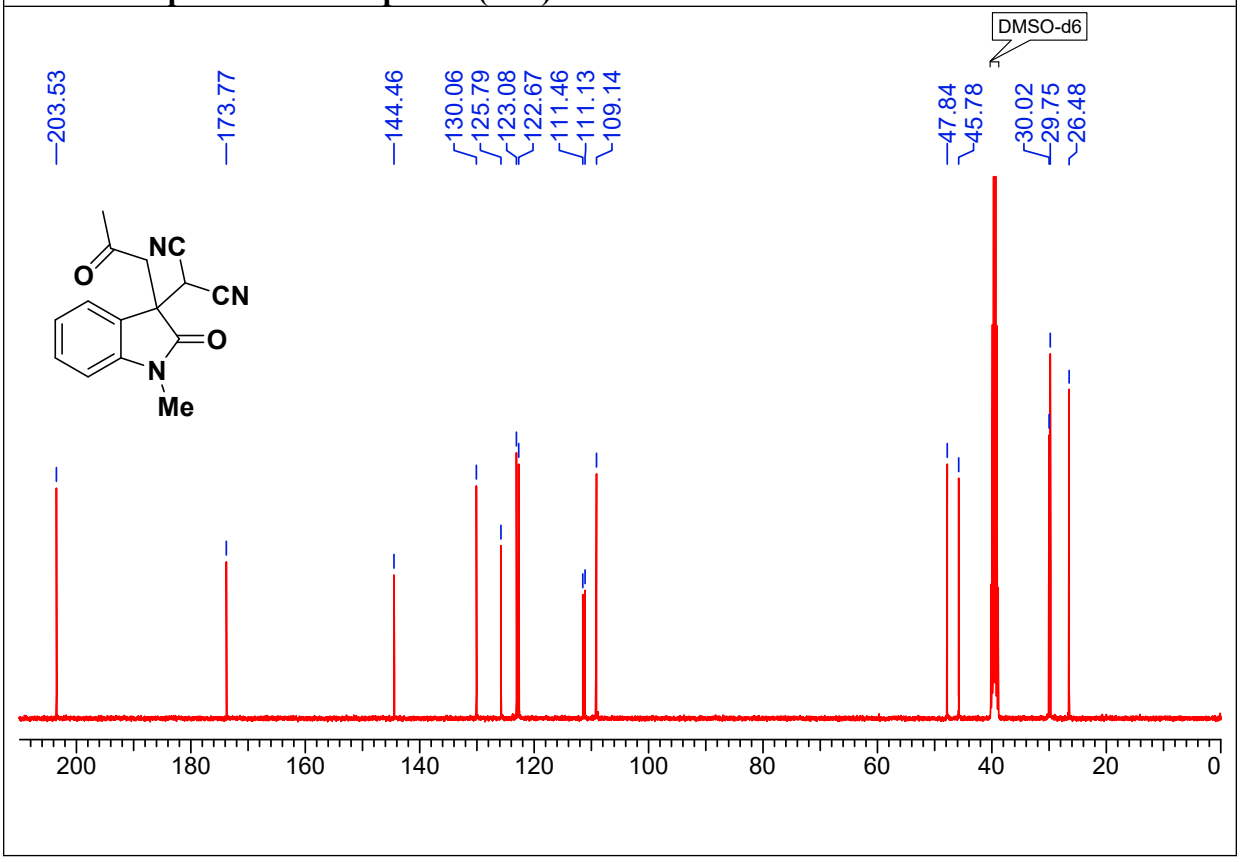

**135 DEPT spectrum of compound (4Al)**


NC
O
CN
O2N
O
N
H
126.93
119.56
109.99
45.68
39.51
29.20
DMSO-d6
200
180
160
140
120
100
80
60
40
20
0

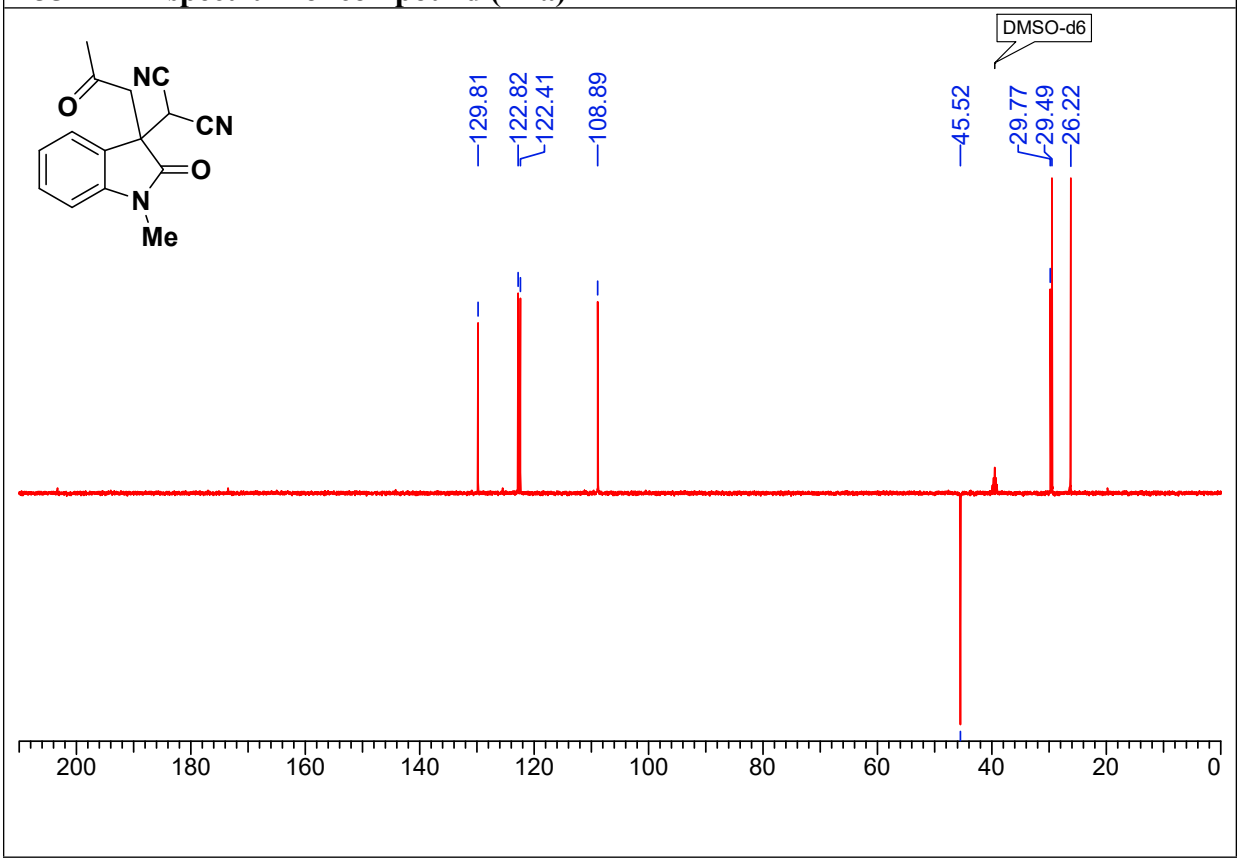
**$^{1}$H NMR spectrum of compound (4Ba)**



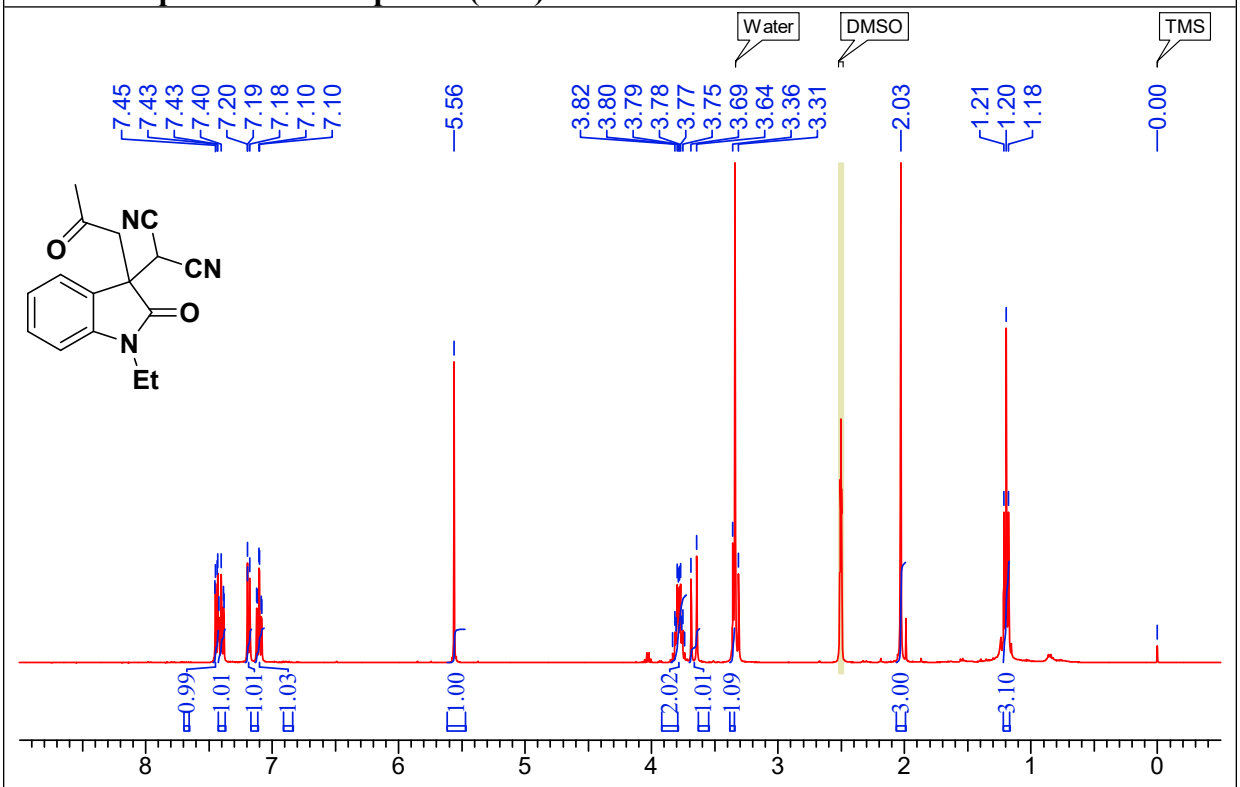

**$^{13}$C NMR spectrum of compound (4Ba)**



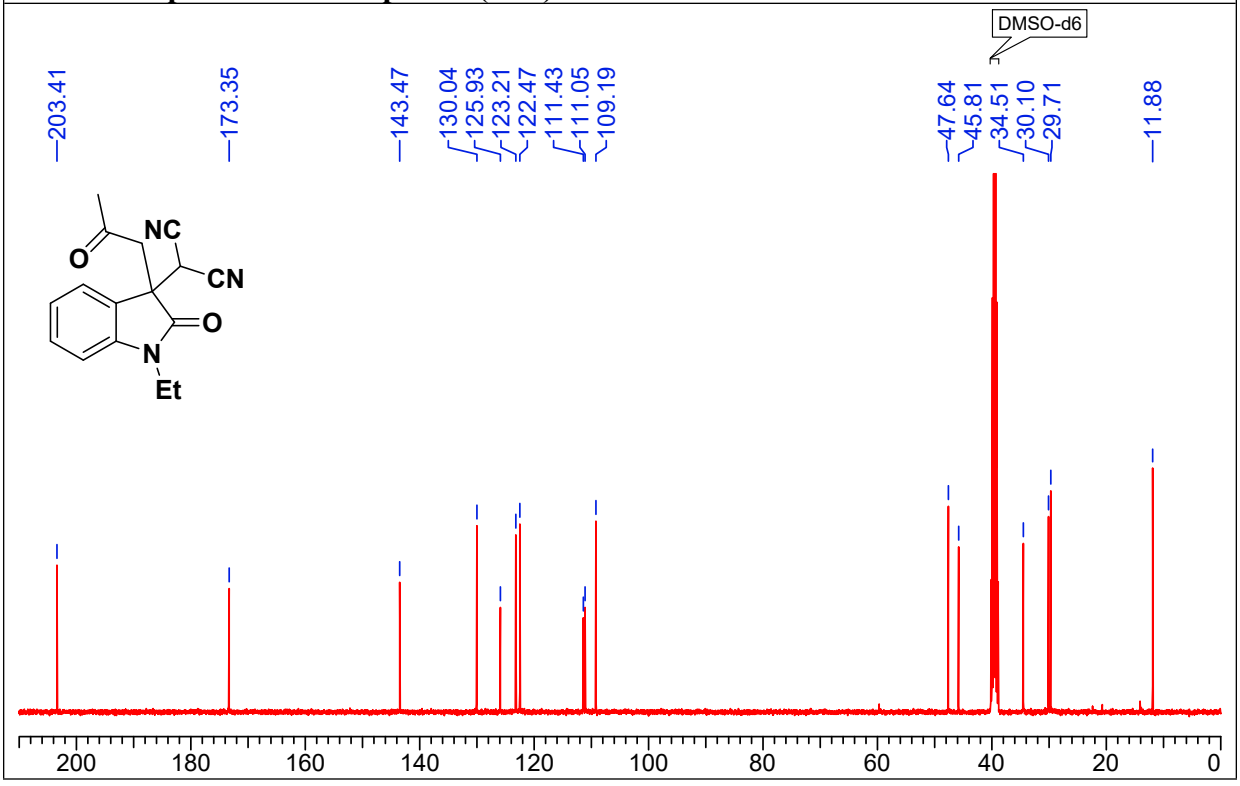
**135 DEPT spectrum of compound (4Aa)**



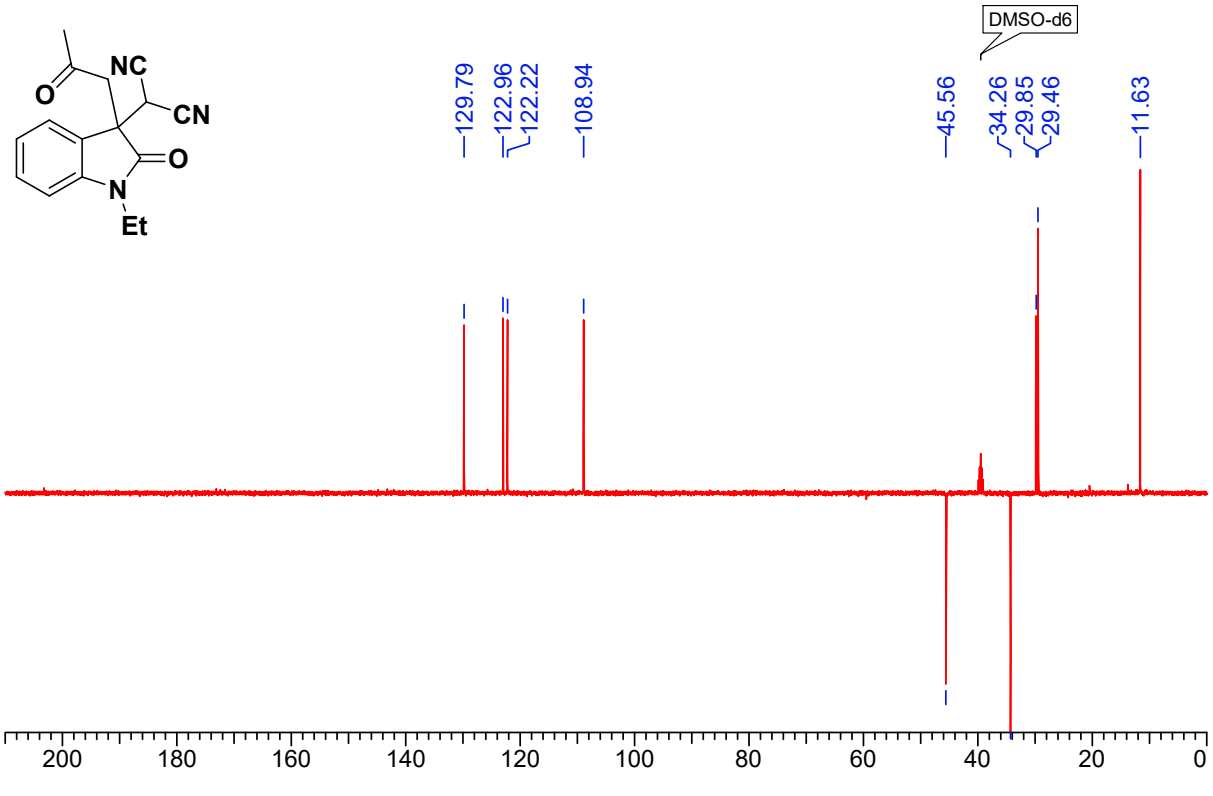
**$^{1}$H NMR spectrum of compound (4Bb)**



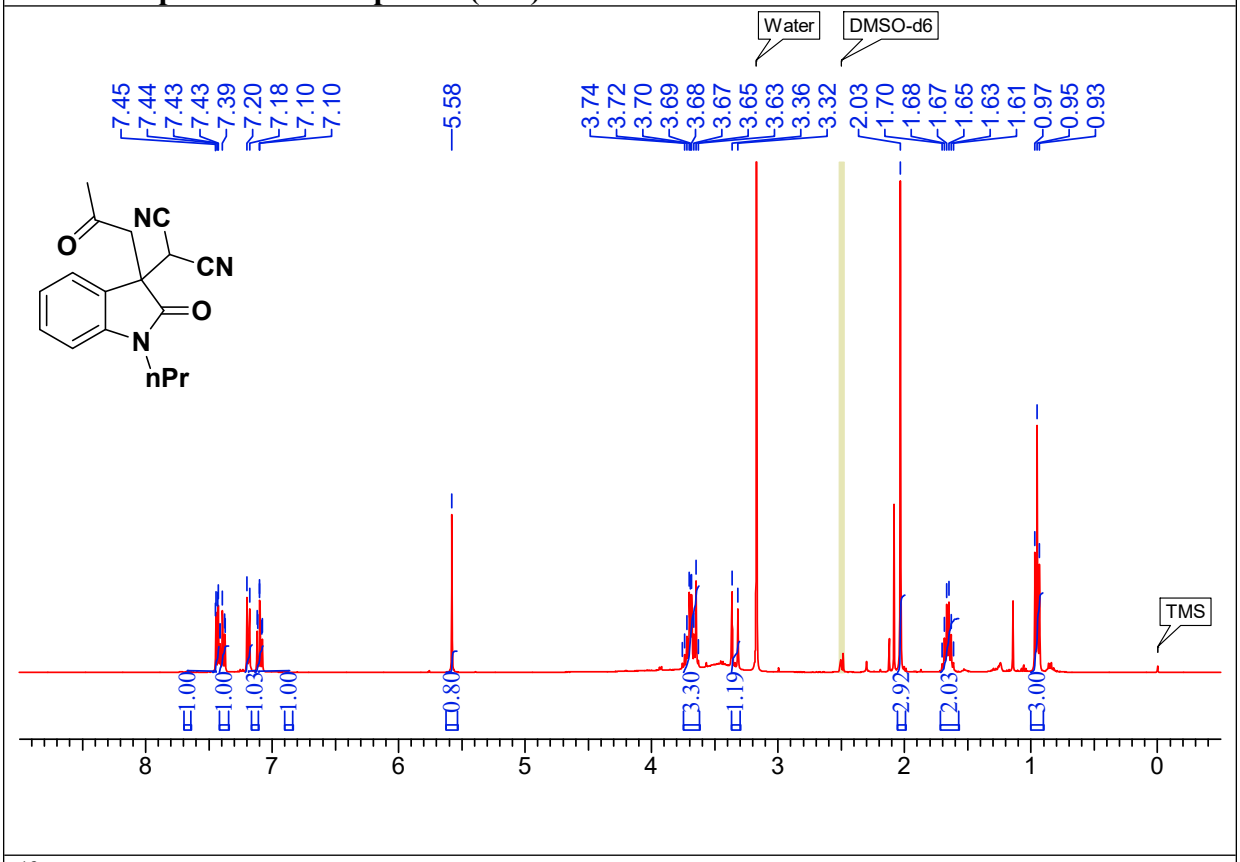

**$^{13}$C NMR spectrum of compound (4Bb)**



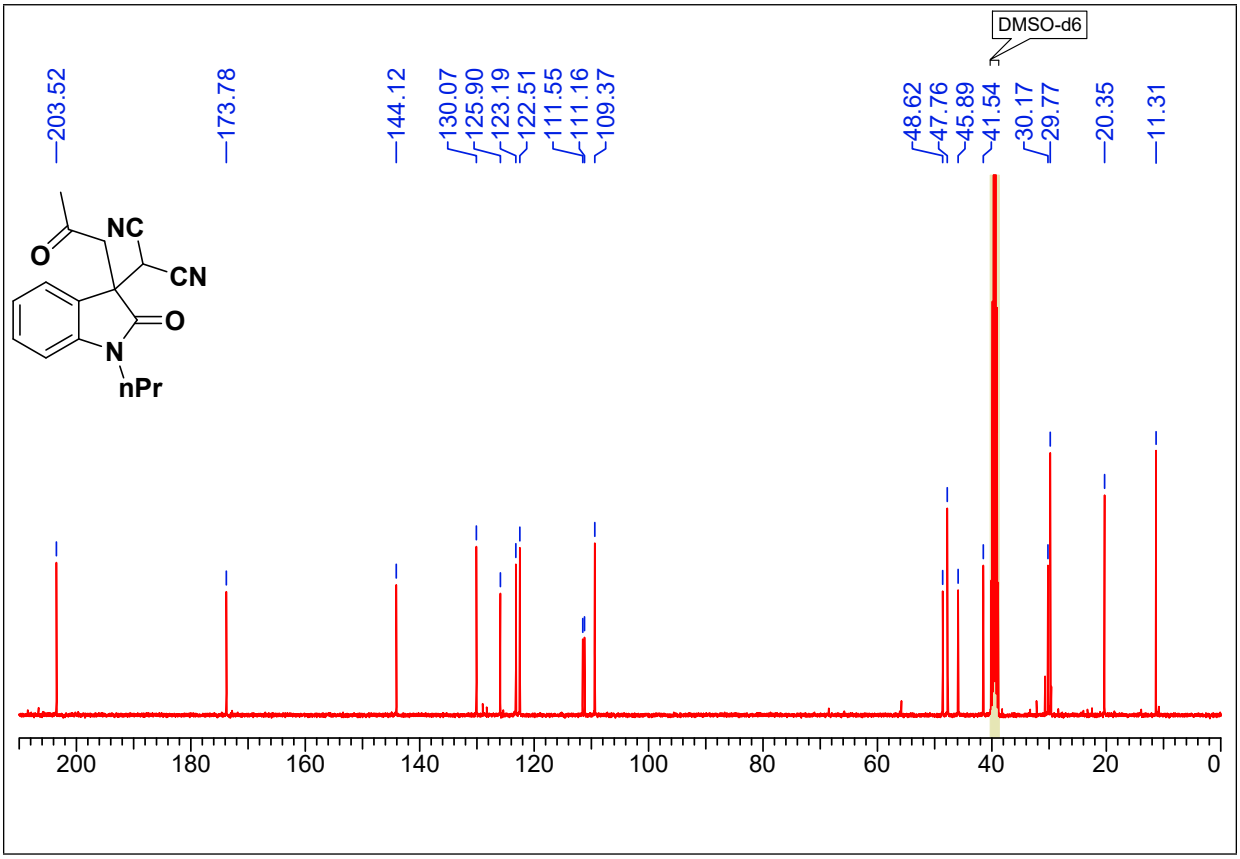
**135 DEPT spectrum of compound (4Bb)**



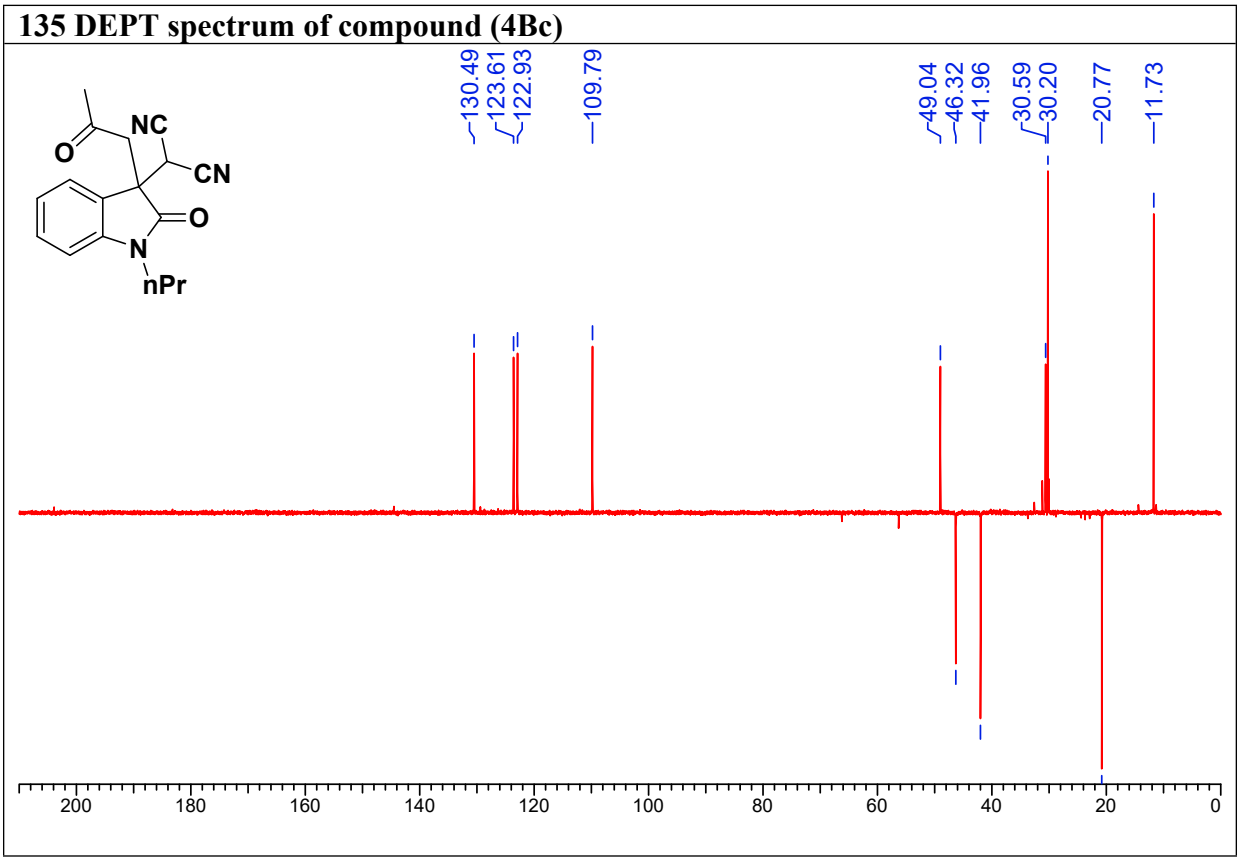
**$^{1}$H NMR spectrum of compound (4Bc)**



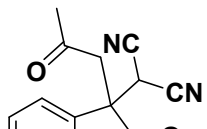

**$^{13}$C NMR spectrum of compound (4Bc)**



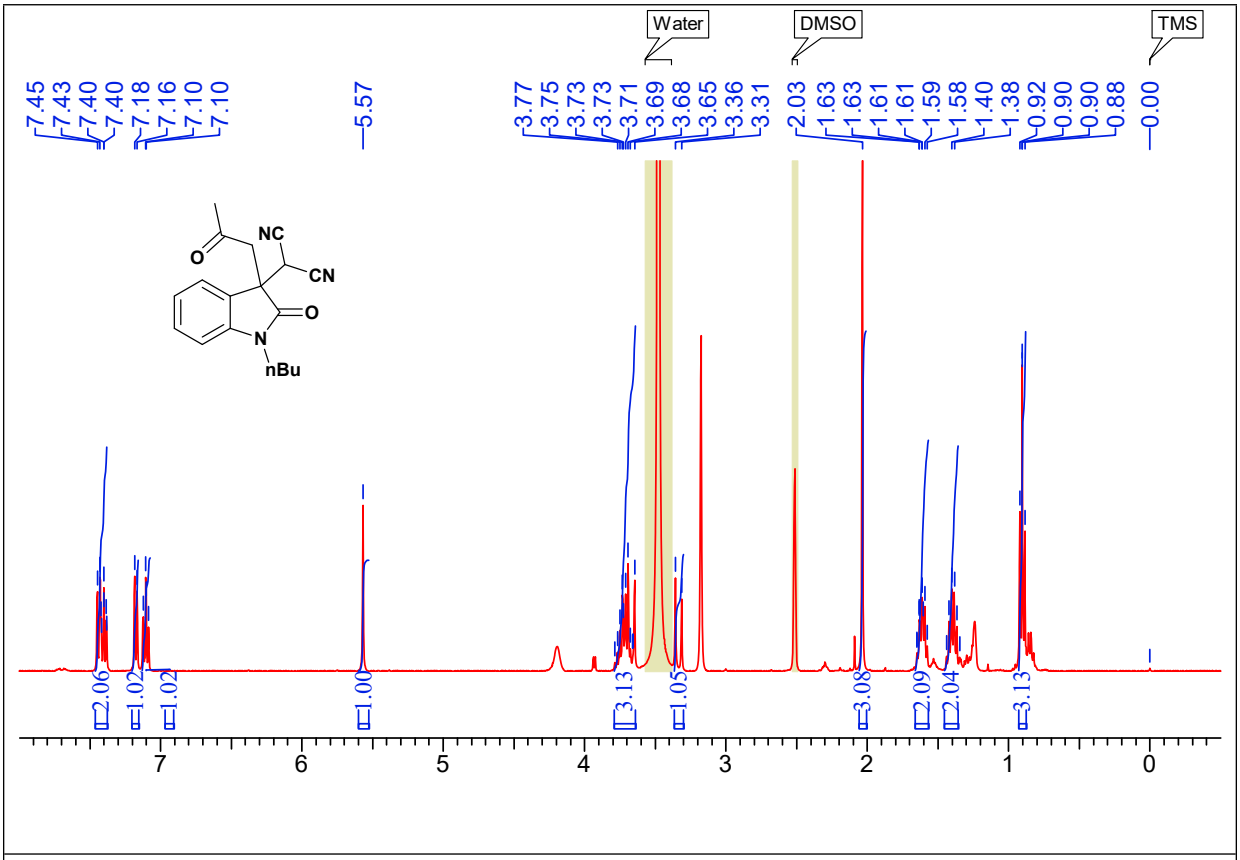

**135 DEPT spectrum of compound (4Bc)**



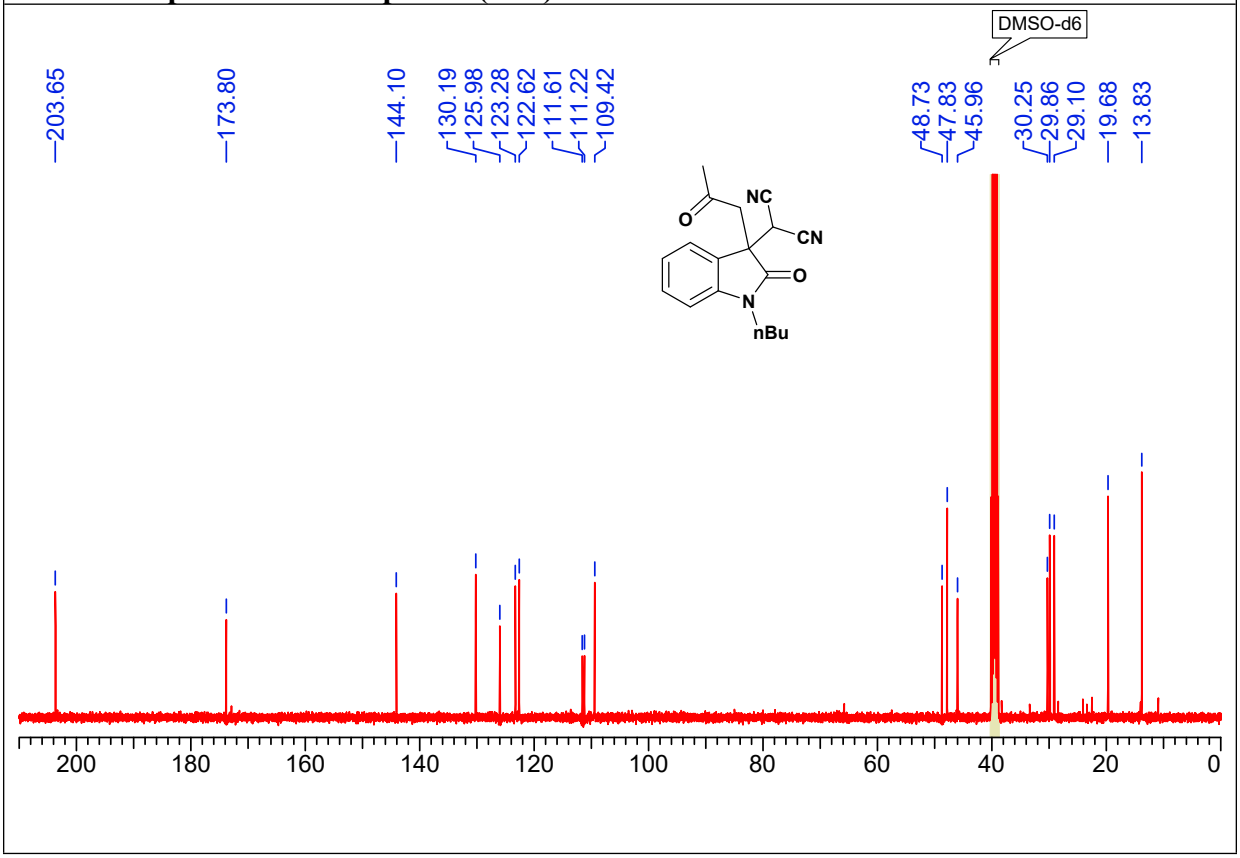


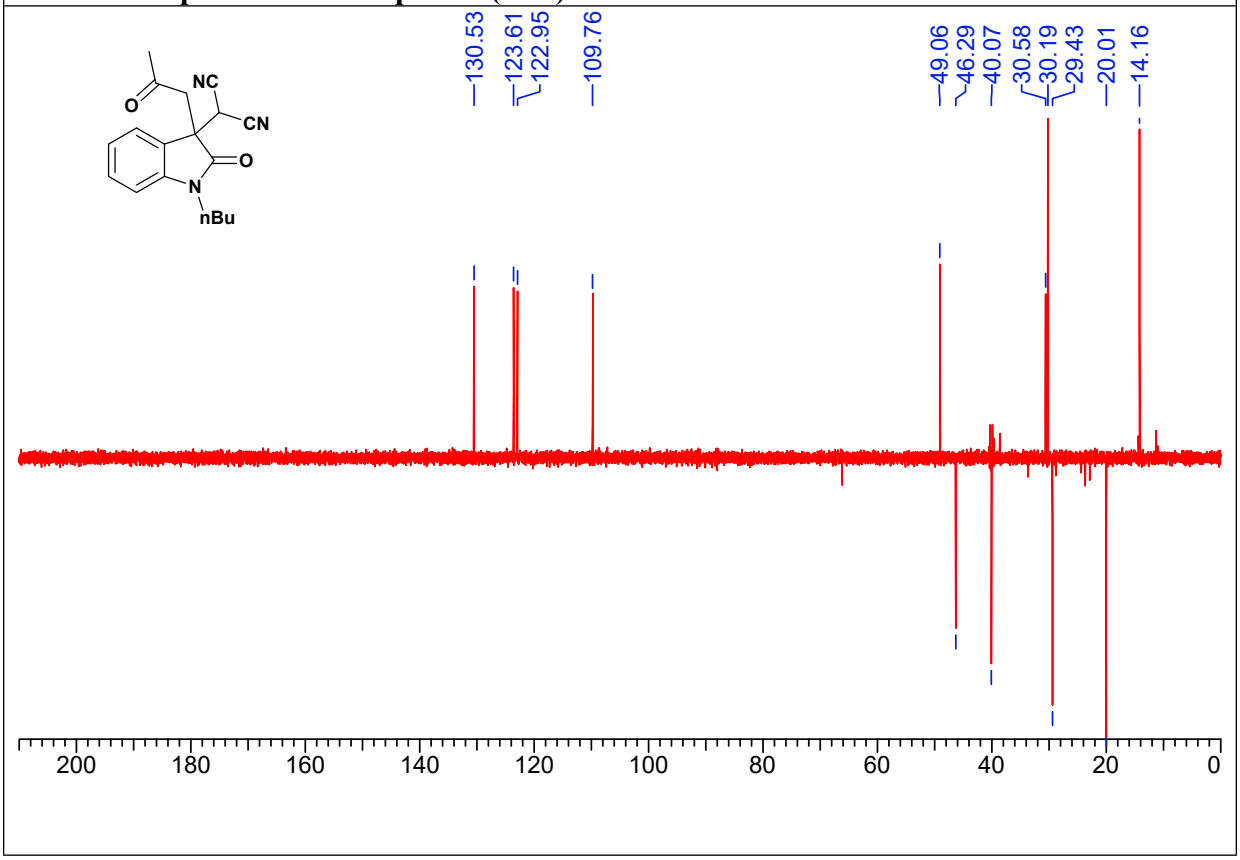
**$^{1}$H NMR spectrum of compound (4Bd)**



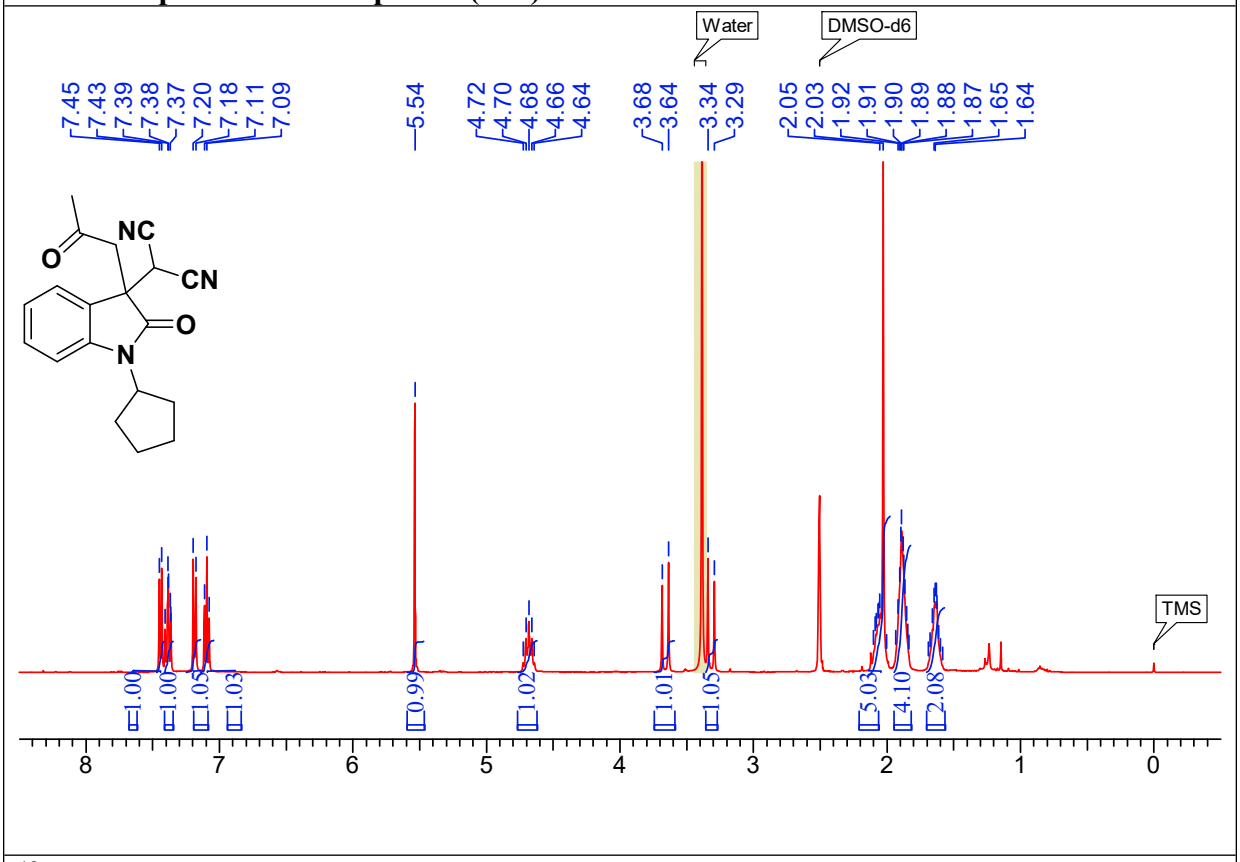

**$^{13}$C NMR spectrum of compound (4Bd)**



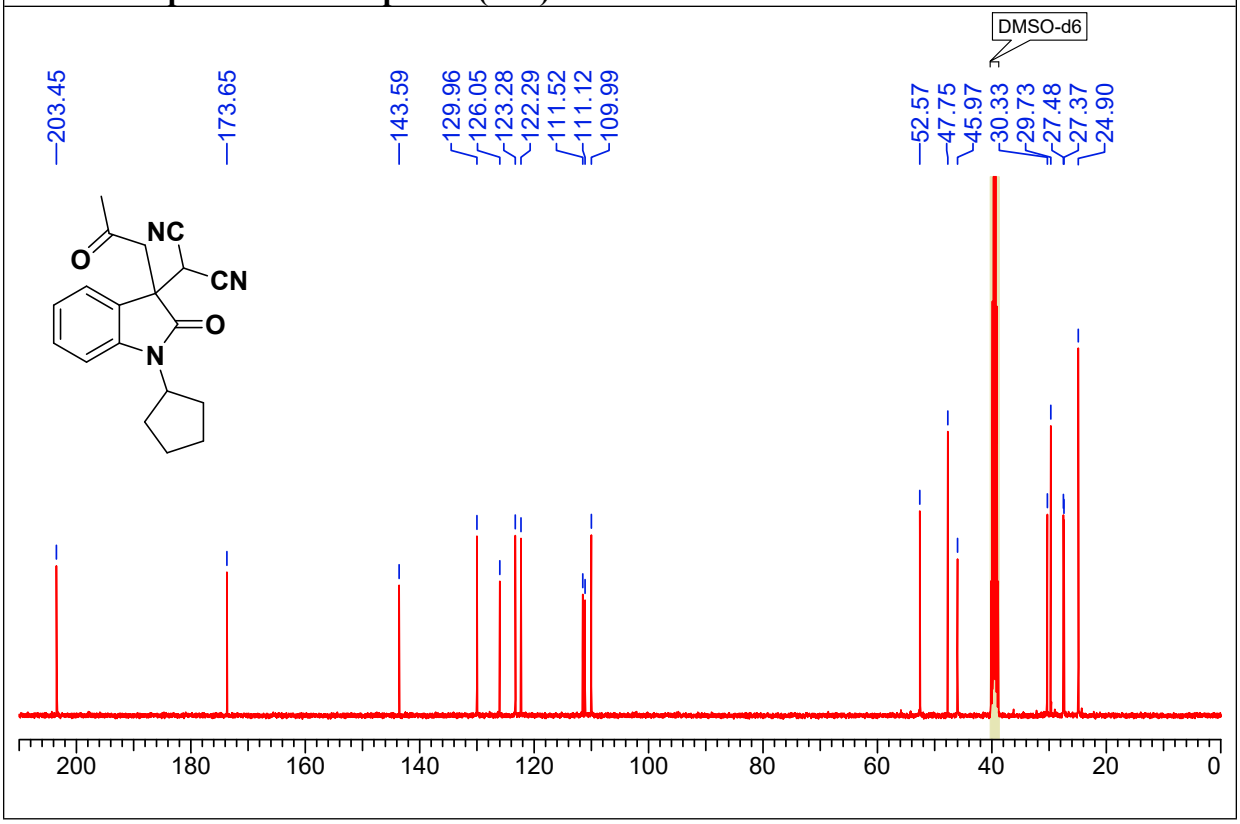
**135 DEPT spectrum of compound (4Bd)**



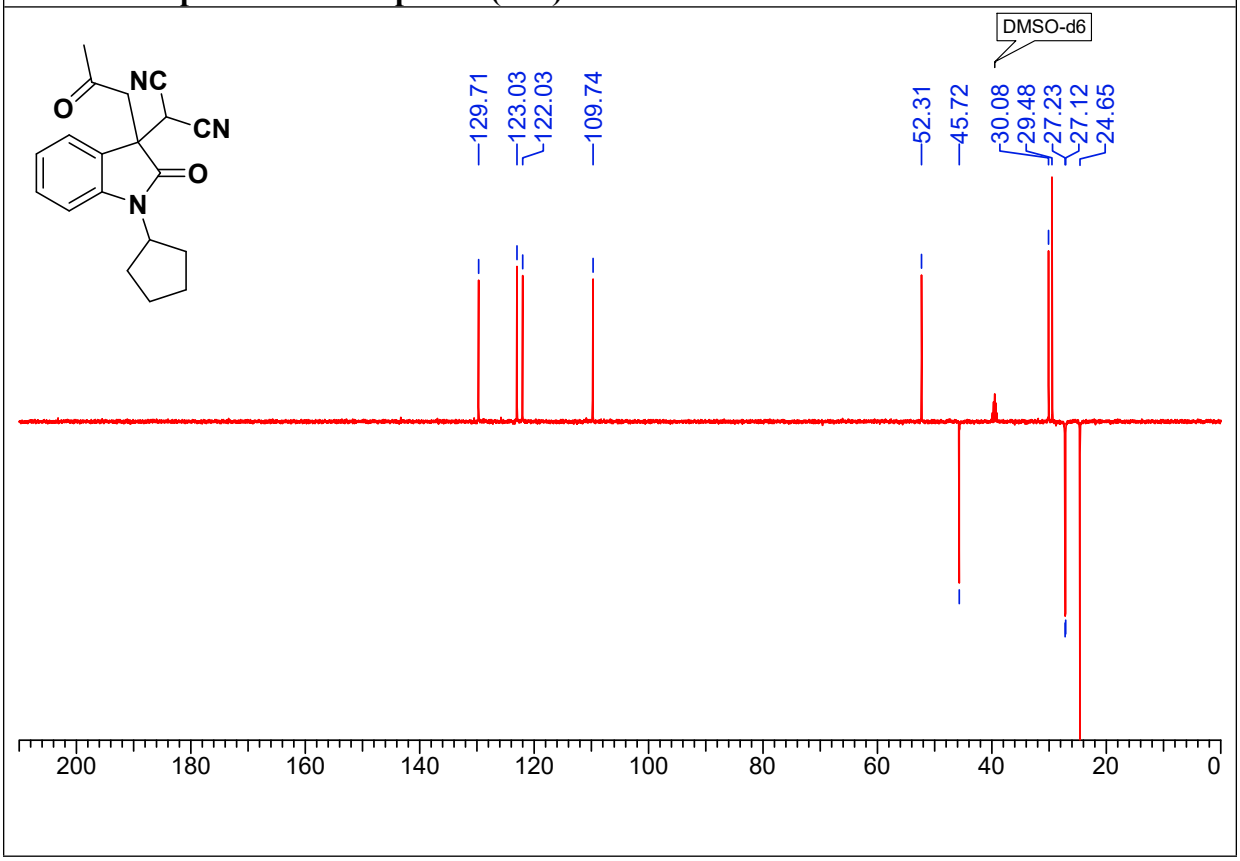
**$^{1}$H NMR spectrum of compound (4Be)**



