Supporting Information

Base controlled rongalite mediated reductive aldol/cyclization and dimerization of isatylidene malononitriles/cyanoacetates

Suryakant S. Chaudhari, [ab] Chandrakant B. Nichinde, [ab] Baliram R. Patil, [ab] Amardipsingh S. Girase [a] Gamidi Rama Krishna [c] and Anil K. Kinage *[ab]

[a] *Chemical Engineering and Process Development Division, CSIR-National Chemical Laboratory, Pune, India-410 008. E-mail: ak.kinage@ncl.res.in*
[b] *Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201 002, India.*
[c] *Organic Chemistry Division, Council of Scientific and Industrial Research-National Chemical Laboratory (CSIR-NCL), Pune 411008, India.*

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1) General information.

All reactions were performed in 10 ml reaction tube. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm, and stanning with basic $KMnO_4$ solution or in I_2 chamber. **^{1}H, ^{13}C, 135 DEPT** and **^{19}F NMR** spectrum were acquired in deuterated solvents at room temperature on Bruker: Ultra shield 400 MHz, chemical shifts (δ) are reported for ^{1}H NMR in ppm from TMS as internal standard and for ^{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 ^{13}C NMR spectra are reported in terms of chemical shift (δ ppm). High resolution mass spectral **(HRMS)** analysis was recorded by using a Thermo Scientific Q-Exactive, Accela 1250 pump. ESI TOF mass analyzer.

2) Single crystal X-ray diffraction study.

SC-XRD Experiments: The single crystals of **2a**, **2aa** and **3a** components were obtained from mixture of ethyl acetate : ethanol solvent, while the crystals of **3h** obtained from the ethyl acetate solvent by slow evaporation method. The X-ray diffraction measurements were performed to determine the crystal structure of all the four components at 100 K using APEX3 (Bruker, 2016; Bruker D8 VENTURE Kappa Duo PHOTON II CPAD) diffractometer having graphite-monochromatized (MoKα = 0.71073 Å). The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of unit cell parameters and an orientation matrix were calculated from 36 frames, and the cell refinement was performed by SAINT-Plus (Bruker, 2016). An optimized strategy used for data collection consisted of different sets of φ and ω scans with 0.5^{o} steps φ/ω. The data were collected with a time frame of 10 sec for both the components by setting the sample to detector distance fixed at 40 cm. All the data points were corrected for Lorentzian, polarization, and absorption effects using SAINT-Plus and SADABS programs (Bruker, 2016). SHELXS-97 (Sheldrick, 2008) was used for structure solution, and full-matrix least-squares refinement on F^{2}.[1, 2] The molecular graphics of ORTEP diagrams were performed by Mercury software. The crystal symmetry of the components was cross-checked by running the cif files through PLATON (Spek, 2020) software and notified that no additional symmetry was observed. The Encifer software was used to correct the cif files.

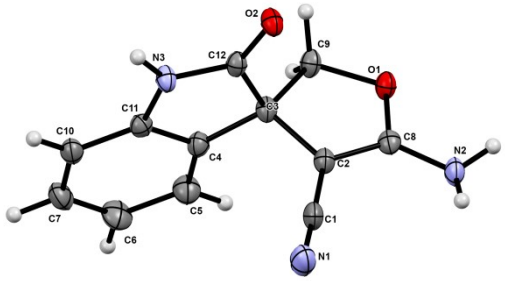


Figure 1. ORTEP diagram of compound **2a**, the asymmetric unit contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

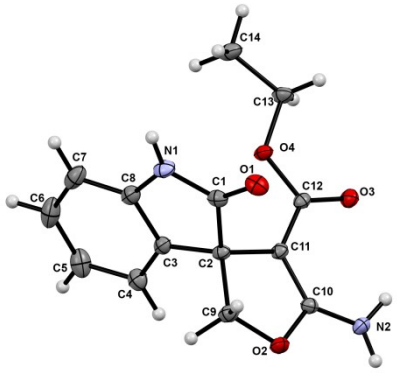


Figure 2. ORTEP diagram of compound **2aa**, the asymmetric unit contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

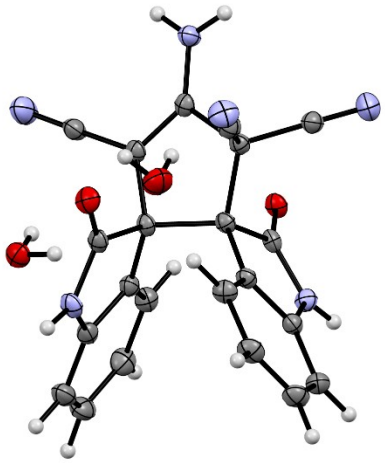


Figure 3. ORTEP diagram of compound **3a**, the asymmetric unit contains a single molecule, along with two water molecules. Herein, the ellipsoids are drawn with a 50% probability.

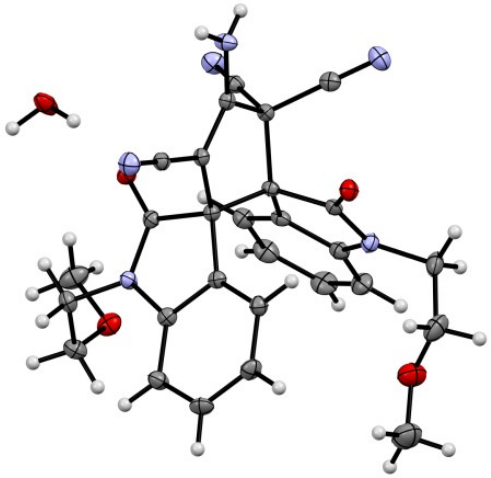


Figure 4. ORTEP diagram of compound **3h**, the asymmetric unit contains a single molecule along with a water molecule. Herein, the ellipsoids are drawn with a 50% probability.

Table 1. Crystallographic information details of compounds **2a**, **2aa**, **3a** and **3h**.

Crystal data	**2a**	**2aa**	**3a**	**3h**
Chemical formula	$C_{12}H_9N_3O_2$	$C_{14}H_{14}N_2O_4$	$C_{22}H_{12}N_6O_2 \cdot 2(H_2O)$	$C_{28}H_{24}N_6O_4 \cdot H_2O$
Formula weight (M_r)	227.22	274.27	428.41	526.55
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	*P-1*	*Pbca*	*Pna2$_1$*	*P2$_1$/c*

Temperature T (K)	100	100	100	100
a (Å)	7.0783 (7)	7.8790 (3)	17.0247 (18)	15.4292 (12)
b (Å)	7.7116 (7)	12.9879 (4)	8.9614 (11)	9.9284 (8)
c (Å)	10.234 (1)	25.3279 (9)	13.2287 (12)	17.7983 (16)
α (°)	84.195 (4)	90	90	90
β (°)	86.746 (4)	90	90	113.305 (3)
γ (°)	82.030 (3)	90	90	90
Z	2	8	4	4
Volume (Å^3)	549.87 (9)	2591.85 (16)	2018.2 (4)	2504.0 (4)
Source of radiation	MoKα	MoKα	MoKα	MoKα
D_{calc} (Mg m^{-3})	1.372	1.406	1.410	1.397
Crystal size (mm)	0.15×0.12×0.11	0.27×0.12×0.09	0.26×0.1×0.08	0.23×0.13×0.09
μ (mm^{-1})	0.10	0.11	0.10	0.10
Data collection				
Diffractometer	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD
Absorption correction	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)
T_{min}, T_{max}	0.6502, 0.7454	0.6015, 0.7458	0.5583, 0.7454	0.6143, 0.7459
No. of measured, independent and observed [I > 2σ(I)] reflections	13478, 2234, 1992	30373, 3358, 2904	17679, 4061, 3975	123205, 5466, 4604
Theta range (°)	2.909-26.422	3.045-28.729	2.39-26.37	2.333−27.000
R_{int}	0.054	0.053	0.046	0.102

Refinement				
R[$F^2 > 2\sigma(F^2)$], wR(F^2)	0.041, 0.096	0.039, 0.103	0.030, 0.079	0.040, 0.103
GOF on F^2	1.06	1.07	1.04	1.04
No. of independent reflections	2234	3358	4061	5466
No. of parameters	166	190	295	371
F_000	236	1152	888	1104
No. of restraints	0	0	1	3
H-atom treatment	Constr	Constr	Constr	Constr
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $A^{\circ-3}$)	0.27, −0.18	0.33, −0.23	0.22, −0.16	0.34, −0.21
CCDC number	2289592	2289593	2289594	2289595

Table 2. Hydrogen-bond geometry (A˚, °) of 2a, 2aa, 3a and 3h components are given as below.