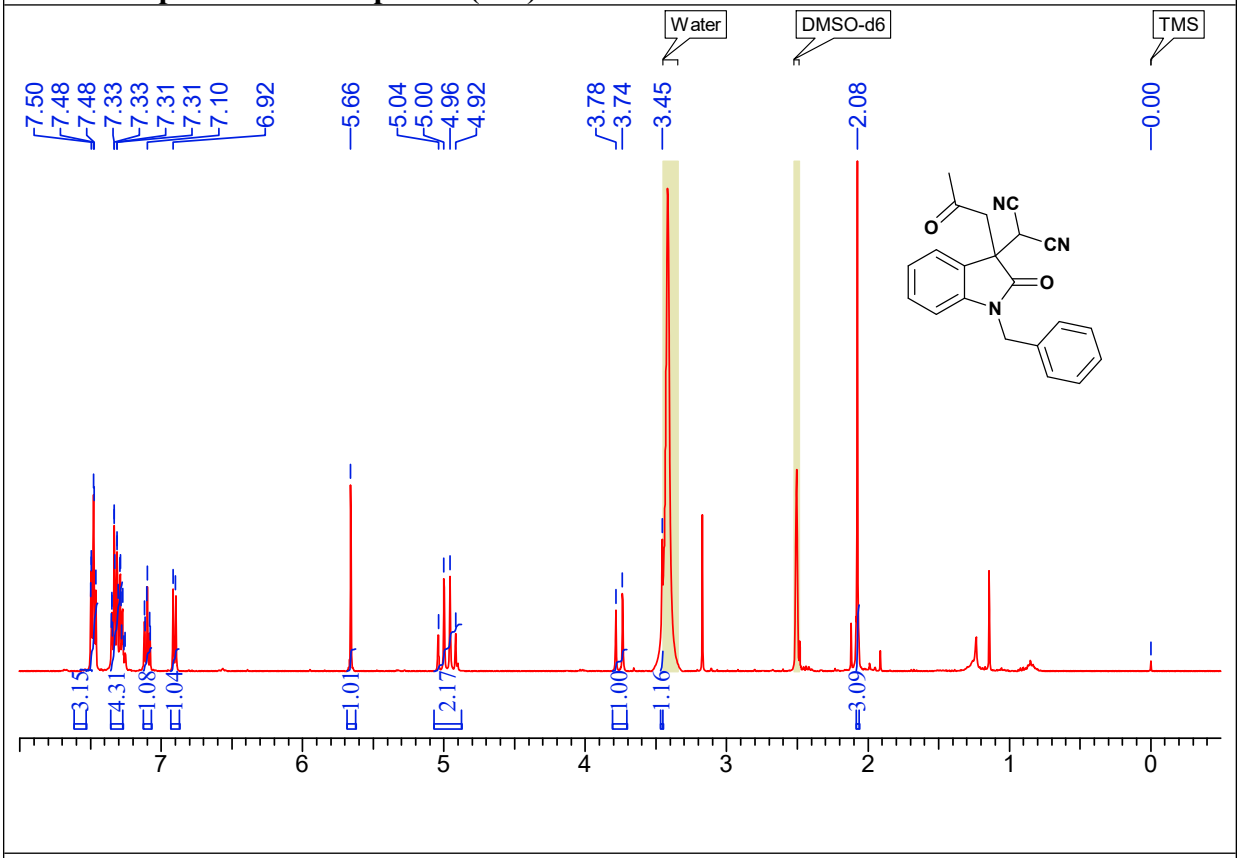

**$^{13}$C NMR spectrum of compound (4Be)**



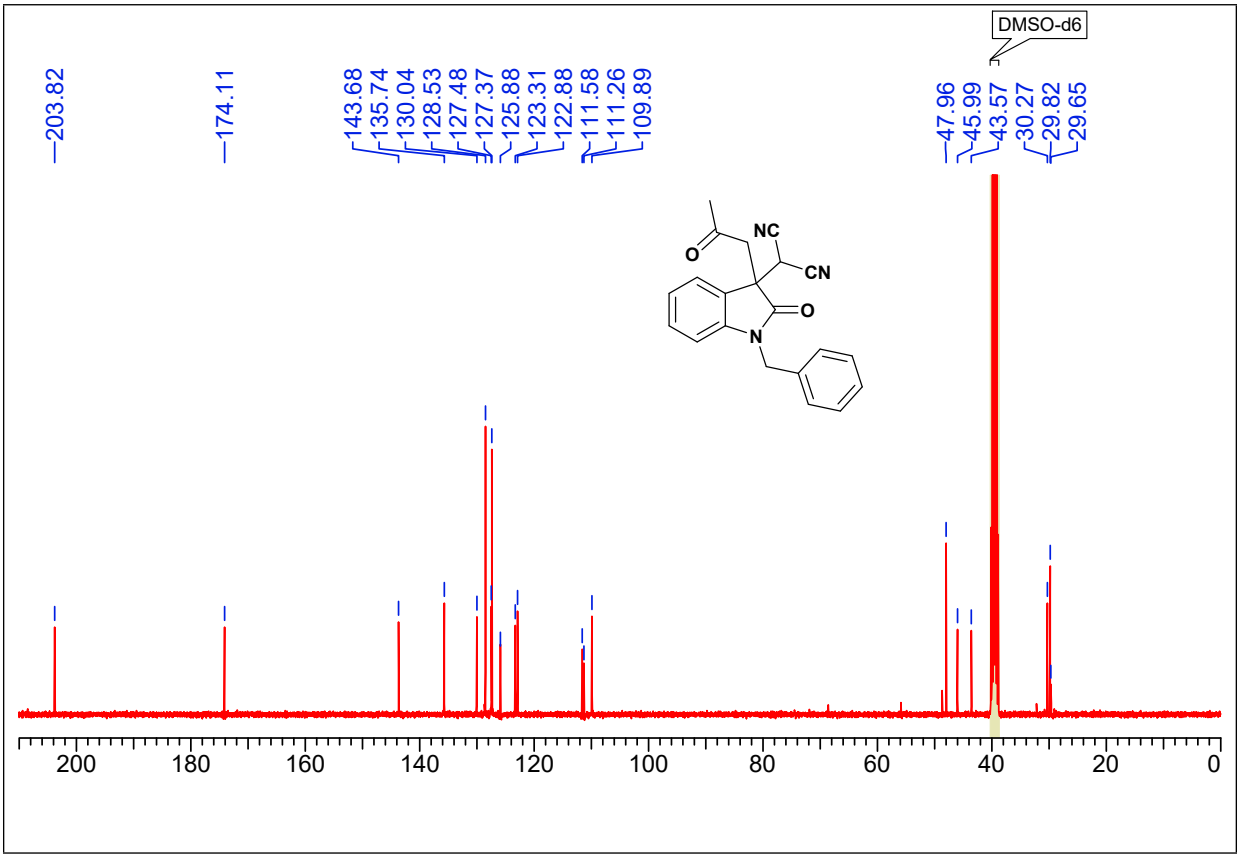
**135 DEPT spectrum of compound (4Be)**



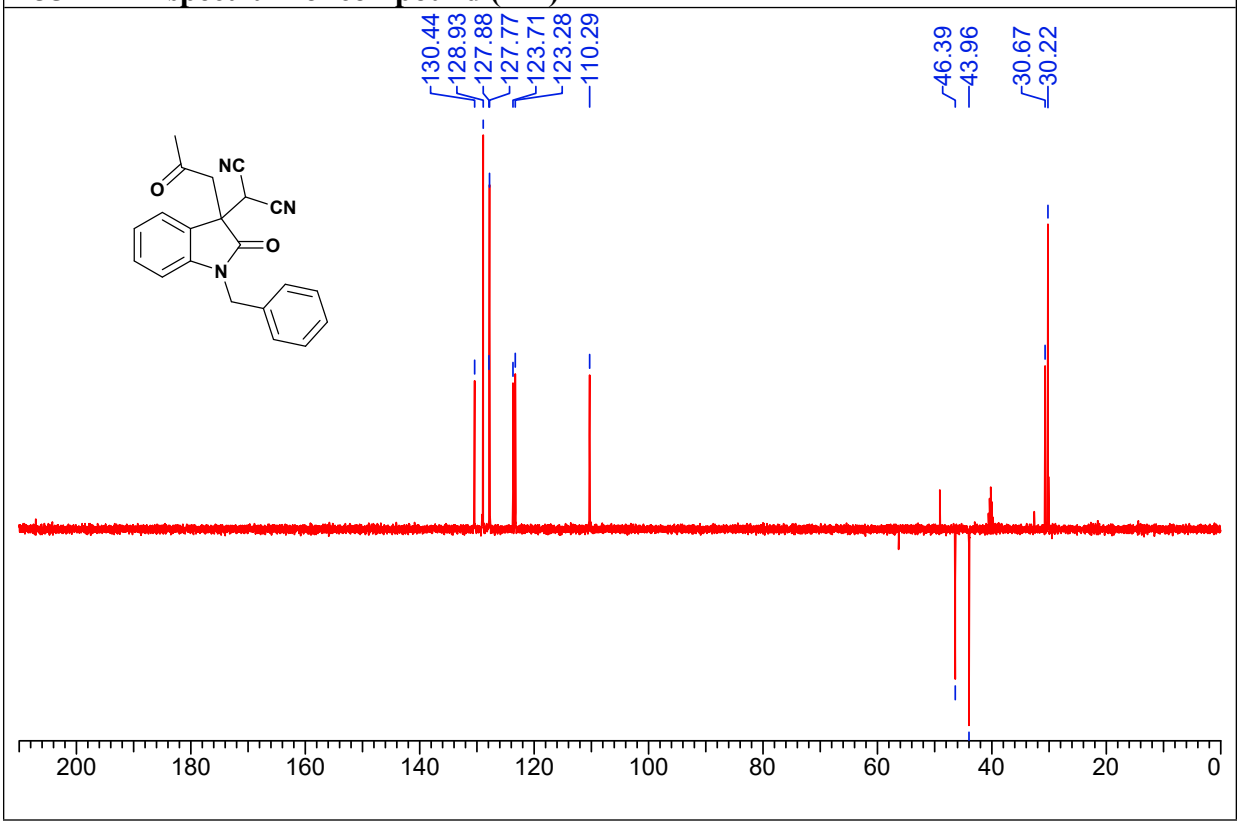
**$^{1}$H NMR spectrum of compound (4Bf)**



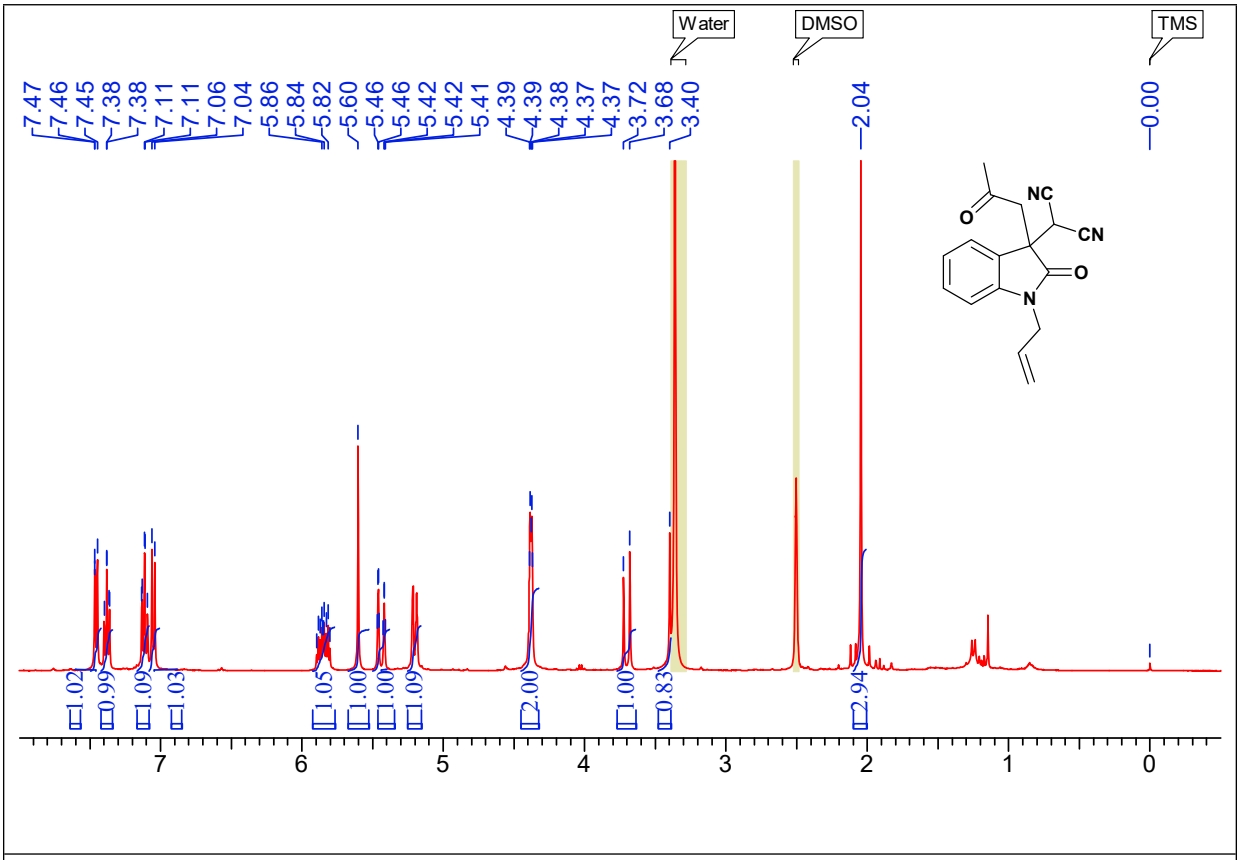

**$^{13}$C NMR spectrum of compound (4Bf)**



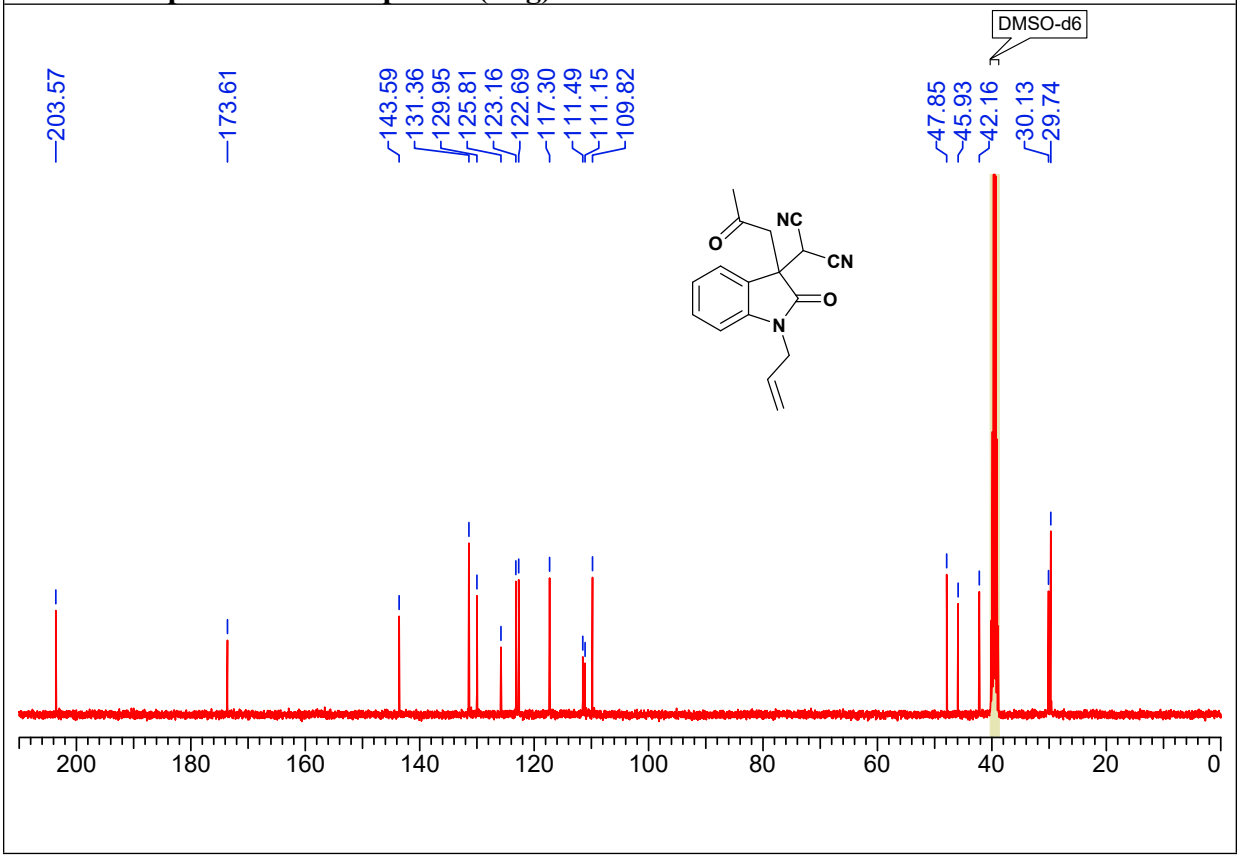

**135 DEPT spectrum of compound (4Bf)**



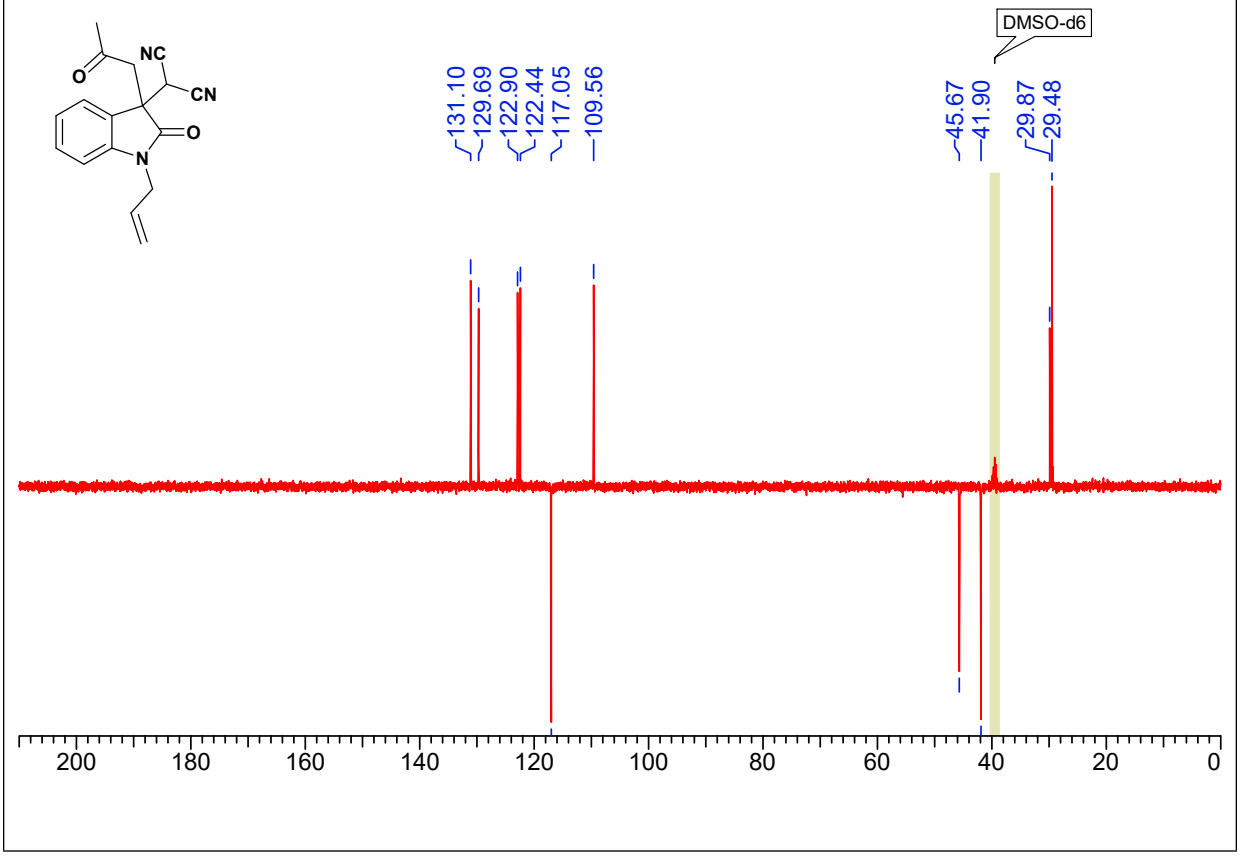
**$^{1}$H NMR spectrum of compound (4Bg)**



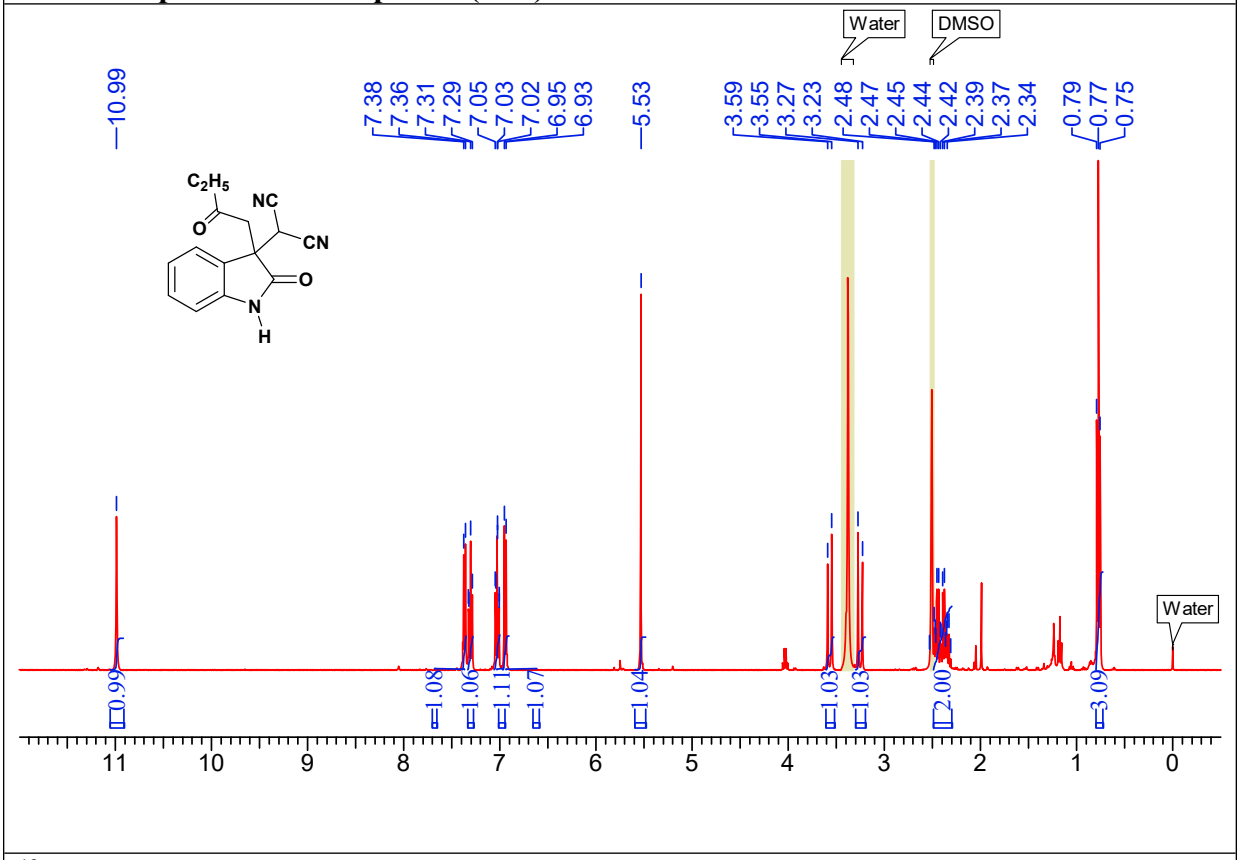

**$^{13}$C NMR spectrum of compound (4Bg)**



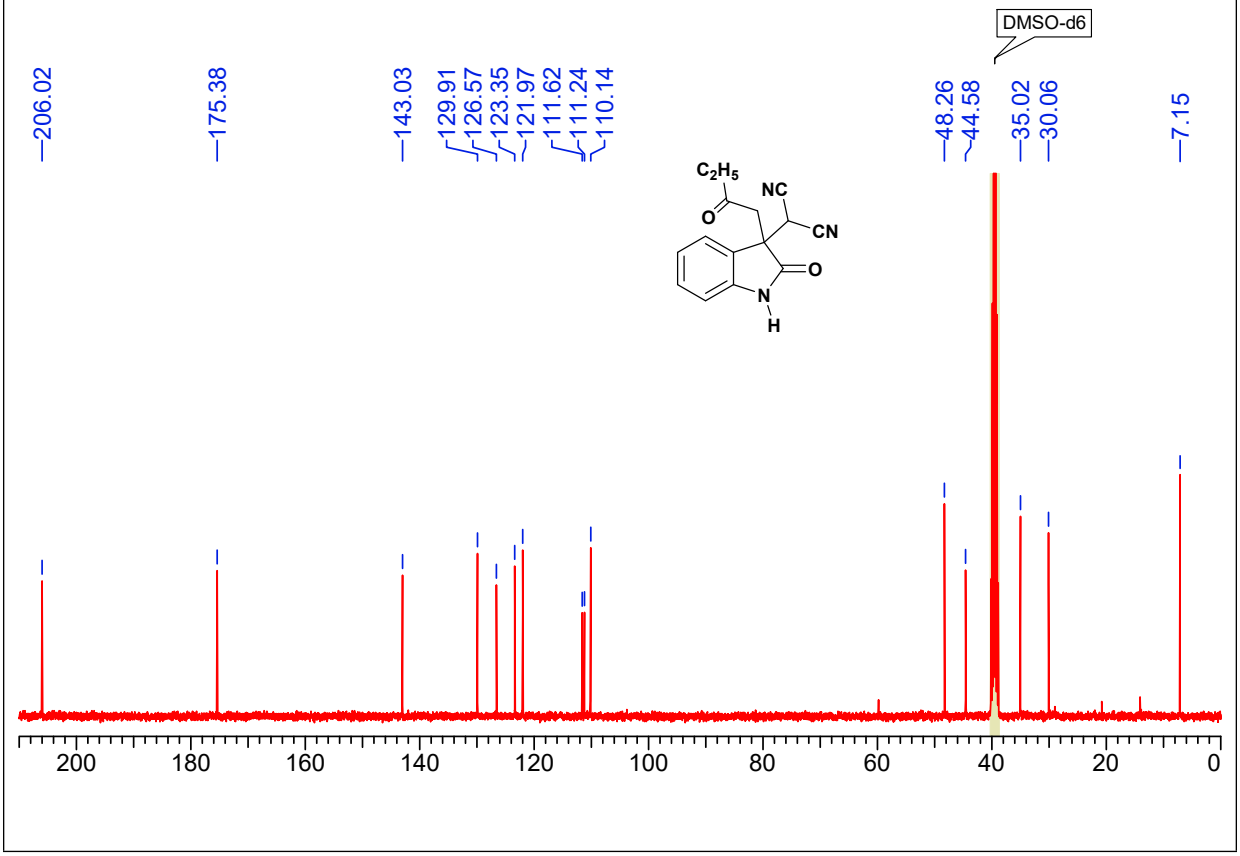
**135 DEPT spectrum of compound (4Bg)**



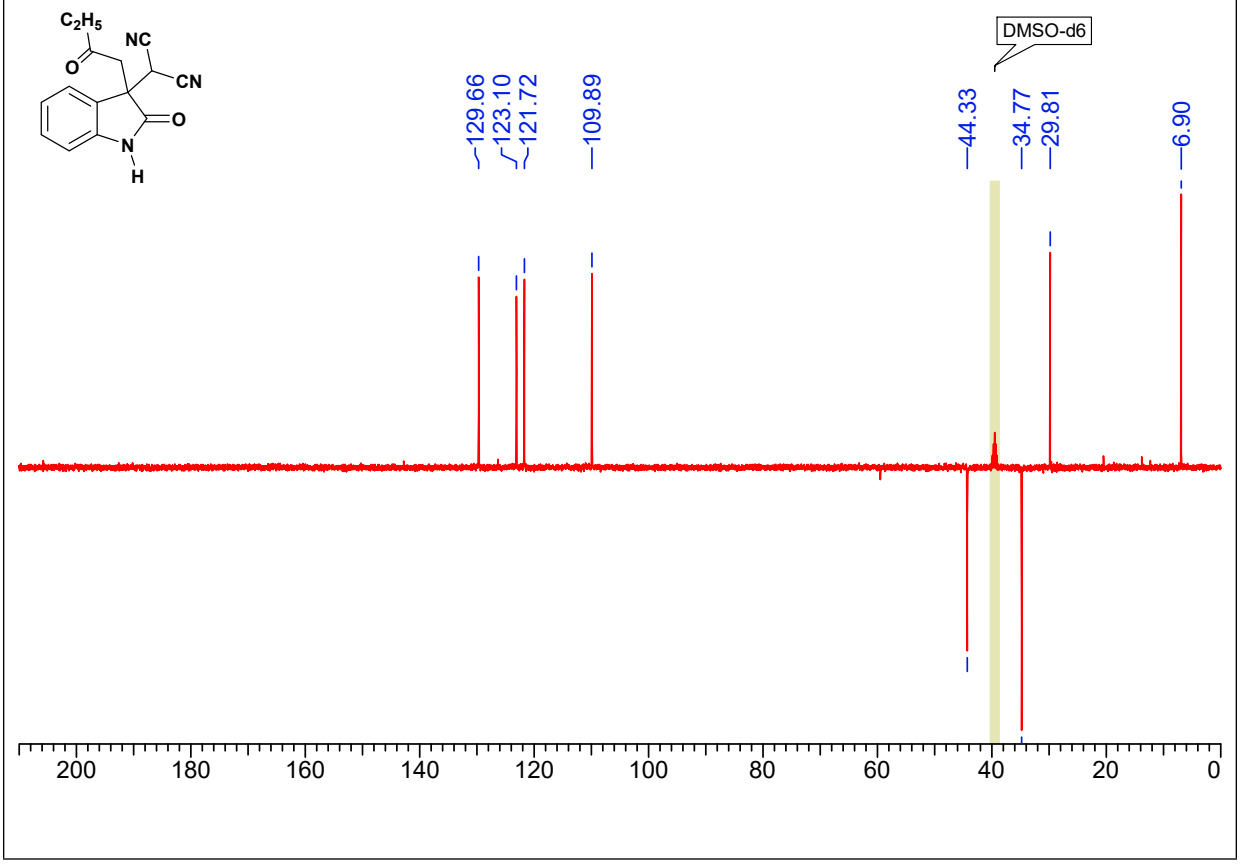
## $^{1}$H NMR spectrum of compound (4Ca)



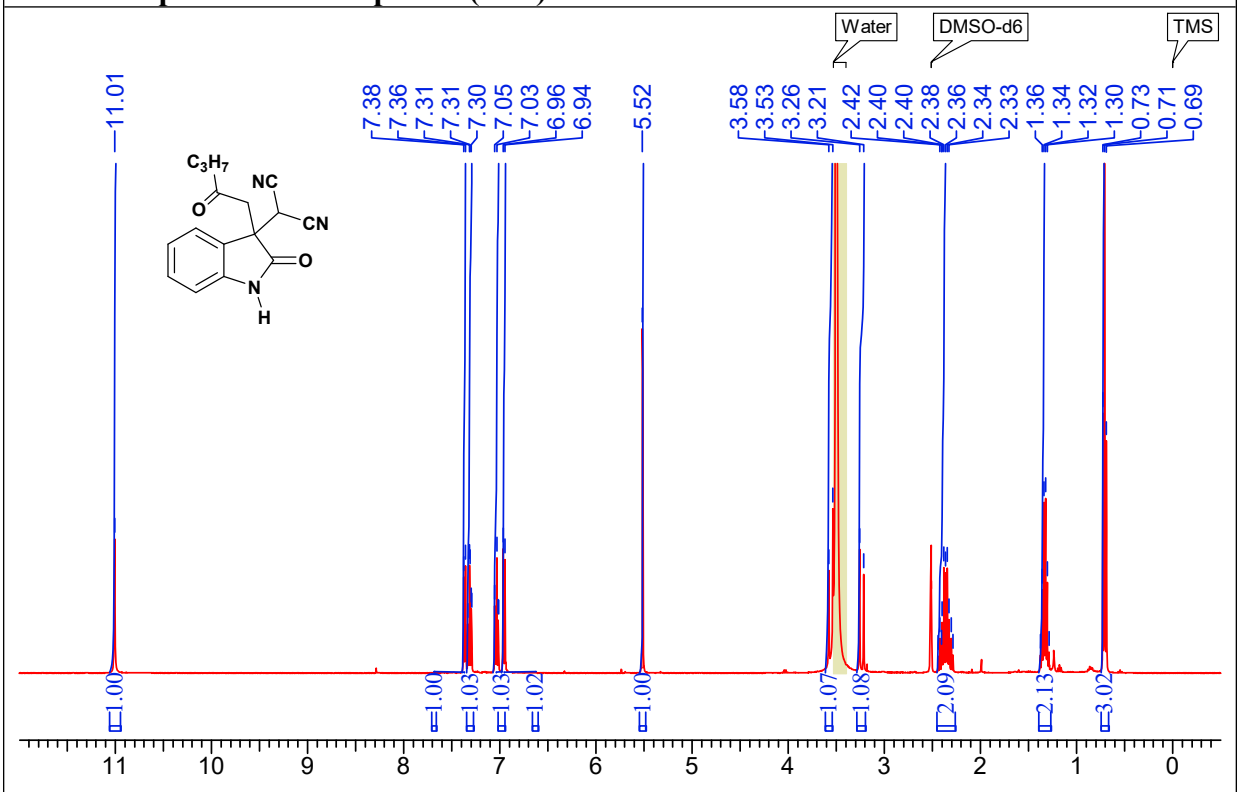

## $^{13}$C NMR spectrum of compound (4Ca)



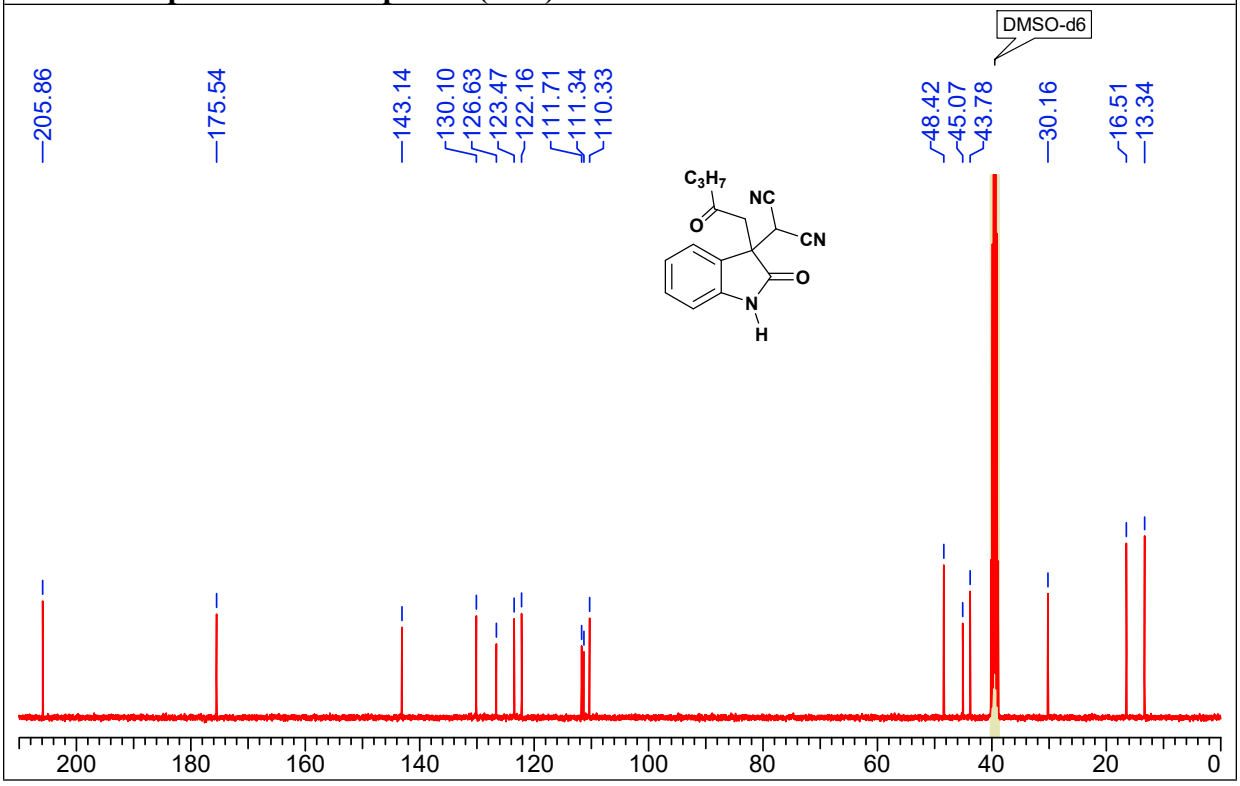
**135 DEPT spectrum of compound (4Ca)**



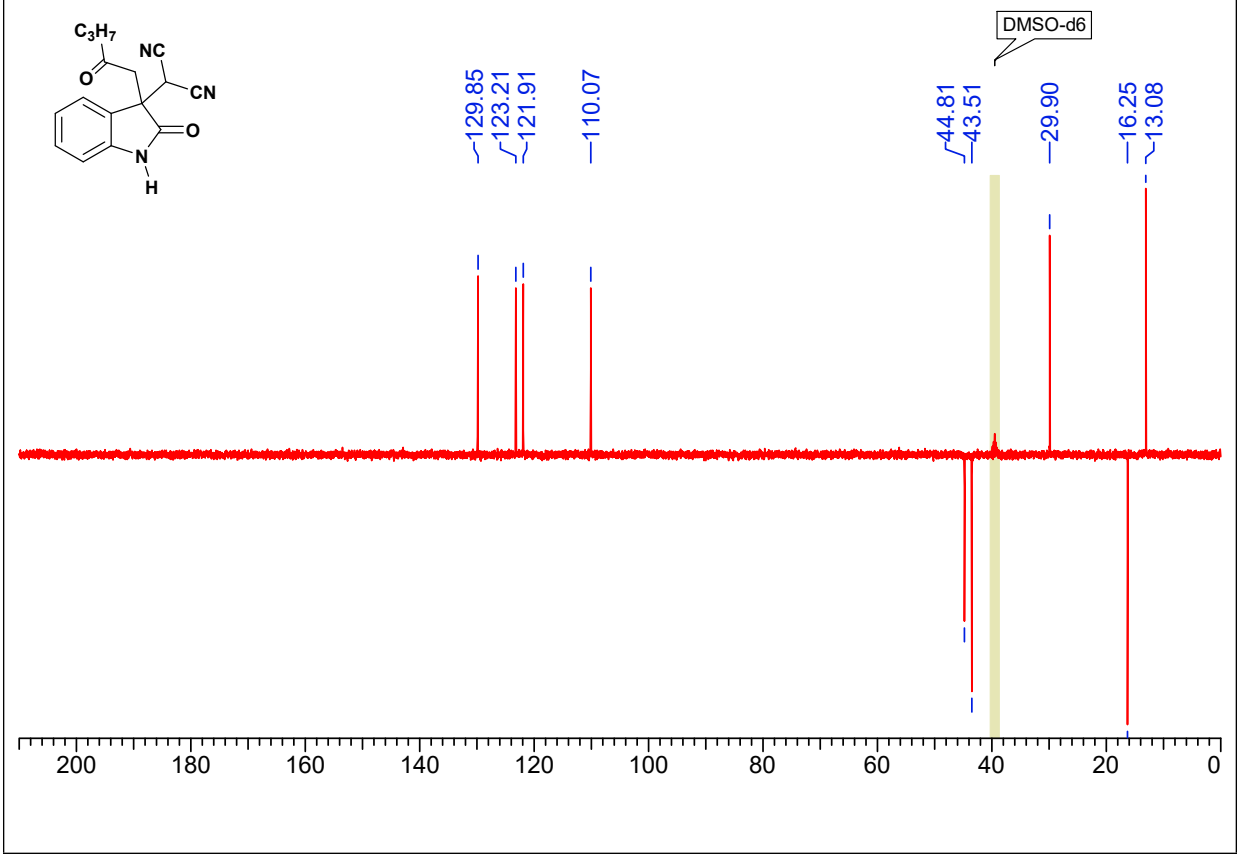
**$^{1}$H NMR spectrum of compound (4Cb)**



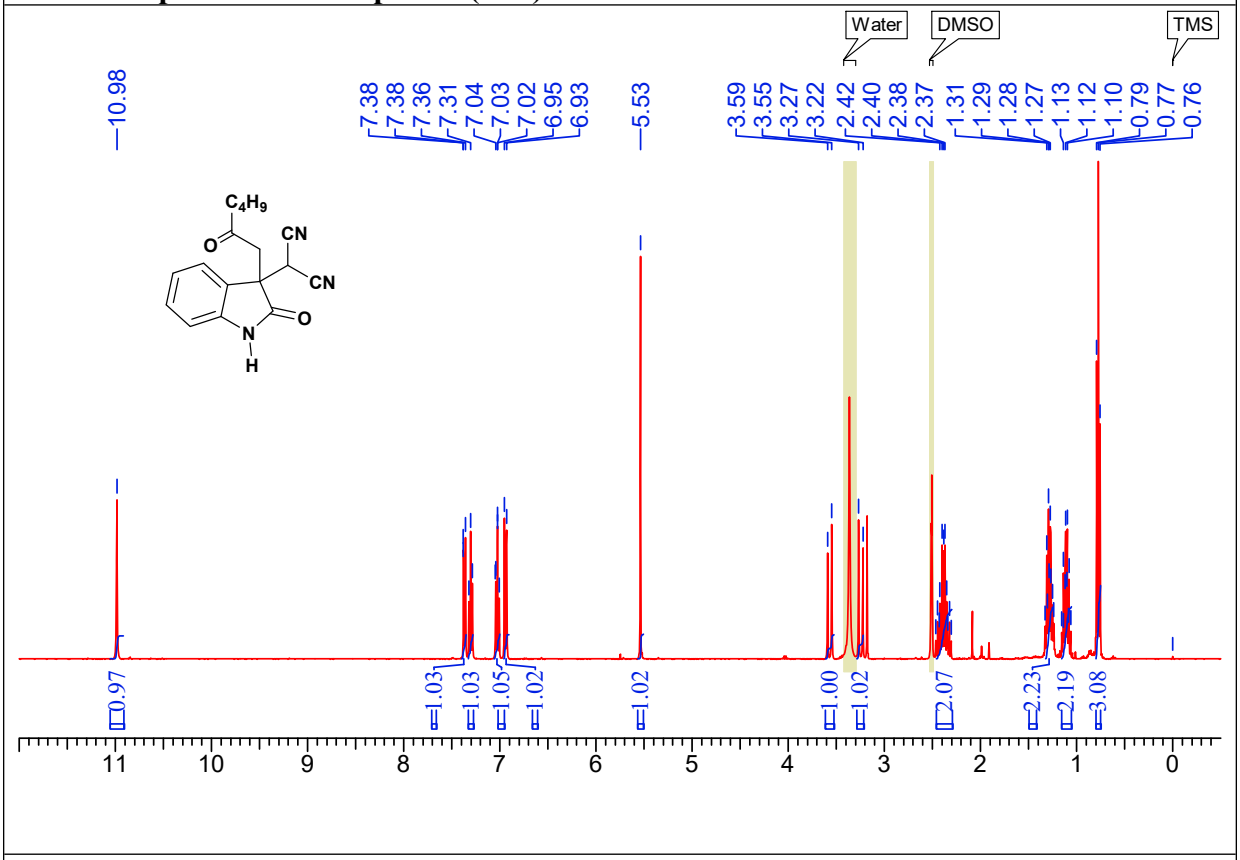

**$^{13}$C NMR spectrum of compound (4Cb)**



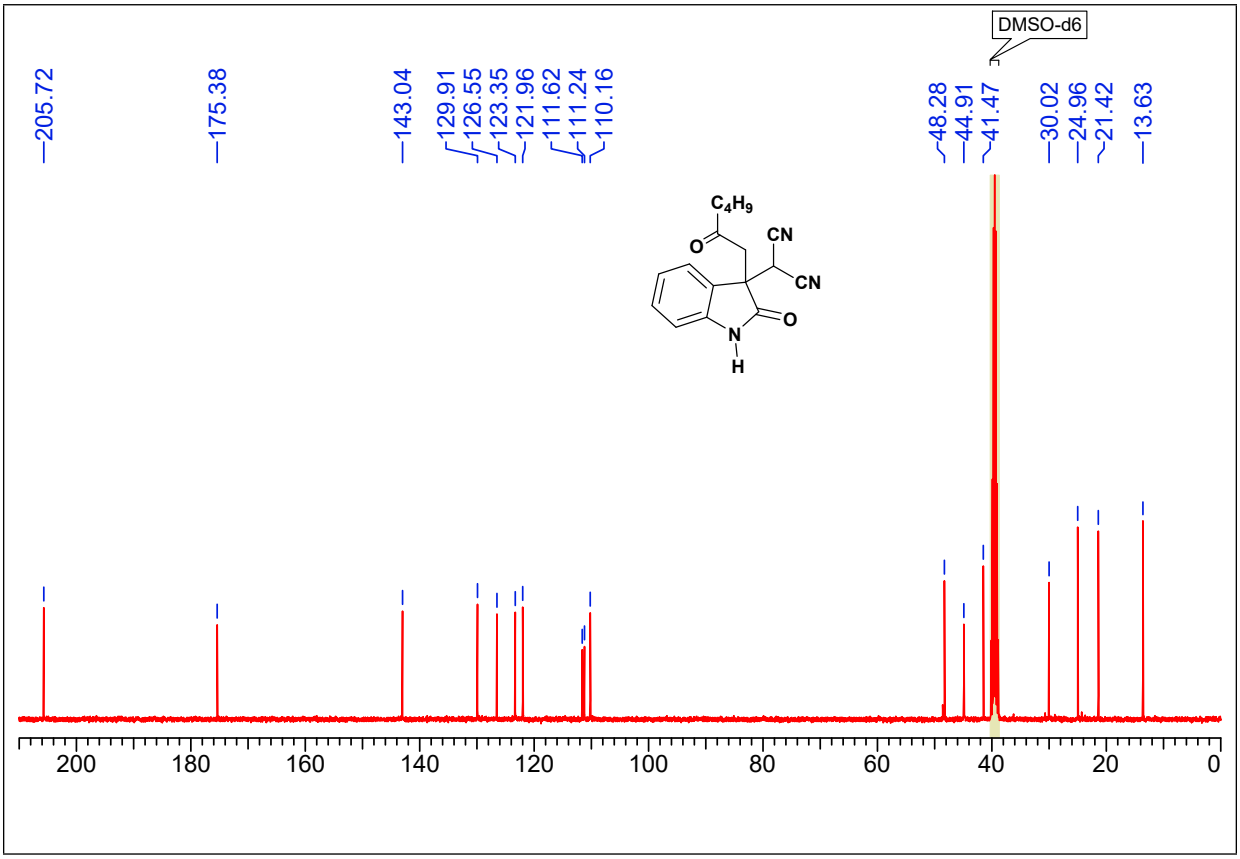
**135 DEPT spectrum of compound (4Cb)**



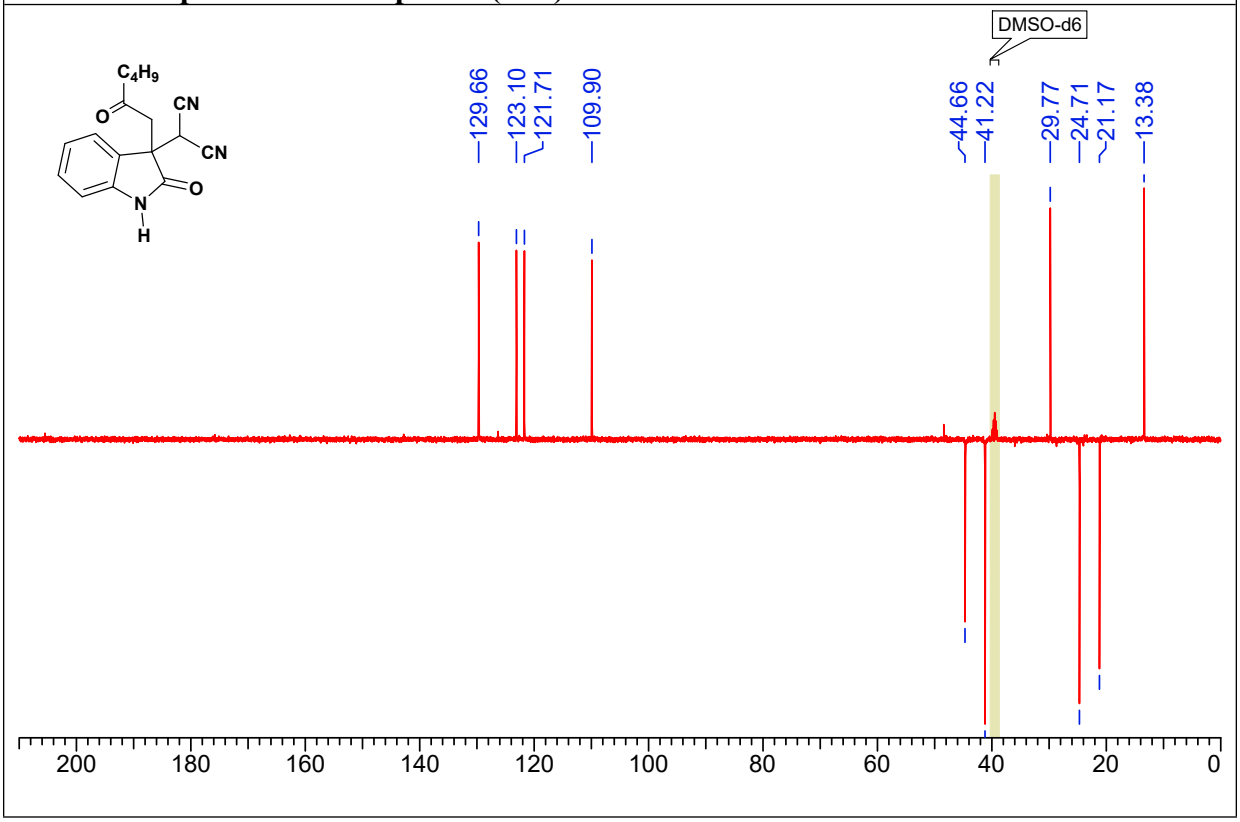
**$^{1}$H NMR spectrum of compound (4Cc)**



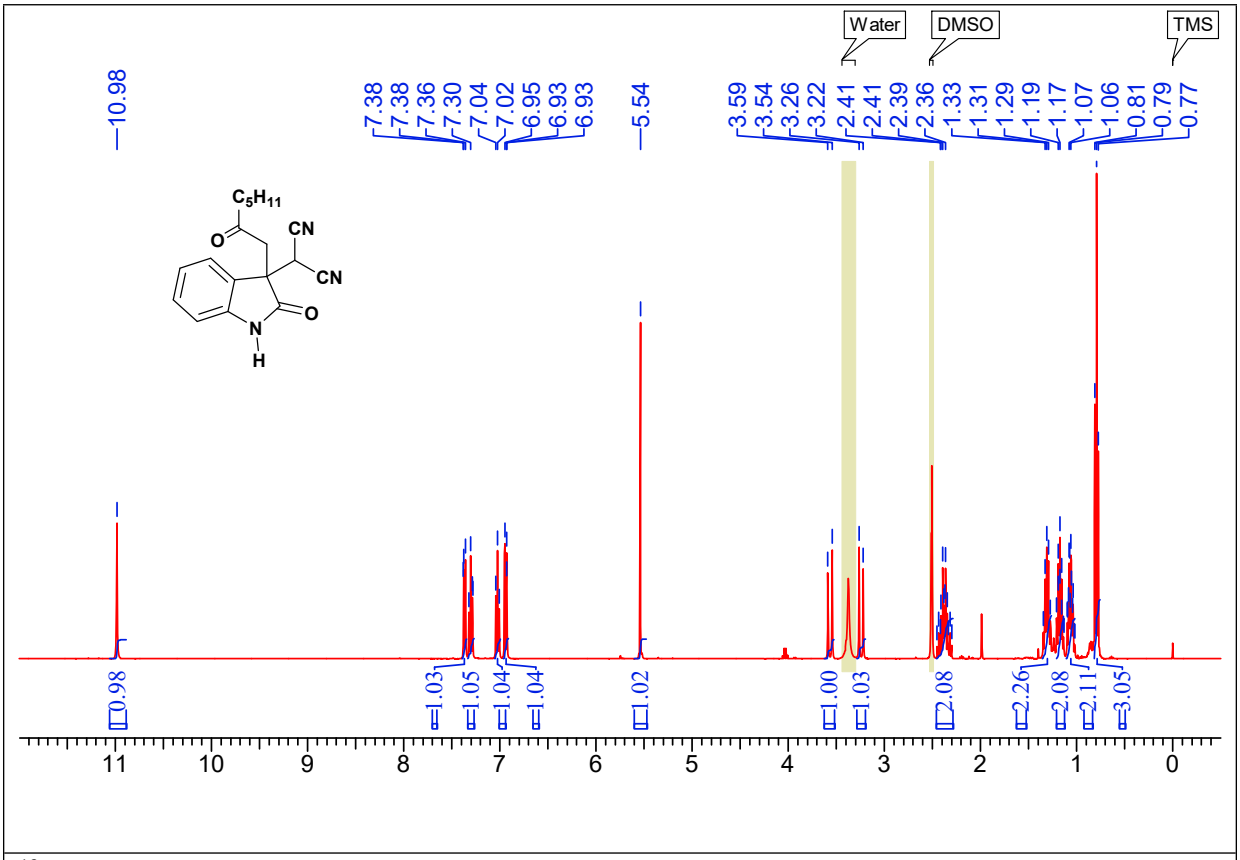

**$^{13}$C NMR spectrum of compound (4Cc)**



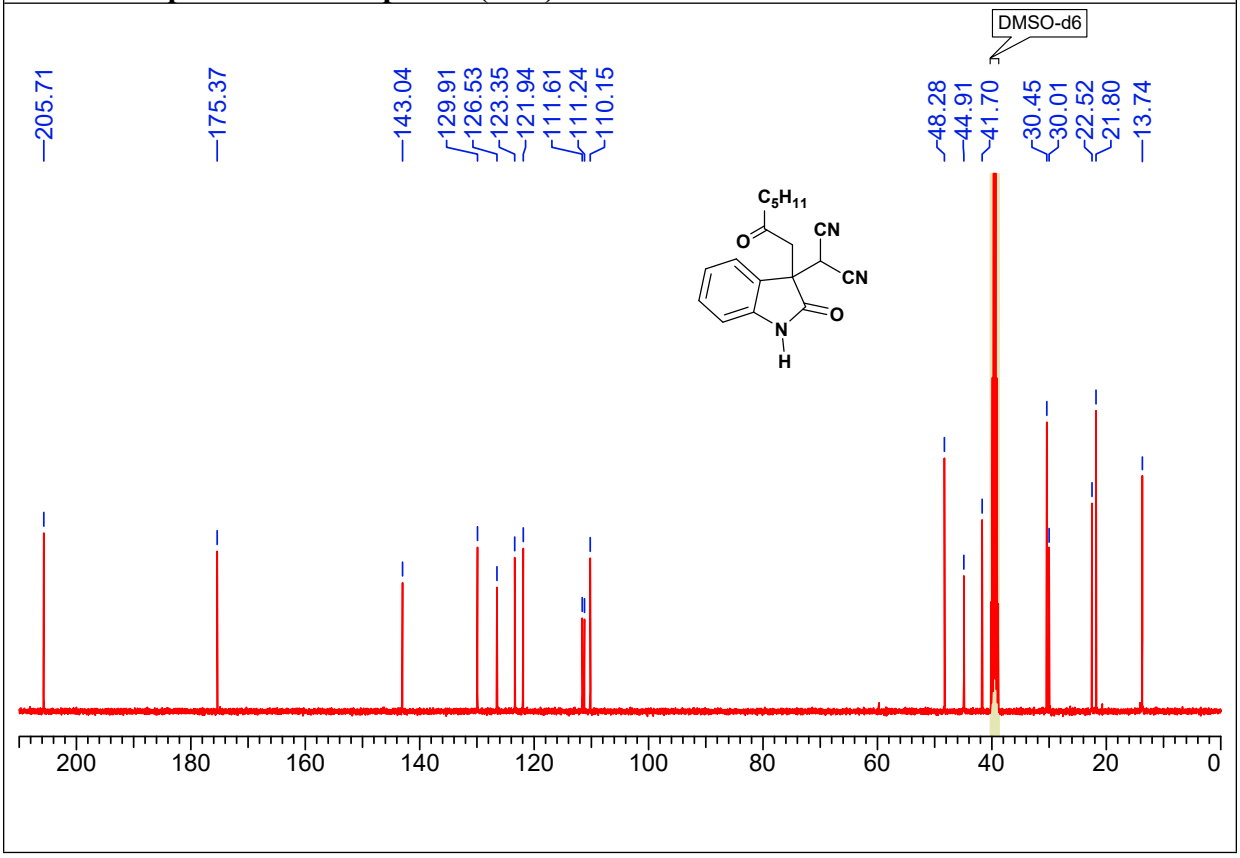

**135 DEPT spectrum of compound (4Cc)**



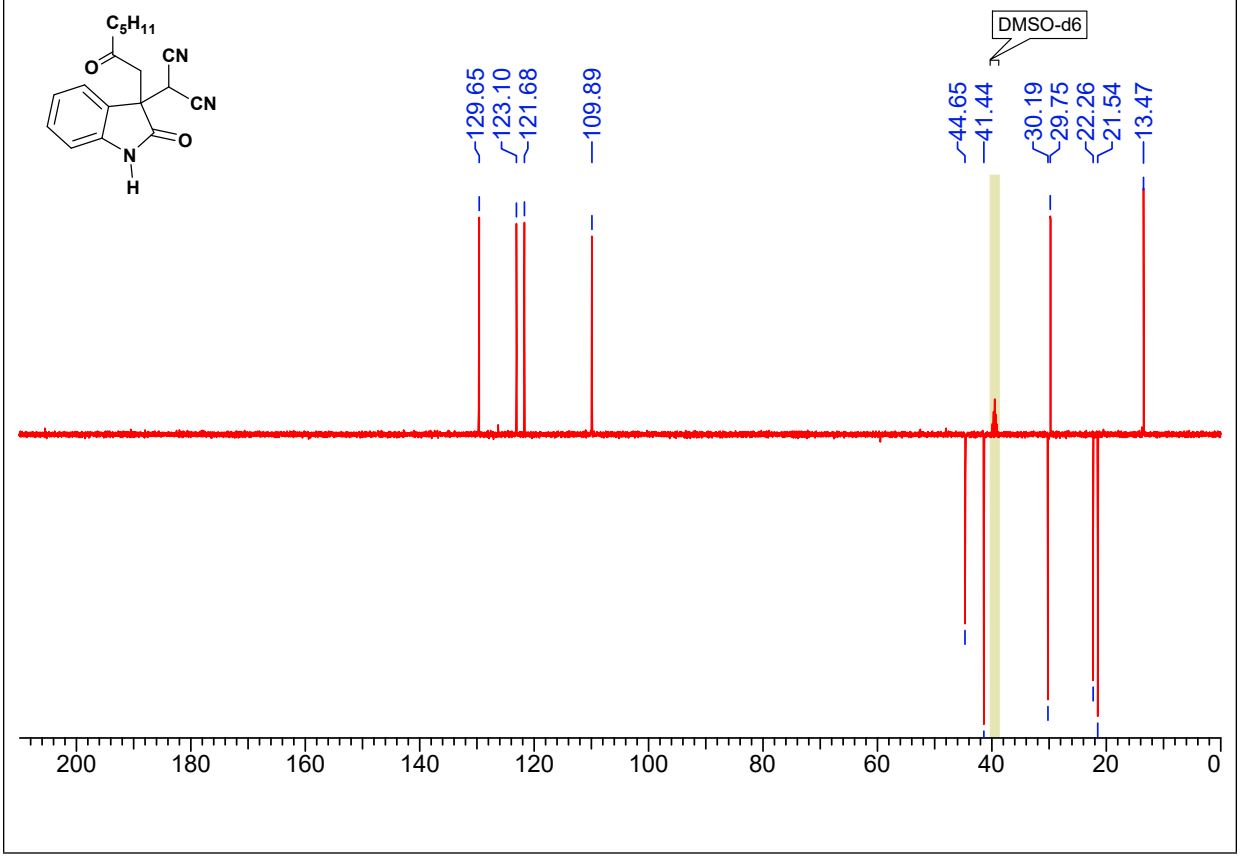
**$^{1}$H NMR spectrum of compound (4Cd)**



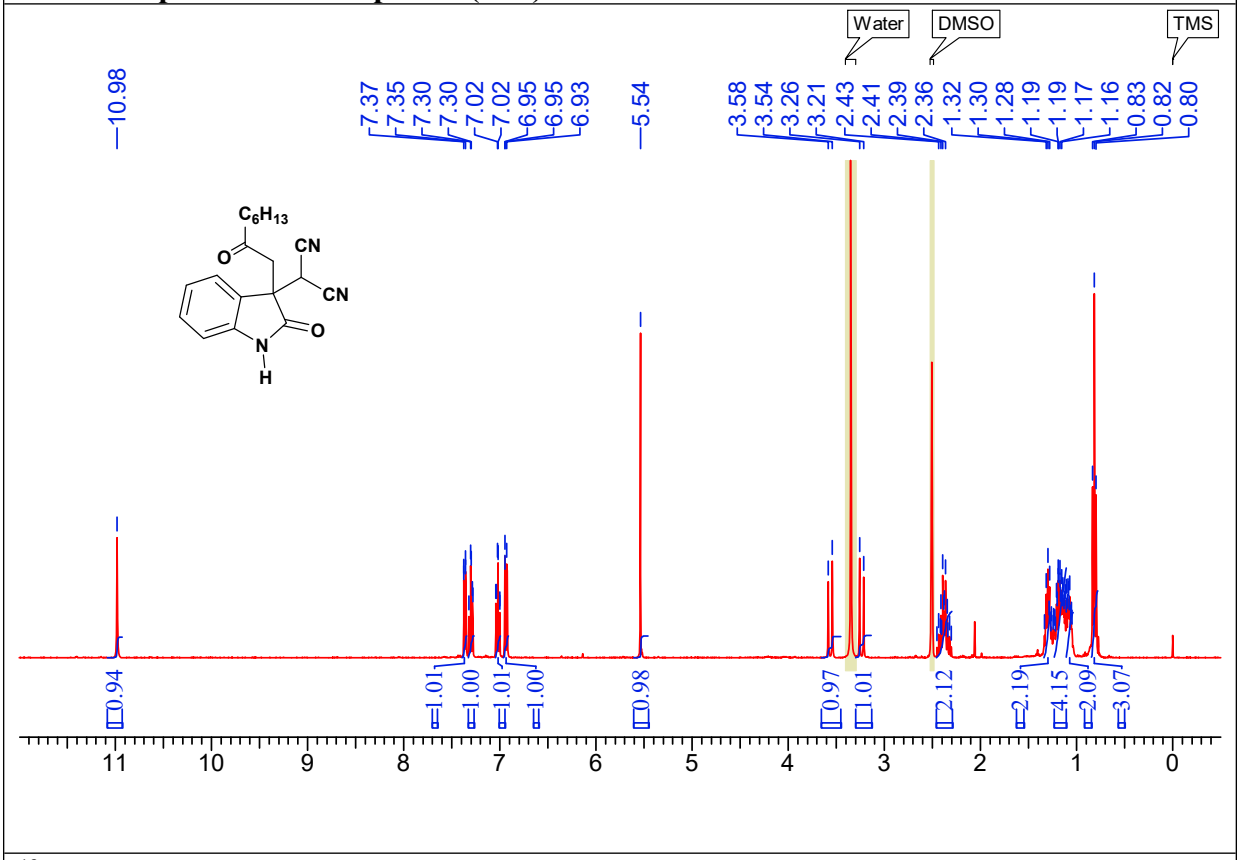

**$^{13}$C NMR spectrum of compound (4Cd)**



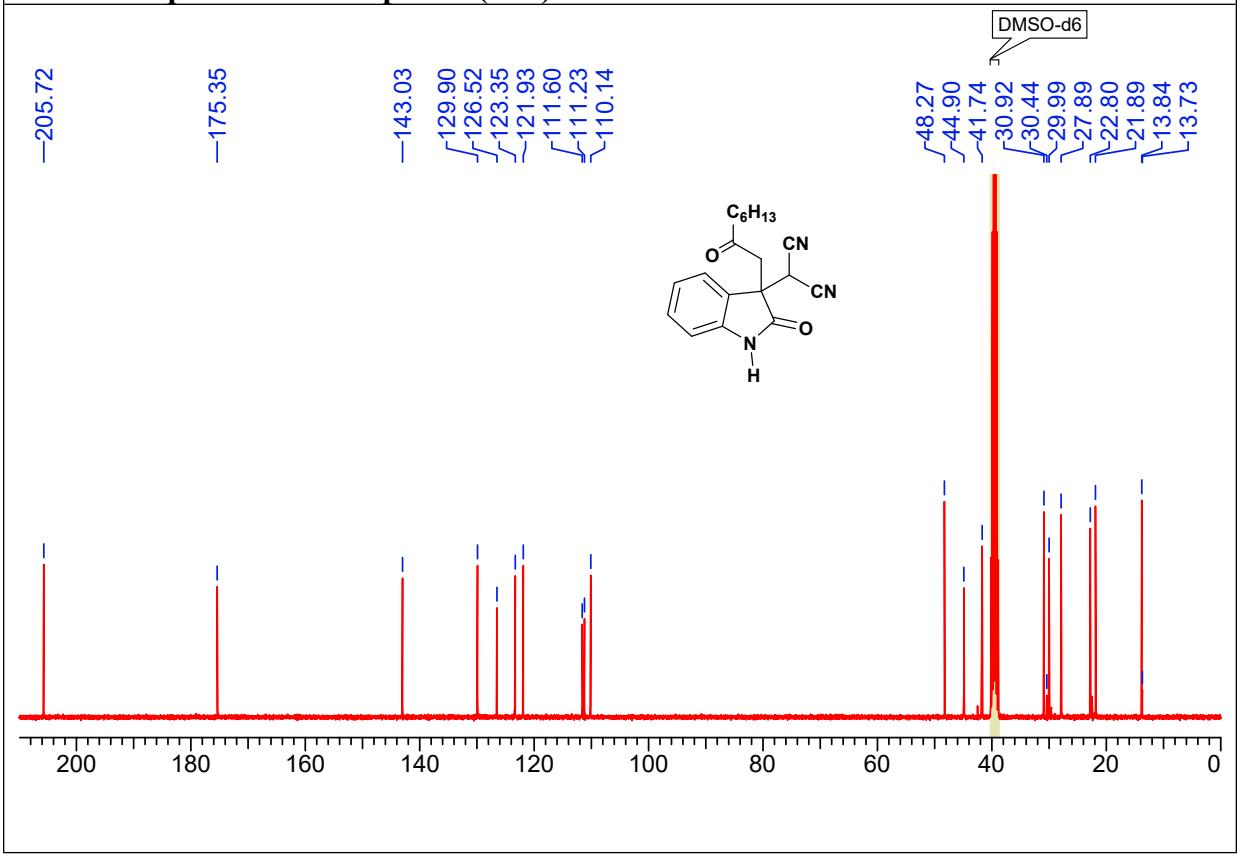
**135 DEPT spectrum of compound (4Cd)**



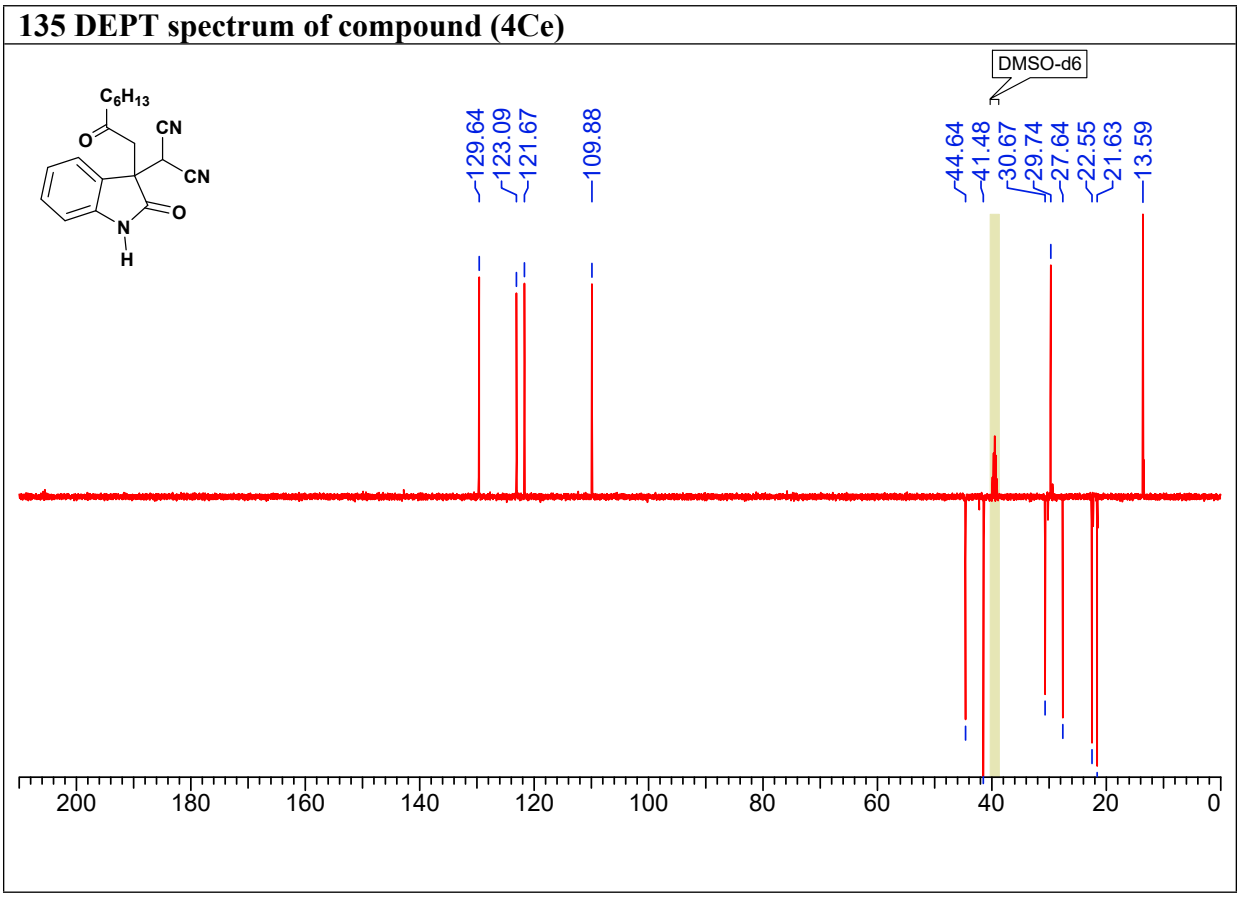
**$^{1}$H NMR spectrum of compound (4Ce)**



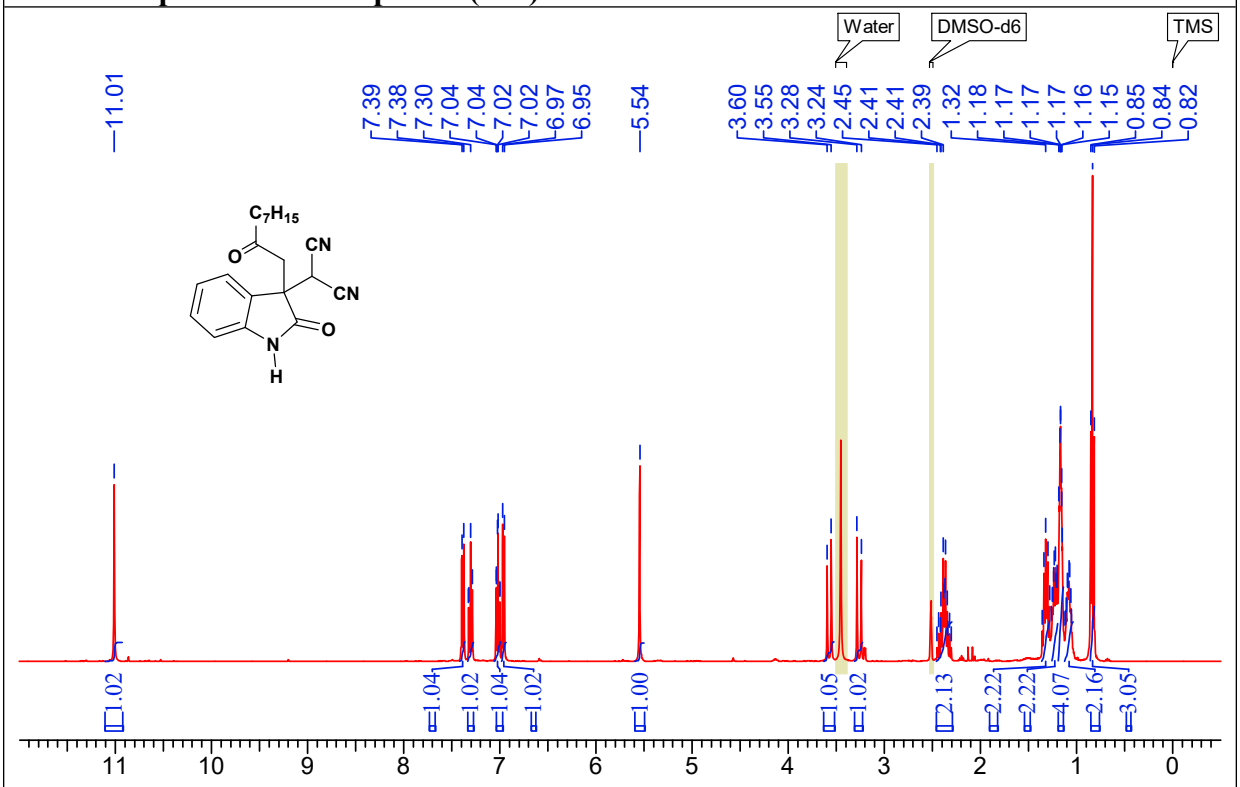

**$^{13}$C NMR spectrum of compound (4Ce)**



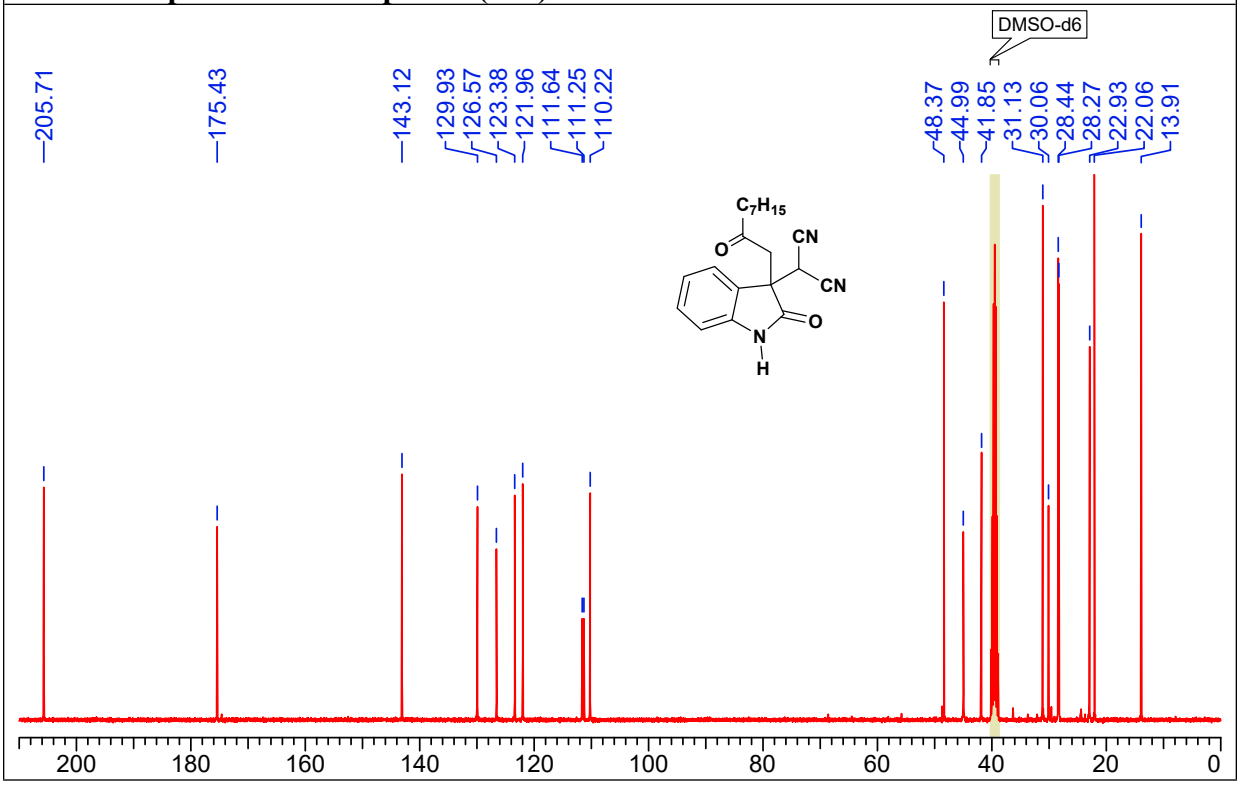
**135 DEPT spectrum of compound (4Ce)**



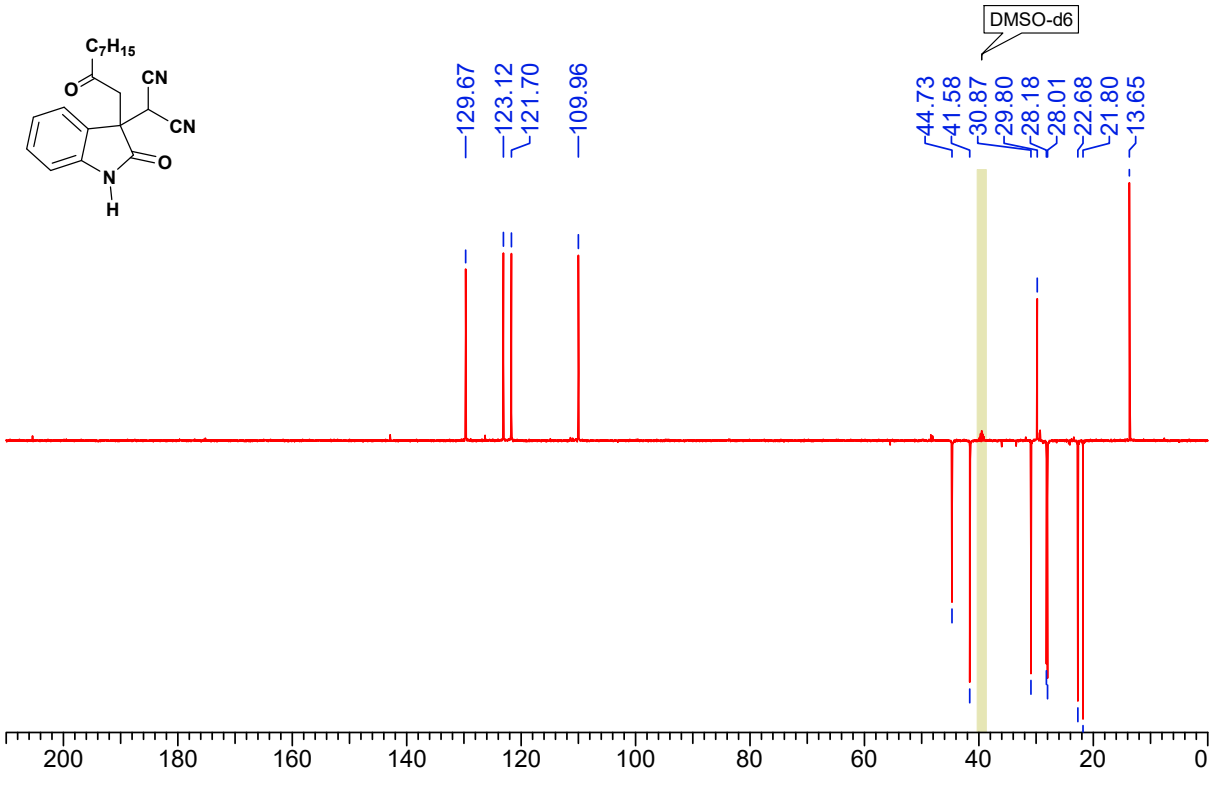
**$^{1}$H NMR spectrum of compound (4Cf)**



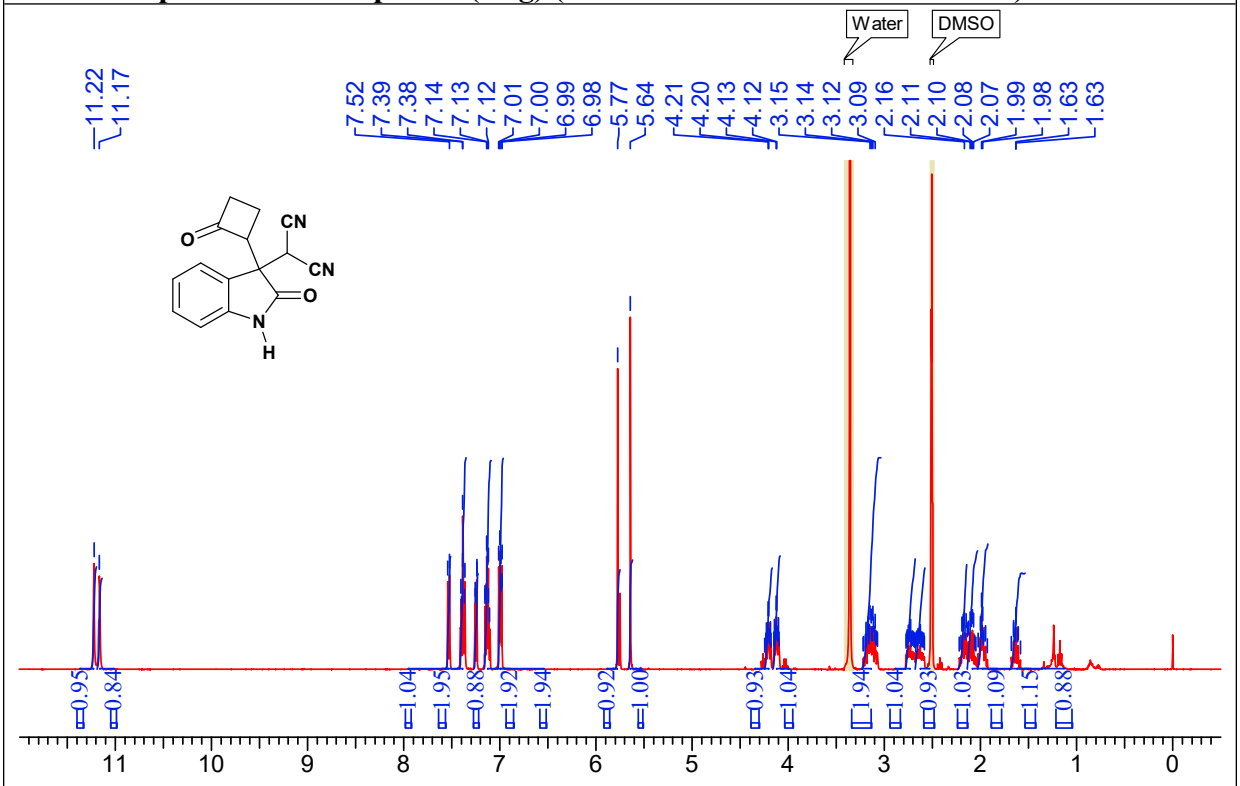

**$^{13}$C NMR spectrum of compound (4Cf)**



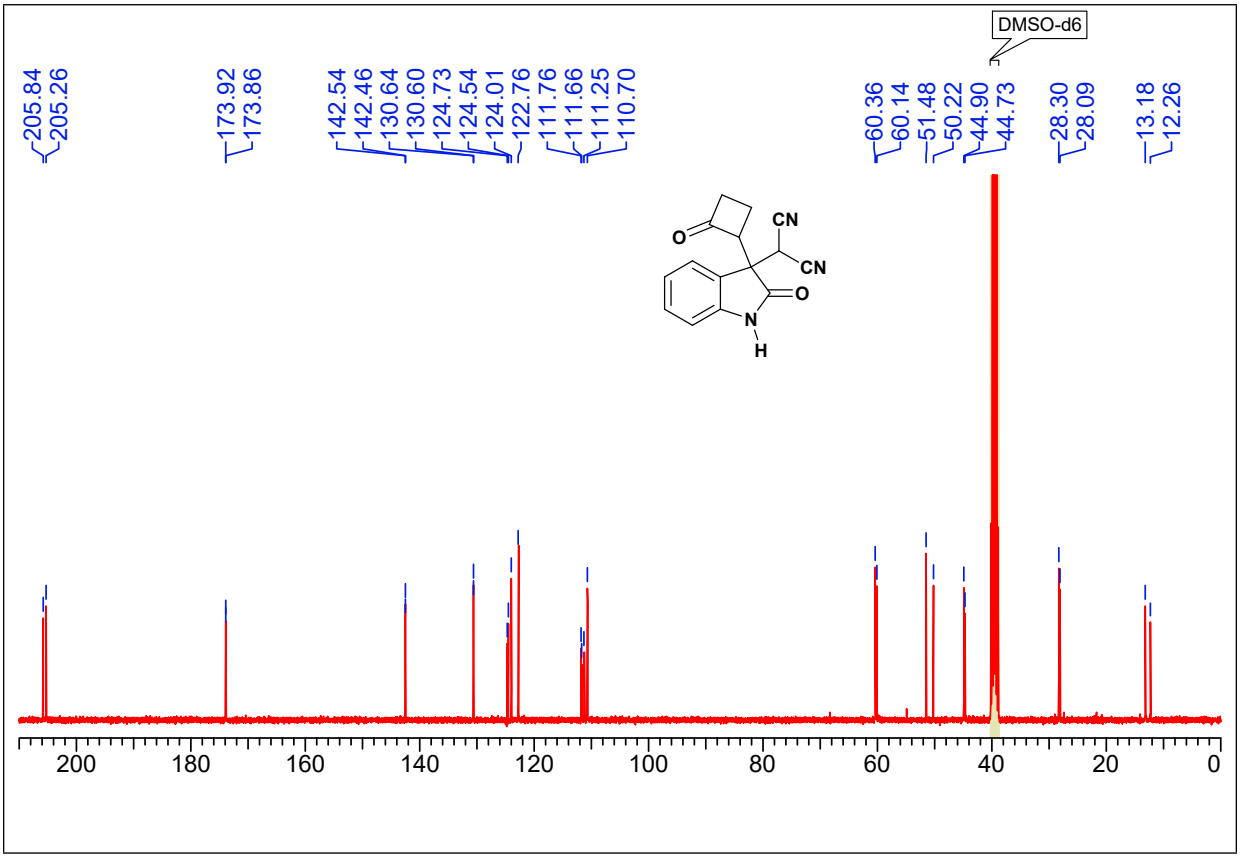
**135 DEPT spectrum of compound (4Cf)**



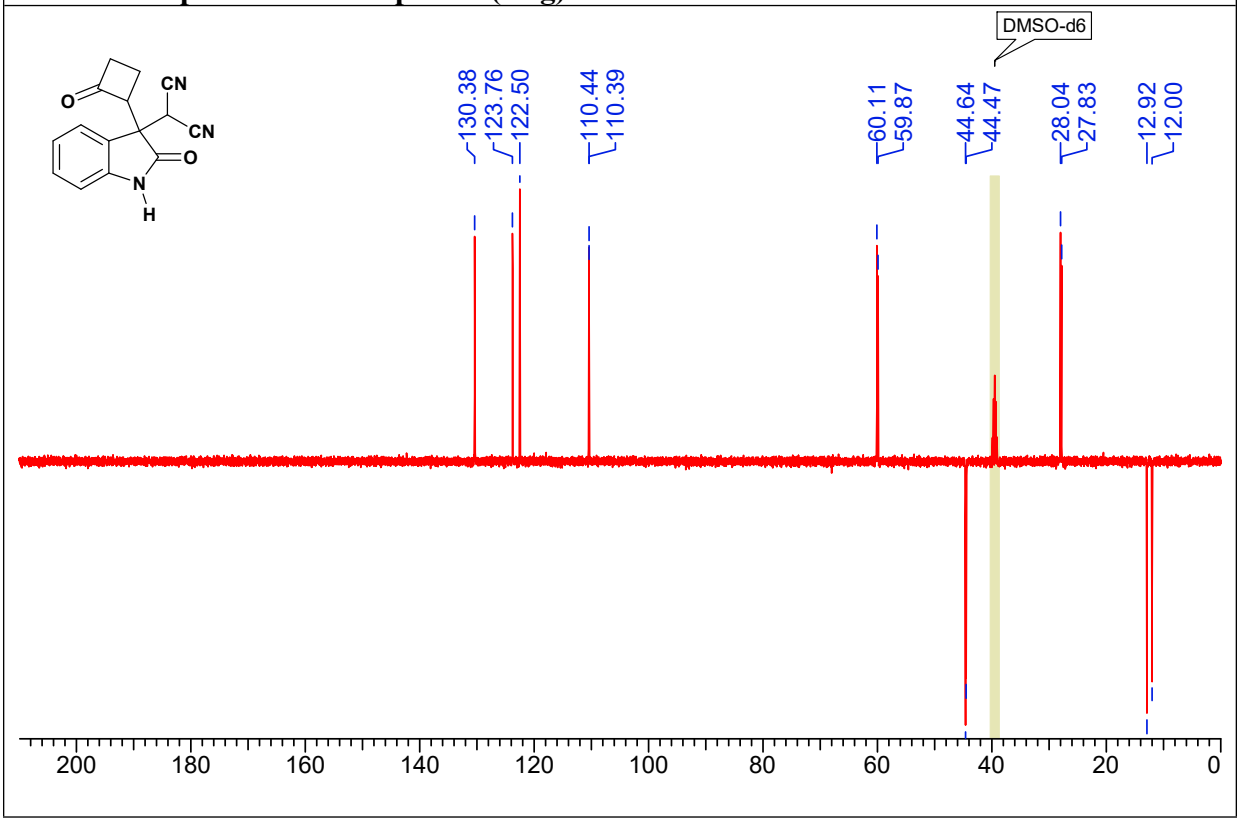
**$^{1}$H NMR spectrum of compound (4Cg) (NMR shows diastereomeric ratio)**