Name of the compound	*D*–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
2a	N2−H2A•••O2	0.8900	2.0100	2.8512(3)	159
	N2−H2B•••N1	0.9000	2.1400	3.0205(3)	165
	N3−H3•••O2	0.9300	1.9100	2.8271(3)	170
	C9−H9B•••N1	0.9900	2.6000	3.4469(3)	143
2aa	N006−H006•••O003	0.8800	2.0800	2.9173(1)	159
	N1−H1A•••O003	0.9000	2.4300	3.0086(1)	122
	N1−H1A•••O002	0.9000	2.3300	3.0038(1)	132
	N1−H1B•••O002	0.8800	1.9600	2.8378(1)	176
3a	N1−H1•••O2	0.8800	2.0500	2.8743(4)	155
	N2−H2•••O3	0.8800	2.1900	3.0074(4)	155
	N2−H2•••N4	0.8800	2.3700	2.9463(4)	123
	N3−H3A•••O4	0.8800	2.1200	2.9974(4)	176
	N3−H3B•••O3	0.8800	1.9800	2.8517(4)	169

	O3−H3C•••O1	0.8700	1.9100	2.7482(3)	162
	O3−H3D•••N4	0.8700	2.1500	2.7881(3)	130
	O4−H4A•••N5	0.8700	2.2400	3.0884(4)	166
	O4−H4B•••N6	0.8700	2.5700	3.2247(4)	133
	C12−H12•••O2	0.9500	2.4900	3.1072(4)	123
	C21−H21•••O1	0.9500	2.5800	3.2202(4)	125
3h	O4−H4A•••O5	0.8500	1.9700	2.8107(3)	168
	O4−H4B•••N4	0.8700	2.0600	2.9206(3)	170
	N5−H5A•••O4	0.8700	1.9600	2.8190(3)	169
	N5−H5B•••O1	0.9200	1.9800	2.8620(3)	159
	C3−H3A•••O5	0.9700	2.5200	2.9003(3)	103
	C19−H19•••O5	0.9300	2.5000	3.1745(3)	130
	C25−H2•••O2	0.9300	2.4000	3.0940(3)	131
	C25−H25••O2	0.9300	2.5500	3.2002(3)	127

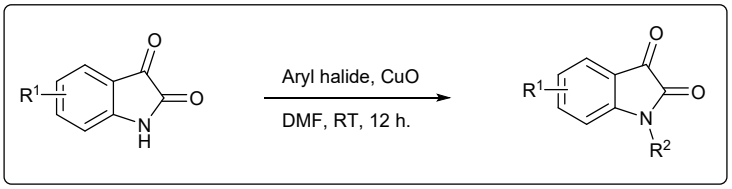
3) General procedure for synthesis of starting materials.

a) Synthesis of N- alkyl protected isatin derivatives.

N-Protected isatin derivatives were synthesized from commercially available isatin alkyl halides and in the presence of potassium carbonate as base in DMF solution. Alkyl halides (12 mmol, 1.2 eq.) was added to a stirred solution of isatin (10 mmol, 1.0 eq.) and K_2CO_3 (12 mmol, 1.2 eq.) in DMF and further stirred at room temperature for 12 h. Reactions were monitored by TLC until completion. After completion of the reaction, the mixture was quenched with water (20 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic phase was 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 derivative.[3-4]

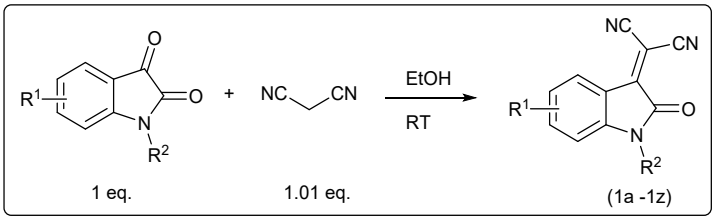
b) Synthesis of N-Aryl substituted isatin derivatives.

N-Arylation of isatin were synthesized from commercially available isatin and aryl halide (1.2eq.) in the presence of CuO (2eq.) in DMF solvent at reflux condition for 5-12 h. After reaction cooled to room temperature and filter to remove CuO. The filtrate was poured in cold water and ethyl acetate was added. The two organic and aqueous layers were separated. The organic layer dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum and resulting crude product was purified by column chromatography to afford product.[5]



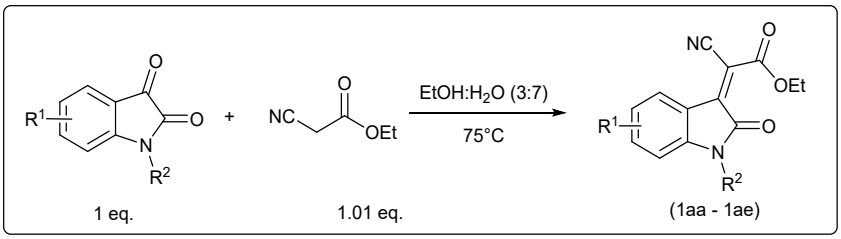
c) Synthesis of Isatyledene malononitrile. (1a-1z)

A mixture of isatin derivatives (0.5 mmol, 1 equiv.), malononitrile (0.51 mmol, 1.01 equiv.) in Ethanol solvent (1 mL) was stirred at room temperature until starting material was completely converted to product (monitored by TLC). After completion of reaction solvent was removed under low pressure. Obtained product was used for next step without any further purification.[6]



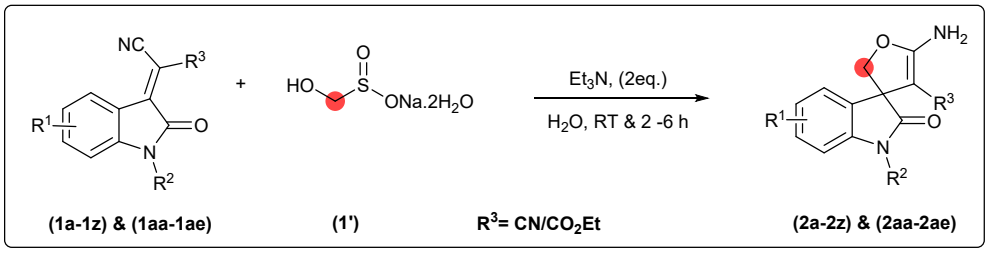
d. Synthesis of Isatyledene ethyl cyanoacetate. (1aa-1ae)

A mixture of isatin/substituted isatin (0.5 mmol, 1 equiv.), ethyl cyanoacetate (0.51 mmol, 1.01 equiv.) in Ethanol: H_2O (3:7) solvent (2 mL) was stirred at 75 °C until the starting material was completely converted to product (monitored by TLC). After completion of reaction solvent was removed under low pressure. Obtained product was used for next step without any further purification.[7]



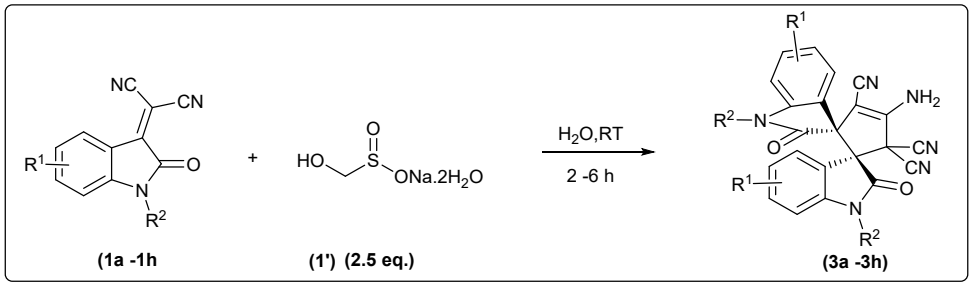
<u>4)Procedure-(A) Synthetic procedure for Spiro[2,3-dihydrofuran-3,3'-oxindole](2 a-2 z & 2 aa-2 ae).</u>

All reactions were carried out in (10 ml) reaction tube. Isatyledene malonitrile/ethyl cyanoacetate (0.2 mmol,1 equiv.), (1') (2 equiv.), triethyl amine (2 equiv.) and H_2O (2 mL) were stirred at room temperature until the starting material was completely converted to product (monitored by TLC). After that, the product was isolated by filtration and washed with H_2O 2-3 times and dry for 80 °C under high vacuum to obtain the spiro [2,3 dihydrofuran-3,3'-oxindole].



5) Procedure-(B) Synthetic procedure for Di-spiro [cyclopent-3'-ene] Bis-oxindoles. (3 a-3 h)

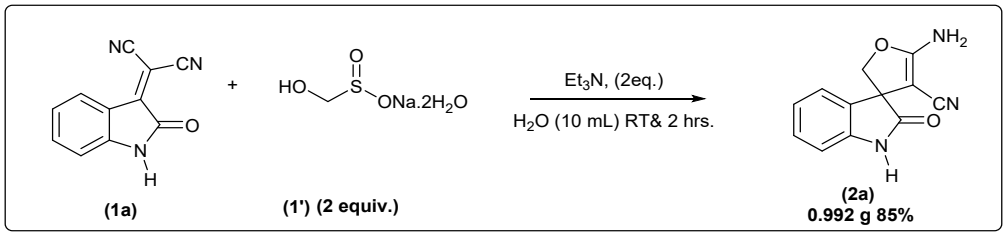
Isatyledene malonitrile (0.2 mmol,1 equiv.), **(1')** (2.5 equiv.) and H_2O (2 mL) were stirred at room temperature, until the starting material was completely converted to product (monitored by TLC). After that, the product was isolated by filtration and then washed with H_2O 2-3 times and dry for 80 °C under high vacuum to obtain Di-spiro [cyclopent-3'-ene] Bis-oxindoles.



6) Synthetic procedure for Gram-scale synthesis.

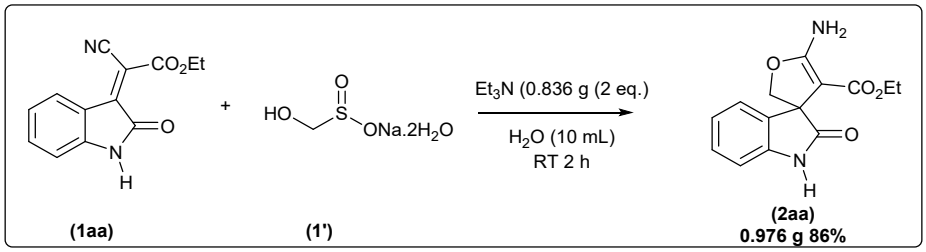
a) Synthesis of 2 a

In 15 mL sealed tube, added sequentially **(1')** (1.57 g), **1a** (1 g 2 equiv.), Et_3N (1.03 g 2 equiv.) and 3mL water and stirred for 5 min. After 5 minutes under stirring second portion of remaining 7 mL water was added slowly and reaction mixture continuously stirred for 2 h at room temperature until the starting material was completely converted to product (monitored by TLC). After the product was isolated by filtration and washed with H_2O and dry for 80 °C under high vacuum to give **2a**.



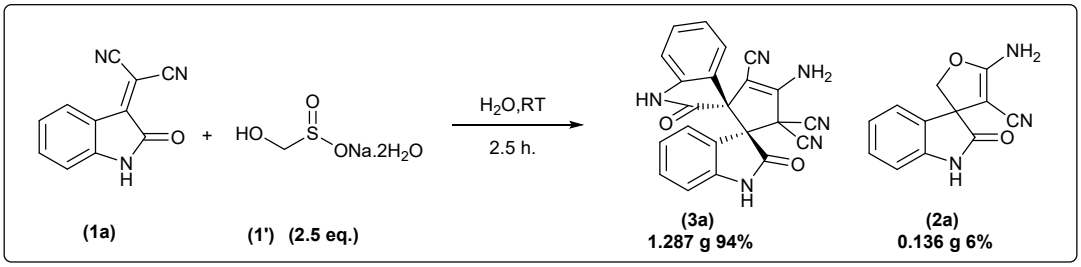
b) Synthesis of 2 aa

In 15 mL sealed tube added sequentially **1'** (1.3 g 2 equiv.), **1aa** (1 g), Et_3N 0.853 g (2 equiv.) and 3 mL water and stirred for 5 min. After 5 minutes under stirring second portion of remaining 7 mL water was added slowly and reaction mixture was continuously stirred for 2 h at room temperature until the starting material was completely converted to product (monitored by TLC). After the product was isolated by filtration and washed with H_2O and dry for 80 °C under high vacuum to give **2aa**.



c) Synthesis of 3 a

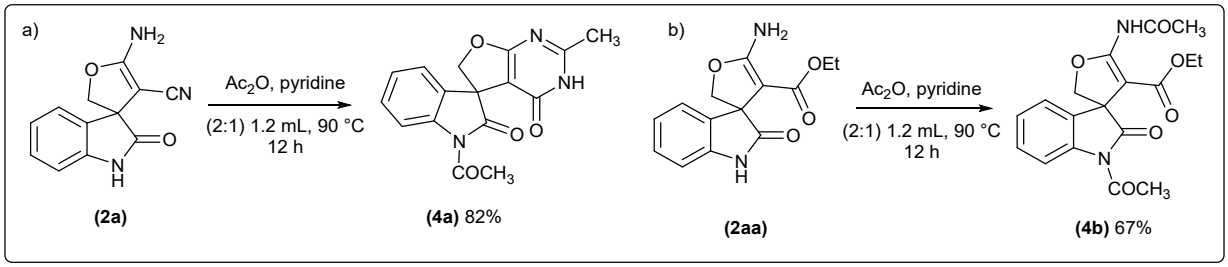
In 50 mL round bottom flask, was added (**1a** 1.3 gm), **(1')** (2.5 equiv.) and (5 mL) water and stirred for 5 min. After that second portion (5 mL) water was added and continuously stirred for 2.5 h at room temperature until the starting material was completely converted to product (monitored by TLC). After the product was isolated by filtration and washed with H_2O and dry for 80° C under high vacuum to give mixture of product **3a** and **2a.**



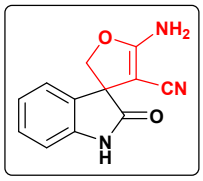
7) General Procedure for synthetic transformation.

(Procedure-c) synthesis of 4 a & 4 b

In 10 mL sealed tube were added (**2a,** 0.2mmol), (1.2 mL, V_{Ac2O} / $V_{Pyridine}$ 2:1 ratio) and stirred at 100 °C for 12 h. After the reaction the crude product was further purified by column chromatography on the silica gel (40% ethyl acetate/ petroleum ether) to give **4 a or 4 b**.

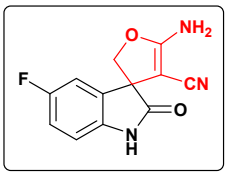


8) Characterization data for compounds.