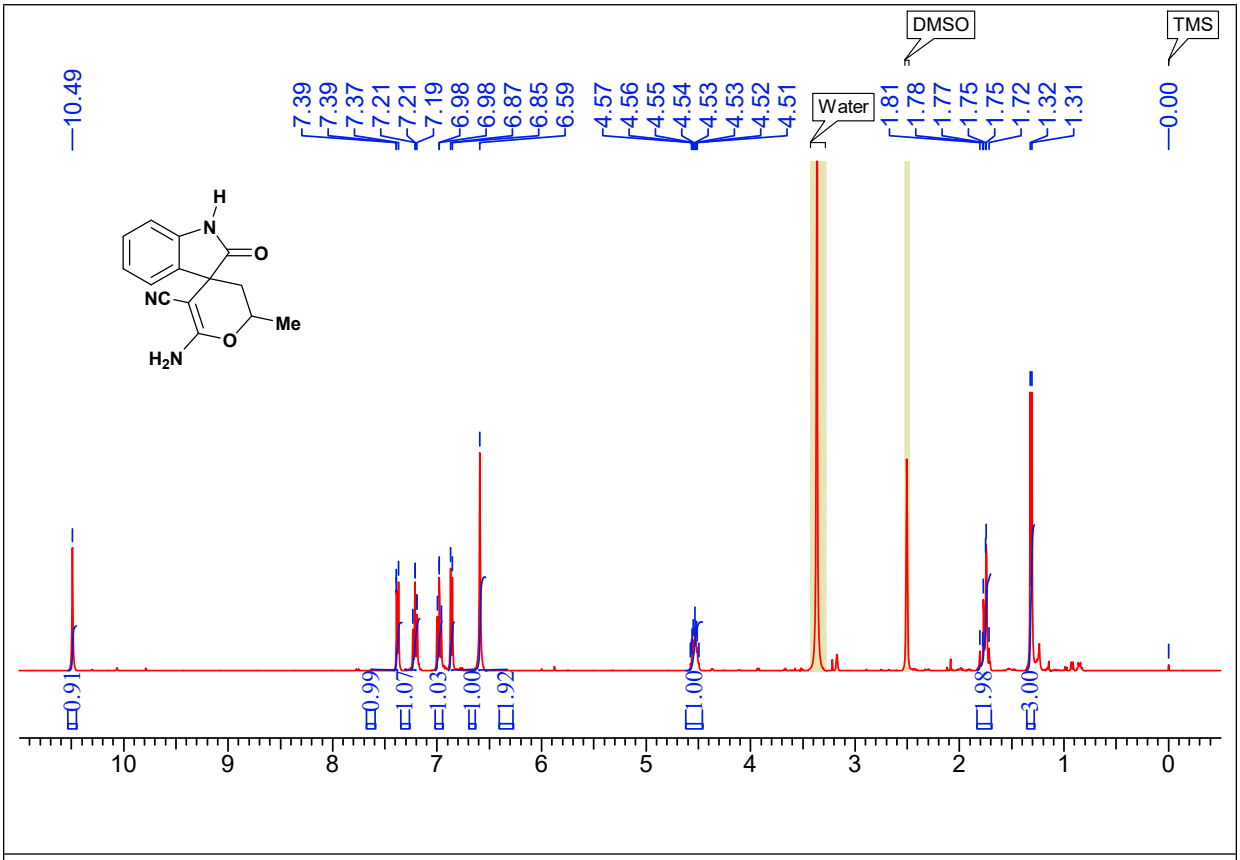

**$^{13}$C NMR spectrum of compound (4Cg)**



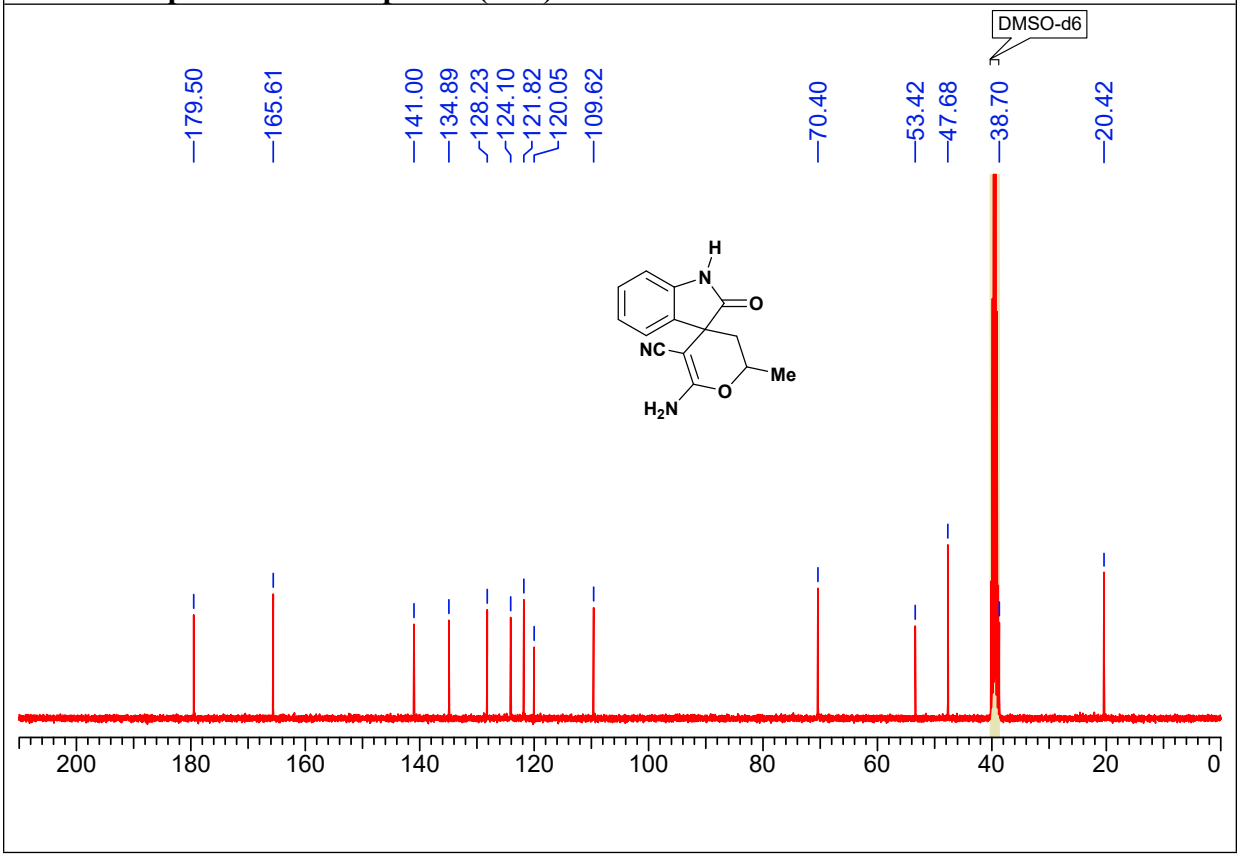

**135 DEPT spectrum of compound (4Cg)**



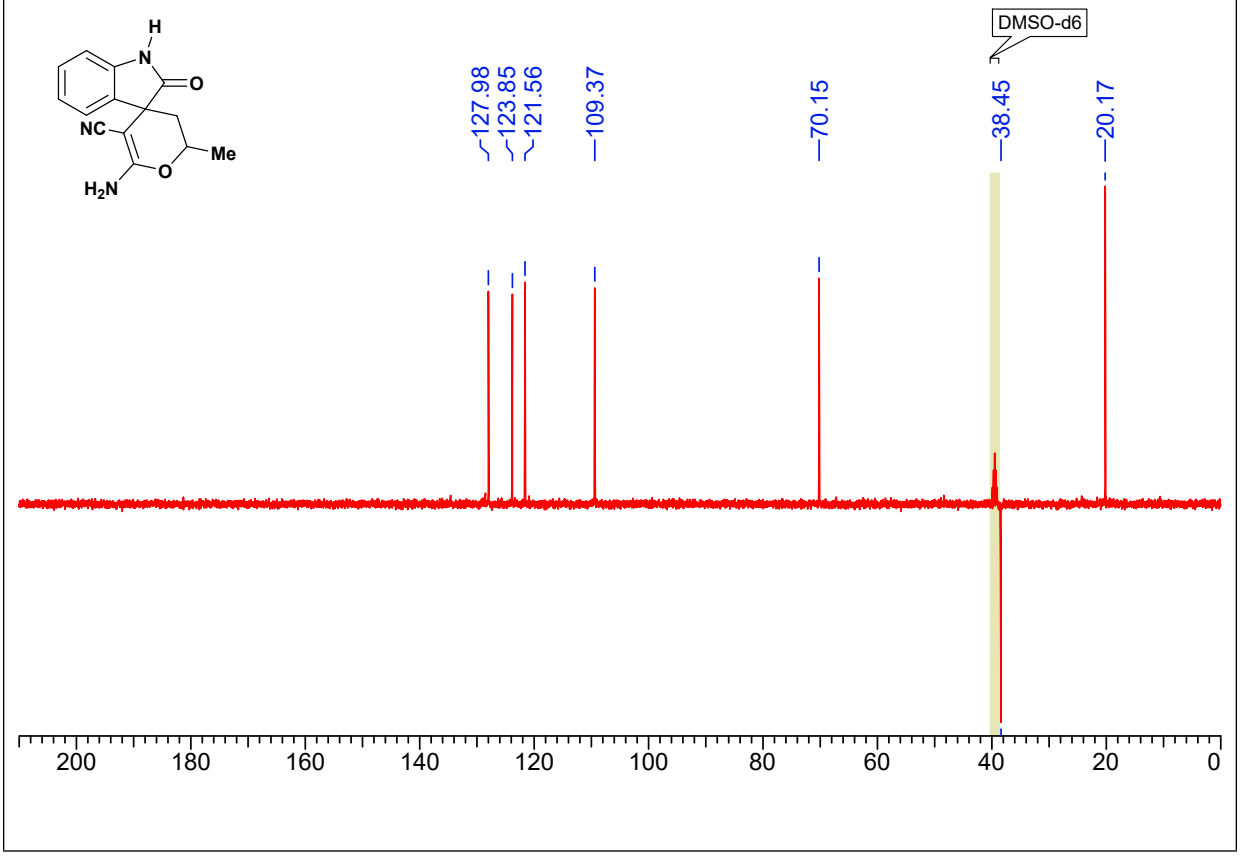
**$^1$H NMR spectrum of compound (5Aa)**



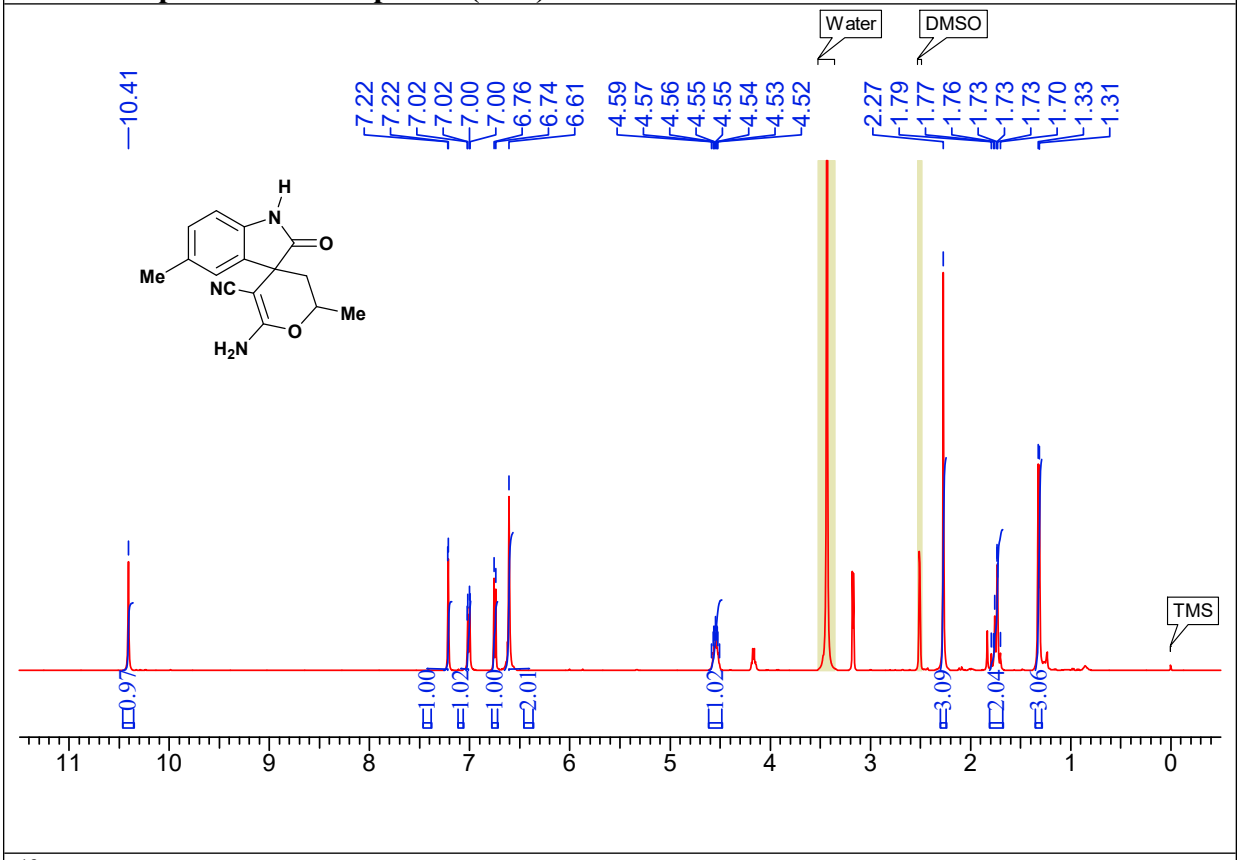

**$^{13}$C NMR spectrum of compound (4Aa)**



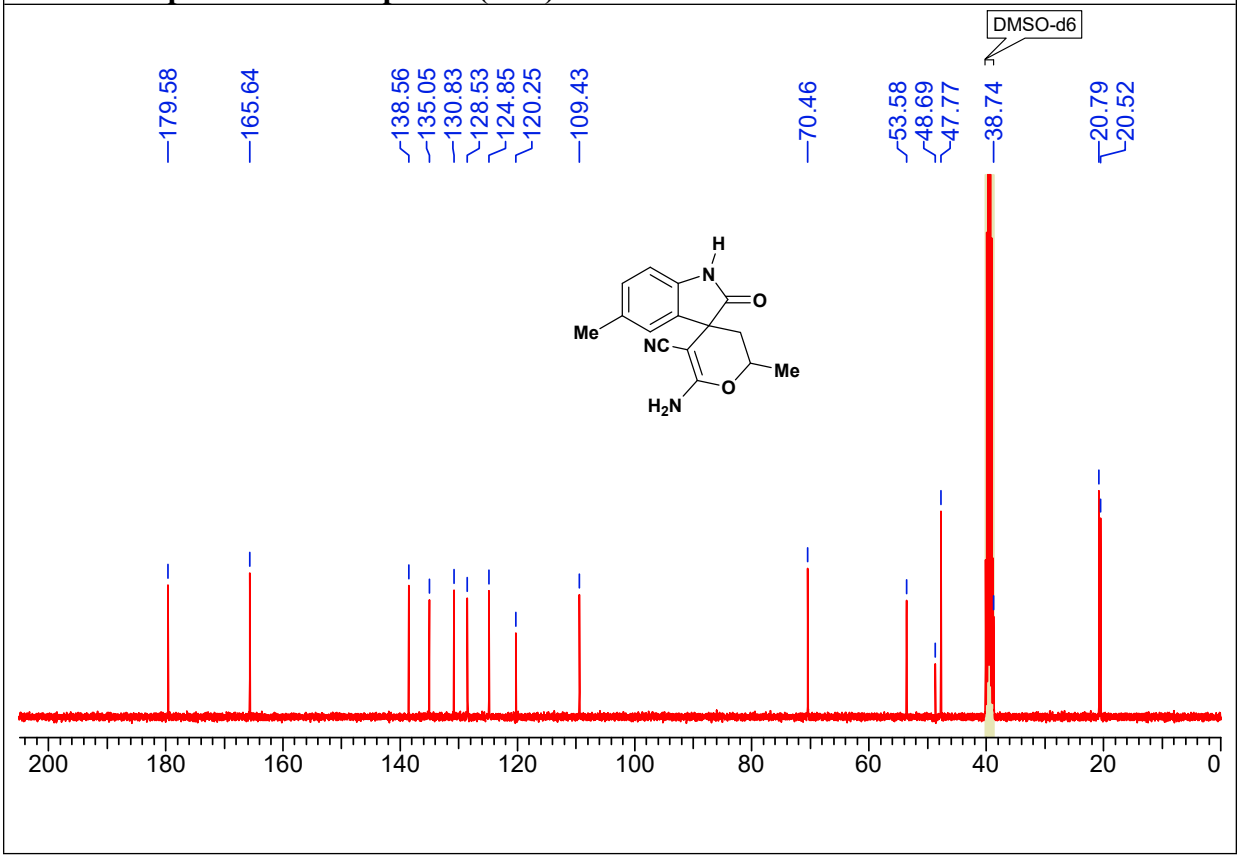
**135 DEPT spectrum of compound (4Aa)**



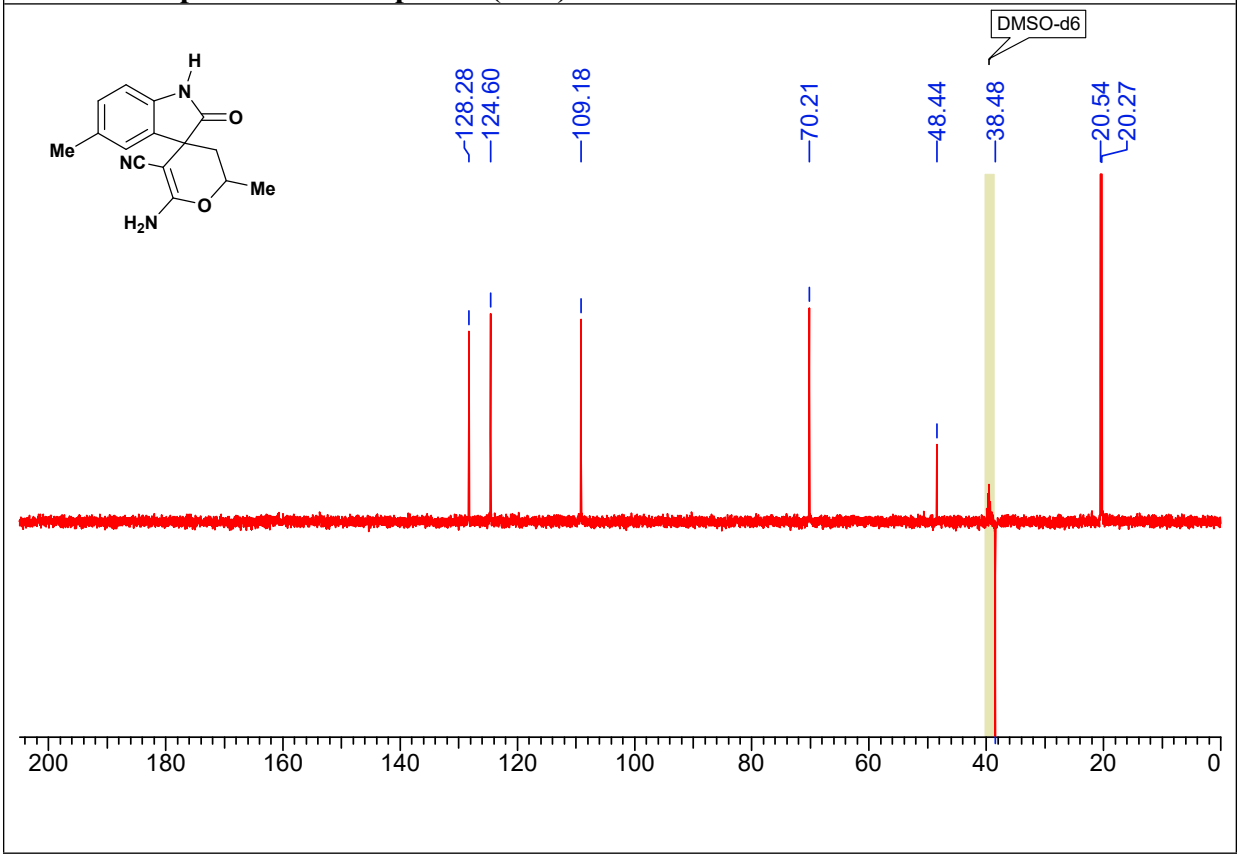
## $^{1}$H NMR spectrum of compound (5Ab)



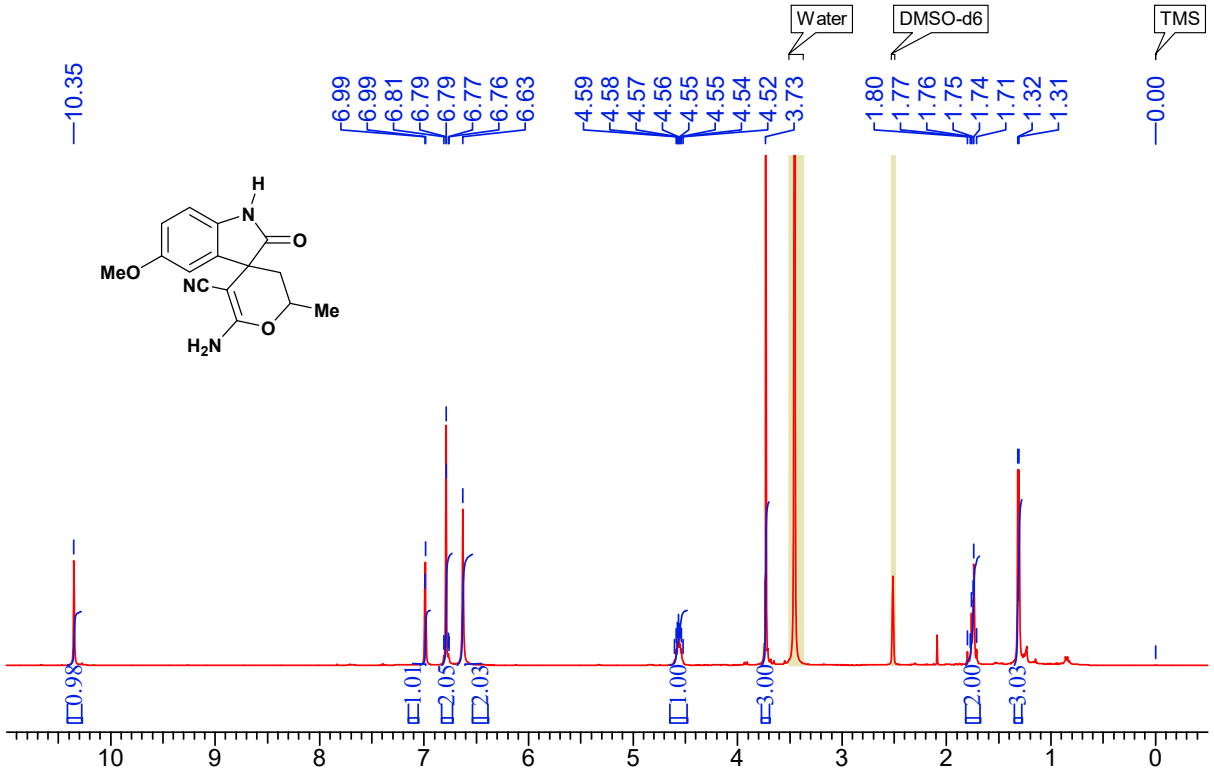

## $^{13}$C NMR spectrum of compound (5Ab)



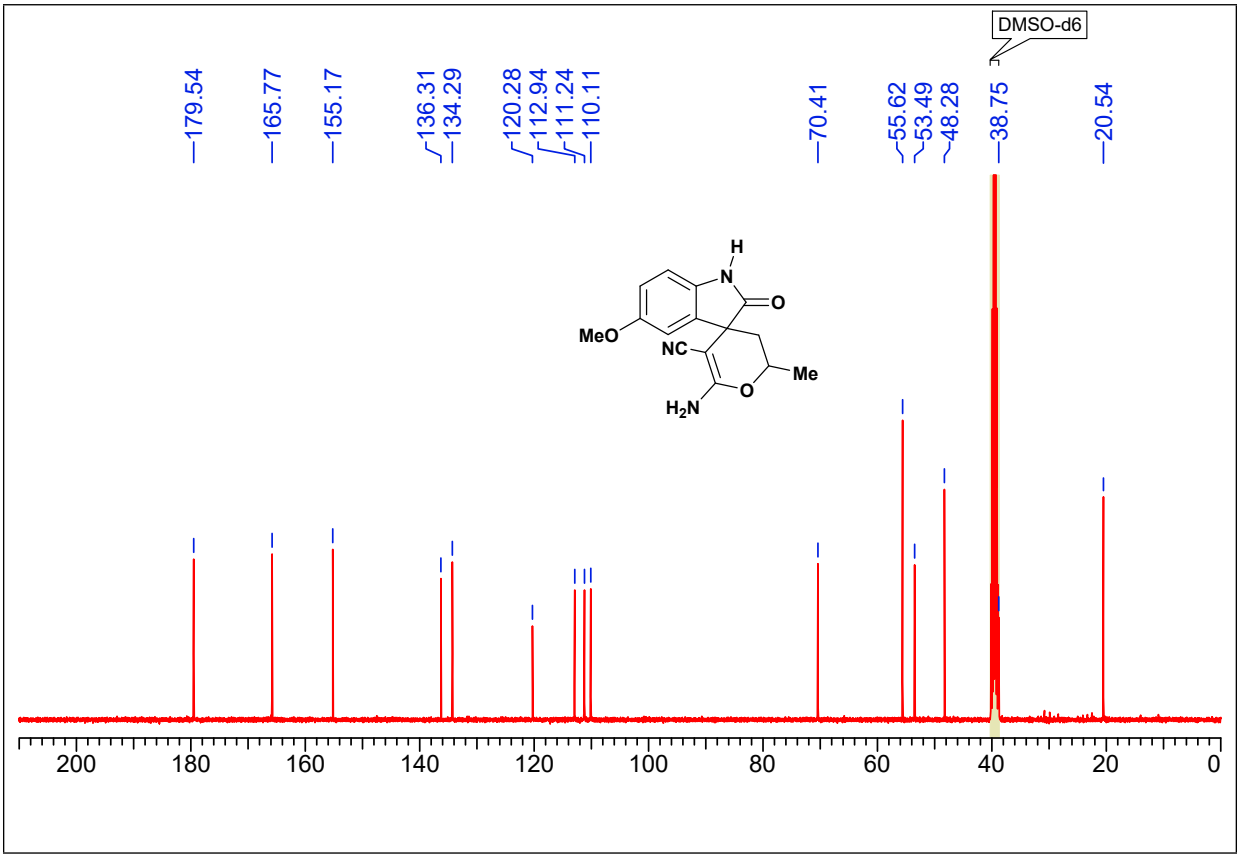
**135 DEPT spectrum of compound (5Ab)**



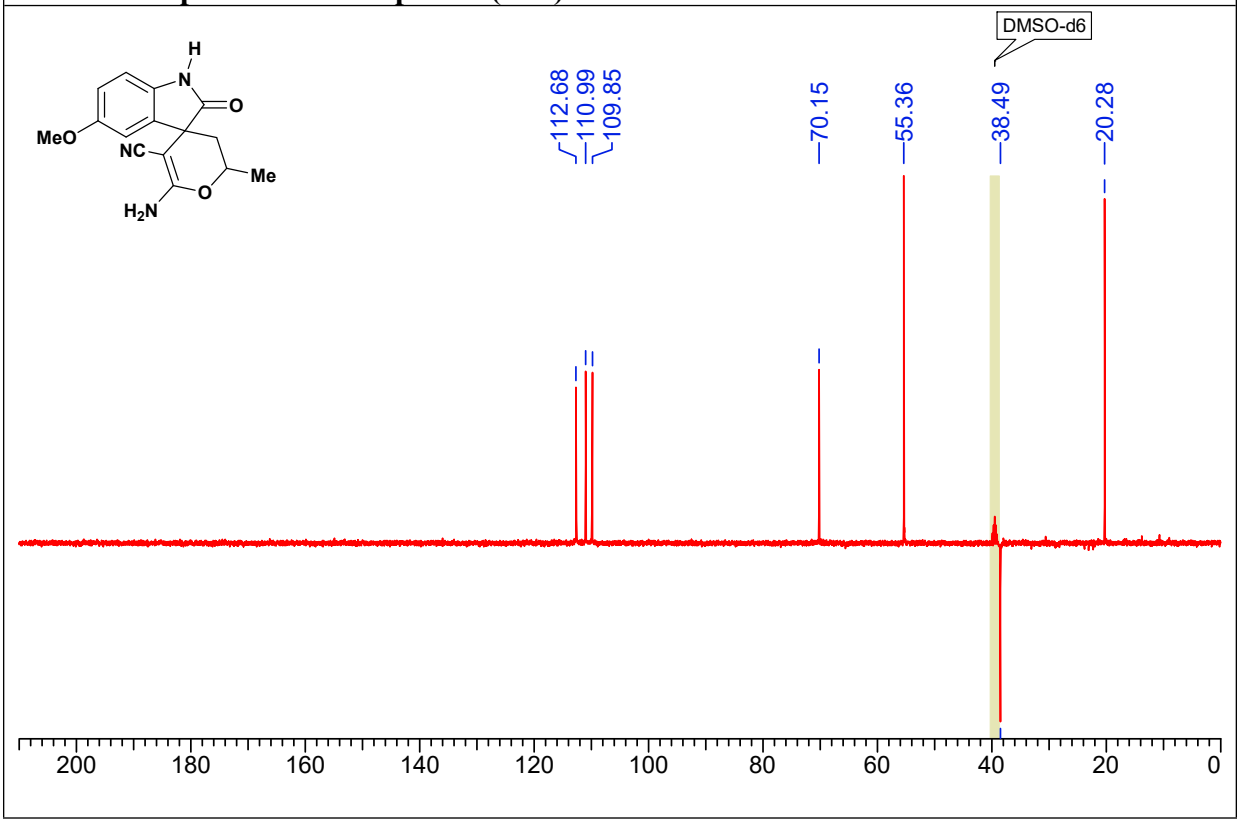
**$^{1}$H NMR spectrum of compound (5Ac)**



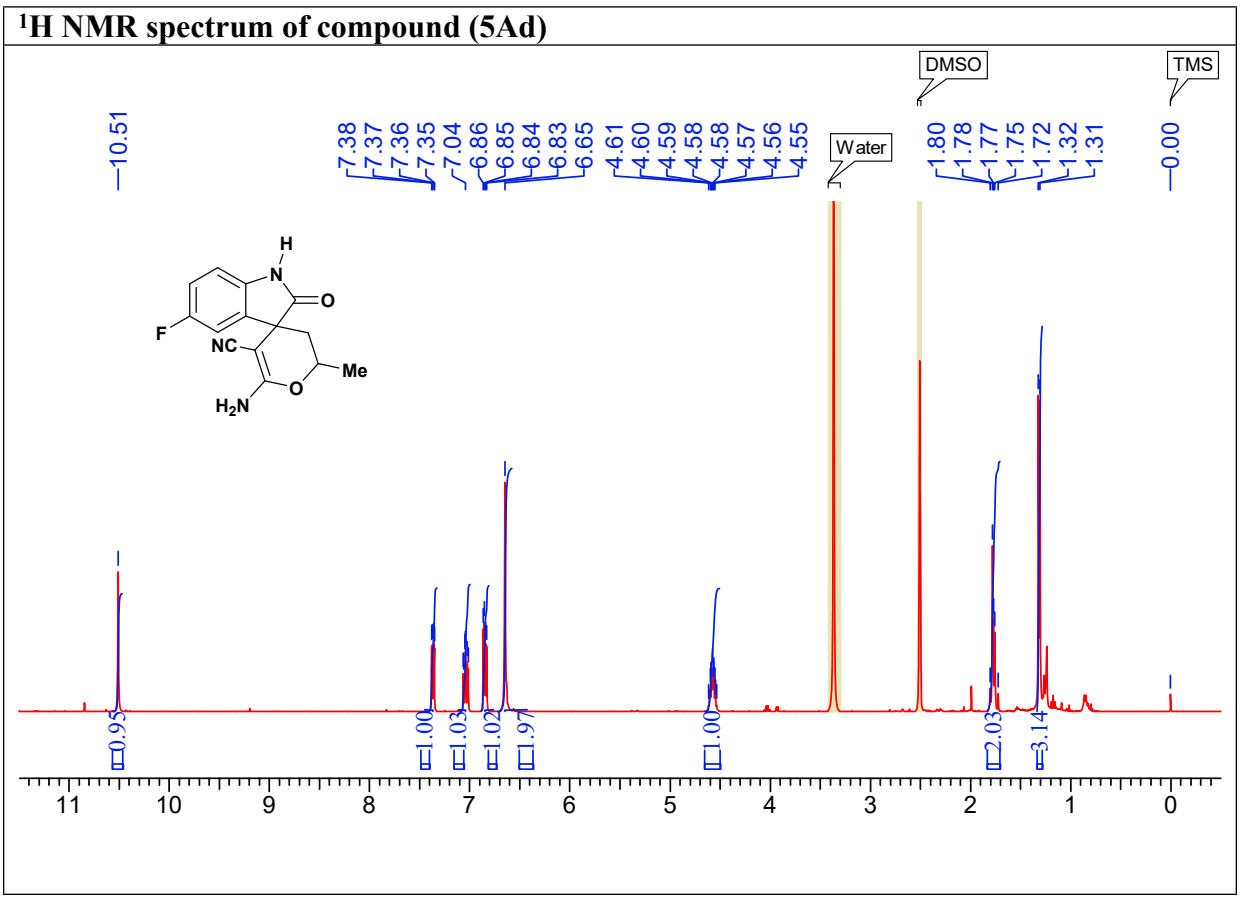

**$^{13}$C NMR spectrum of compound (5Ac)**



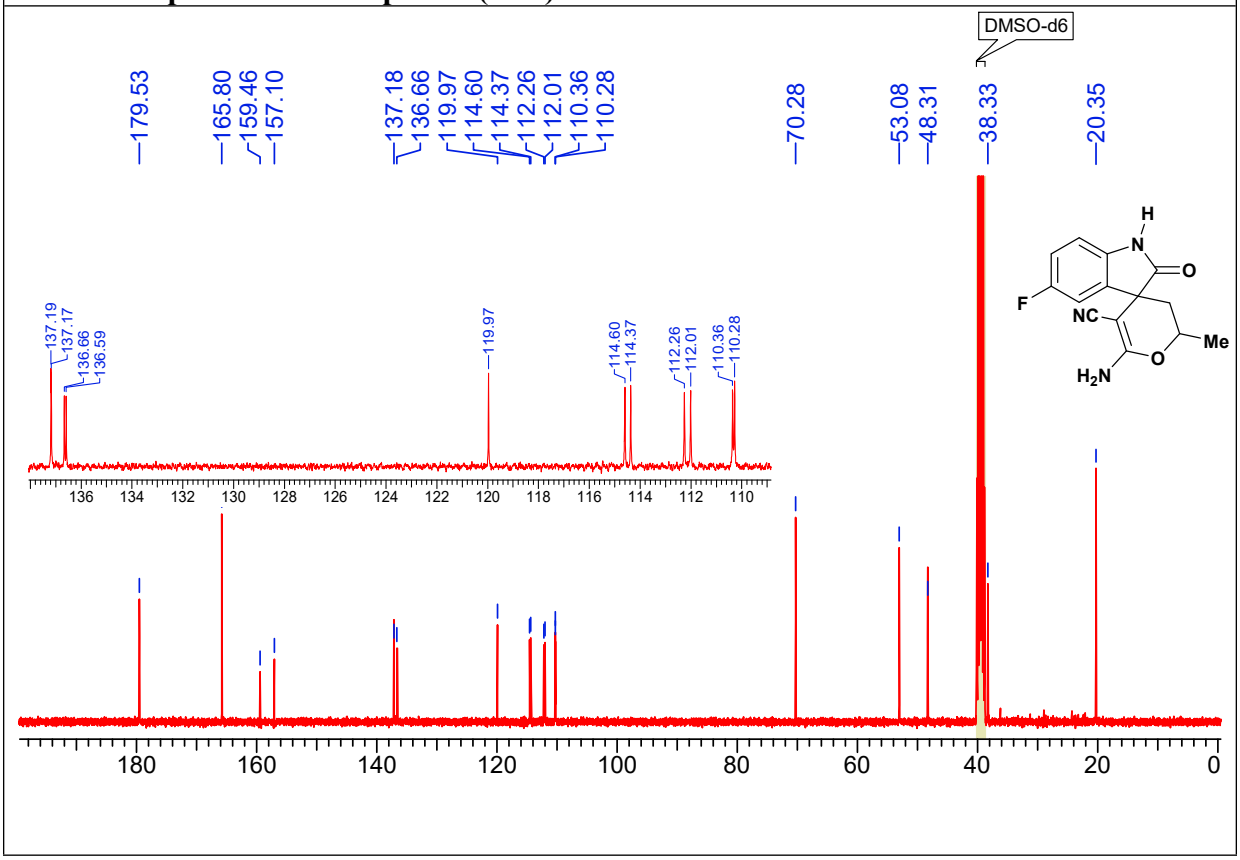

**135 DEPT spectrum of compound (5Ac)**



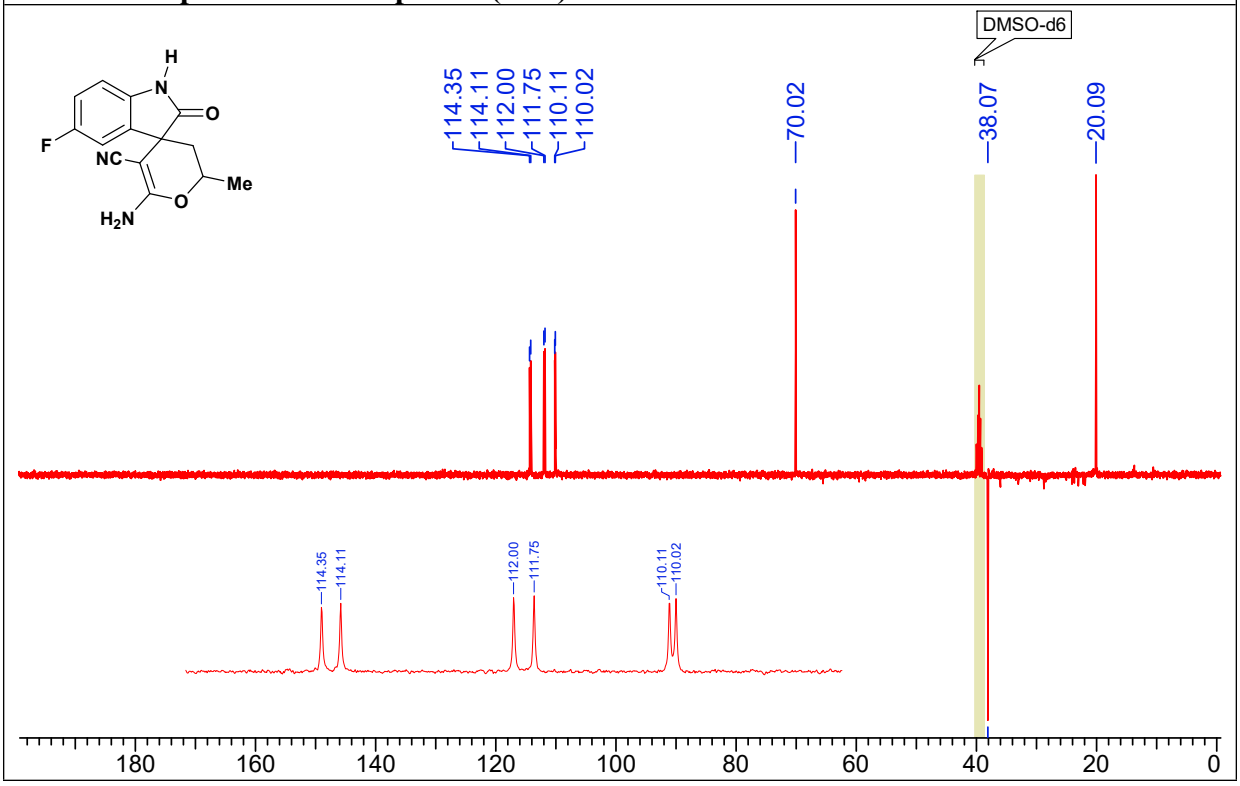
**$^{1}$H NMR spectrum of compound (5Ad)**



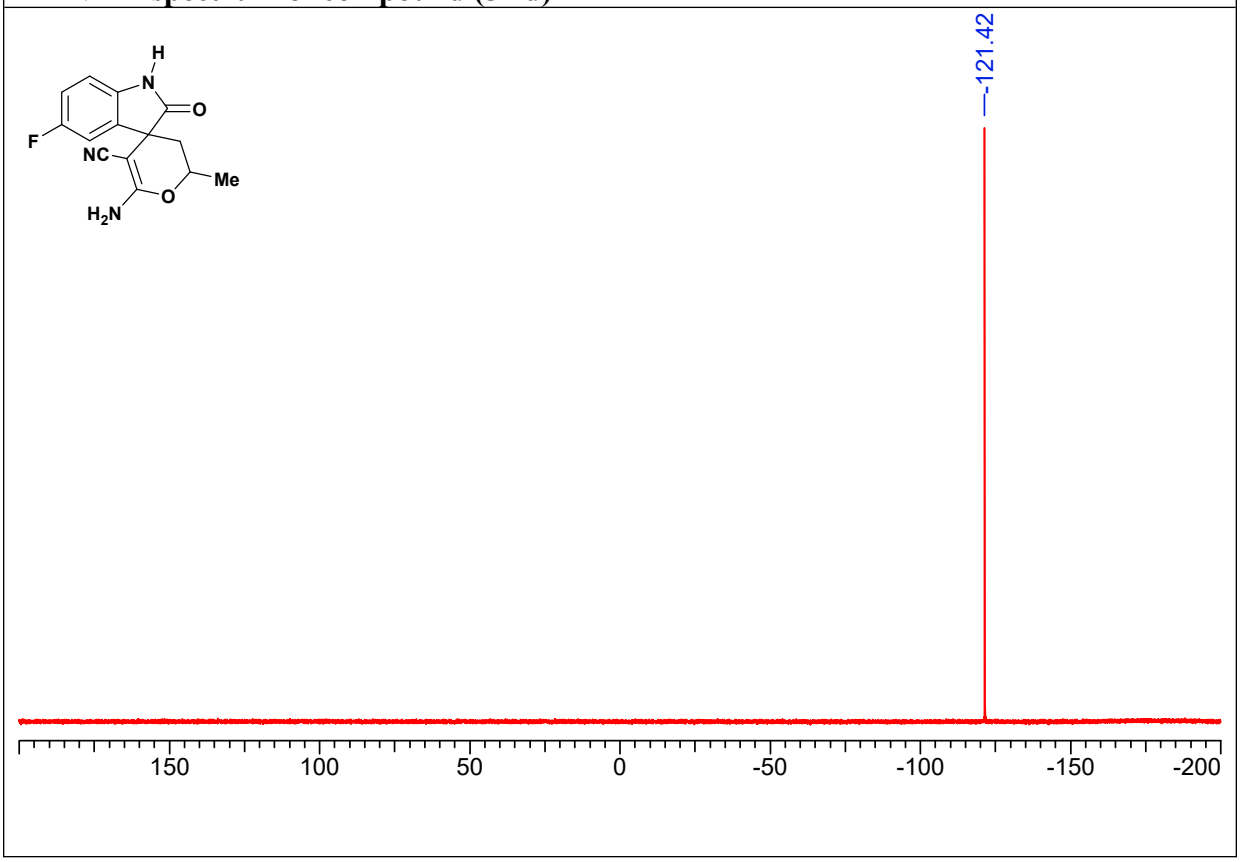
## $^{13}$C NMR spectrum of compound (5Ad)



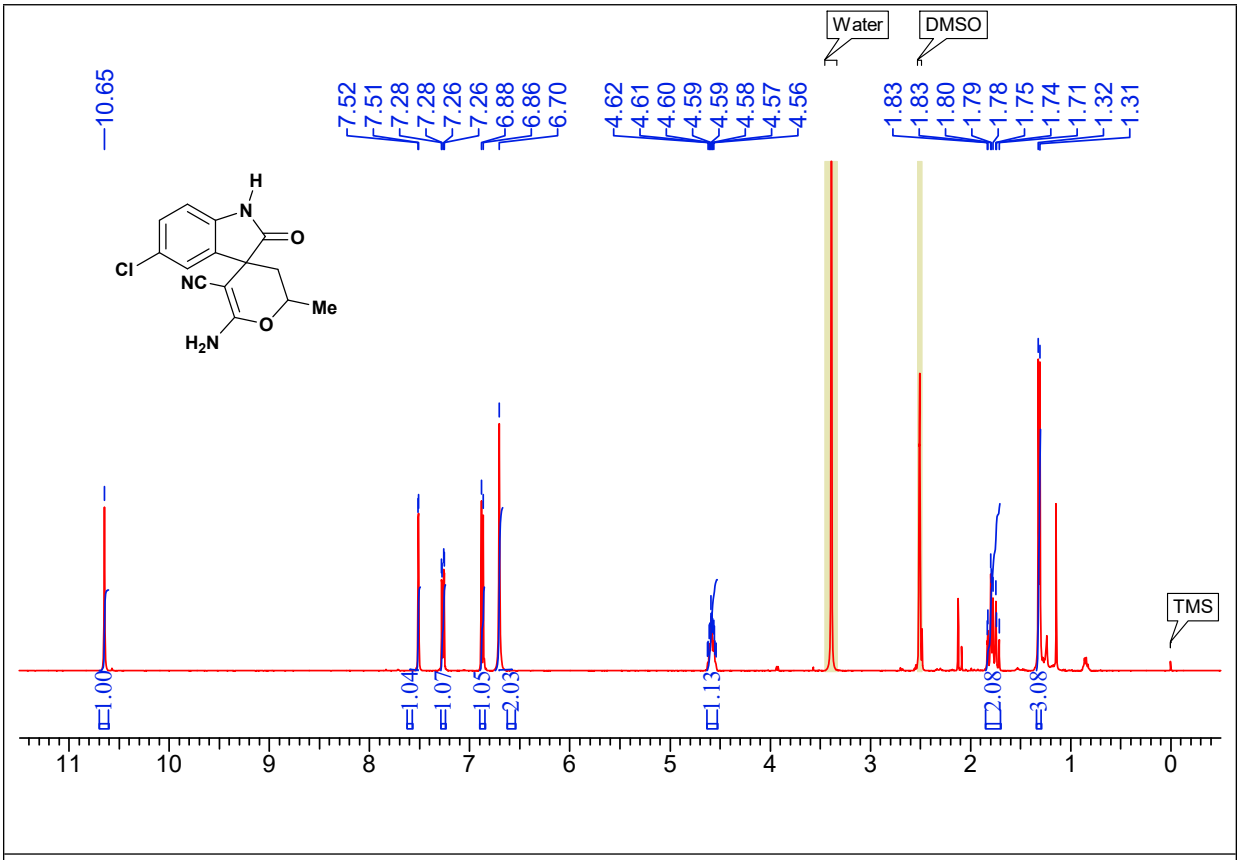

## 135 DEPT spectrum of compound (5Ad)



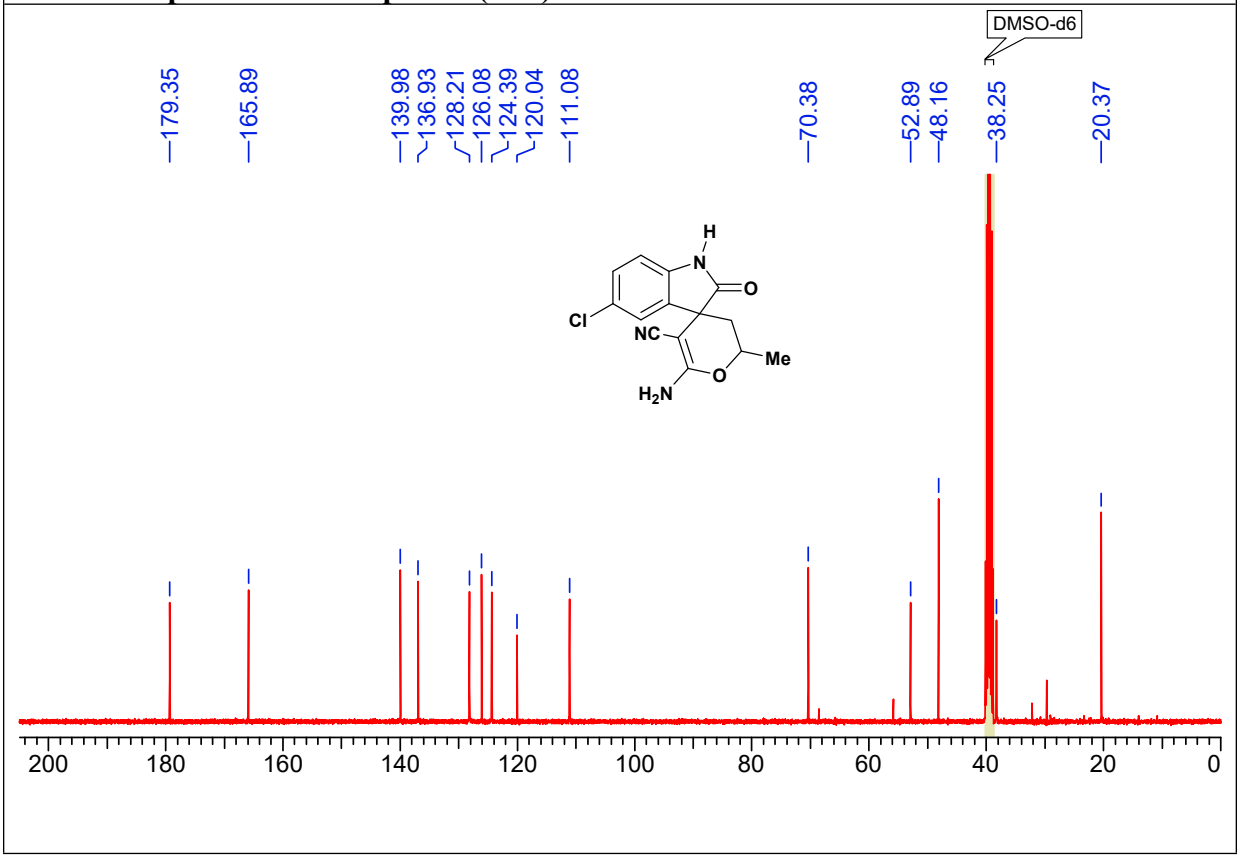
**$^{19}$F NMR spectrum of compound (5Ad)**



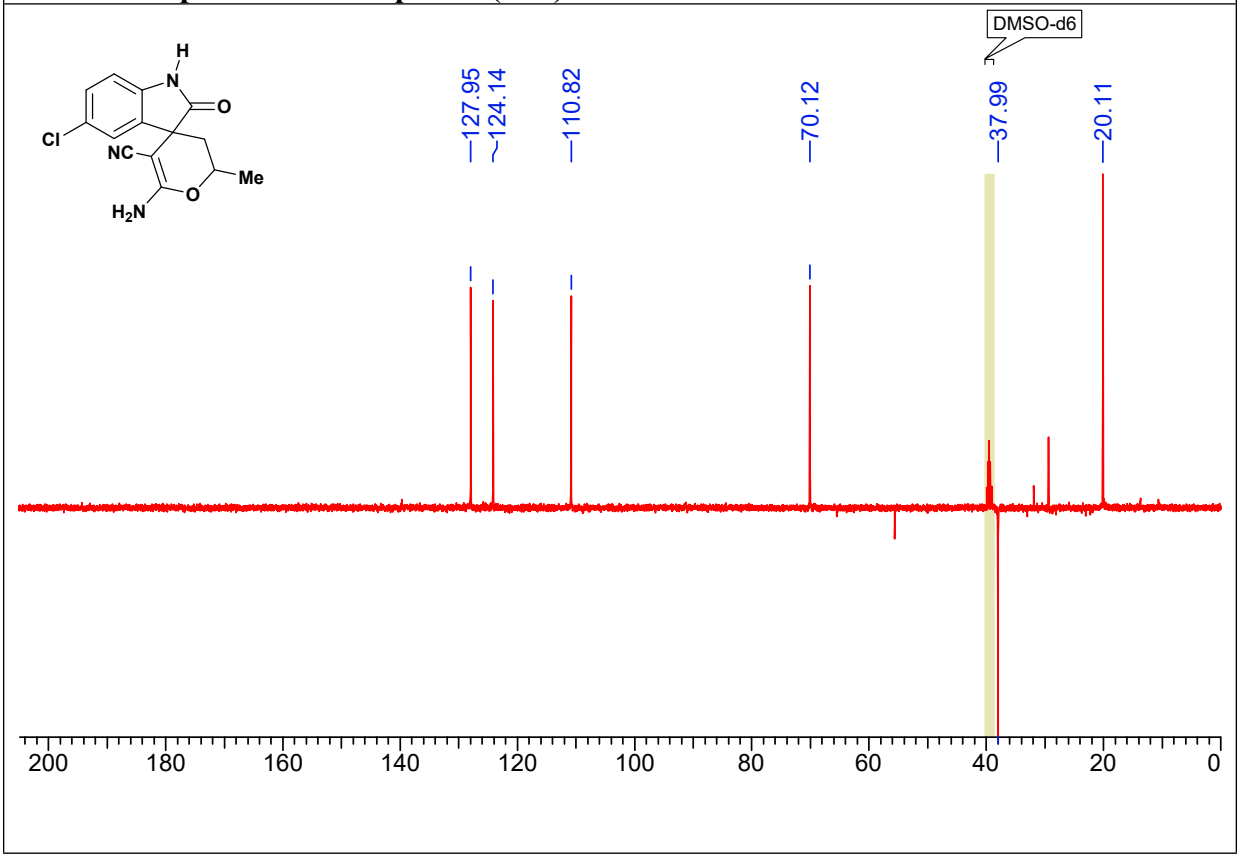

**$^{1}$H NMR spectrum of compound (5Ae)**



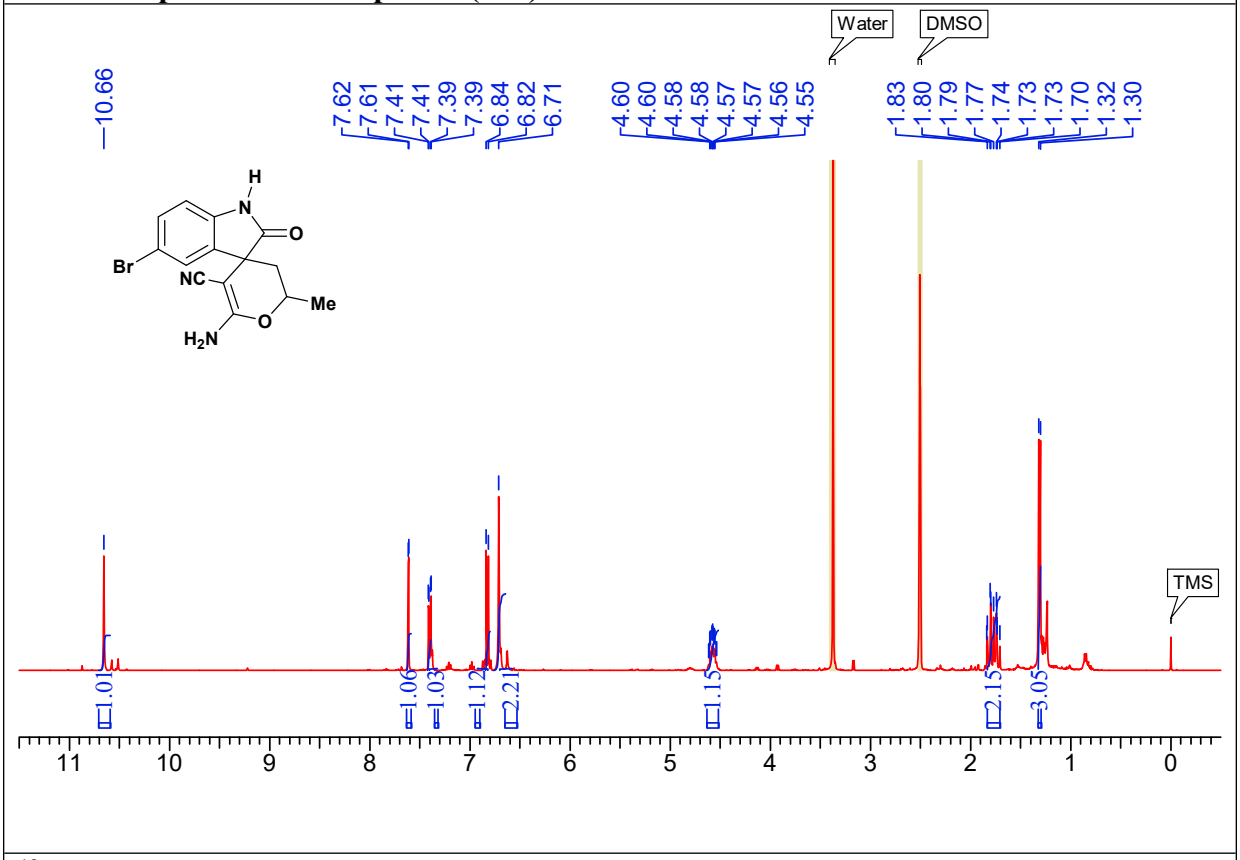

**$^{13}$C NMR spectrum of compound (5Ae)**



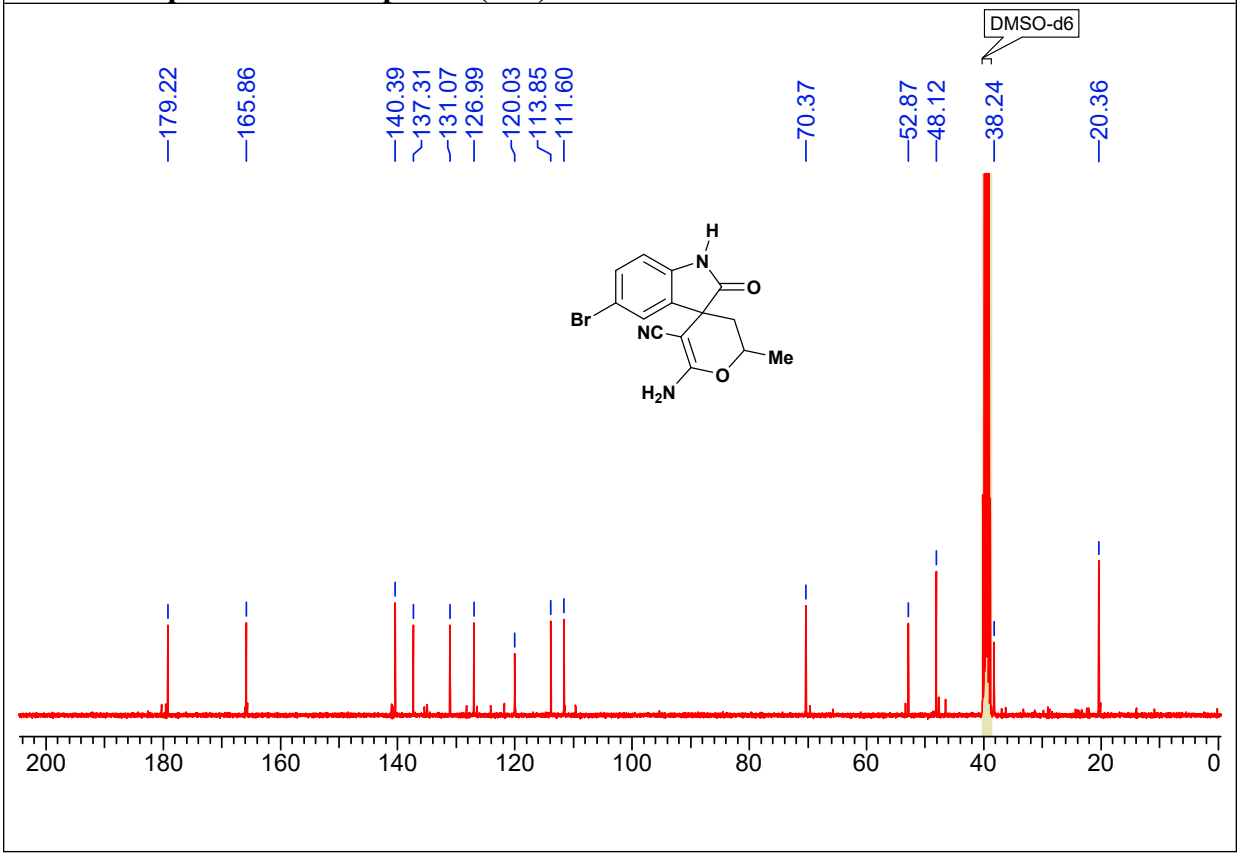
**135 DEPT spectrum of compound (5Ae)**



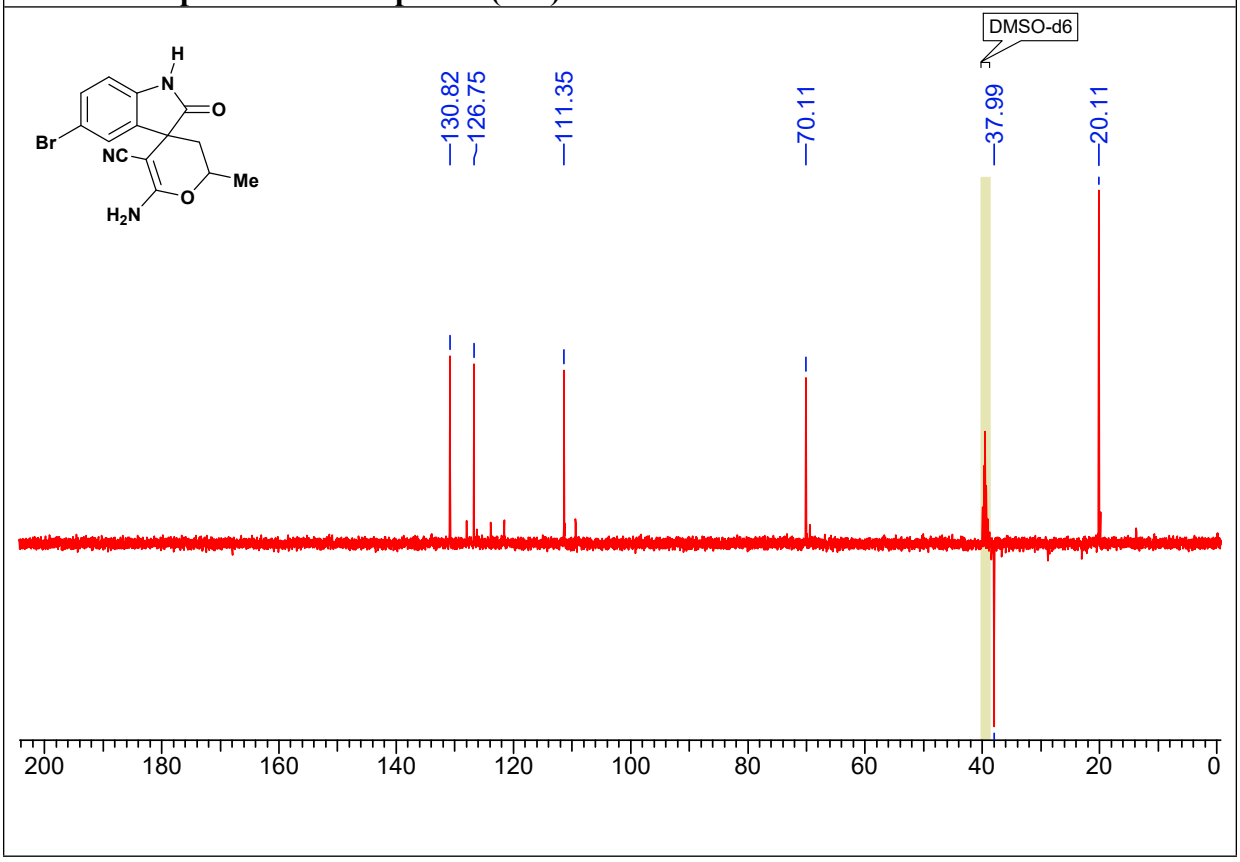
## $^{1}$H NMR spectrum of compound (5Af)



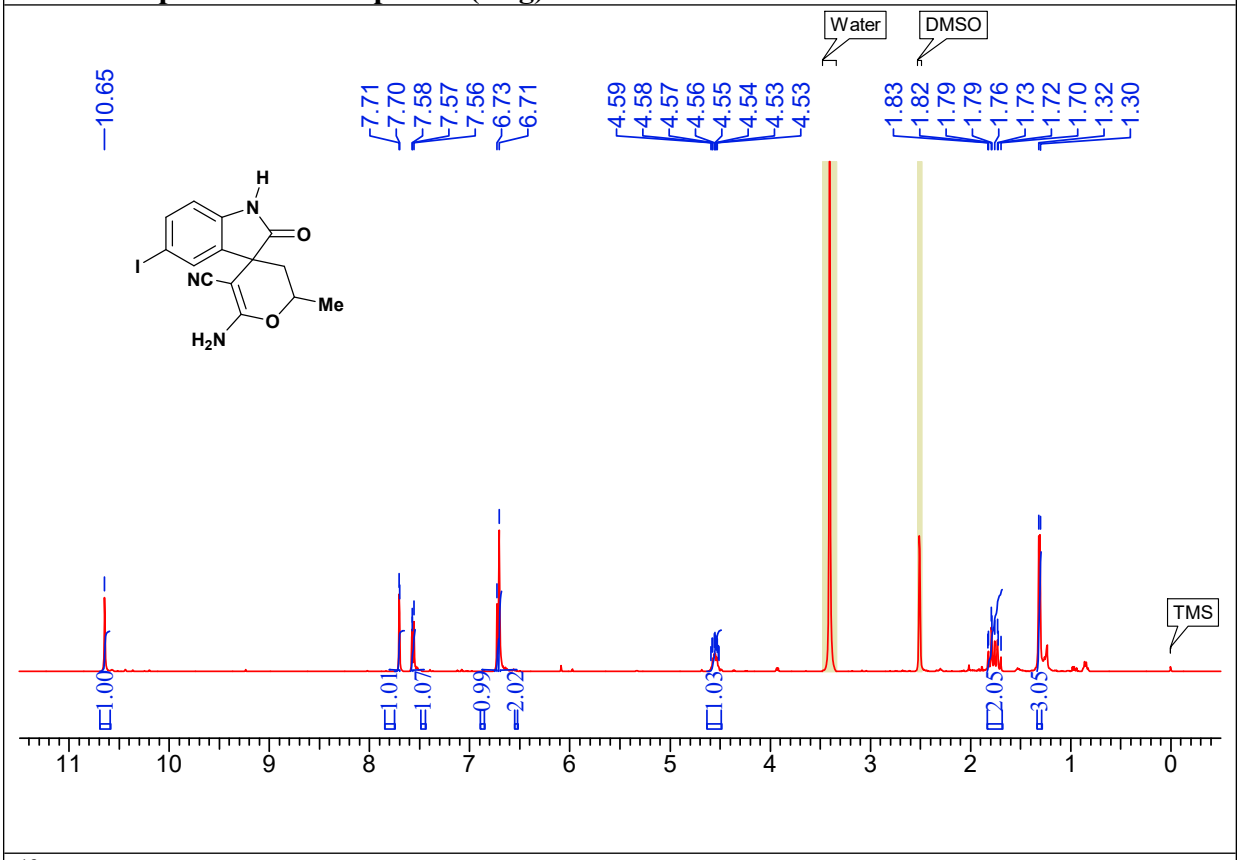

## $^{13}$C NMR spectrum of compound (5Af)



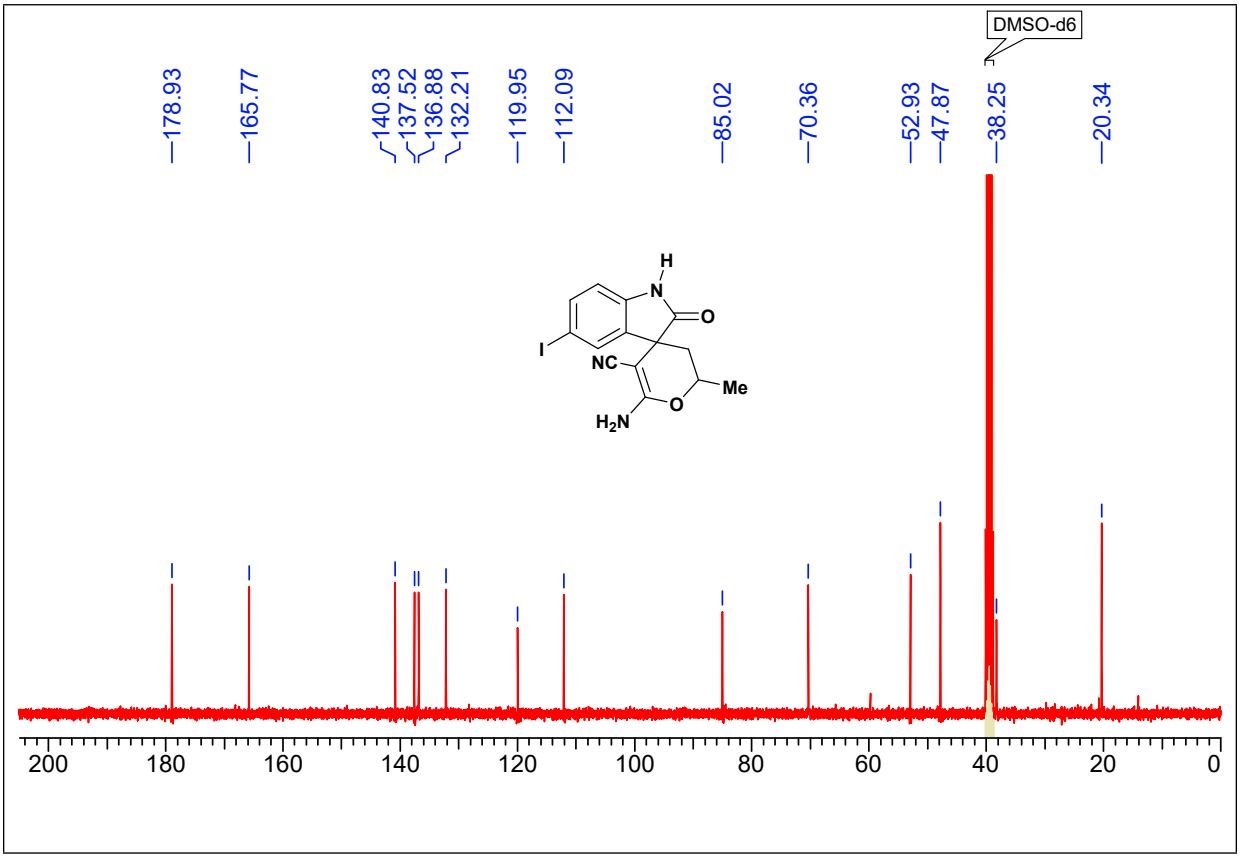
**135 DEPT spectrum of compound (5Af)**



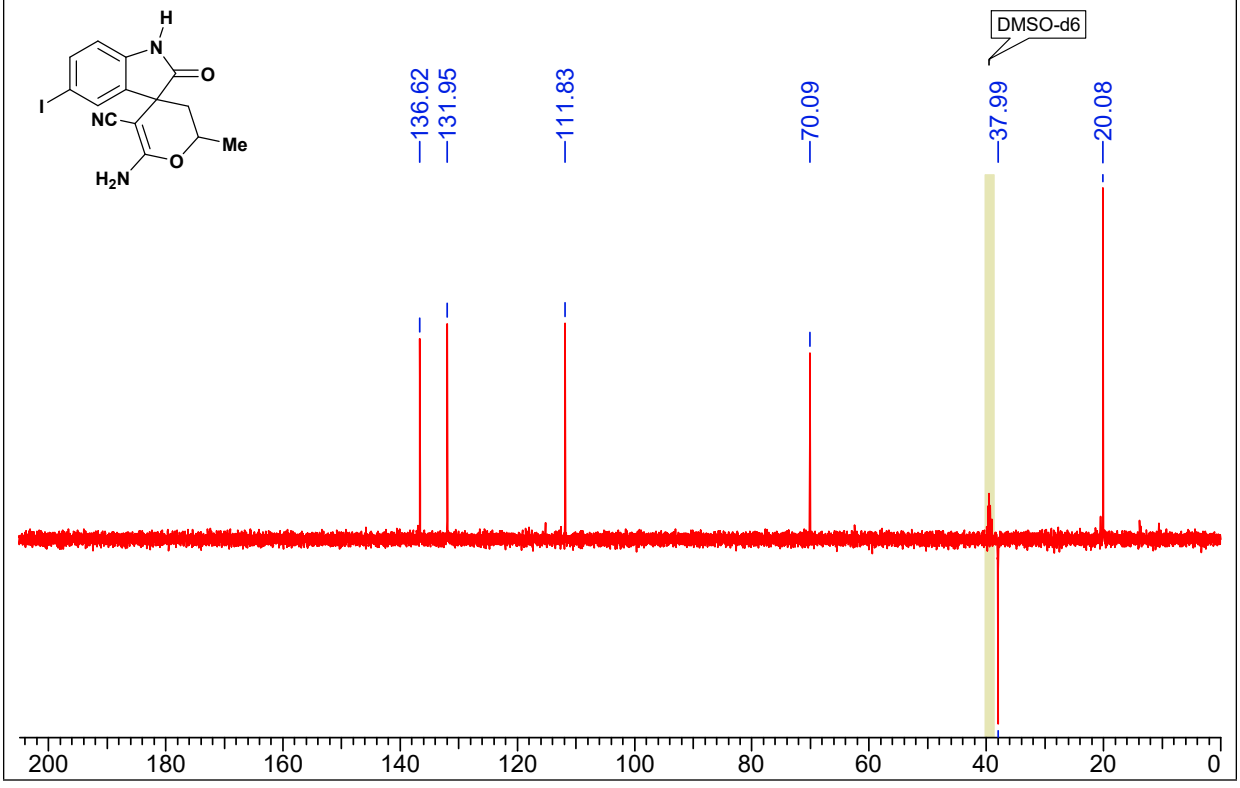
**$^{1}$H NMR spectrum of compound (5Ag)**



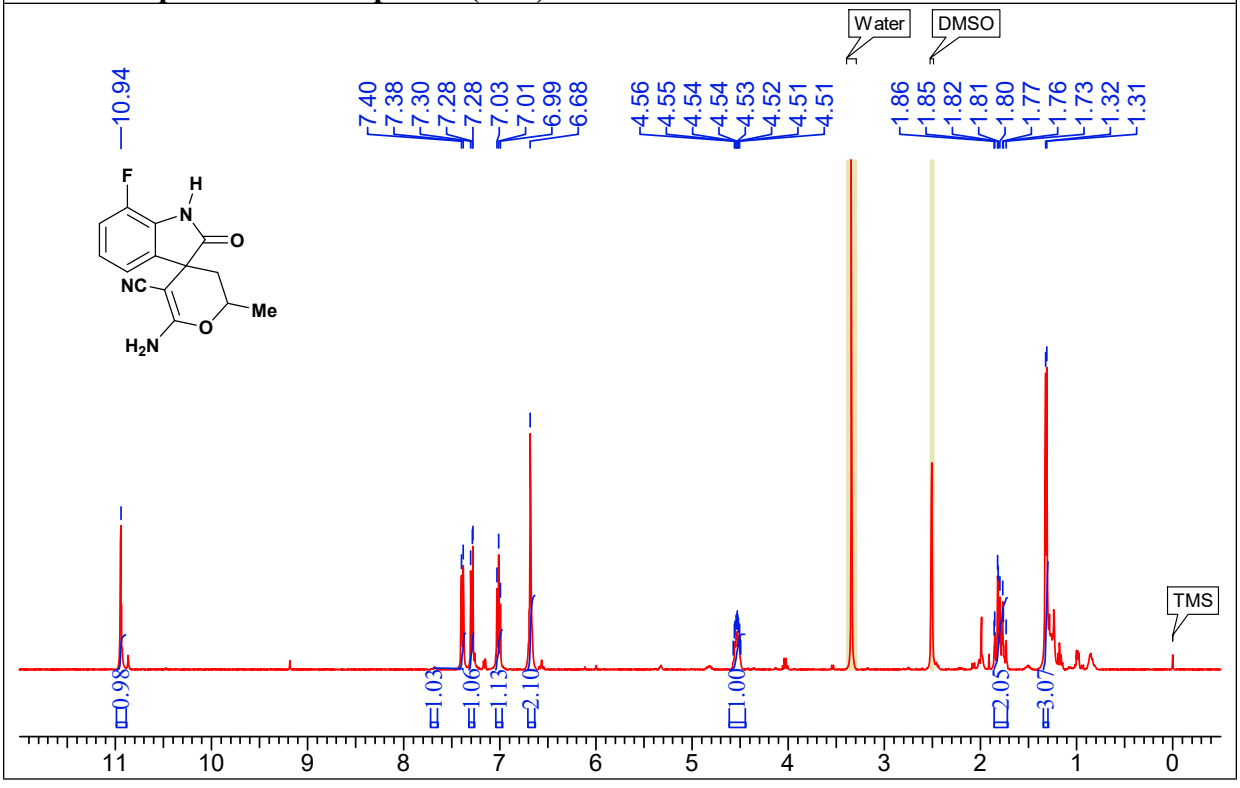

**$^{13}$C NMR spectra of (5Ag)**



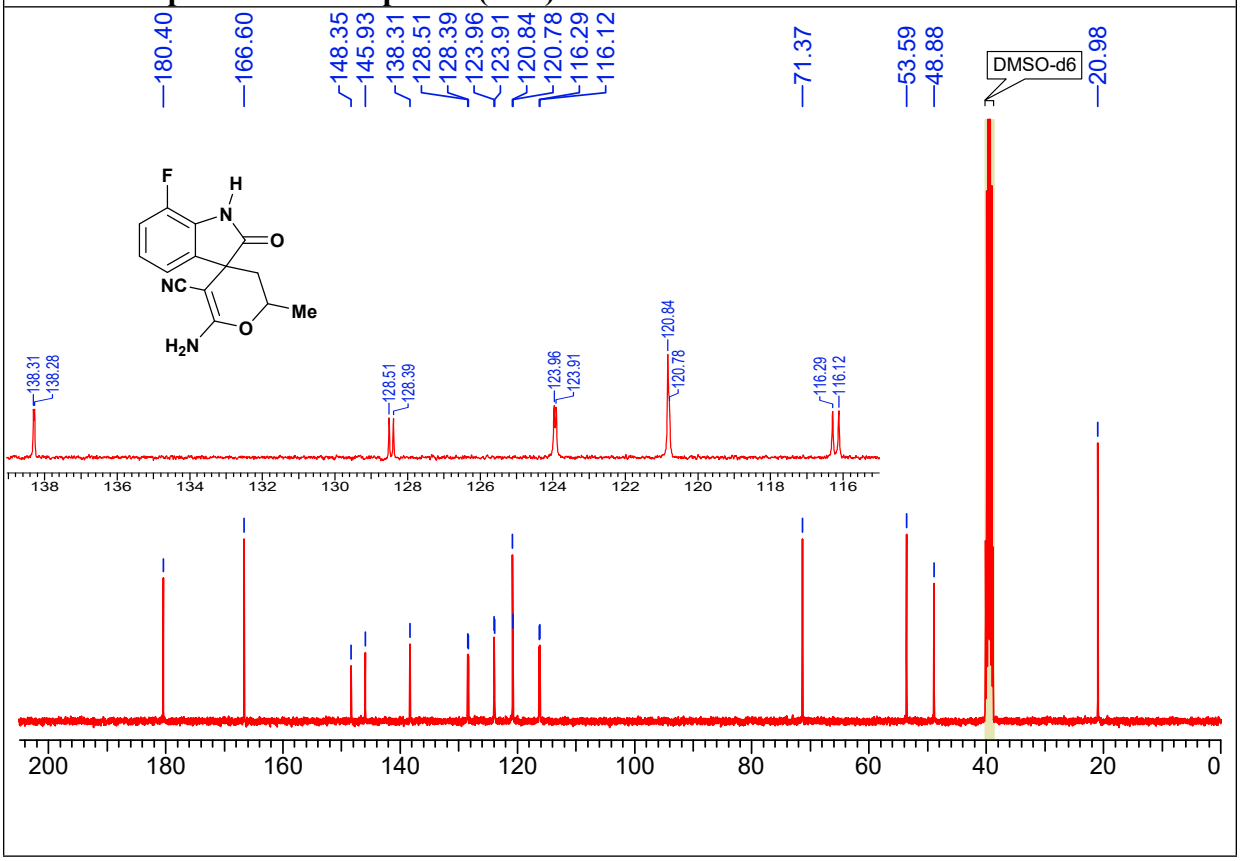

**135 DEPT spectrum of compound (5Ag)**



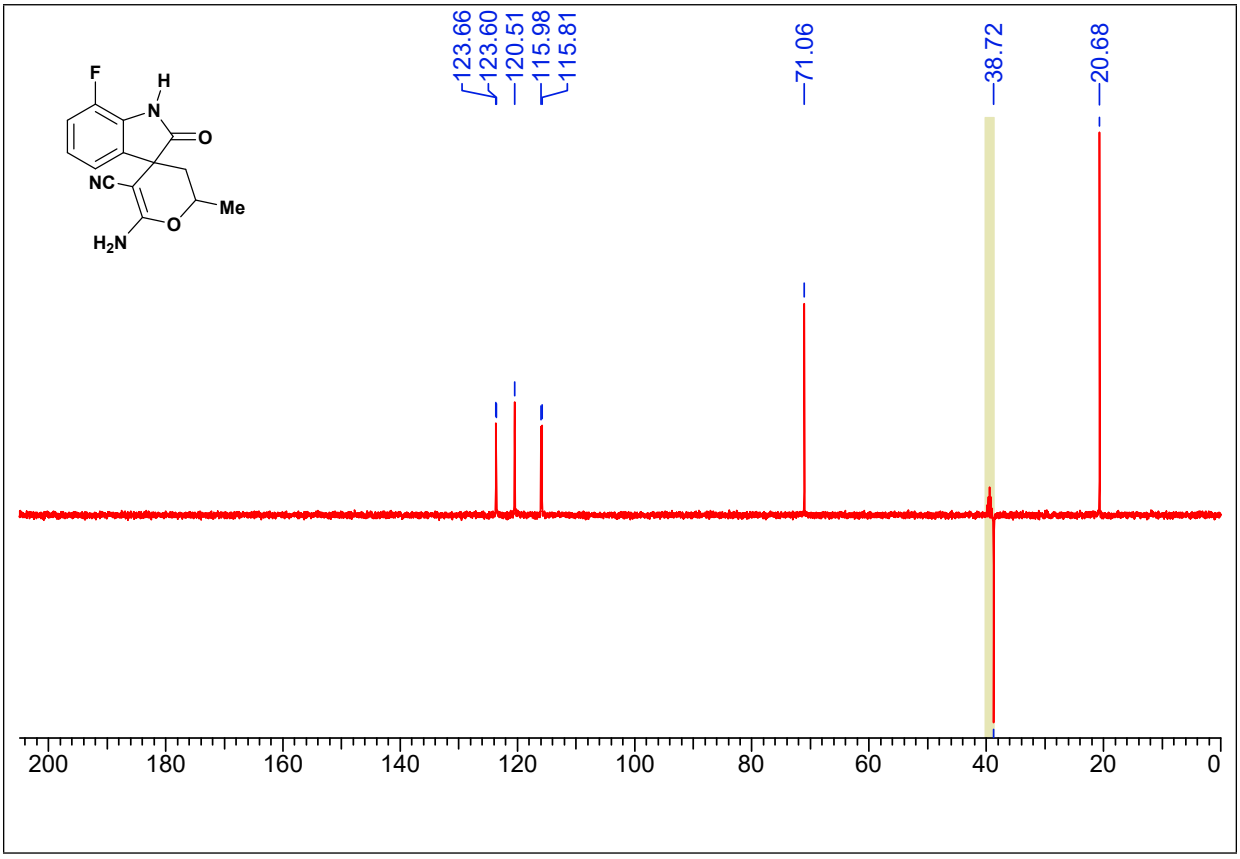
**$^1$H NMR spectrum of compound (5Ah)**



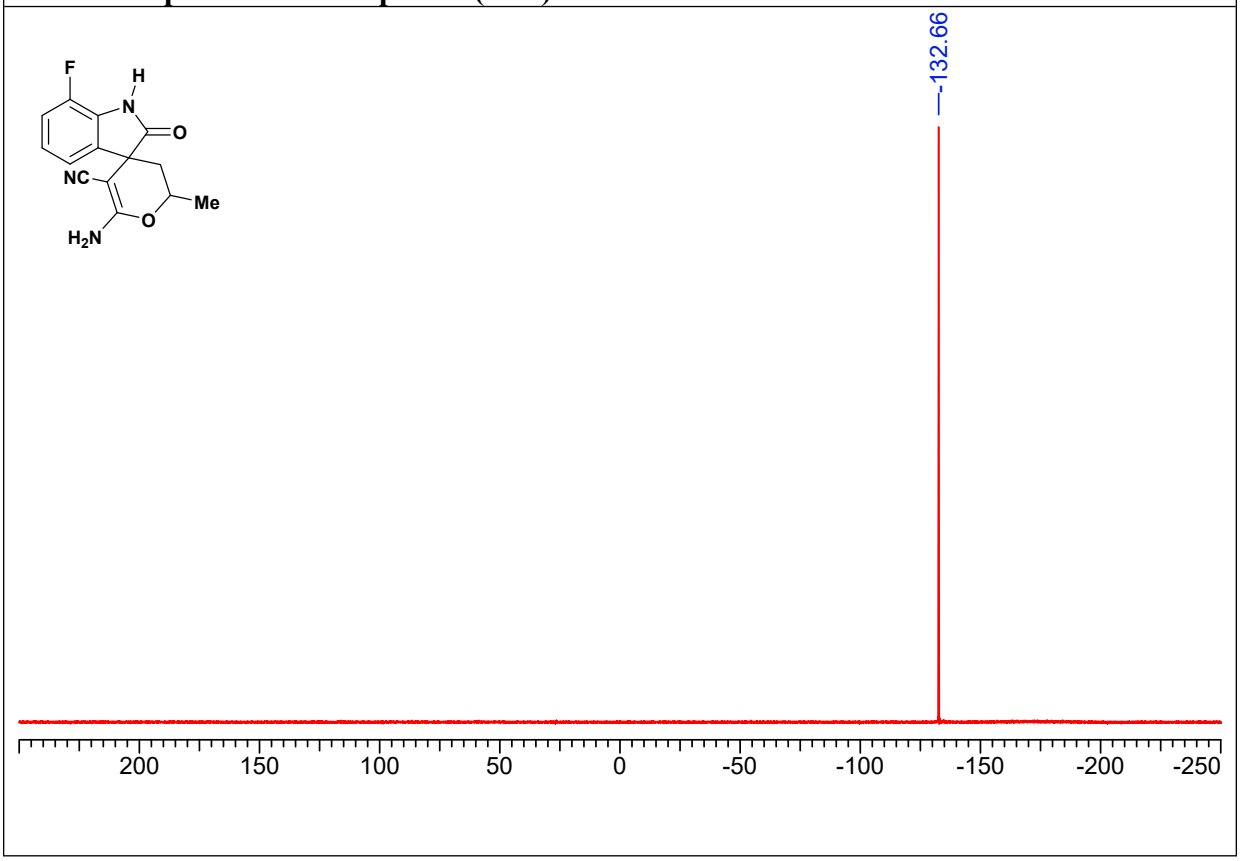
## $^{13}$C NMR spectrum of compound (5Ah)