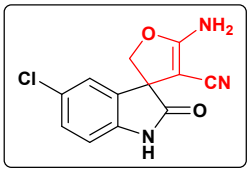
(2a) 5-amino-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (43.1 mg, 93% yield), M. P. 224-226 °C., Rf (Ethyl acetate/Pet. ether;1:1) = 0.3

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.44 (s, 1 H), 7.46 (s, 2 H), 7.30 (d, *J*=7.3 Hz, 1 H), 7.23 (t, *J*=7.1 Hz, 1 H), 7.03 (t, *J*=7.2 Hz, 1 H), 6.84 (d, *J*=7.6 Hz, 1 H), 4.55 (d, *J*=9.3 Hz, 1 H), 4.43 (d, *J*=9.1 Hz, 1 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 178.8, 169.3, 141.5, 130.9, 128.7, 123.9, 122.1, 117.6, 109.5, 77.4, 56.8, 54.6; **HRMS** (ESI) m/z calculated for $C_{12}H_9N_3O_2$+H 228.0773, found: 228.0771



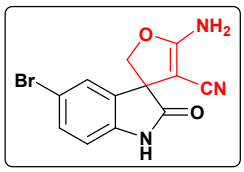
(2b) 5-amino-5'-fluoro-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (45 mg, 92% yield), M. P. 258-260 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.3

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 10.47 (br. s., 1H), 7.51 (s, 2H), 7.25 (d, *J*=8.1 Hz, 1H), 7.07 (t, *J*=9.0 Hz, 1H), 6.83 (dd, *J*=8.2, 4.1 Hz, 1H), 4.56 (d, *J*=9.3 Hz, 1H), 4.48 (d, *J*=9.3 Hz, 1H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 179.2, 169.5, 159.6, 157.2, 137.9, 132.9, 117.7, 115.4, 115.1, 112.1, 111.9, 110.5, 110.4, 77.2, 57.6, 54.6; **^{19}F NMR** (376 MHz, *DMSO-d_6*) δ -121.0; **HRMS** (ESI) m/z calculated for $C_{12}H_8FN_3O_2$+H 246.0679, found: 246.0673



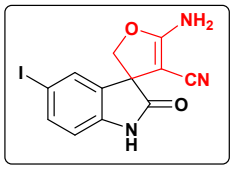
(2c) 5-amino-5'-chloro-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (46.4 mg, 89%yield), M. P. 234-236 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.3

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.57 (s, 1 H), 7.52 (s, 2 H), 7.40 (d, *J*=1.9 Hz, 1 H), 7.28 (dd, *J*=8.3, 2.0 Hz, 1 H), 6.85 (d, *J*=8.3 Hz, 1 H), 4.53 - 4.61 (m, 2 H), 4.44 - 4.53 (m, 2 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 178.9, 169.5, 140.7, 133.2, 128.8, 126.2, 124.3, 117.6, 111.1, 77.2, 57.3, 54.5 **HRMS:** (ESI) m/z calculated for $C_{12}H_8ClN_3O_2$+H: 262.0383, found: 262.0378



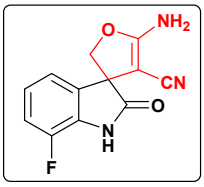
(2d) 5-amino-5'-bromo-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (54.8 mg, 90% yield), M. P. 254-256 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.3

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 10.57 (s, 1H), 7.52 (s, 2H), 7.50 (d, *J*=2.1 Hz, 1H), 7.41 (dd, *J*=8.3, 2.1 Hz, 1H), 6.80 (d, *J*=8.3 Hz, 1H), 4.55 (d, J=9.3 Hz, 1H), 4.50 (d, J=9.3 Hz, 1H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 178.7, 169.5, 141.1, 133.6, 131.6, 127.1, 117.6, 113.8, 111.6, 77.2, 57.2, 54.5; **HRMS:** (ESI) m/z calculated for $C_{12}H_8BrN_3O_2$+H: 305.9878, found: 305.9873



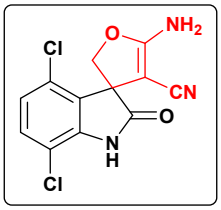
(2e) 5-amino-5'-iodo-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (60.7 mg, 86% yield), M. P. 244-246 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.3

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 10.56 (s, 1H), 7.61 (d, *J*=1.8 Hz, 1H), 7.57 (dd, *J*=8.1, 1.8 Hz, 1H), 7.51 (s, 2H), 6.70 (d, *J*=8.1 Hz, 1H), 4.53 (d, J=9.5 Hz, 1H), 4.49 (d, J=9.5 Hz, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 178.4, 169.5, 141.5, 137.4, 133.9, 132.4, 117.7, 112.1, 85.1, 77.2, 57.1, 54.5; **HRMS:** (ESI) m/z calculated for $C_{12}H_8IN_3O_2$+H: 353.9739, found: 353.9734



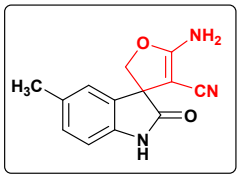
(2f) 5-amino-7'-fluoro-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (44.6 mg, 91% yield), M. P. 256-258 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.4

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (br. s., 1 H), 7.52 (br. s., 2 H), 7.11 - 7.22 (m, 2 H), 7.00 - 7.11 (m, 1 H), 4.58 (d, *J*=9.3 Hz, 1 H), 4.46 (d, *J*=9.4 Hz, 1 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 178.9, 169.5, 147.5, 145.1, 134.3, 128.7, 123.2, 120.1, 117.6, 115.9, 77.5, 57.4, 54.7; **^{19}F NMR** (376 MHz, *DMSO-d_6*) δ -133.2; **HRMS:** (ESI) m/z calculated for $C_{12}H_8FN_3O_2$+H: 246.0679, found: 246.0676



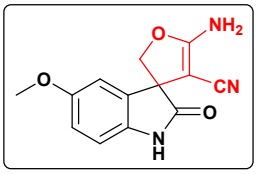
(2g) 5-amino-4',7'-dichloro-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (54.2 mg, 92% yield), M. P. 276-278°C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.4

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.15 (br. s., 1 H), 7.54 (s, 2 H), 7.37 (d, *J*=8.8 Hz, 1 H), 7.09 (d, *J*=8.6 Hz, 1 H), 4.64 (d, *J*=9.8 Hz, 1 H), 4.47 (d, *J*=9.8 Hz, 1 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 178.1, 169.9, 141.1, 130.3, 129.2, 128.6, 123.7, 117.3, 113.1, 75.1, 58.9, 51.9; **HRMS:** (ESI) m/z calculated for $C_{12}H_7Cl_2N_3O_2$+H: 295.9994, found: 295.9993



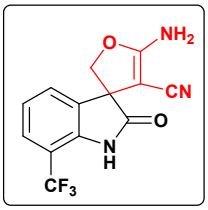
(2h) 5-amino-5'-methyl-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (40.4 mg, 84% yield), M. P. 242-244 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.2

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.34 (s, 1 H), 7.44 (s, 2 H), 7.11 (s, 1 H), 7.03 (d, *J*=7.8 Hz, 1 H), 6.72 (d, *J*=7.8 Hz, 1 H), 4.53 (d, *J*=9.1 Hz, 1 H), 4.42 (d, *J*=9.1 Hz, 1 H), 2.27 (s, 3 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 178.9, 169.4, 139.2, 131., 131.2, 129.1, 124.6, 117.8, 109.4, 77.7, 57.1, 54.9, 20.7; **HRMS:** (ESI) m/z calculated for $C_{13}H_{11}N_3O_2$+H: 242.0930, found: 242.0924



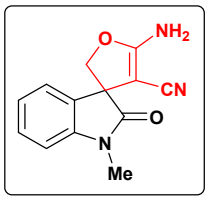
(2i) 5-amino-5'-methoxy-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (40.5 mg, 79% yield), M. P. 248-250 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.3

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.26 (s, 1 H), 7.45 (s, 2 H), 6.93 (s, 1 H), 6.78 - 6.83 (m, 1 H), 6.71 - 6.78 (m, 1 H), 4.54 (d, *J*=9.3 Hz, 1 H), 4.45 (d, *J*=9.3 Hz, 1 H), 3.73 (s, 3 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 179.1, 169.4, 155.4, 134.9, 132.3, 117.8, 113.8, 110.7, 110.1, 77.5, 57.5, 55.5, 54.9; **HRMS:** (ESI) m/z calculated for $C_{13}H_{11}N_3O_3$+H: 258.0879, found: 258.0873.