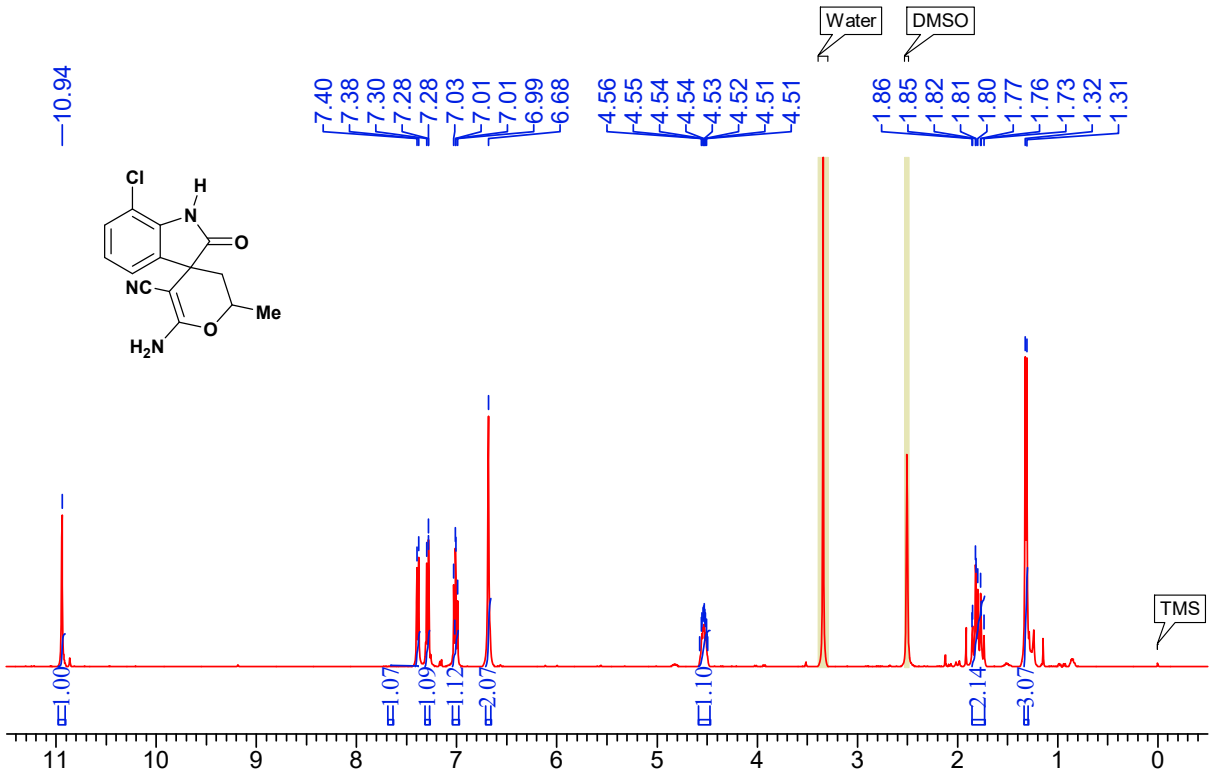

## 135 DEPT spectrum of compound (5Ah)



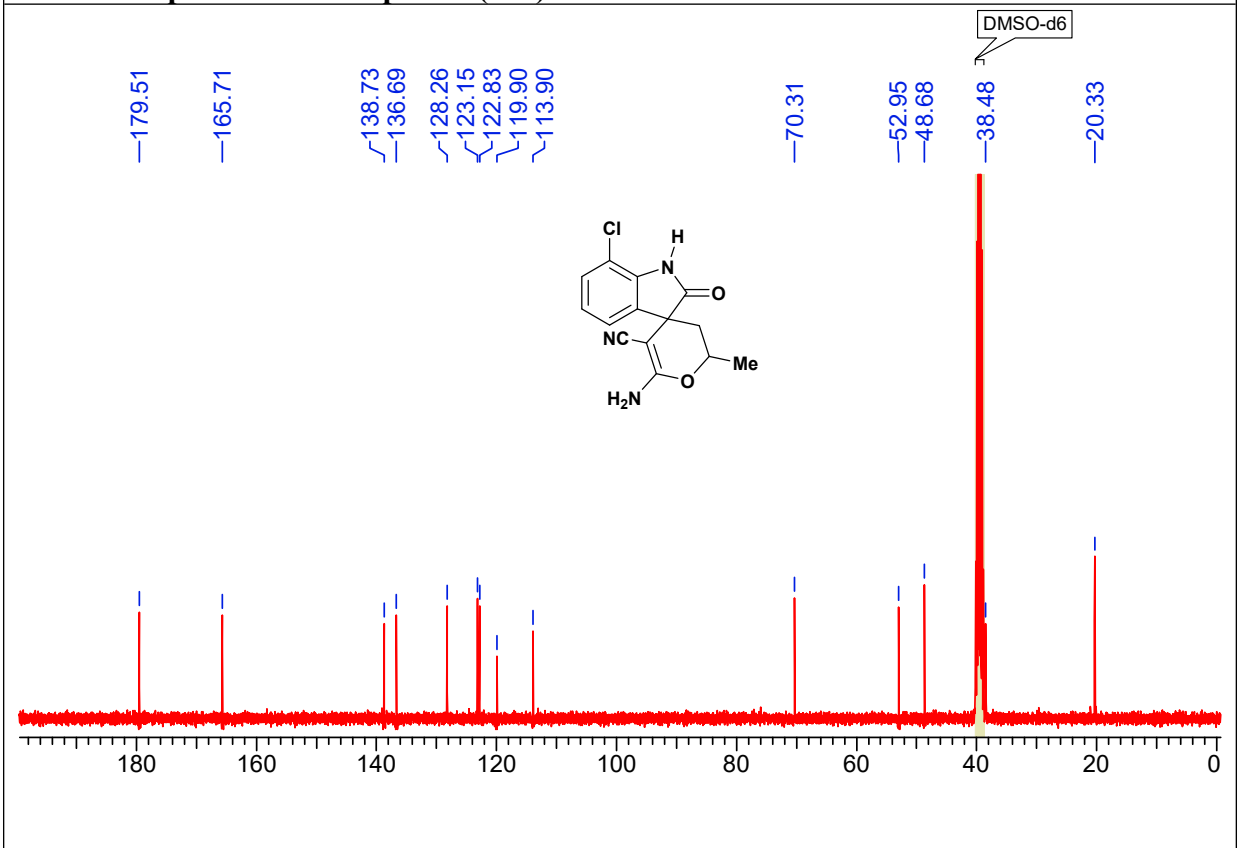

**$^{19}$F NMR spectrum of compound (5Ah)**



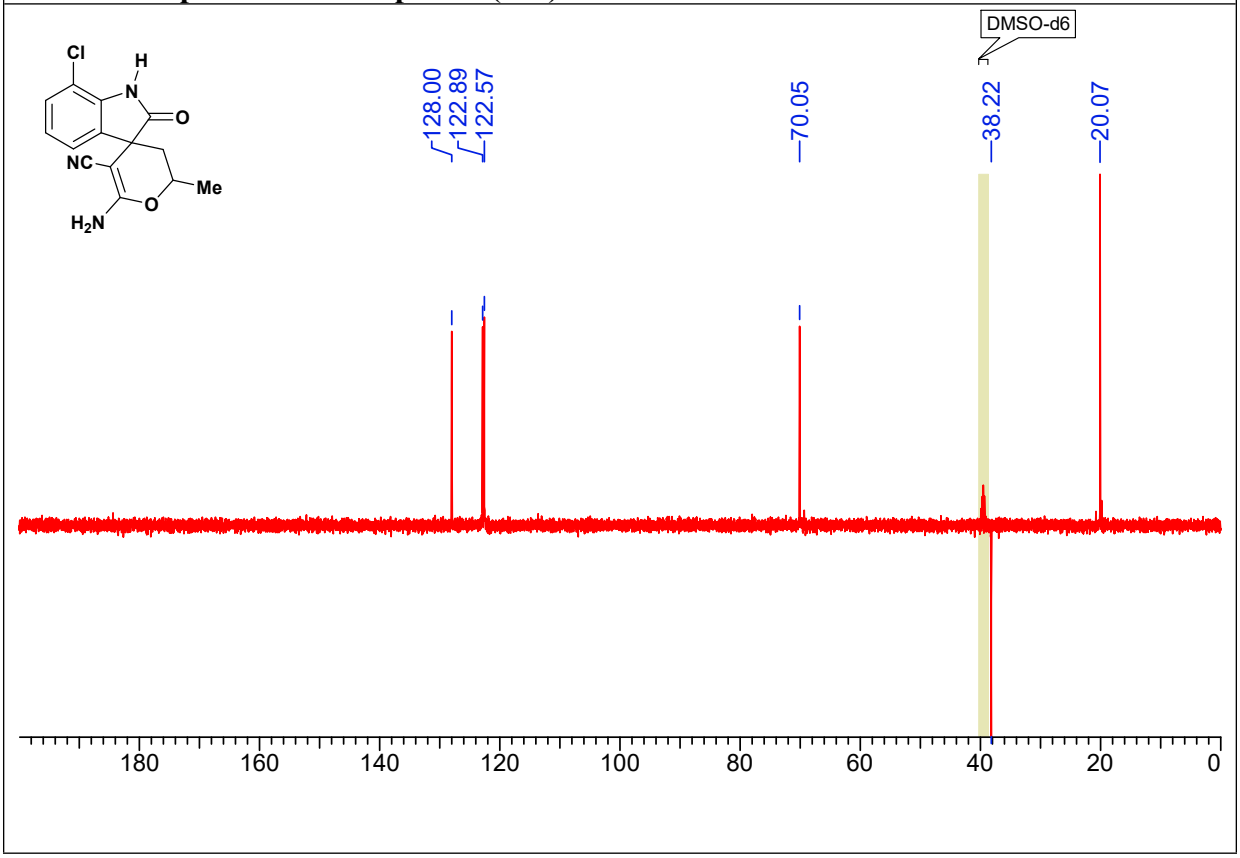
## $^{1}$H NMR spectrum of compound (5Ai)



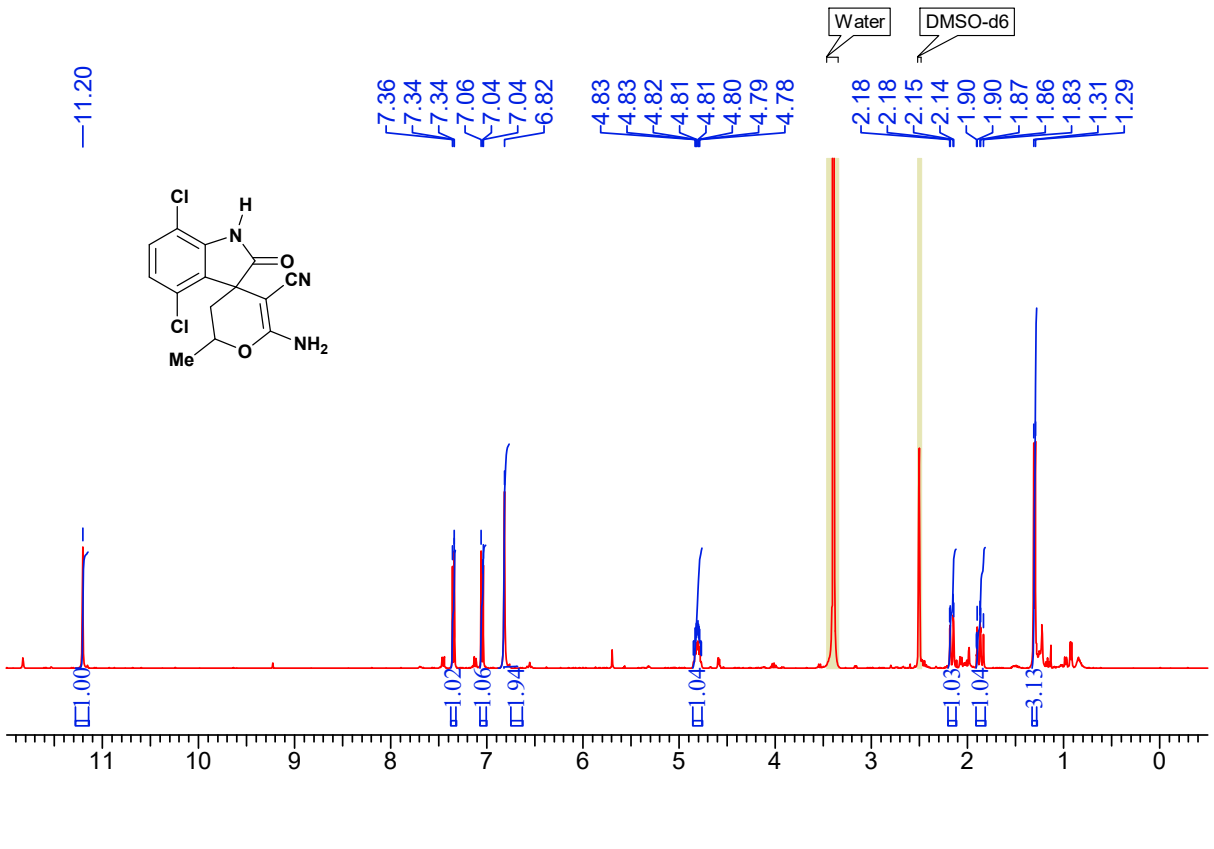

## $^{13}$C NMR spectrum of compound (5Ai)



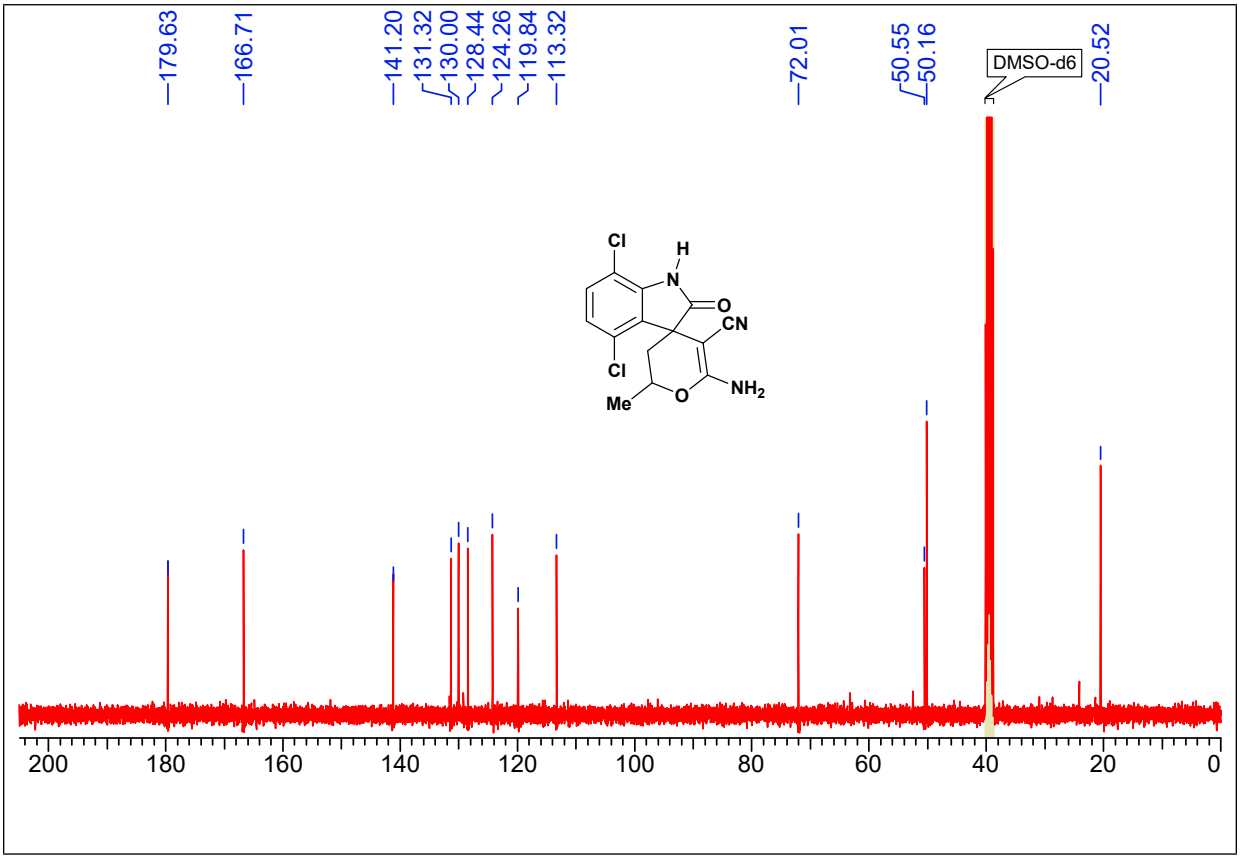
**135 DEPT spectrum of compound (5Ai)**



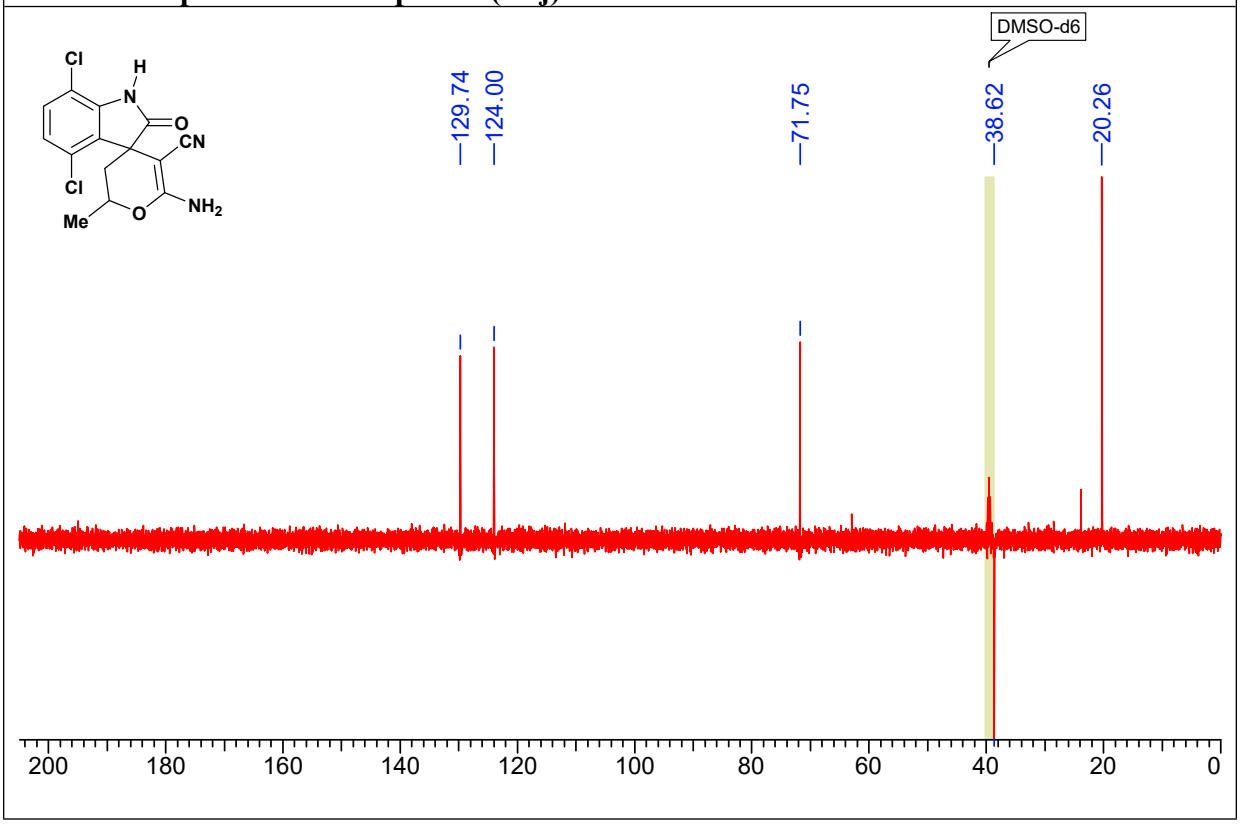
**$^{1}$H NMR spectrum of compound (5Aj)**



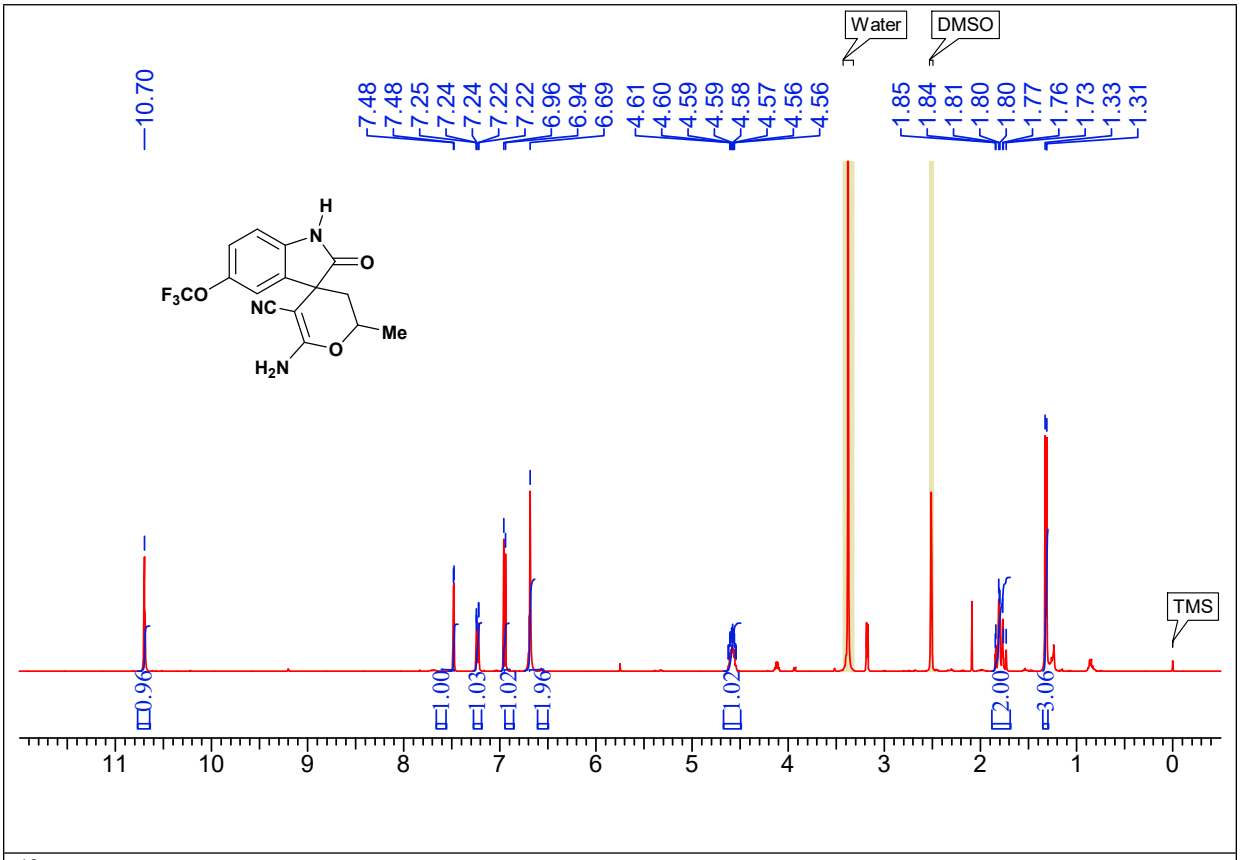

**$^{13}$C NMR spectrum of compound (4Aj)**



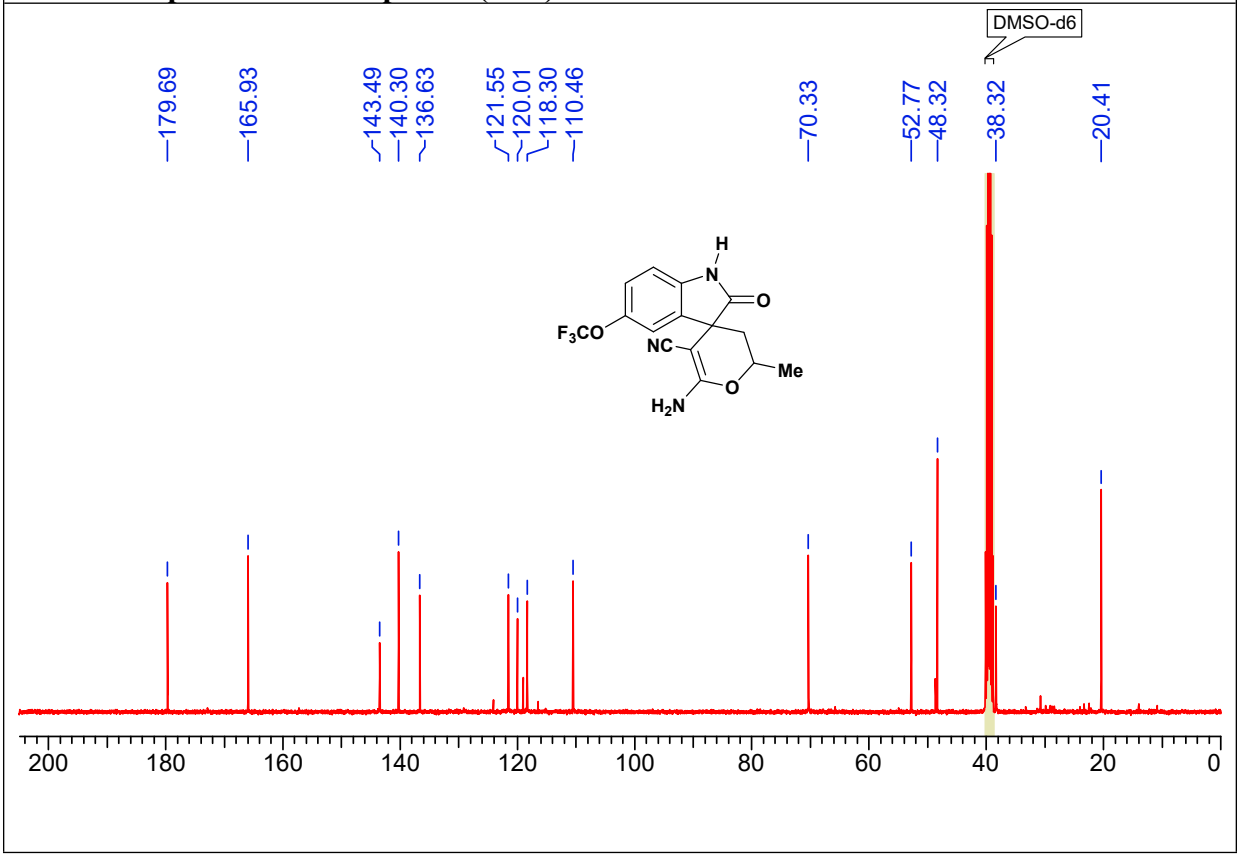

**135 DEPT spectrum of compound (5Aj)**



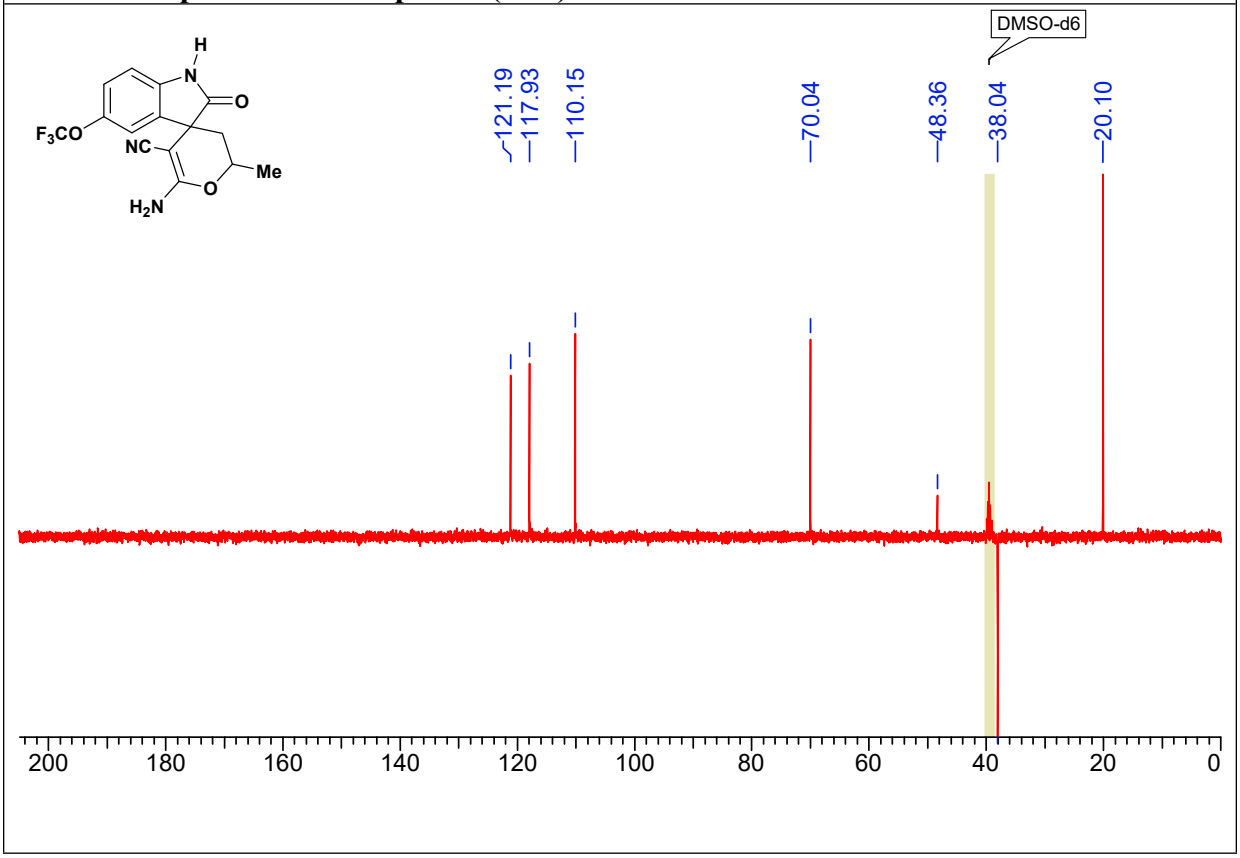
**$^1$H NMR spectrum of compound (5Ak)**



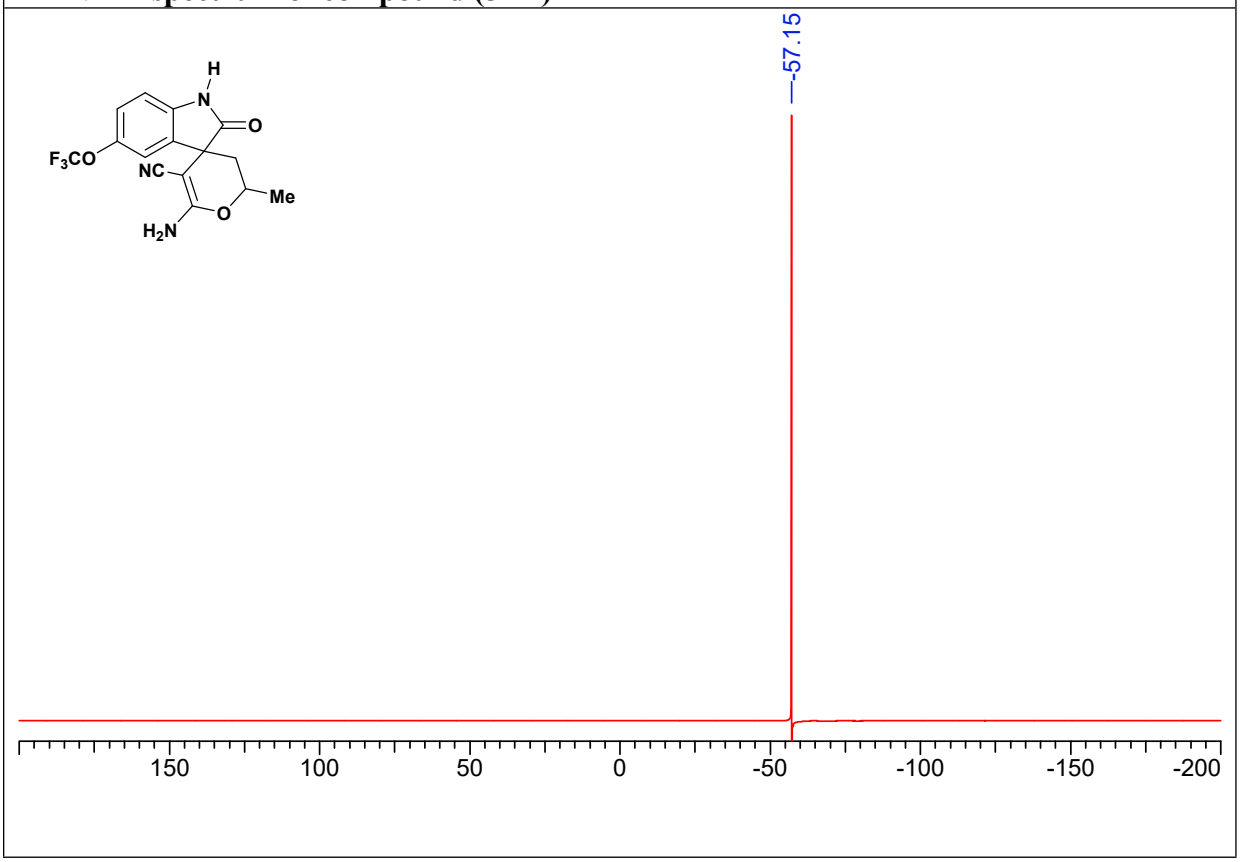

**$^{13}$C NMR spectrum of compound (5Ak)**



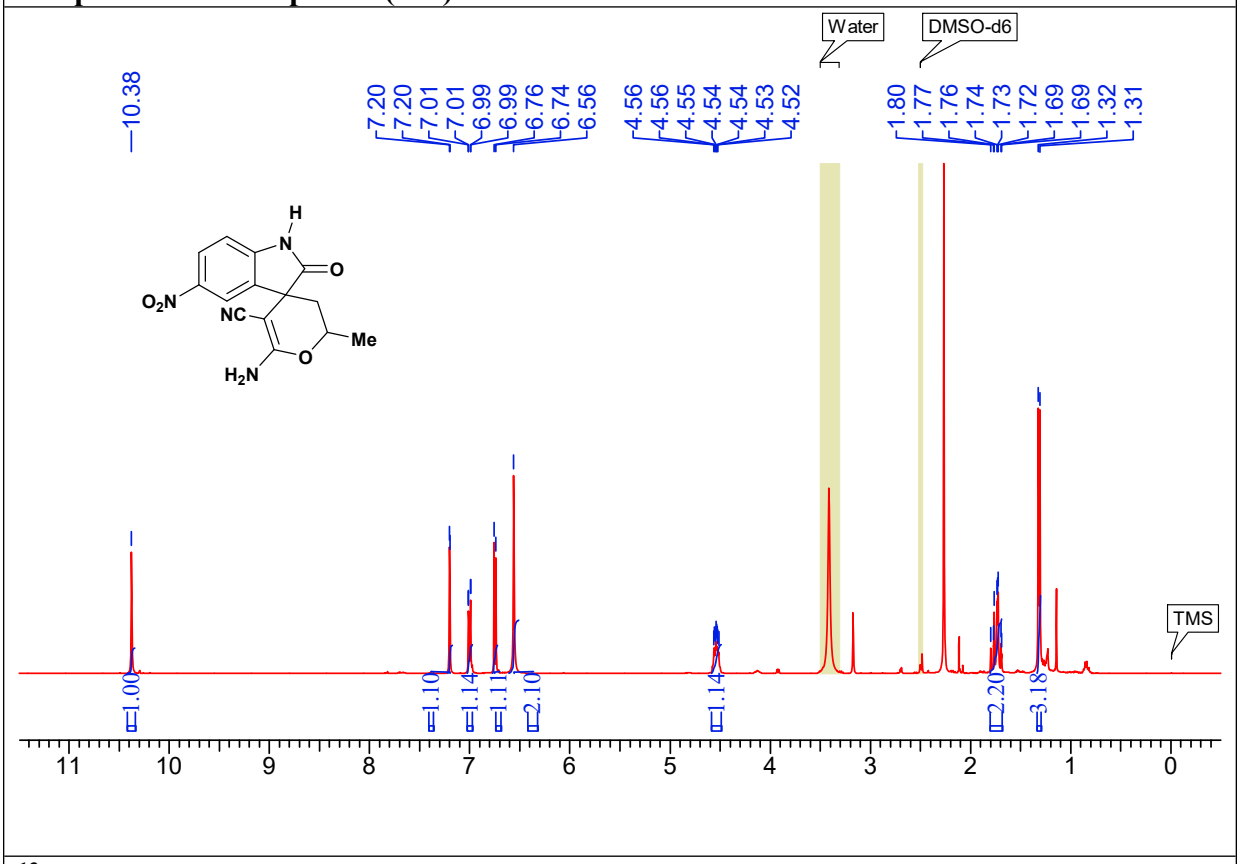
## 135 DEPT spectrum of compound (5Ak)



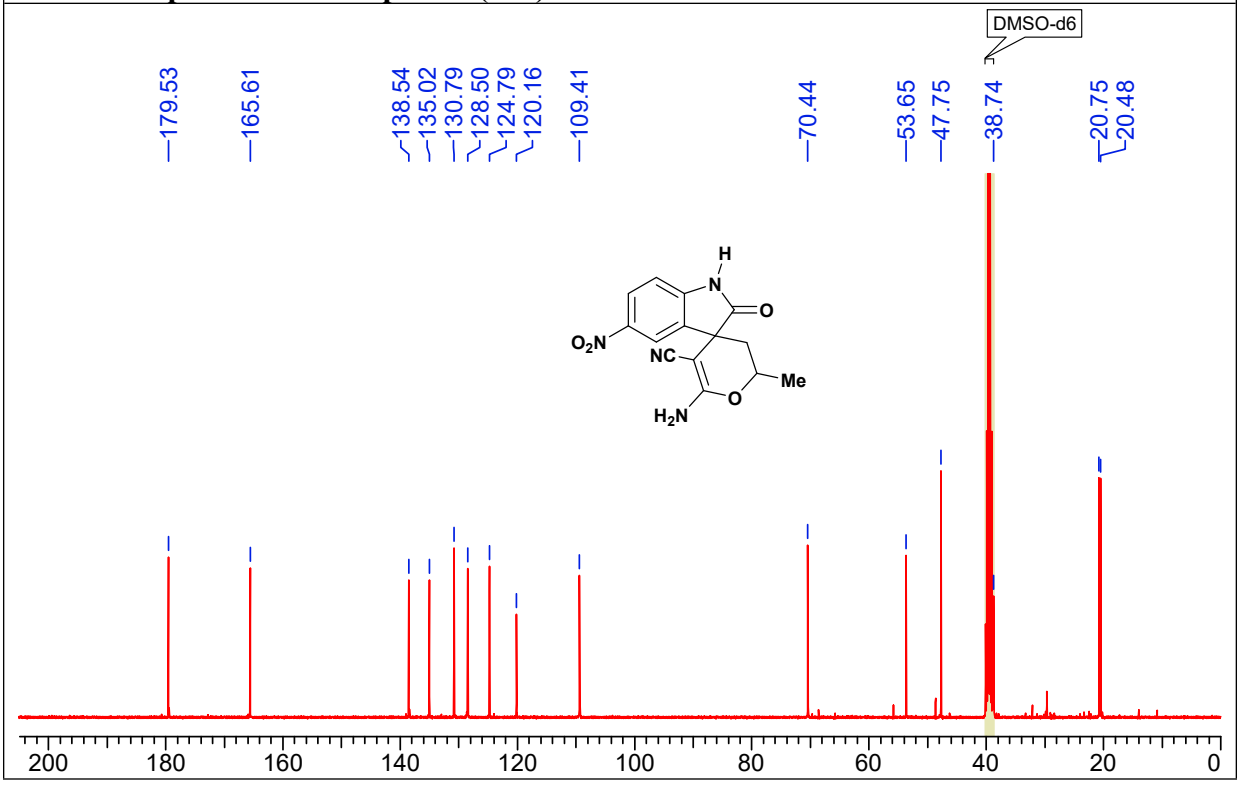

## $^{19}$F NMR spectrum of compound (5Ak)



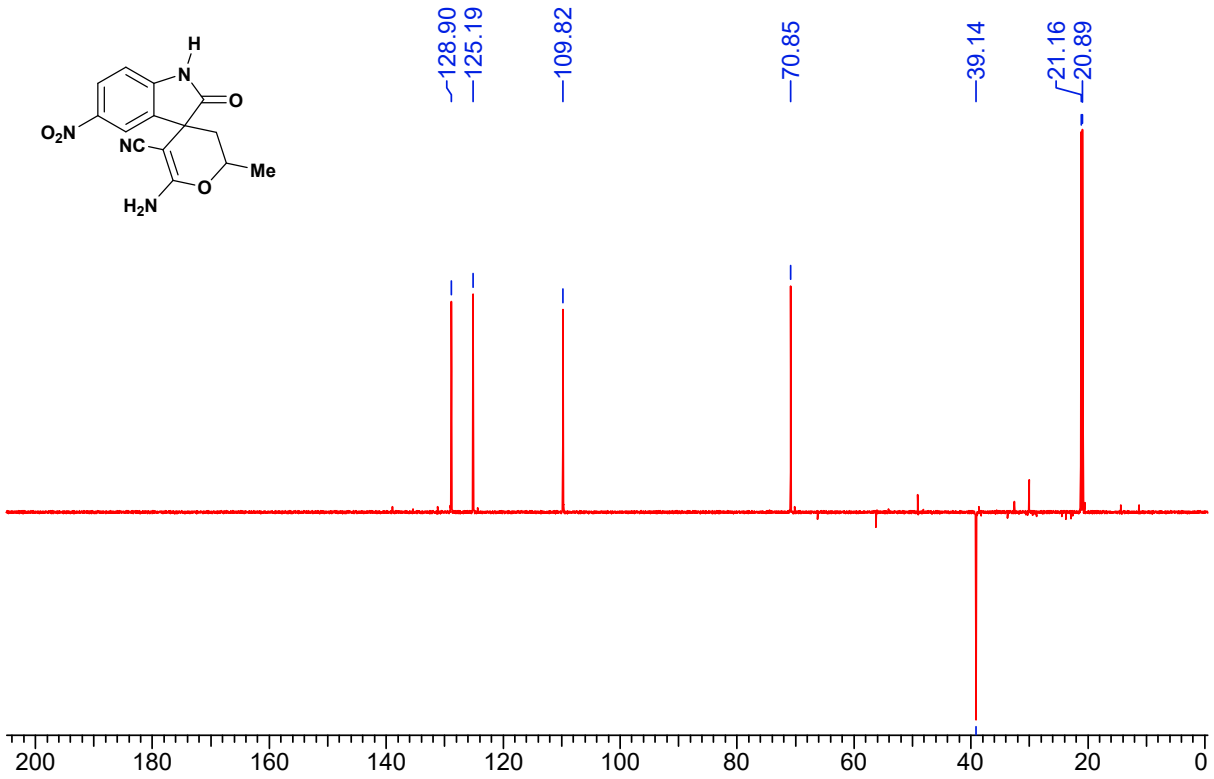
**$^{1}$H spectrum of compound (5Al)**



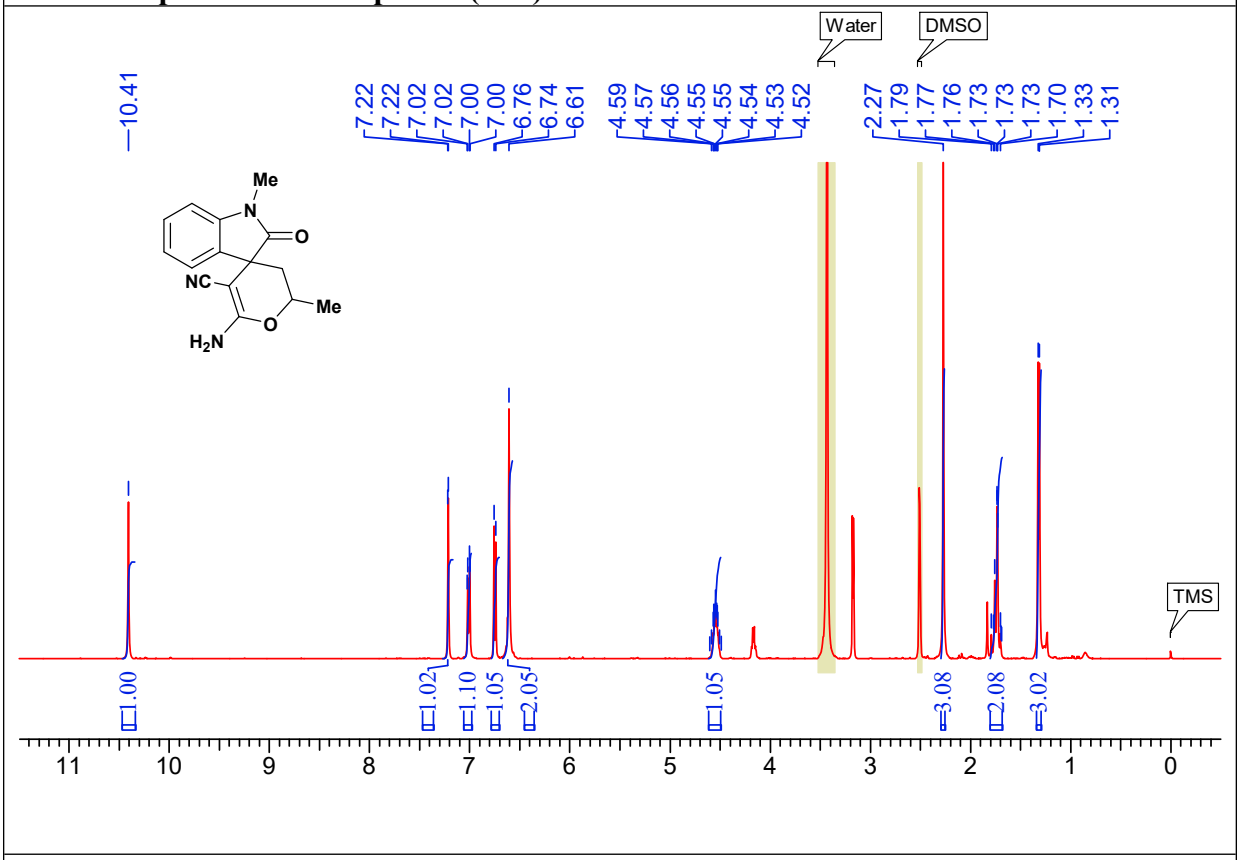

**$^{13}$C NMR spectrum of compound (5Al)**



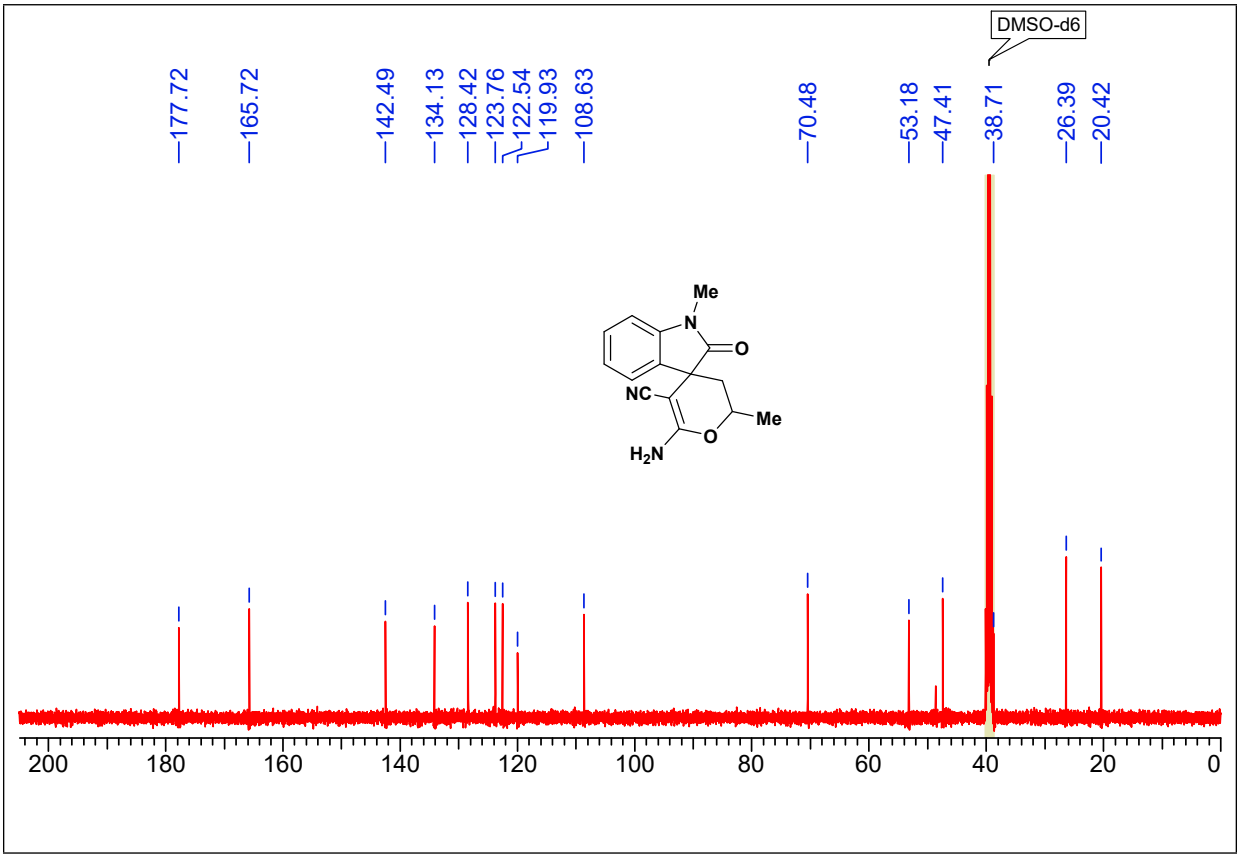
**135 DEPT spectrum of compound (5Al)**



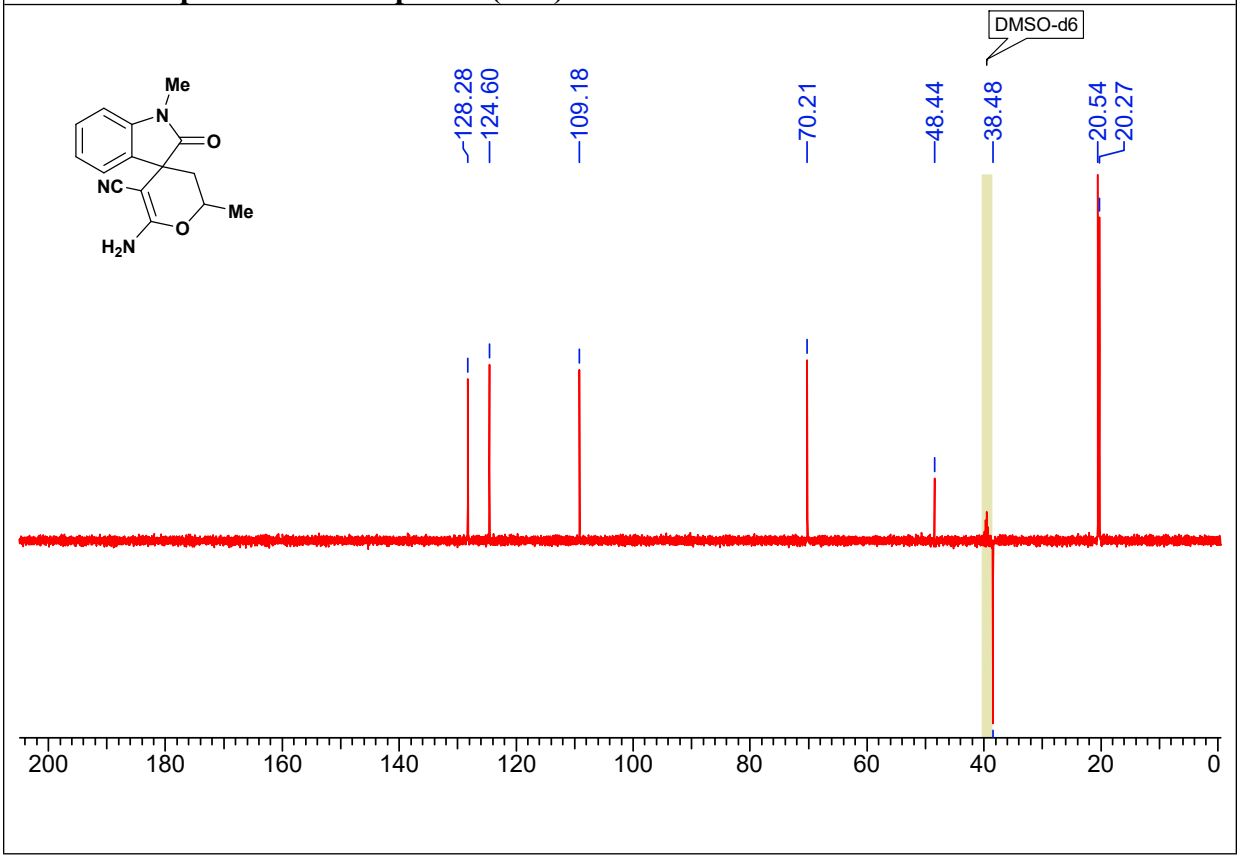
**$^{1}$H NMR spectrum of compound (5Ba)**