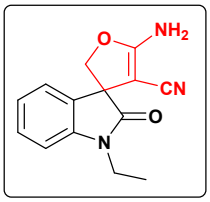
(2j) 5-amino-2'-oxo-7'-(trifluoromethyl)-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized **procedure-(A)**, obtained as a solid (51.9 mg, 88% yield), **M. P.** 226-228°C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.6

^{1}H NMR (400 MHz, *DMSO-d$_6$*) δ 10.94 (br. s., 1H), 7.62 (d, *J*=7.1 Hz, 1H), 7.57 (br. s., 2H), 7.53 (d, *J*=8.0 Hz, 1H), 7.21 (t, *J*=7.3 Hz, 1H), 4.60 (d, *J*=9.4 Hz, 1H), 4.50 (d, *J*=9.3 Hz, 1H); **^{13}C NMR (101 MHz, *DMSO-d$_6$*)** δ 179.5, 169.6, 139.1, 133.3, 128.2, 125.4, 122.4, 117.5, 110.9, 110.5, 77.5, 56.2, 54.5; **^{19}F NMR** (376 MHz, DMSO-*d*$_6$) δ -59.9; **HRMS:** (ESI) m/z calculated for $C_{13}H_8F_3N_3O_2$+H: 296.0647, found: 296.0641.



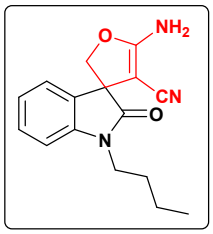
(2l) 5-amino-1'-methyl-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (43.4 mg, 90% yield), M. P. 220-222°C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.7

^{1}H NMR (400 MHz, *DMSO-d$_6$*) δ 7.50 (s, 2H), 7.39 - 7.30 (m, 2H), 7.17 - 7.07 (m, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 4.55 (d, *J* = 9.3 Hz, 1H), 4.44 (d, *J* = 9.3 Hz, 1H), 3.14 (s, 3H); **^{13}C NMR** (101 MHz, *DMSO-d$_6$*) δ 177.2, 169.6, 143.2, 130.3, 129.1, 123.7, 122., 117.6, 108.6, 77.6, 56.6, 54.4, 26.3; **HRMS:** (ESI) m/z calculated for $C_{13}H_{11}N_3O_2$+H: 242.0930, found: 242.0924



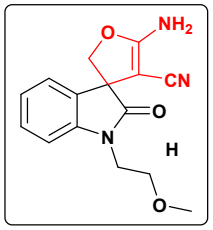
(2m) 5-amino-1'-ethyl-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (46.8 mg, 92%yield), M. P. 202-204 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.7

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.49 (s, 2 H), 7.36 (d, *J*=7.4 Hz, 2 H), 7.33 (td, *J*=7.7, 1.2 Hz, 1 H), 7.06 - 7.12 (m, 2 H), 4.55 (d, *J*=9.4 Hz, 1 H), 4.45 (d, *J*=9.3 Hz, 1 H), 3.66 - 3.75 (m, 2 H), 1.14 (t, *J*=7.1 Hz, 3 H); **^{13}C NMR** (101 MHz, *DMSO-d$_6$*) δ 177.1, 169.7, 142.3, 130.7, 129.4, 124.1, 123.1, 117.8, 109.1, 77.7, 56.8, 54.9, 34.7, 12.8; **HRMS:** (ESI) m/z calculated for $C_{14}H_{13}N_3O_2$+H: 256.1086, found: 256.1084



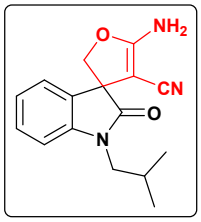
(2n) 5-amino-1'-butyl-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimize procedure-(A), obtained as a solid (53.8 mg, 95% yield), M. P. 230-232°C., Rf (Ethyl acetate/Pet. ether;1:1) = 0.7

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 7.49 (s, 2H), 7.36 (d, *J*=7.3 Hz, 1H), 7.32 (t, *J*=7.8 Hz, 1H), 7.08 - 7.14 (m, 1H), 7.06 (d, *J*=7.9 Hz, 1H), 4.54 (d, *J*=9.3 Hz, 1H), 4.46 (d, J=9.3 Hz, 1H), 3.69 - 3.79 (m, 1H), 3.61 (dt, *J*=13.9, 6.8 Hz, 1H), 1.51 - 1.61 (m, 2H), 1.25 - 1.36 (m, 2H), 0.88 (t, *J*=7.3 Hz, 3H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 177.1, 169.5, 142.5, 130.5, 129.0, 123.9, 122.7, 117.5, 108.8, 77.5, 56.6, 54.8, 28.9, 19.3, 13.6; **HRMS:** (ESI) m/z calculated for $C_{16}H_{17}N_3O_2$+H: 284.1399, found: 284.1394



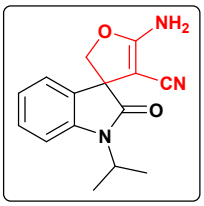
(2o) 5-amino-1'-(2-methoxyethyl)-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (49.6 mg, 87% yield), M. P. 196-198 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.4

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 7.49 (s, 2H), 7.29 - 7.38 (m, 2H), 7.06 - 7.13 (m, 2H), 4.54 (d, *J*=9.3 Hz, 1H), 4.45 (d, *J*=9.3 Hz, 1H), 3.80 - 3.87 (m, 2H), 3.53 (t, *J*=5.7 Hz, 2H), 3.22 (s, 3H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 177.4, 169.5, 142.7, 130.2, 128.9, 123.8, 122.8, 117.5, 109.2, 77.6, 68.9, 58.2, 56.5, 54.6; **HRMS:** (ESI) m/z calculated for $C_{15}H_{15}N_3O_3$+H: 286.1192, found: 286.1186.



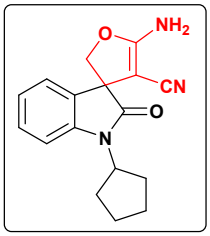
(2p) 5-amino-1'-isobutyl-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (50.3mg, 89% yield), M. P. 190-192 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.5

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.49 (s, 2 H), 7.36 (d, *J*=7.4 Hz, 1 H), 7.27 - 7.34 (m, 1 H), 7.04 - 7.13 (m, 2 H), 4.54 (d, *J*=9.3 Hz, 1 H), 4.46 (d, *J*=9.3 Hz, 1 H), 3.55 (dd, *J*=13.8, 8.2 Hz, 1 H), 3.40 (dd, *J*=13.8, 6.8 Hz, 1 H), 2.00 - 2.11 (m, 1 H), 0.88 (dd, *J*=14.0, 6.6 Hz, 6 H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 177.5, 169.4, 142.8, 130.4, 128.9, 123.8, 122.7, 117.6, 109.1, 77.5, 56.6, 54.8, 46.7, 26.3, 19.9, 19.7; **HRMS:** (ESI) m/z calculated for $C_{16}H_{17}N_3O_2$ +H: 284.1399, found: 284.1394



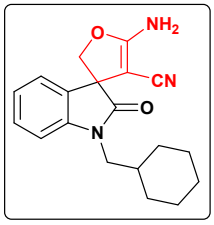
(2q) 5-amino-1'-isopropyl-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (47.3 mg, 89% yield), M. P. 194-196 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.5

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 7.46 (s, 2H), 7.36 (d, *J*=8.4 Hz, 1H), 7.27 - 7.32 (m, 1H), 7.18 (d, *J*=7.8 Hz, 1H), 7.05 - 7.12 (m, 1H), 4.53 - 4.56 (m, 1H), 4.46 - 4.52 (m, 1H), 4.44 - 4.46 (m, 1H), 1.40 (d, *J*=3.3 Hz, 3H), 1.39 (d, *J*=3.4 Hz, 3H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 176.9, 169.3, 141.7, 130.9, 128.9, 124.0, 122.4, 117.4, 109.8, 77.4, 56.5, 55.1, 43.7, 19.2, 18.9; **HRMS:** (ESI) m/z calculated for $C_{15}H_{15}N3O_2$+H: 270.1243, found: 270.1237



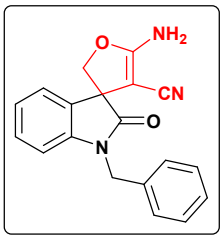
(2r) 5-amino-1'-cyclopentyl-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (51.9 mg, 88% yield), M. P. 188-190 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.6