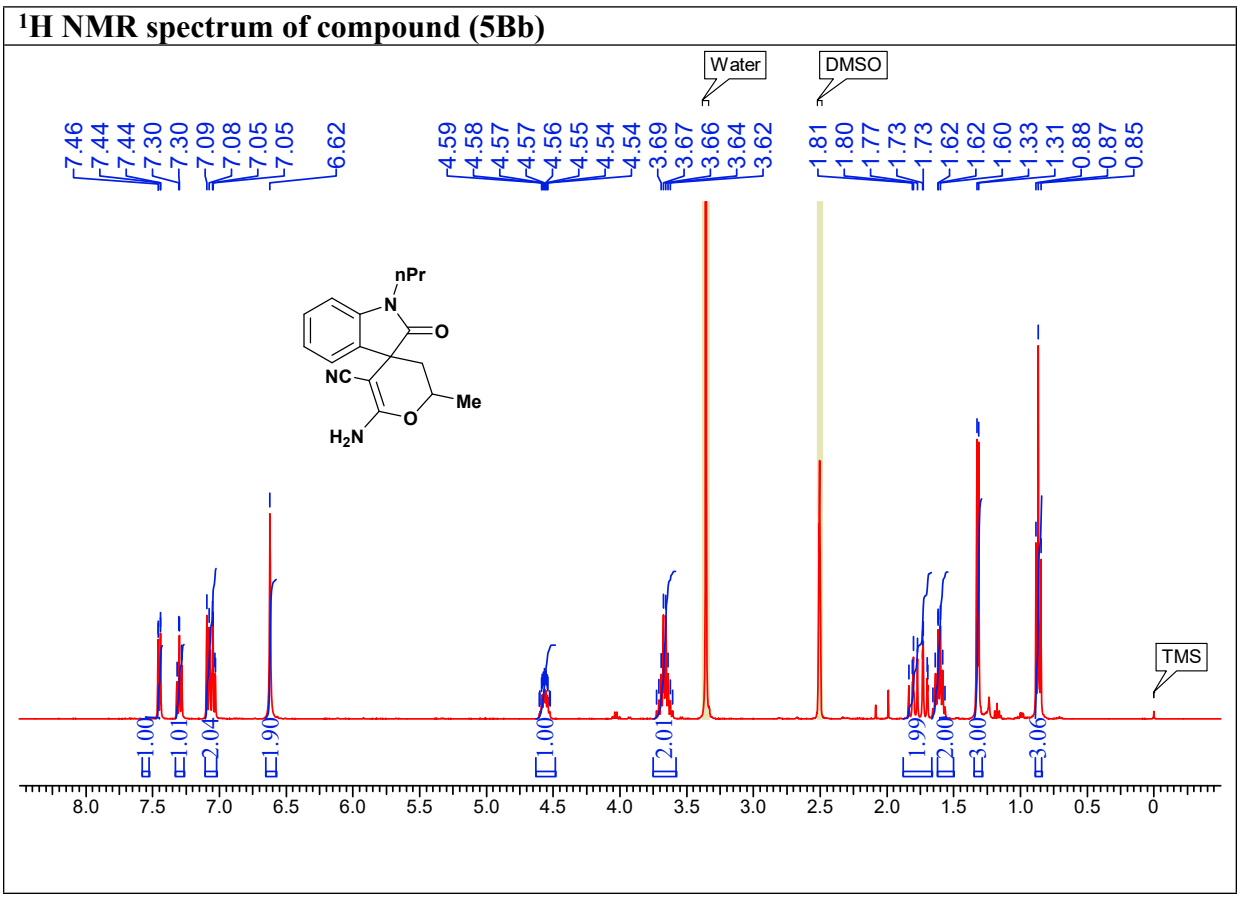

**$^{13}$C NMR spectrum of compound (5Ba)**



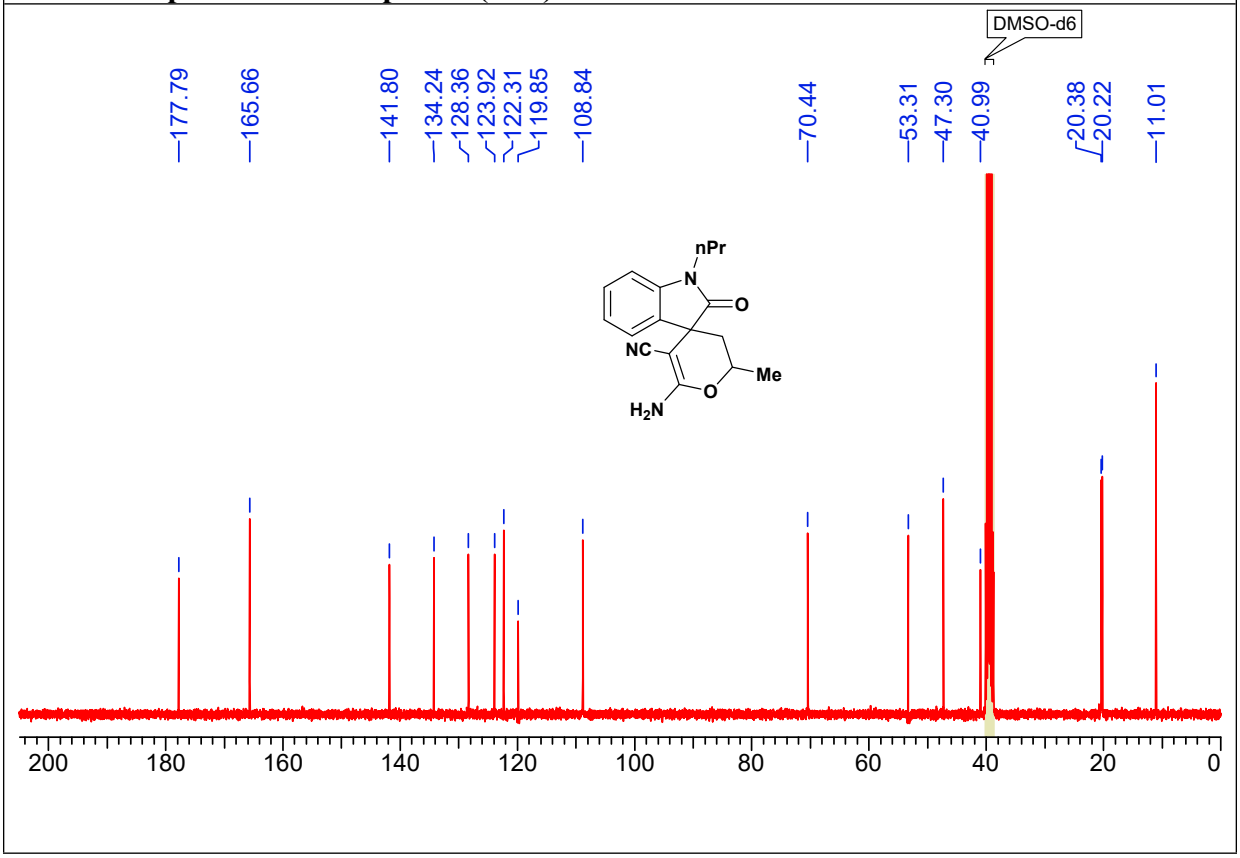

**135 DEPT spectrum of compound (5Ba)**



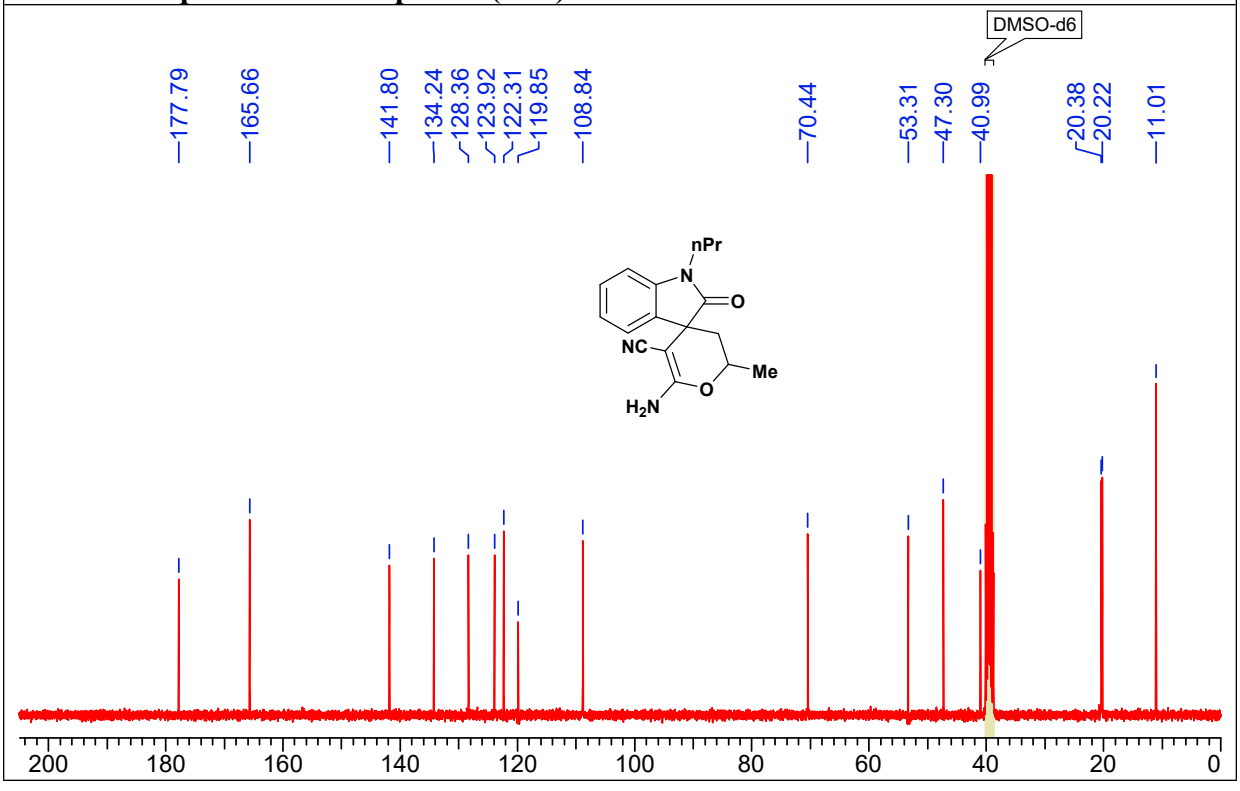
**$^1$H NMR spectrum of compound (5Bb)**



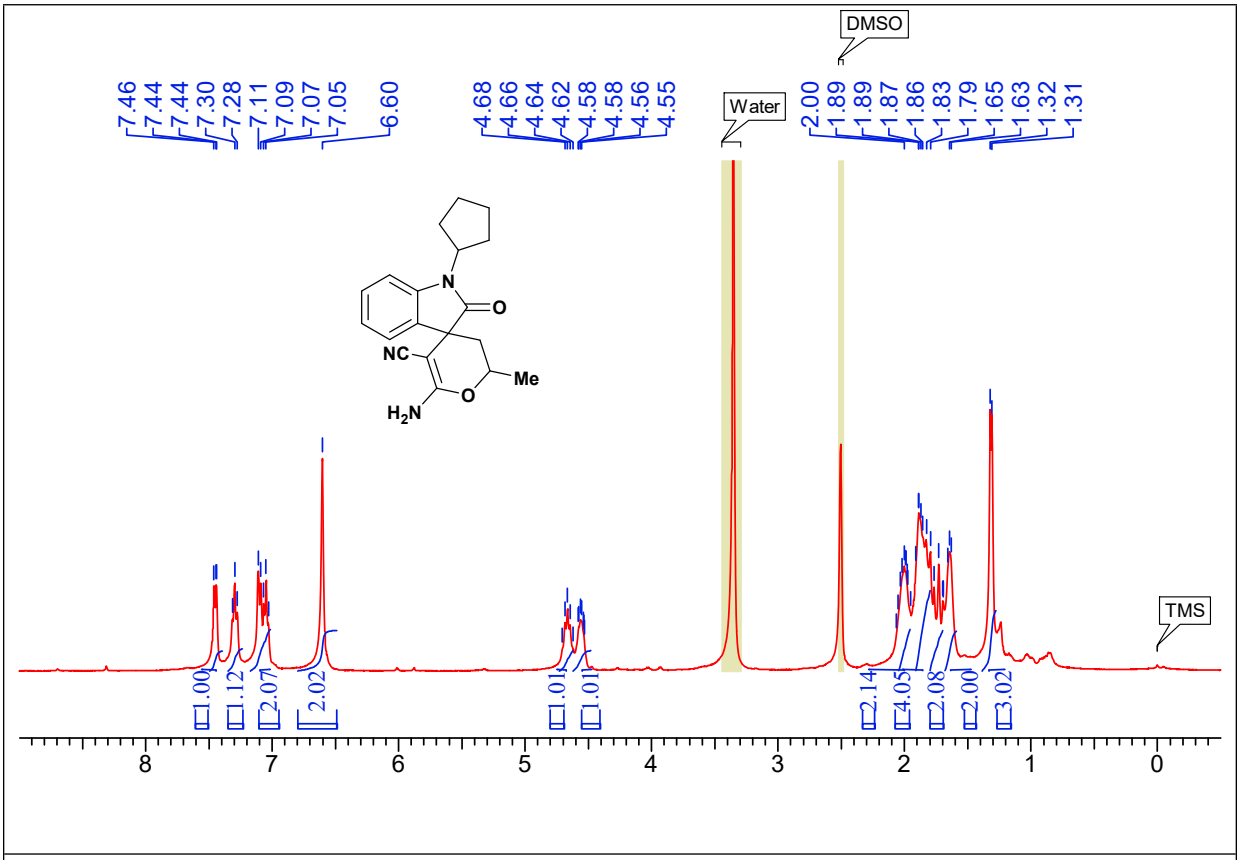
## $^{13}$C NMR spectrum of compound (5Bb)



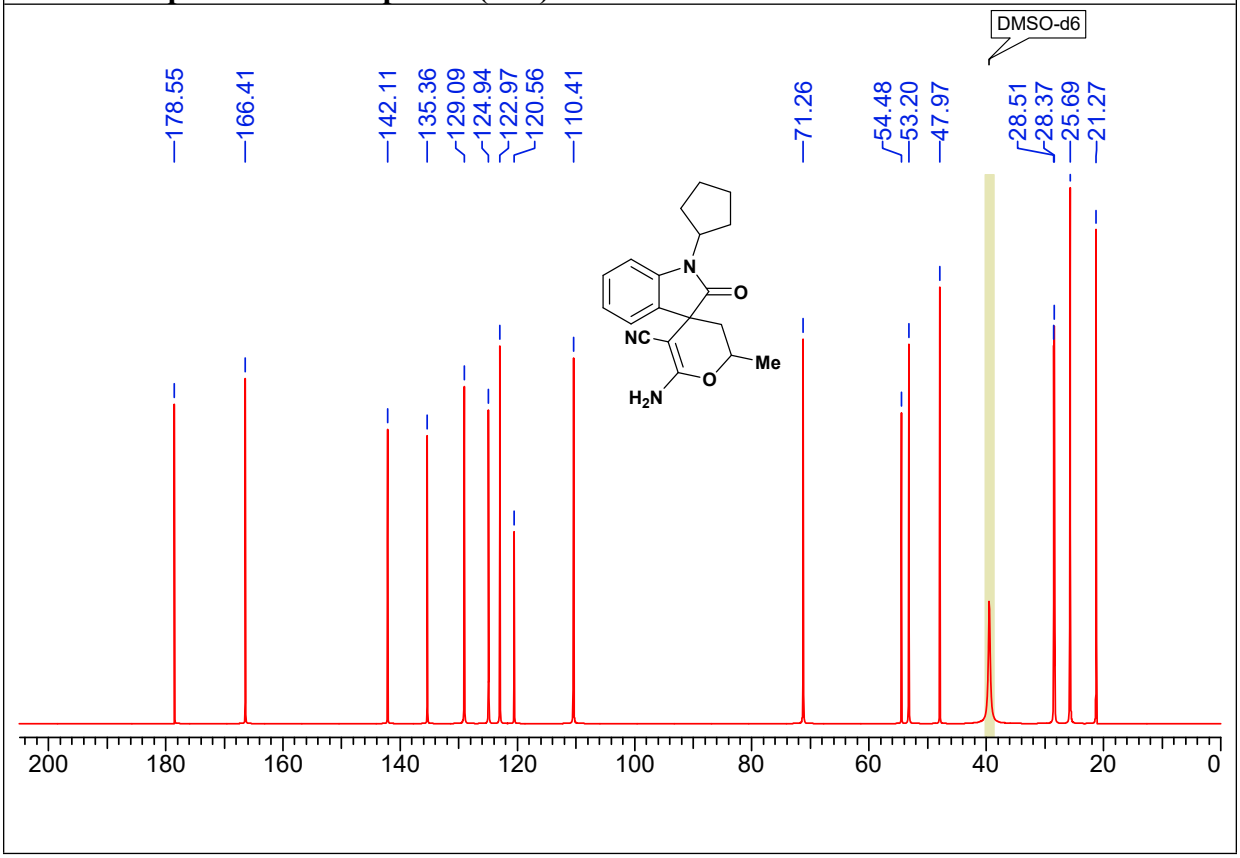

## 135 DEPT spectrum of compound (5Bb)



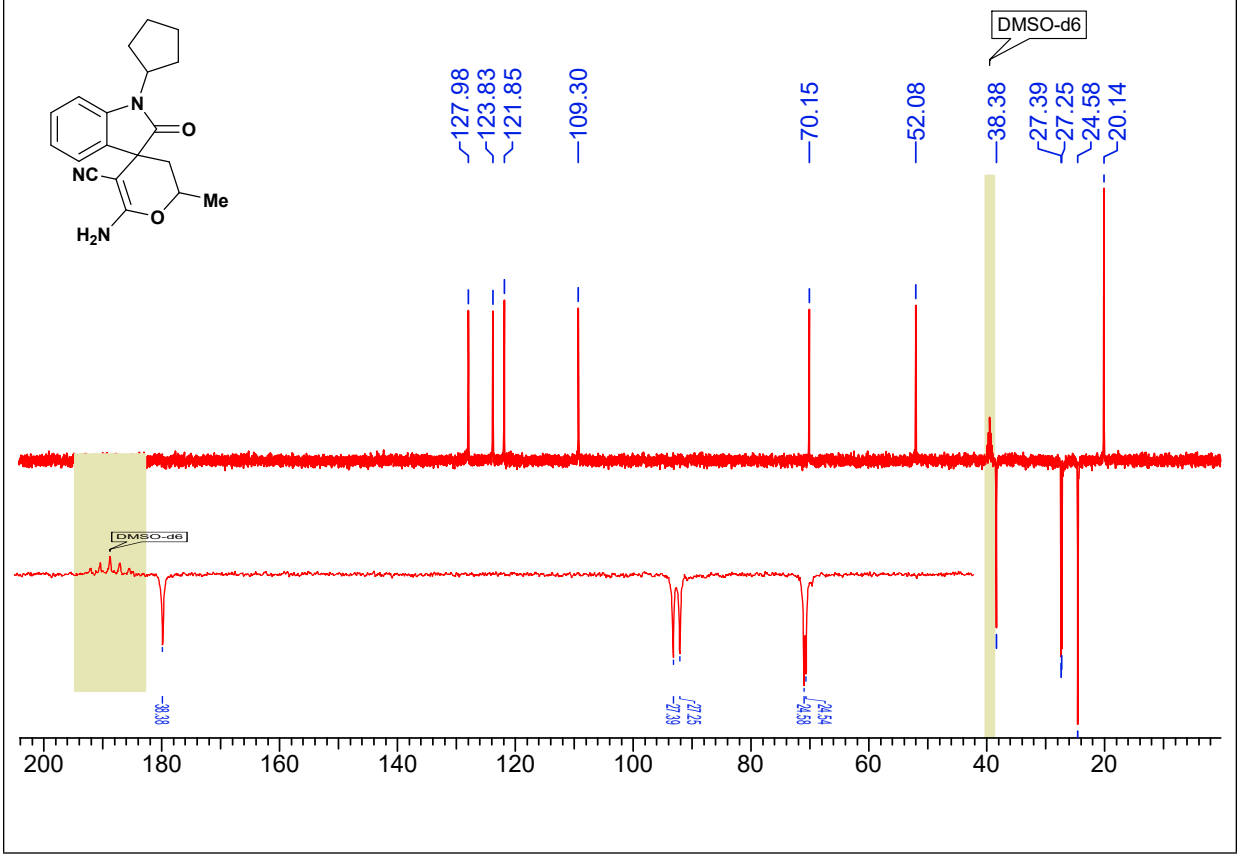
**$^{1}$H NMR spectrum of compound (5Bc)**



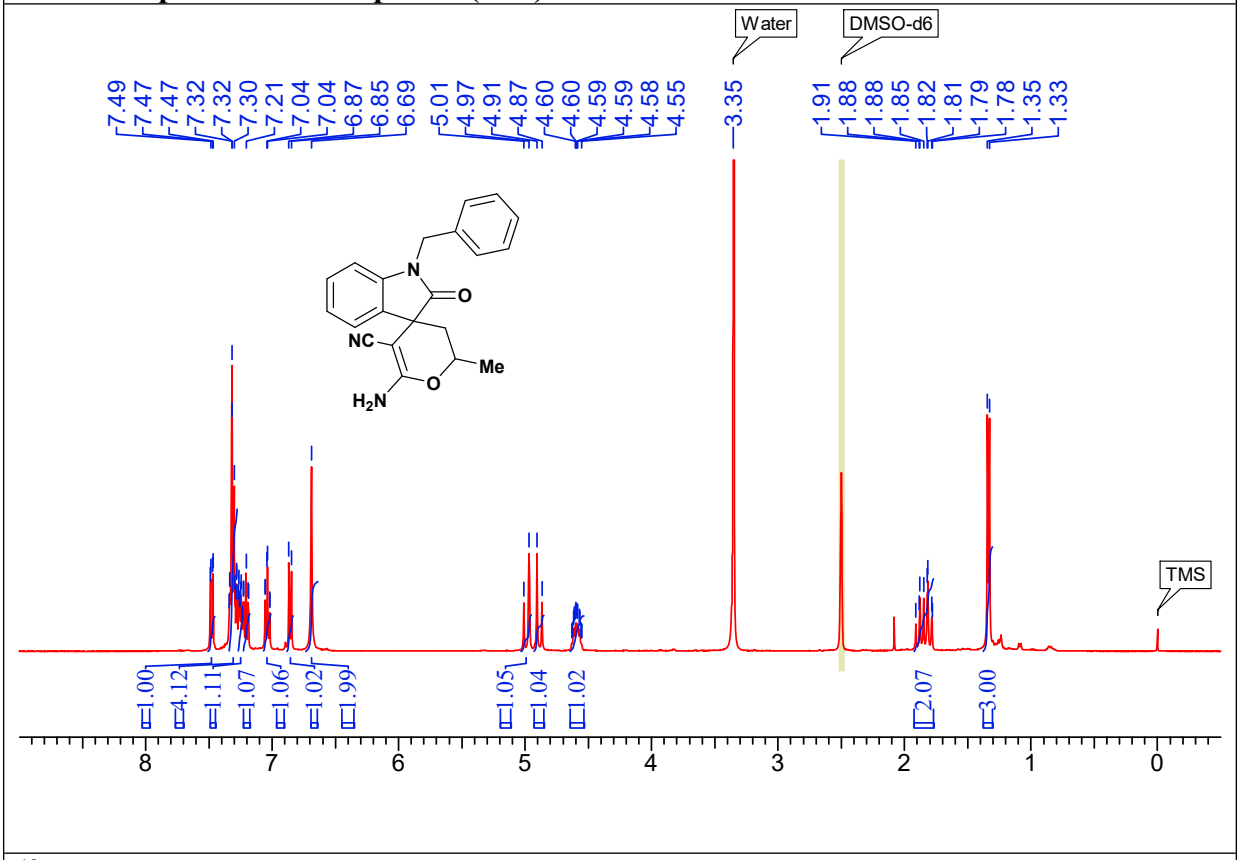

**$^{13}$C NMR spectrum of compound (5Bc)**



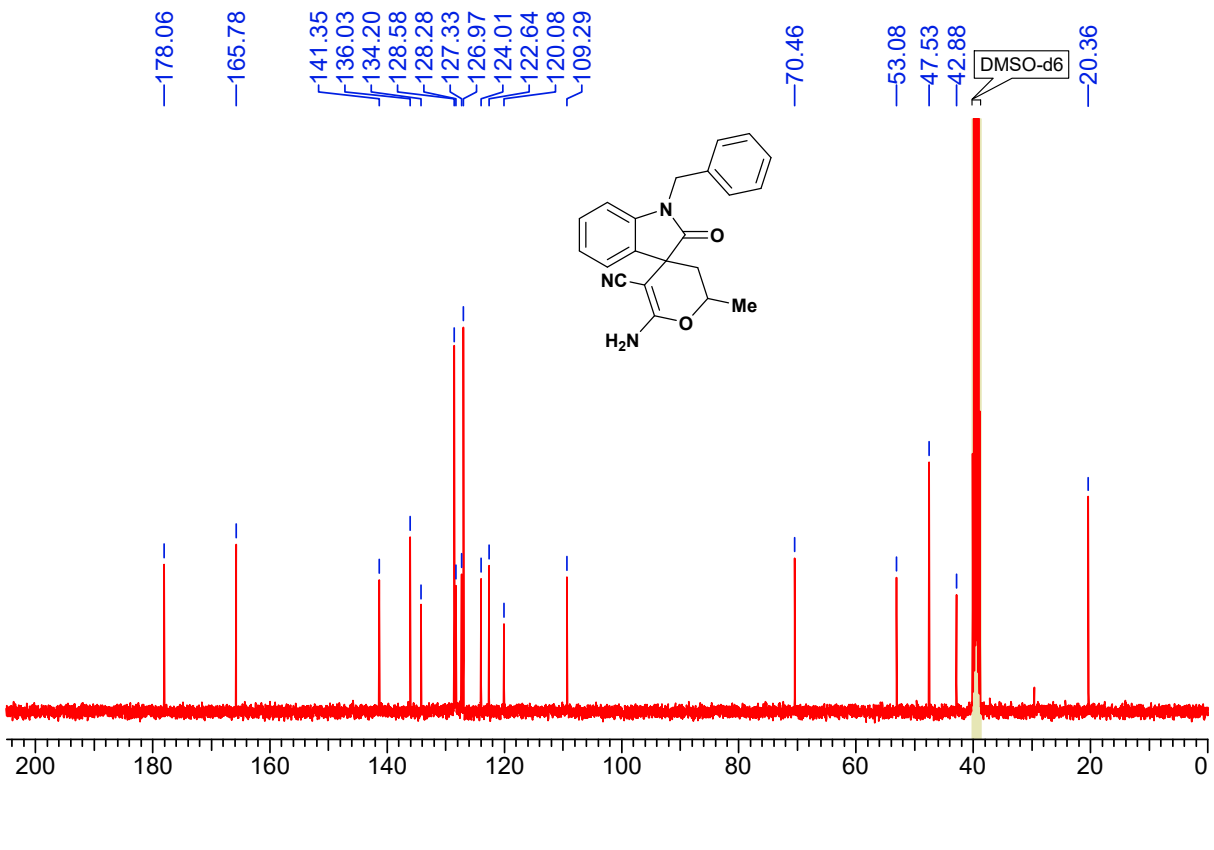
**135 DEPT spectrum of compound (5Bc)**



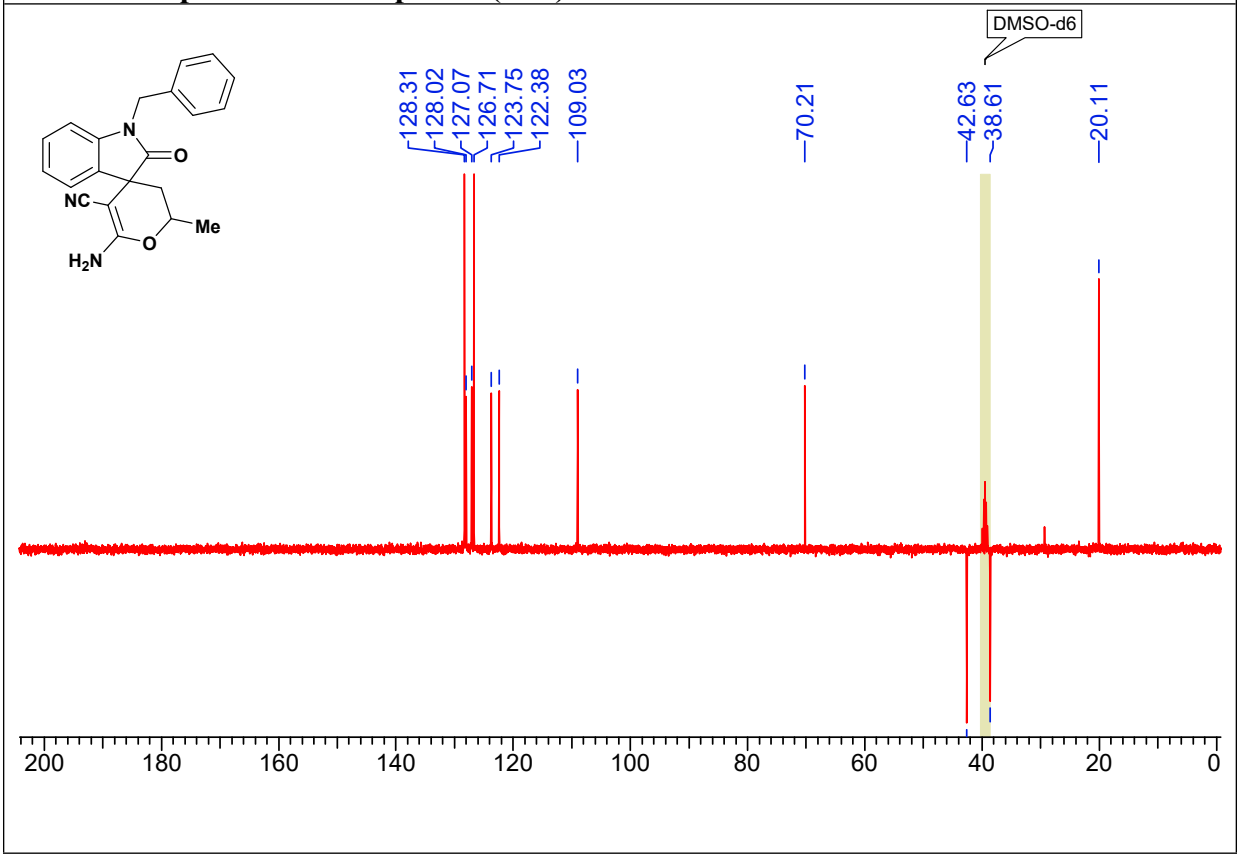
## $^{1}$H NMR spectrum of compound (5Bd)



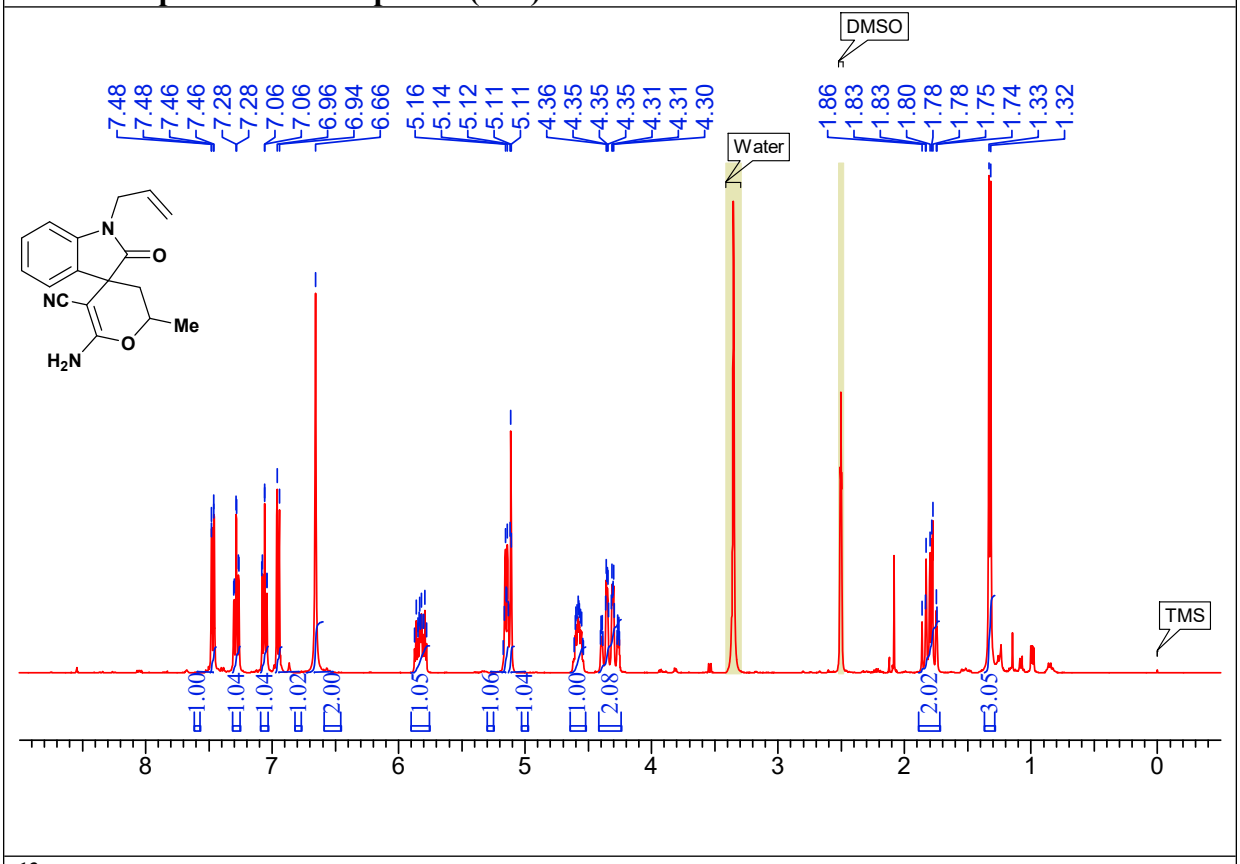

## $^{13}$C NMR spectrum of compound (5Bd)



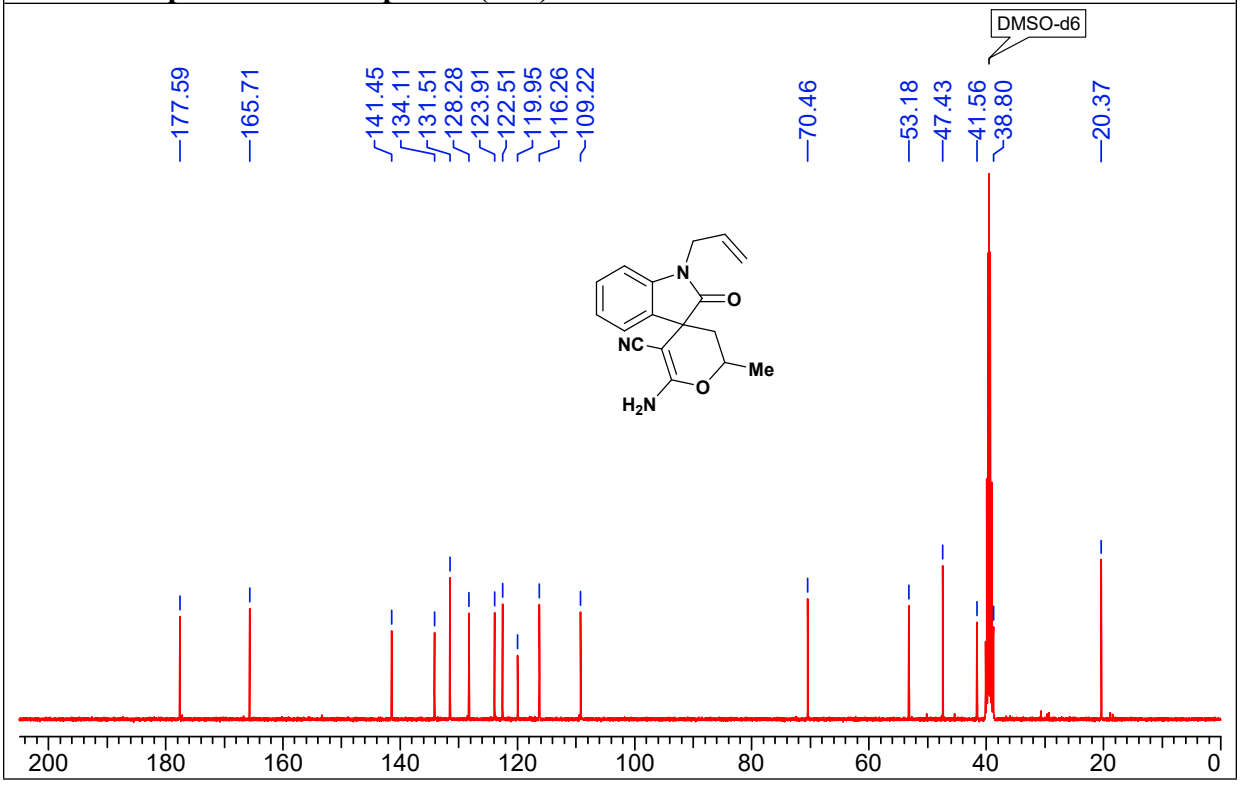
**135 DEPT spectrum of compound (5Bd)**



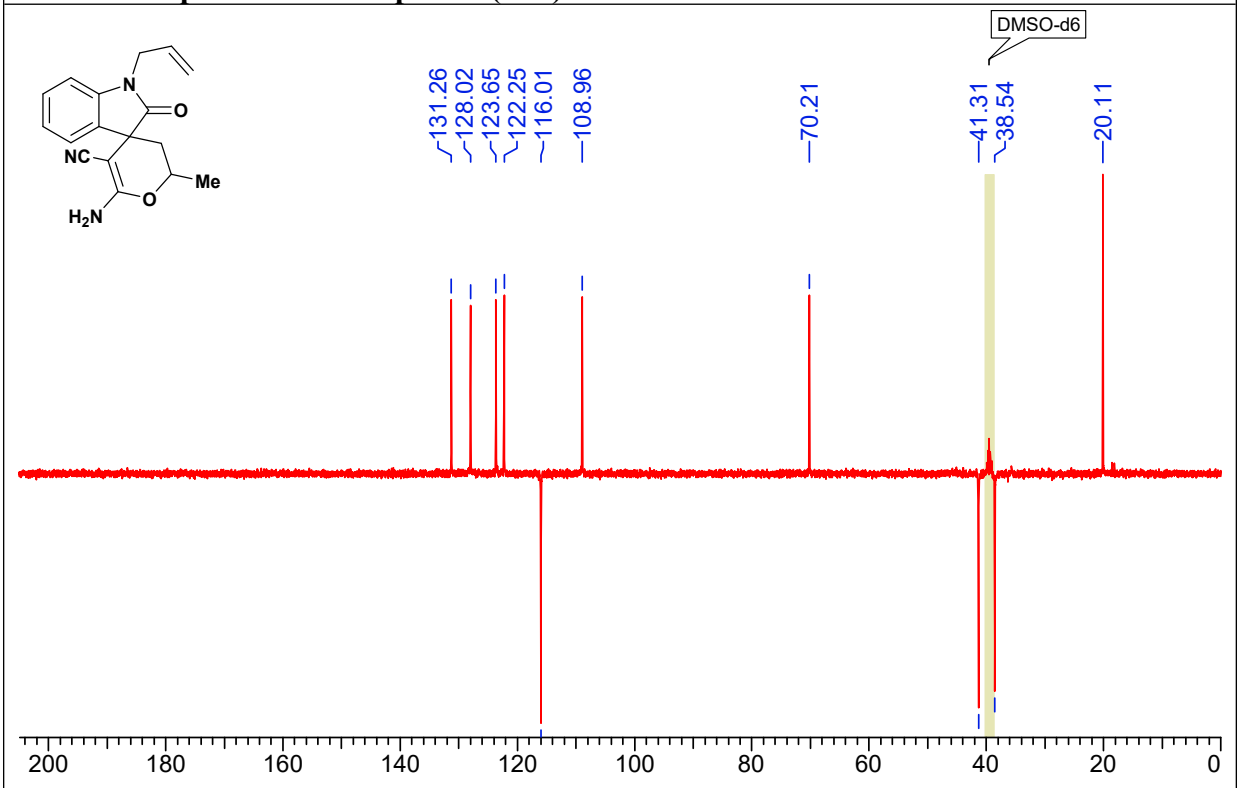
**$^{1}$H NMR spectrum of compound (5Be)**



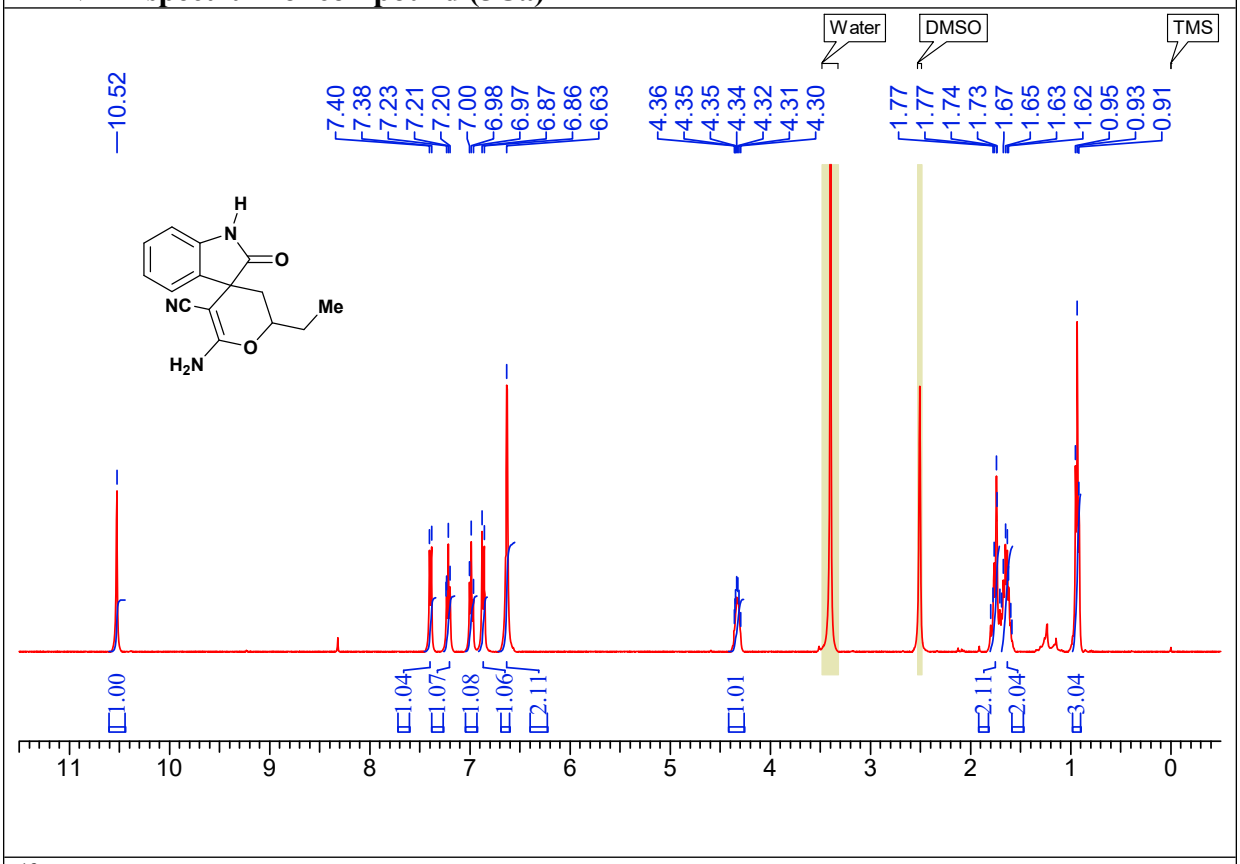

**$^{13}$C NMR spectrum of compound (5Be)**



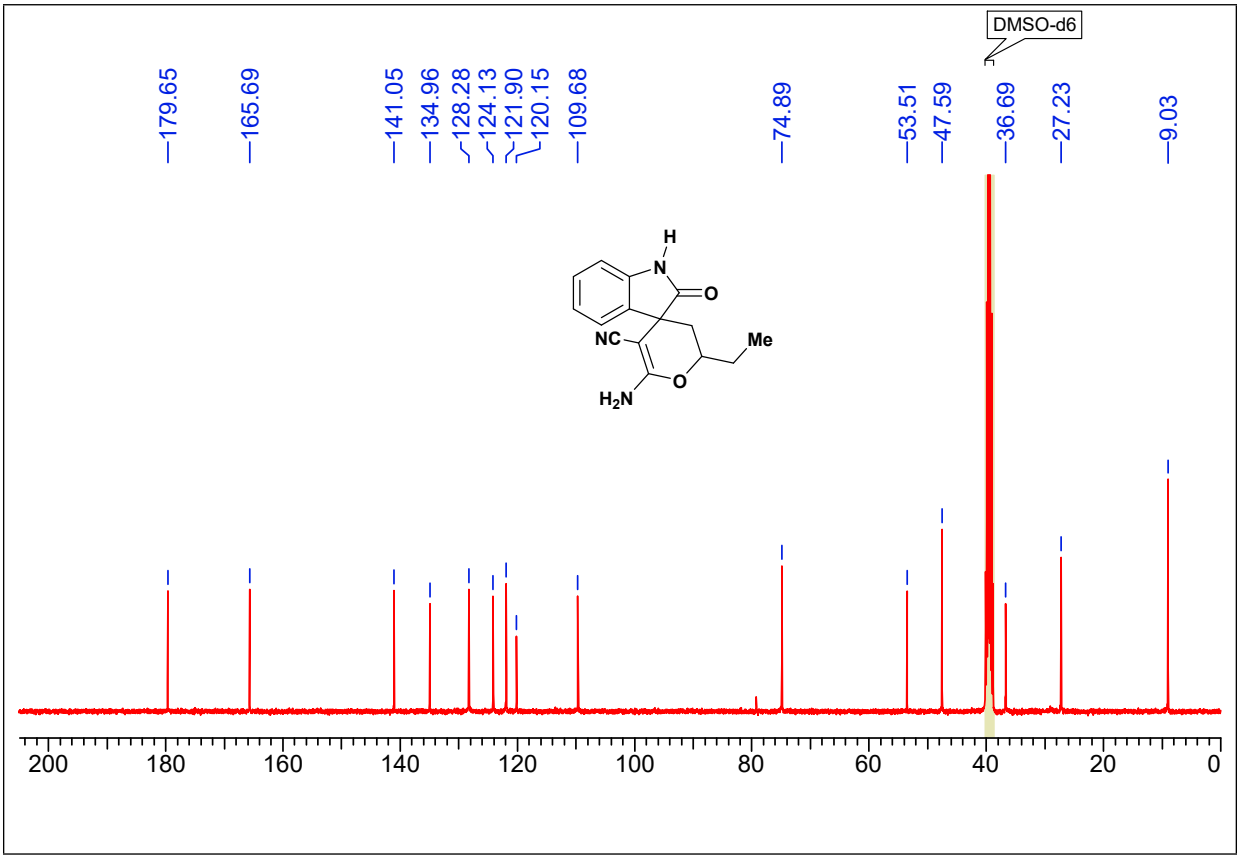
**135 DEPT spectrum of compound (5Be)**



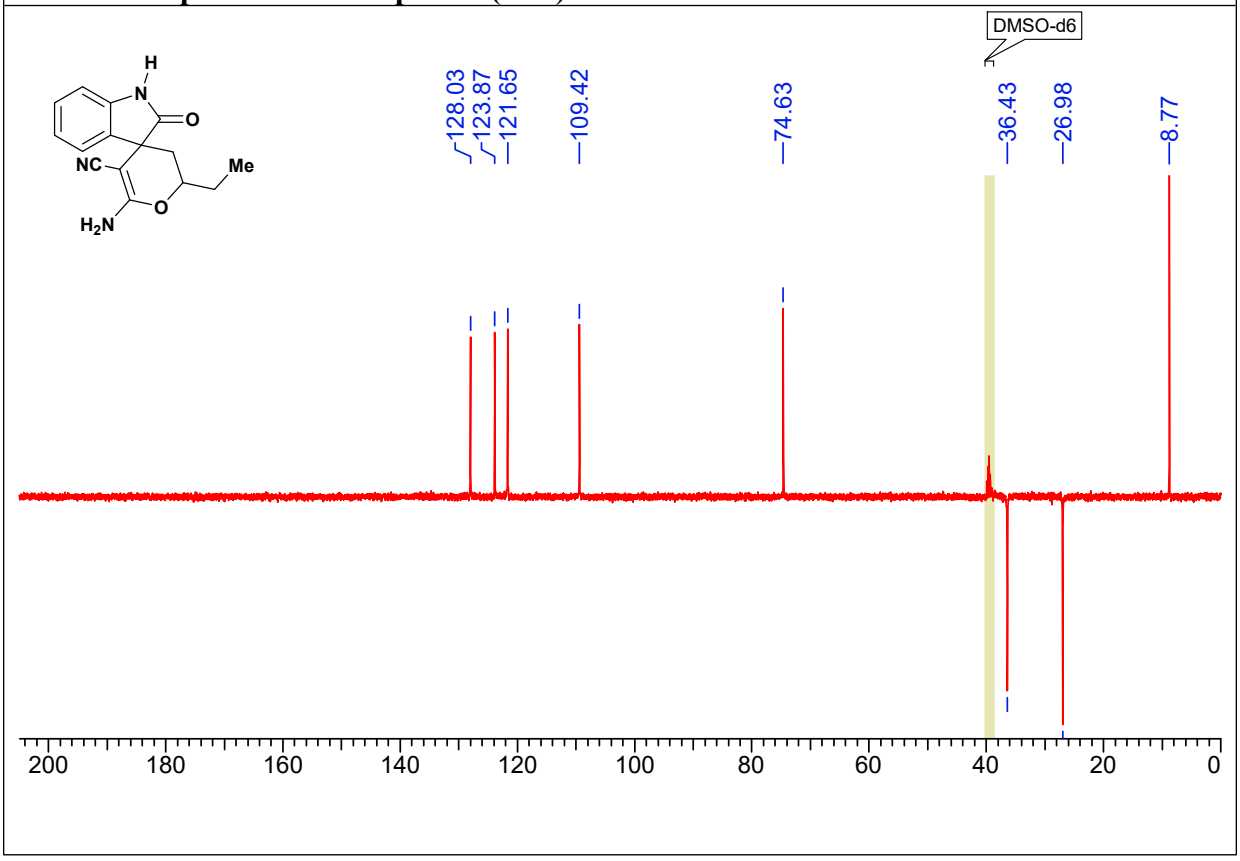
**$^{1}$H NMR spectrum of compound (5Ca)**



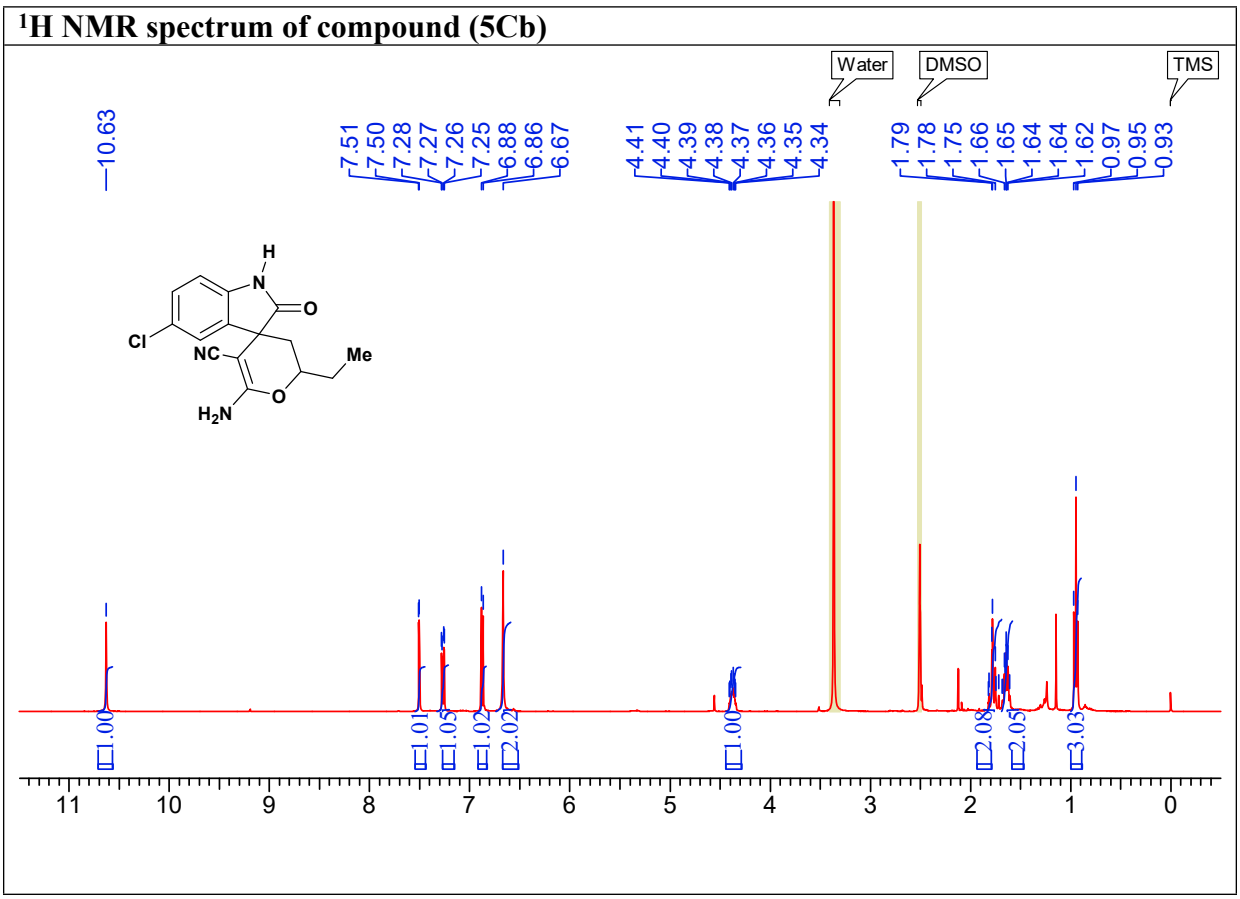

**$^{13}$C NMR spectrum of compound (5Ca)**



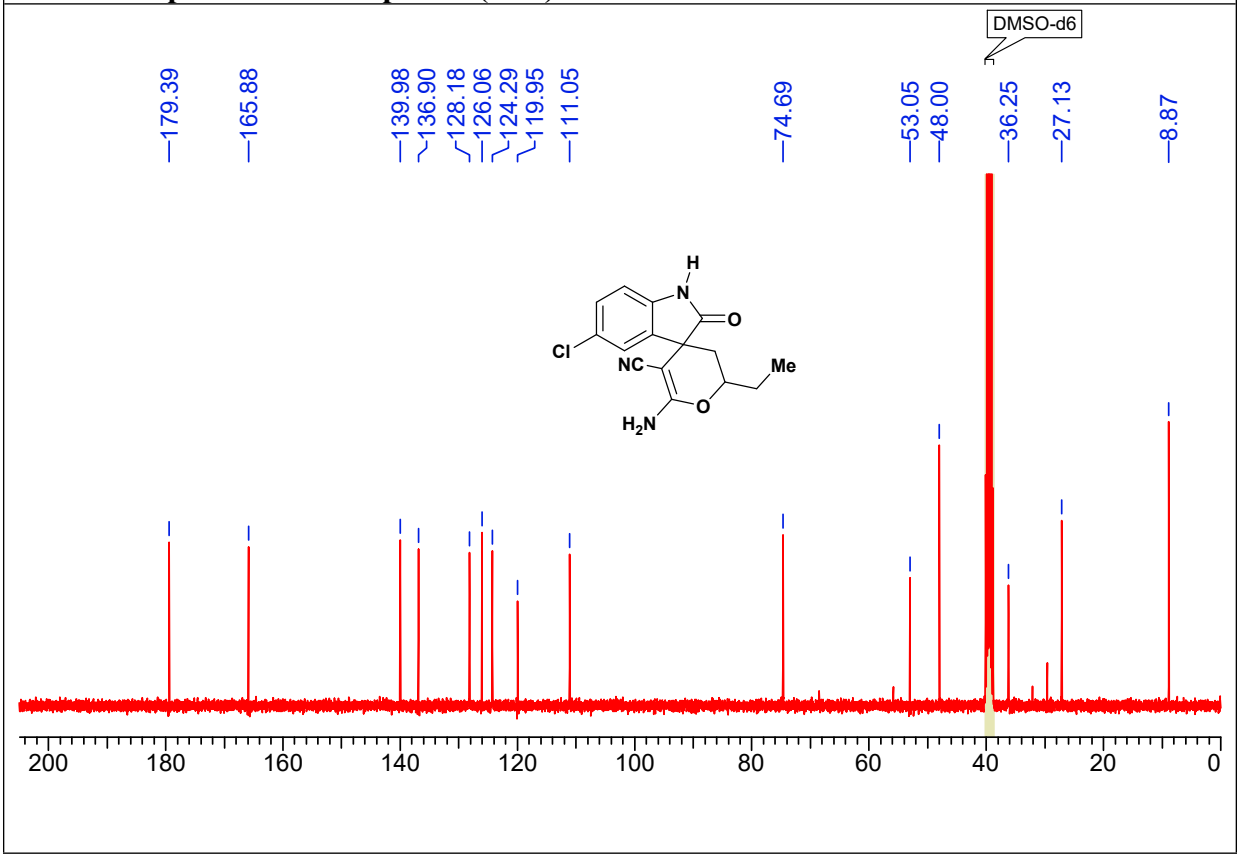

**135 DEPT spectrum of compound (5Ca)**



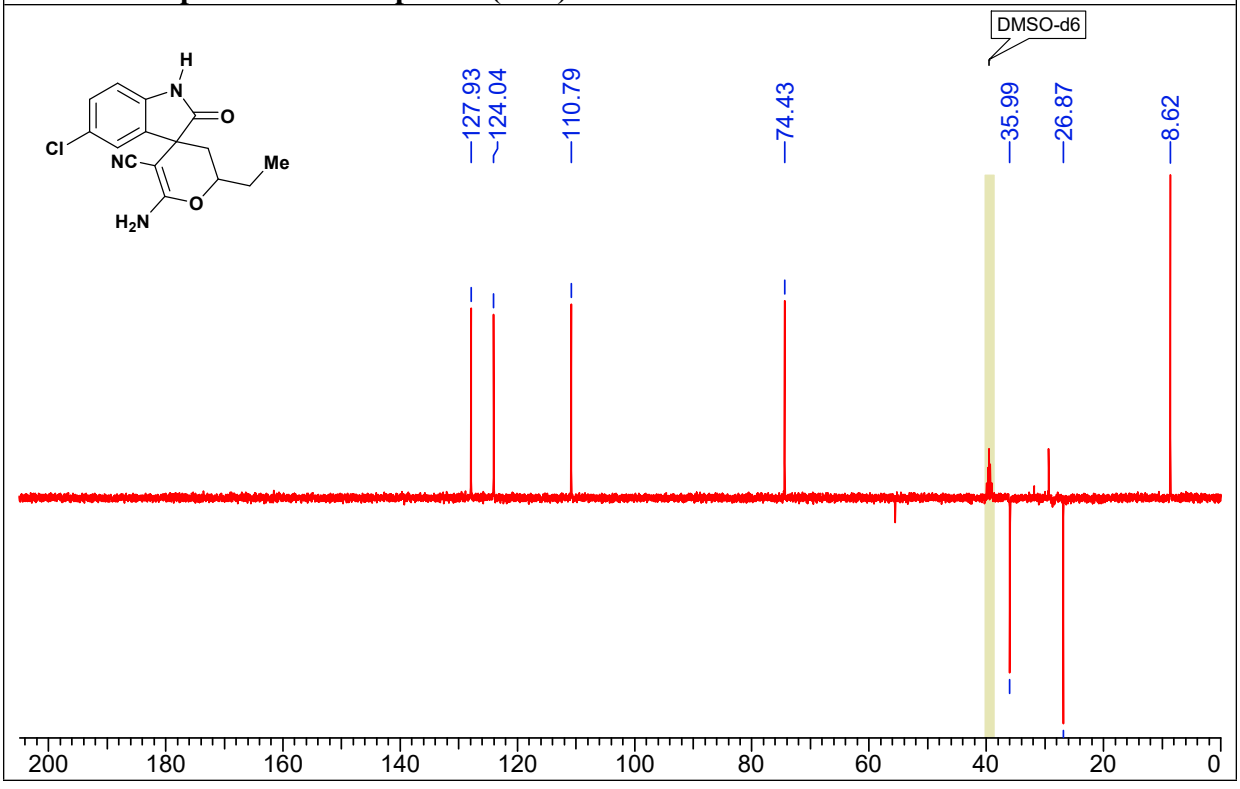
**$^1$H NMR spectrum of compound (5Cb)**



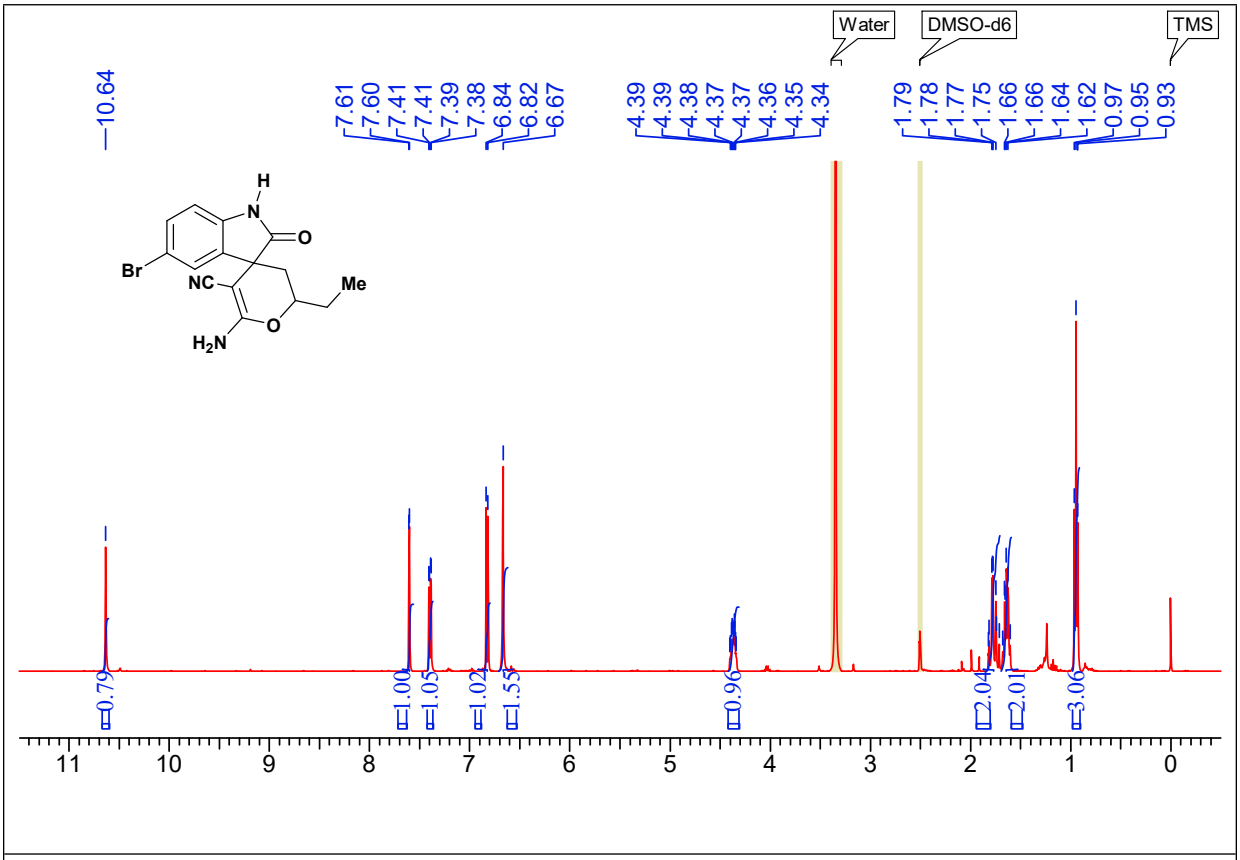
## $^{13}$C NMR spectrum of compound (5Cb)



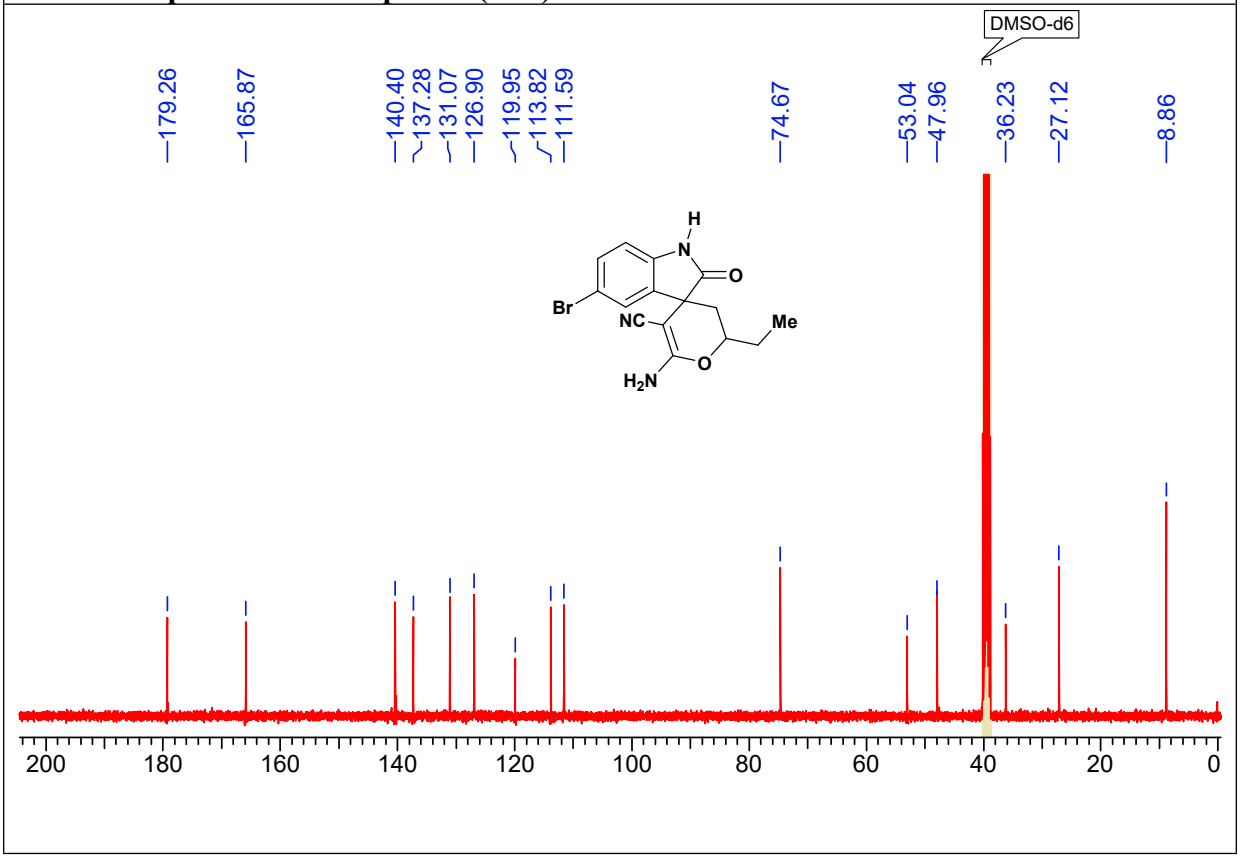

## 135 DEPT spectrum of compound (5Cb)



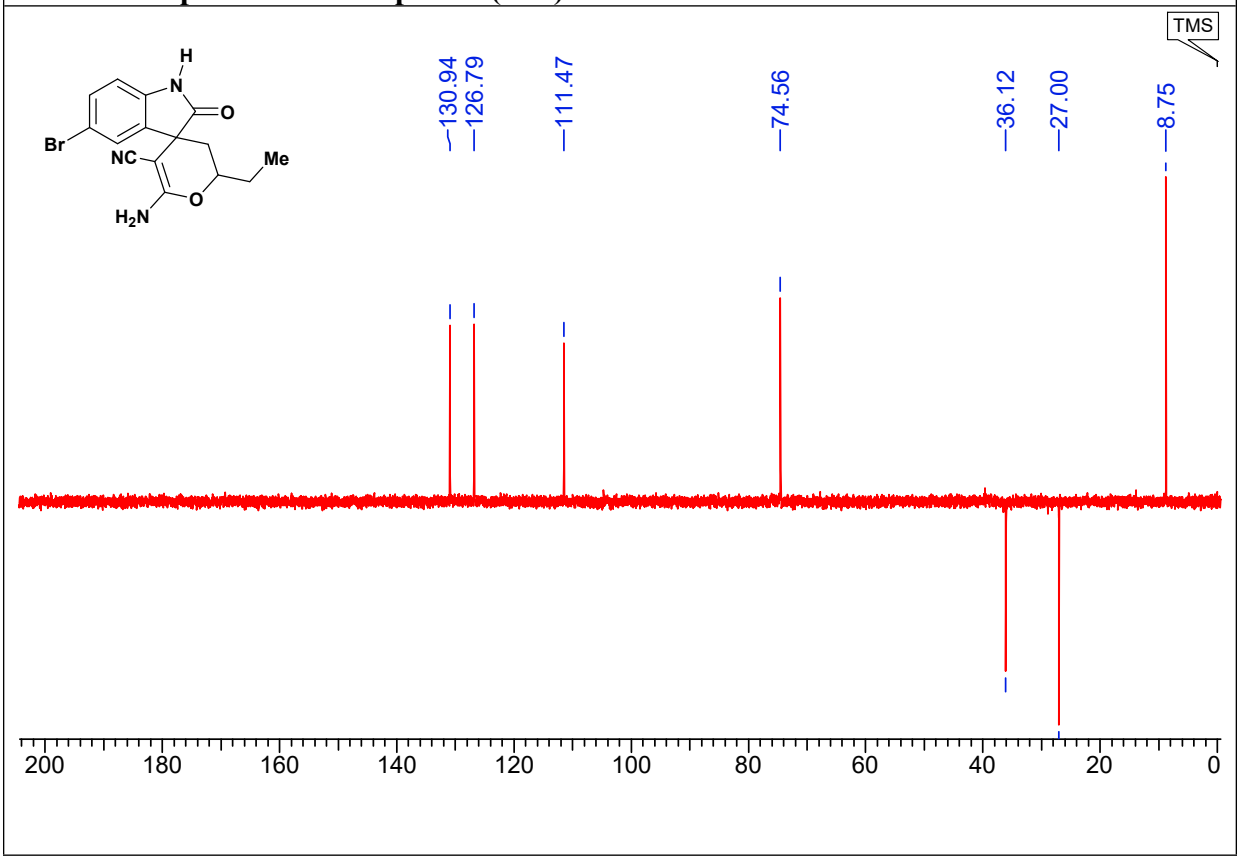
**$^{1}$H NMR spectrum of compound (5Cc)**



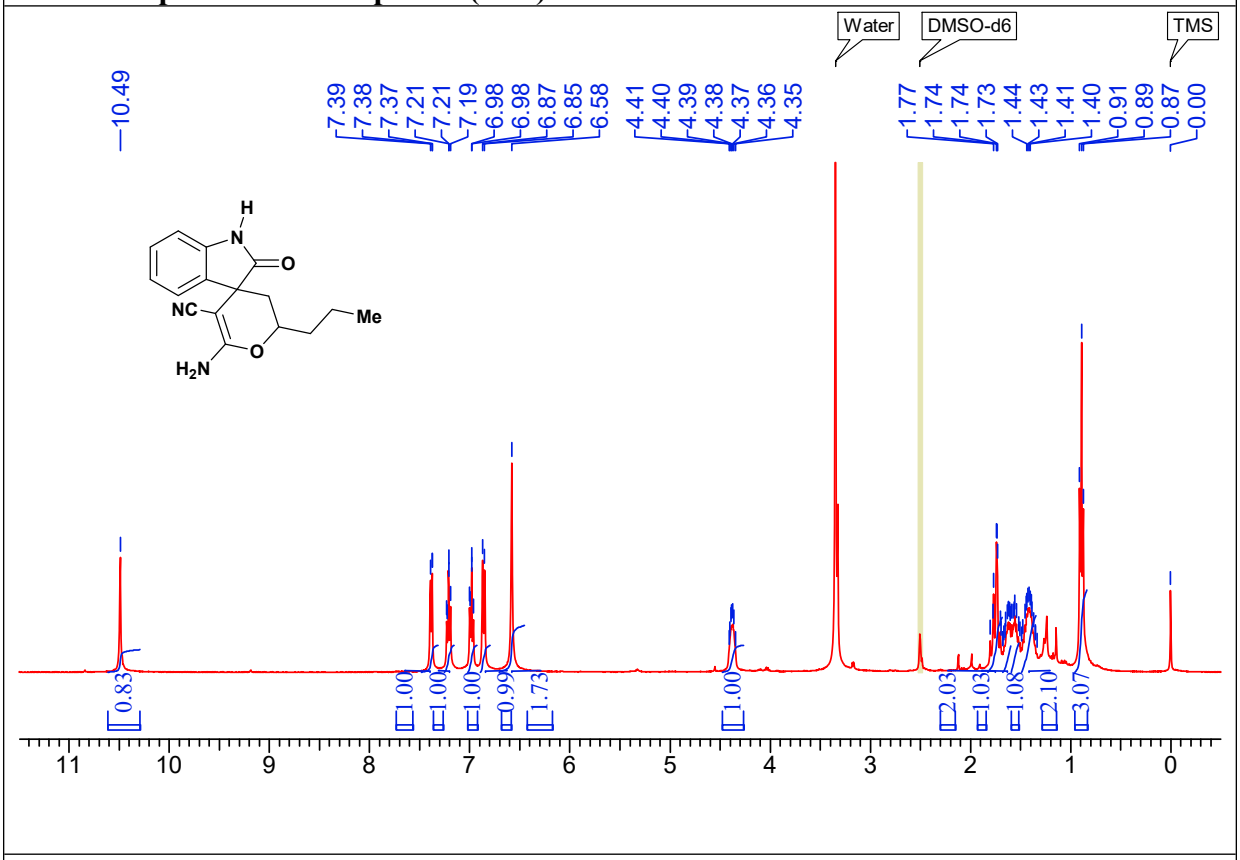

**$^{13}$C NMR spectrum of compound (5Cc)**



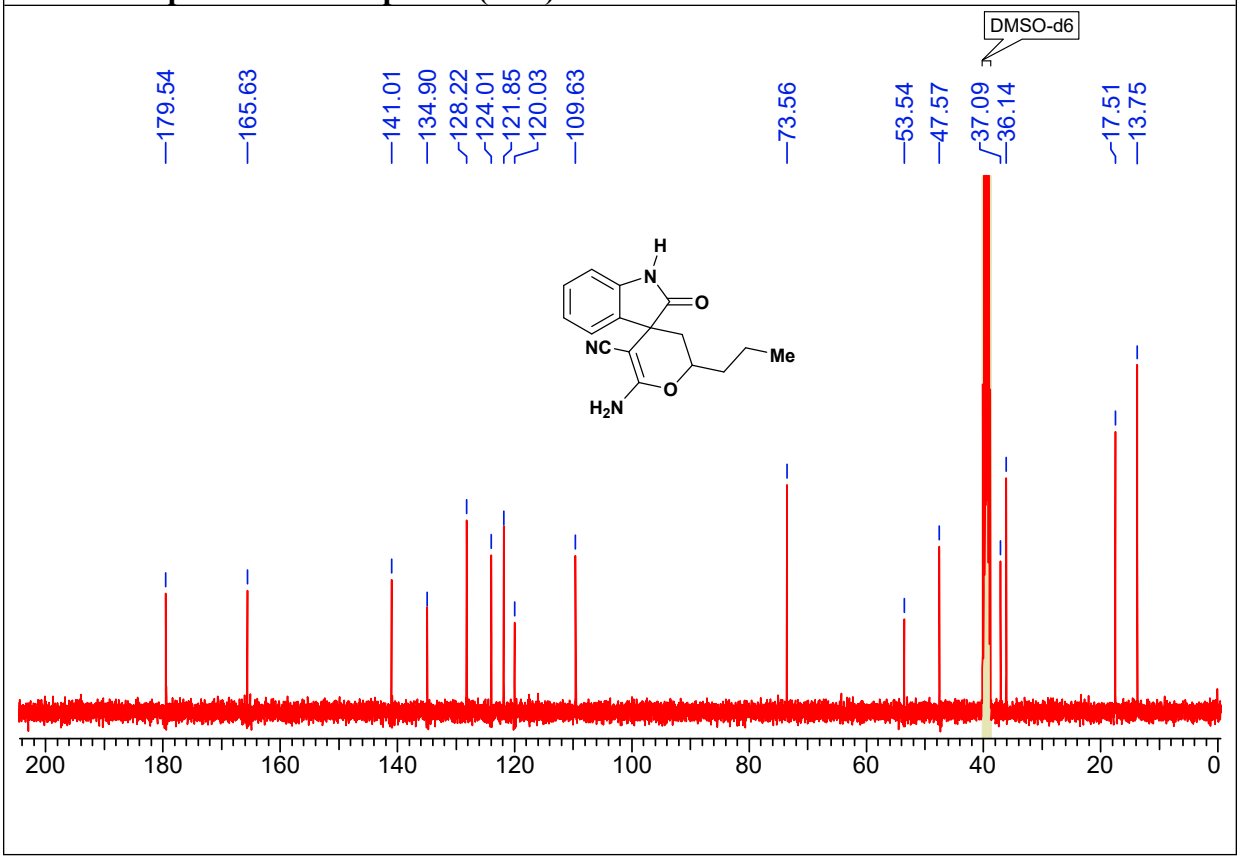
**135 DEPT spectrum of compound (5Cc)**



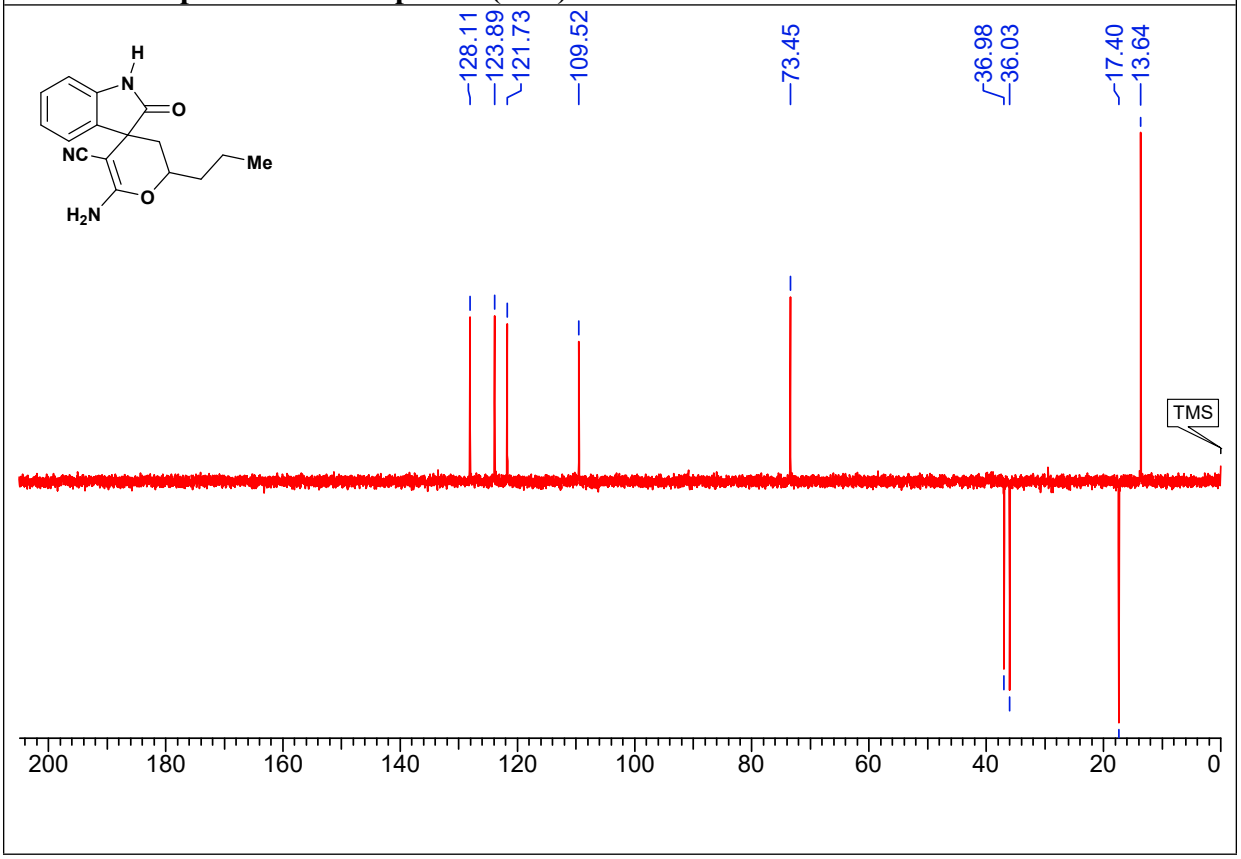
**$^{1}$H NMR spectrum of compound (5Cd)**



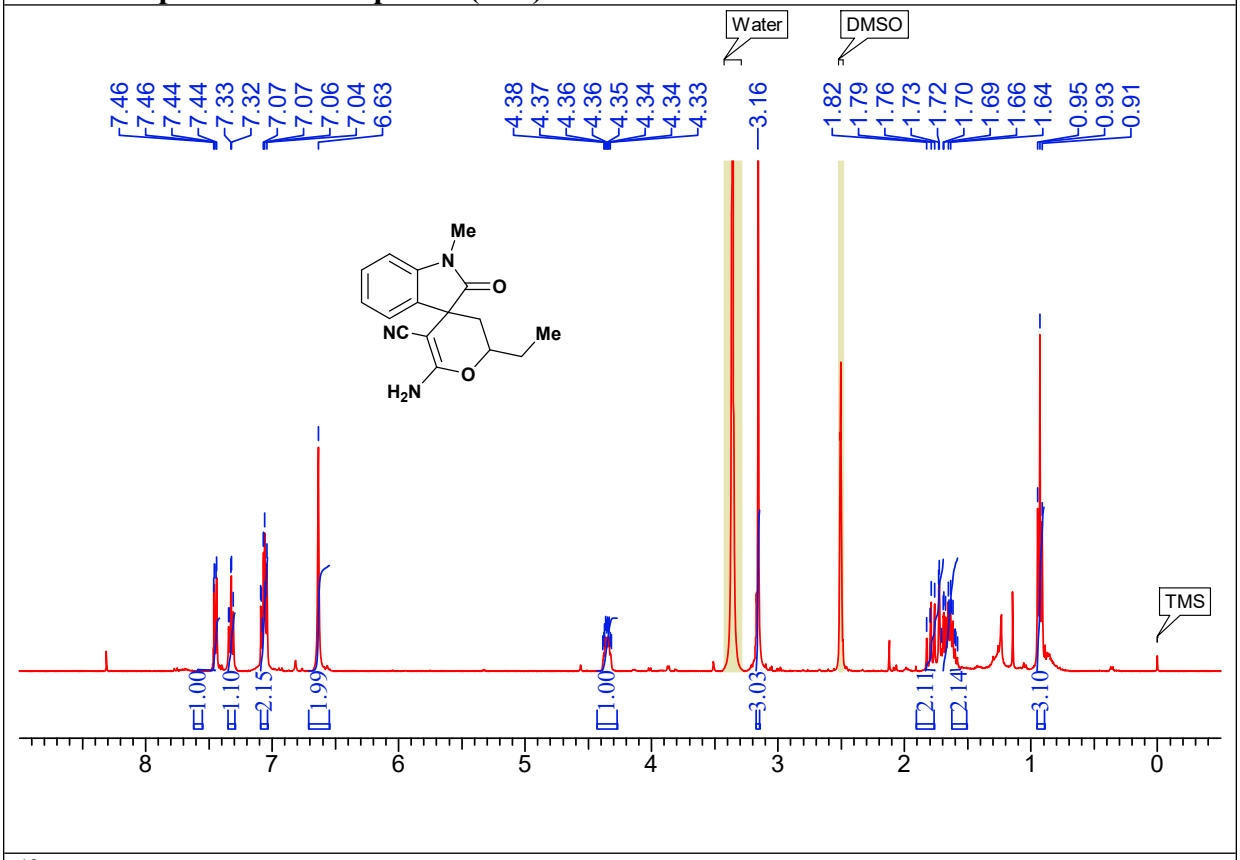

**$^{13}$C NMR spectrum of compound (5Cd)**



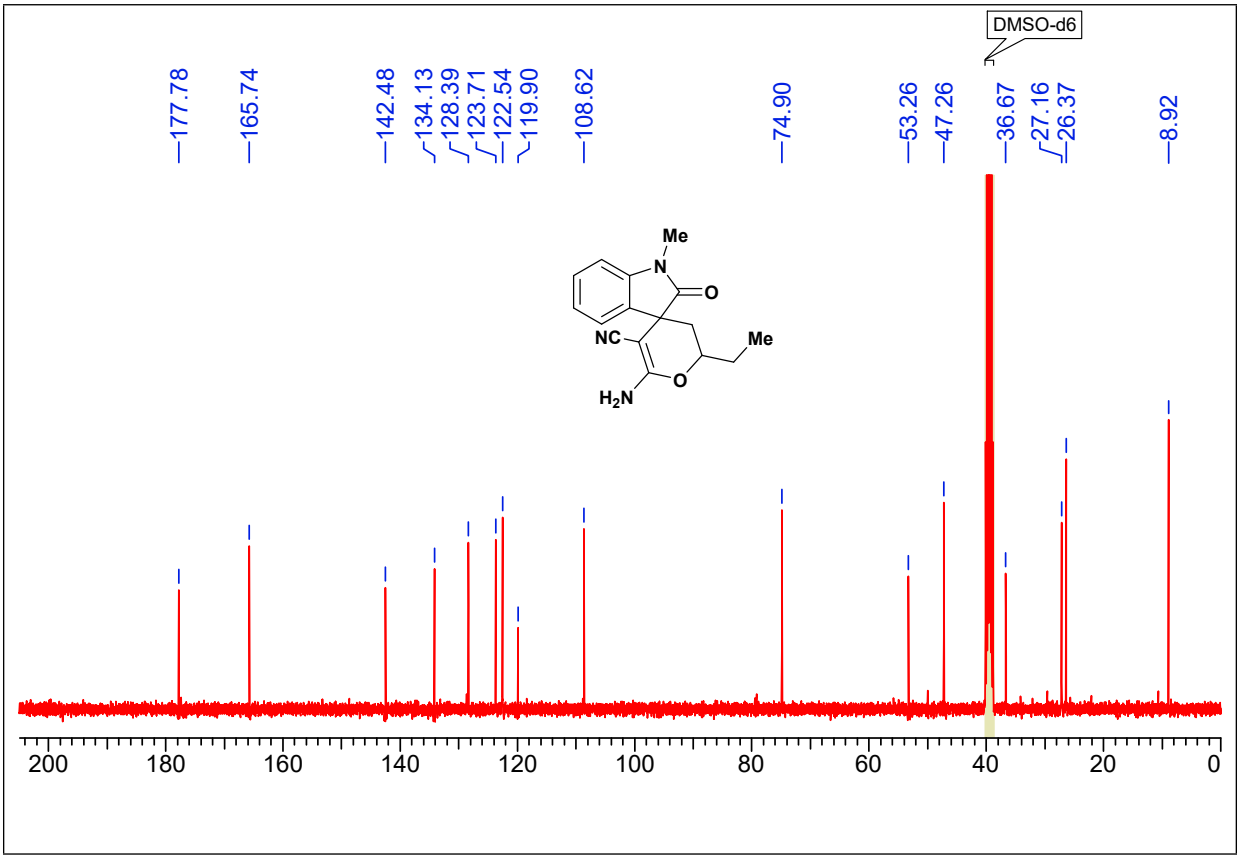
**135 DEPT spectrum of compound (5Cd)**



**$^{1}$H NMR spectrum of compound (5Ce)**




**$^{13}$C NMR spectrum of compound (5Ce)**




**135 DEPT spectrum of compound (5Ce)**