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 7.47 (s, 2H), 7.36 (d, *J*=7.1 Hz, 1H), 7.28 - 7.34 (m, 1H), 7.06 - 7.13 (m, 2H), 4.64 (quin, *J*=8.5 Hz, 1H), 4.55 (d, *J*=9.3 Hz, 1H), 4.44 (d, J=9.3 Hz, 1H), 1.94 - 2.04 (m, 2H), 1.77 - 1.92 (m, 4H), 1.60 - 1.67 (m, 2H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 177.1, 169.4, 141.9, 130.8, 128.9, 124.0, 122.5, 117.5, 109.6, 77.5, 56.6, 55., 52.3, 27.6, 27.5, 24.7, 24.7; **HRMS:** (ESI) m/z calculated for $C_{17}H_{17}N_3O_2$ +H: 296.1399, found: 296.1394



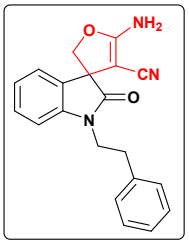
(2s) 5-amino-1'-(cyclohexylmethyl)-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (56.2 mg, 87% yield), M. P**.** 246-248 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.6

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 7.48 (s, 2H), 7.28 - 7.38 (m, 2H), 7.04 - 7.12 (m, 2H), 4.54 (d, *J*=9.3 Hz, 1H), 4.46 (d, *J*=9.3 Hz, 1H), 3.51 - 3.67 (m, 1H), 3.43 (dd, *J*=13.9, 6.6 Hz, 1H), 1.61 - 1.71 (m, 4H), 1.49 - 1.60 (m, 1H), 1.09 - 1.17 (m, 4H), 0.94 - 1.01 (m, 2 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 177.4, 169.4, 142.9, 130.4, 128.9, 123.8, 122.6, 117.5, 109.1, 77.5, 56.6, 54.8, 45.7, 45.5, 35.5, 30.1, 29.9, 25.8, 25.3, 25.2; **HRMS:** (ESI) m/z calculated for: $C_{19}H_{21}N_3O_2$+H, 324.1712 found: 324.1704



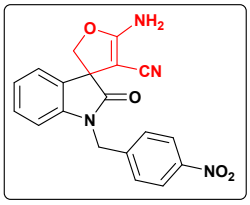
(2t) 5-amino-1'-benzyl-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimize procedure-(A), obtained as a solid (55.1 mg, 87% yield), M. P. 242-244 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.7

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.56 (s, 2 H), 7.39 (d, *J*=7.4 Hz, 1 H), 7.32 - 7.25 (m, 5 H), 7.19 - 7.24 (m, 1 H), 7.09 (t, *J*=7.4 Hz, 1 H), 6.85 (d, *J*=7.8 Hz, 1 H), 5.01 (d, *J*=15.9 Hz, 1 H), 4.81 (d, *J*=15.9 Hz, 1 H), 4.64 (d, *J*=9.3 Hz, 1 H), 4.52 (d, *J*=9.3 Hz, 1 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 177.5, 169.5, 142.1, 135.9, 130.4, 128.9, 128.6, 127.4, 126.9, 123.9, 123.1, 117.7, 109.3, 77.5, 56.8, 54.7, 42.9; **HRMS:** (ESI) m/z calculated for: $C_{19}H_{15}N_3O_2$ +H, 318.1243 found: 318.1242.



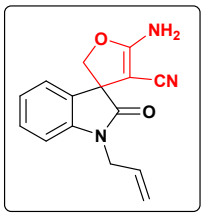
(2u) 5-amino-2'-oxo-1'-phenethyl-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (60.2 mg, 91% yield), M. P. 214-216 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.7

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 7.50 (s, 2H), 7.32 - 7.37 (m, 1H), 7.22 - 7.32 (m, 3H), 7.14 - 7.22 (m, 3H), 7.09 (t, *J*=7.5 Hz, 1H), 7.02 (d, *J*=7.9 Hz, 1H), 4.24 - 4.47 (m, 2H), 3.89 (t, *J*=7.1 Hz, 2H), 2.88 (t, *J*=6.8 Hz, 2H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 177.1, 169.5, 142.3, 138.2, 130.2, 128.9, 128.9, 128.3, 126.3, 123.8, 122.7, 117.6, 108.9, 77.6, 56.5, 54.3, 41.1, 32.9; **HRMS:** (ESI) m/z calculated for: $C_{20}H_{17}N_3O_2$ +H, 332.1399 found: 332.1394.



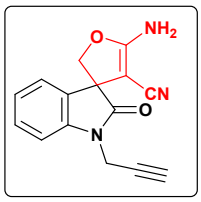
(2v) 5-amino-1'-(4-nitrobenzyl)-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (63 mg, 87% yield), M. P. 210-212 °C, Rf (Ethyl acetate/Pet. Ether; 1:1) = 0.5

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 8.13 - 8.21 (m, 2H), 7.59 - 7.61 (m, 1H), 7.57 - 7.59 (m, 2H), 7.40 - 7.45 (m, 1H), 7.22 - 7.29 (m, 1H), 7.08 - 7.16 (m, 1H), 6.91 (d, *J*=7.8 Hz, 1H), 5.15 (d, *J*=16.8 Hz, 1H), 5.02 (d, *J*=16.6 Hz, H), 4.68 (d, *J*=9.4 Hz, 1H), 4.55 (d, *J*=9.5 Hz, 1H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ ppm 178.2, 169.9, 147.4, 144.5, 142.3, 130.9, 129.5, 128.7, 124.6, 124.1, 123.8, 118.2, 109.6, 77.9, 57.3, 55.2, 42.9; **HRMS:** (ESI) m/z calculated for: $C_{19}H_{14}N_4O_4$ +H, 363.1093 found: 363.1088



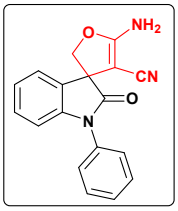
(2w) 1'-allyl-5-amino-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (50.2 mg, 94% yield), M. P. 224-226°C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.6

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 7.52 (s, 2H), 7.36 - 7.41 (m, 1H), 7.30 (td, *J*=7.7, 1.2 Hz, 1H), 7.07 - 7.14 (m, 1H), 6.94 (d, *J*=7.8 Hz, 1H), 5.78 - 5.89 (m, 1H), 5.08 - 5.16 (m, 2H), 4.58 (d, *J*=9.4 Hz, 1H), 4.49 (d, *J*=9.3 Hz, 1H), 4.34 - 4.43 (m, 1H), 4.19 - 4.27 (m, 1H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 177.1, 169.5, 142.3, 131.5, 130.3, 128.9, 123.9, 122., 117.6, 116.3, 109.2, 77.5, 56.7, 54.7, 41.6; **HRMS:** (ESI) m/z calculated for: $C_{15}H_{13}N_3O_2$+H, 268.1086 found: 267.1081



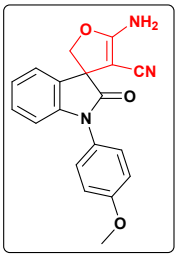
(2x) 5-amino-2'-oxo-1'-(prop-2-yn-1-yl)-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (49.3 mg, 93% yield), M. P. 220-222 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.6

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 7.54 (s, 2H), 7.40 (d, *J*=7.8 Hz, 1H), 7.36 (dd, *J*=7.8, 1.1 Hz, 1H), 7.14 - 7.19 (m, 1H), 7.12 (d, *J*=7.9 Hz, 1H), 4.54 - 4.62 (m, 2H), 4.51 (d, *J*=2.5 Hz, 1H), 4.45 - 4.48 (m, 1H), 3.27 (t, *J*=2.4 Hz, 1H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 176.6, 169.6, 141.3, 130.1, 129.1, 123.9, 123.3, 117.4, 109.4, 77.9, 77.5, 74.6, 56.6, 54.3, 29.1; **HRMS:** (ESI) m/z calculated for: $C_{15}H_{11}N_3O_2$ +H, 266.0930 found: 266.0924



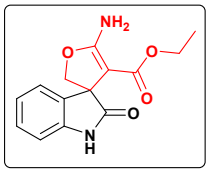
(2y) 5-amino-2'-oxo-1'-phenyl-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (52.6 mg, 87% yield), M. P. 208-210 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.6

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.57 - 7.64 (m, 2 H), 7.56 (s, 2 H), 7.45 - 7.51 (m, 2 H), 7.41 (d, *J*=7.1 Hz, 2 H), 7.25 - 7.32 (m, 1 H), 7.13 - 7.21 (m, 1 H), 6.75 (d, *J*=7.8 Hz, 1 H), 4.73 (d, *J*=9.5 Hz, 1 H), 4.57 (d, *J*=9.4 Hz, 1 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 176.9, 169.5, 142.9, 134.2, 130.3, 129.6, 129.1, 128.2, 126.6, 124.3, 123.5, 117.6, 109.1, 77.7, 56.9, 55.1; **HRMS:** (ESI) m/z calculated for: $C_{18}H_{13}N_3O_2$ +H, 304.1086 found: 304.1081



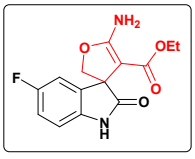
(2z) 5-amino-1'-(4-methoxyphenyl)-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carbonitrile, the titled compound was prepared by following the optimize procedure-(A), obtained as a solid (53.2 mg, 80% yield), M. P. 154-156 °C, Rf (Ethyl acetate/Pet. ether;1:1) = 0.6

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.56 (s, 2 H), 7.45 (d, *J*=6.6 Hz, 1 H), 7.29 - 7.35 (m, 2 H), 7.23 - 7.29 (m, 1 H), 7.16 (d, *J*=7.4 Hz, 1 H), 7.12 (d, *J*=9.0 Hz, 2 H), 6.68 (d, *J*=7.8 Hz, 1 H), 4.71 (d, *J*=9.4 Hz, 1 H), 4.56 (d, *J*=9.4 Hz, 1 H), 3.83 (s, 3 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 177.1, 169.5, 158.7, 143.4, 130.2, 129.1, 128.1, 126.7, 124.2, 123.3, 117.6, 114.8, 108.9, 77.7, 56.8, 55.4, 55.0; **HRMS:** (ESI) m/z calculated for: $C_{19}H_{15}N_3O_3$ +H, 334.1192 found: 334.1186



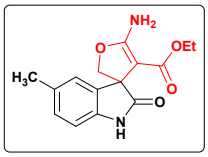
(2aa) Ethyl 5-amino-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carboxylate, the titled compound was prepared by following the optimize procedure-(A), obtained as a solid (49.3 mg, 90% yield), M. P. 212-214 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.3

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.28 (s, 1 H), 7.25 (br. s., 2 H), 7.08 - 7.15 (m, 2 H), 6.89 - 6.96 (m, 1 H), 6.77 (d, *J*=7.5 Hz, 1 H), 4.47 (d, *J*=9.1 Hz, 1 H), 4.37 (d, *J*=9.0 Hz, 1 H), 3.71 (br. s., 2 H), 0.74 (br. s., 3 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 179.9, 142.1, 133.9, 128.0, 123.1, 121.8, 109.1, 78.2, 57.7, 14.1; **HRMS:** (ESI) m/z calculated for: $C_{14}H_{14}N_2O_4$+H, 275.1032 found: 275.1026



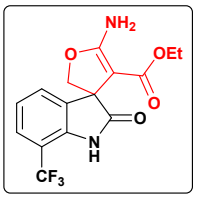
(2ab) ethyl 5-amino-5'-fluoro-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carboxylate, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (53.1 mg, 91% yield), M. P. 186-188 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.3

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 10.30 (s, 1H), 7.29 (br. s., 2H), 7.02 (dd, *J*=8.3, 2.5 Hz, 1H), 6.88 - 6.99 (m, 1H), 6.75 (dd, *J*=8.4, 4.4 Hz, 1H), 4.48 (d, *J*=9.1 Hz, 1H), 4.42 (d, *J*=9.1 Hz, 1H), 3.60 - 3.89 (m, 2H), 0.66 - 0.96 (m, 3H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 179.8, 159.3, 156.9, 138.3, 135.6, 135.5, 114.1, 113.8, 111.1, 110.8, 109.5, 109.4, 77.6, 57.5, 13.9; **^{19}F NMR** (376 MHz, DMSO-d_6) d ppm -122.1; **HRMS:** (ESI) m/z calculated for: $C_{14}H_{13}FN_2O_4$ +H, 293.0938 found: 293.0932.



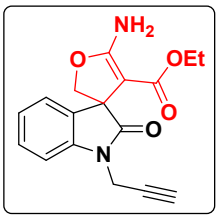
(2ac) ethyl 5-amino-5'-methyl-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carboxylate, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (44.8 mg 79% yield), M. P. 232-234°C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.2

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.18 (s, 1 H), 7.21 (br. s.,2 H), 6.78 - 7.00 (m, 2 H), 6.66 (d, *J*=7.9 Hz, 1 H), 4.45 (d, *J*=9.0 Hz, 1 H), 4.36 (d, *J*=8.9 Hz, 1 H), 3.59 - 3.89 (m, 2 H), 2.23 (s, 3 H), 0.77 (br. s., 3 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 179.6, 139.5, 133.9, 130.3, 128.1, 123.6, 123.6, 108.6, 78.1, 57.4, 20.6, 13.9; **HRMS:** (ESI) m/z calculated for: $C_{15}H_{16}N_2O_4$+H, 289.1188, found:289.1183



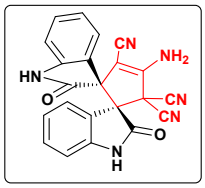
(2ad) ethyl 5-amino-2'-oxo-7'-(trifluoromethyl)-2H-spiro[furan-3,3'-indoline]-4-carboxylate, the titled compound was prepared by following the optimize procedure-(A), obtained as a solid (51.6 mg, 76% yield), M. P. 240-242 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.3

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.77 (s, 1 H), (NH2 replaced), 7.43 (dd, *J*=7.6, 3.1 Hz, 2 H), 7.10 (t, *J*=7.5 Hz, 1 H), 4.53 (d, *J*=9.3 Hz, 1 H), 4.46 (d, *J*=9.0 Hz, 1 H), 3.65 - 3.68 (m, 2 H), 0.53 - 0.81 (m, 3 H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 180.3, 139.5, 135.9, 127.1, 125.1, 124.0, 122.4, 121.7, 110.2, 109.9, 77.7, 57.5, 57.5, 13.3; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -60.03: **HRMS:** (ESI) m/z calculated for: $C_{15}H_{13}F_3N_2O_4$ +H, 343.0906, found: 343.0900



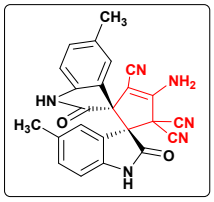
(2ae) ethyl5-amino-2'-oxo-1'-(prop-2-yn-1-yl)-2H-spiro[furan-3,3'-indoline]-4-carboxylate, the titled compound was prepared by following the optimized procedure-(A), obtained as a solid (42.7 mg 70% yield), M. P. 120-122 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.6

^{1}H NMR (400 MHz, DMSO-d_6) δ (NH_2 replaced) 7.28 (t, *J*=7.6 Hz, 1 H), 7.21 (d, *J*=7.4 Hz, 1 H), 7.05 (d, *J*=5.8 Hz, 2 H), 4.51 - 4.76 (m, 1 H), 4.50 (d, *J*=9.8 Hz, 2 H), 4.42 (d, *J*=9.4 Hz, 1 H), 3.66 (br. s., 2 H), 3.25 (br. s., 1 H), 0.69 (br. s., 3 H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 177.2, 141.6, 132.9, 127.9, 122.8, 122.7, 108.5, 78.1, 77.8, 74.2, 57.4, 28.9, 14.1; **HRMS:** (ESI) m/z calculated for: $C_{17}H_{16}N_2O_4$+H 313.1188, found: 313.1183.



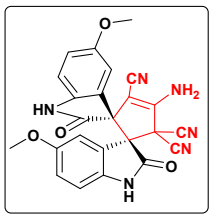
(3a) 4'-amino-2,2''-dioxodispiro[indoline-3,1'-cyclopentane-2',3''-indolin]-3'-ene-3',5',5'tricarbonitrile, the titled compound was prepared by following the optimized procedure-(B), obtained as a solid, (33.1 mg, 85% yield, 20:1 dr.) diastereomeric ratio calculated by ^{1}H NMR of crude product, M. P. 228-230 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.4

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.22 (s, 1 H), 10.76 (s, 1 H), 8.37 (s, 2 H), 7.71 (d, *J*=7.9 Hz, 1 H), 7.29 - 7.39 (m, 2 H), 7.21 (t, *J*=7.7 Hz, 1 H), 7.12 (t, *J*=7.8 Hz, 1 H), 7.00 (t, *J*=7.6 Hz, 1 H), 6.79 (d, *J*=7.8 Hz, 1 H), 6.67 (d, *J*=7.8 Hz, 1 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 176.3, 172.6, 153.4, 142.9, 142.8, 131.7, 130.6, 126.6, 126.5, 123.1, 122.7, 122.5, 119.4, 115.0, 112.2, 111.5, 110.5, 110.2, 75.9, 62.4, 62.1, 46.4; **HRMS:** (ESI) m/z calculated for: $C_{22}H_{12}N_6O_2$ +H, 393.1100 found: 393.1095



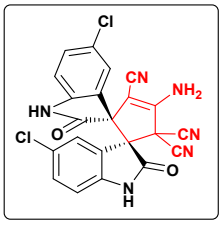
(3b) 4'-amino-5,5''-dimethyl-2,2''-dioxodispiro[indoline-3,1'-cyclopentane-2',3''-indolin]-3'-ene-3',5',5'-tricarbonitrile, the titled compound was prepared by following the optimized procedure-(B), obtained as a solid, (35.1 mg, 84% yield & d. r. 20:1), diastereomeric ratio calculated by **^{1}H NMR** of crude product, M. P. 238-240 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.5

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 11.15 (s, 1H), 10.68 (s, 1H), 8.31 (br. s., 2H), 7.53 (s, 1H), 7.09 - 7.23 (m, 2H), 6.96 - 7.05 (m, 1H), 6.63 - 6.72 (m, 1H), 6.50 - 6.60 (m, 1H), 2.26 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 176.2, 172.6, 153.3, 140.4, 140.3, 131.8, 131.4, 131.1, 130.8, 127.1, 127.0, 123.1, 119.5, 115.0, 112.2, 111.4, 110.1, 109.8, 76.1, 62.3, 61.9, 46.5, 20.9, 20.8; **HRMS:** (ESI) m/z calculated for: $C_{24}H_{16}N_6O_2$ +Na, 443.1232 found: 443.1227



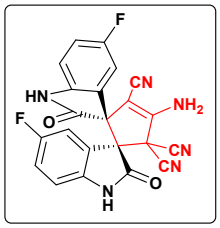
(3c) 4'-amino-5,5''-dimethoxy-2,2''-dioxodispiro[indoline-3,1'-cyclopentane-2',3''-indolin]-3'-ene-3',5',5'-tricarbonitrile, the titled compound was prepared by following the optimized procedure-(B), obtained as a solid, (39.1 mg, 87% yield & d. r. 20:1), diastereomeric ratio calculated by **^{1}H NMR** of crude product, M. P. 230-232 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.5

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 11.10 (s, 1H), 10.58 - 10.72 (m, 1 H), 8.35 (br. s., 2 H), 7.30 - 7.42 (m, 1 H), 6.89 - 7.01 (m, 2 H), 6.76 - 6.84 (m, 1 H), 6.67 - 6.76 (m, 1 H), 6.61 (dd, *J*=8.5, 1.6 Hz, 1 H), 3.71 (s, 3 H), 3.68 (s, 3 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 176.1, 172.4, 154.9, 153.3, 135.9, 135.6, 124.3, 120.6, 115.6, 114.9, 114.5, 114.3, 113.9, 112.1, 111.4, 110.8, 110.4, 75.9, 62.6, 62.1, 55.5, 55.3, 46.5; **HRMS:** (ESI) m/z calculated for: $C_{24}H_{16}N_6O_4$ +Na, 475.1131 found: 475.1125



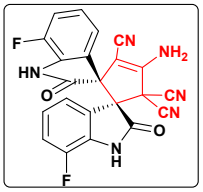
(3e) (4'-amino-5,5''-dichloro-2,2''-dioxodispiro[indoline-3,1'-cyclopentane-2',3''-indolin]-3'-ene-3',5',5'-tricarbonitrile, the titled compound was prepared by following the optimized procedure-(B), obtained as a solid, (34.8 mg, 76% yield & d. r. 20:1), diastereomeric ratio calculated by **^{1}H NMR** of crude product, M. P. 232-234 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.4

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 11.62 (s, 1H), 11.15 (s, 1H), 8.54 (s, 2H), 7.67 (d, *J*=2.3 Hz, 1H), 7.47 (dd, *J*=8.4, 2.1 Hz, 1H), 7.33 (dd, *J*=8.4, 2.3 Hz, 1H), 7.27 (d, *J*=2.3 Hz, 1H), 6.88 (d, *J*=8.5 Hz, 1H), 6.76 (d, *J*=8.4 Hz, 1H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 175.9, 172.2, 153.5, 141.8, 141.7, 131.9, 130.9, 126.8, 126.5, 126.3, 124.7, 120.1, 114.6, 112.4, 112.1, 111.7, 111.1, 74.8, 62.4, 61.6, 46.2; **HRMS:** (ESI) m/z calculated for: $C_{22}H_{10}Cl_2N_6O_2$+Na, 483.0140 found: 483.0135



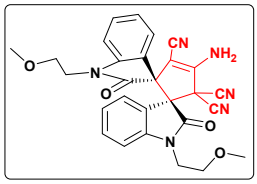
(3f) 4'-amino-5,5''-difluoro-2,2''-dioxodispiro[indoline-3,1'-cyclopentane-2',3''-indolin]-3'-ene-3',5',5'-tricarbonitrile, the titled compound was prepared by following the optimized procedure-(B), obtained as a solid, (32 mg, 81% yield & d. r. 20:1), diastereomeric ratio calculated by **^{1}H NMR** of crude product, M. P. 250-252 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.4

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.46 (s, 1 H), 10.99 (s, 1 H), 8.51 (s, 2 H), 7.47 (dd, *J*=9.1, 2.6 Hz, 1 H), 7.27 (td, *J*=8.9, 2.7 Hz, 1 H), 7.07 - 7.16 (m, 2 H), 6.86 (dd, *J*=8.6, 4.5 Hz, 1 H), 6.74 (dd, *J*=8.5, 4.5 Hz, 1 H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 176.1, 172.4, 159.1, 159.0, 156.8, 156.6, 153.4, 139.1, 124.4, 120.7, 118.8, 118.5, 117.7, 117.4, 114.6, 114.4, 114.2, 113.9, 111.9, 111.8, 111.5, 111.1, 75.1, 62.6, 61.7, 46.2; **^{19}F NMR** (376 MHz, DMSO-d_6) d -119.40 (s, 1 F), -120.04 (s, 1 F); **HRMS:** (ESI) m/z calculated for: $C_{22}H_{10}F_2N_6O_2$+Na,451.0731 found: 451.0726



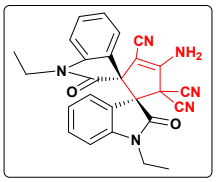
(3g) 4'-amino-7,7''-difluoro-2,2''-dioxodispiro[indoline-3,1'-cyclopentane-2',3''-indolin]-3'-ene-3',5',5'-tricarbonitrile, the titled compound was prepared by following the optimized procedure-(B), obtained as a solid, (34 mg, 80% yield & d. r. 20:1), diastereomeric ratio calculated by **^{1}H NMR** of crude product. M. P. 226-228 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.4

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 11.93 (s, 1H), 11.44 (s, 1H), 8.53 (br. s., 2H), 7.50 - 7.61 (m, 1H), 7.31 - 7.41 (m, 1H), 7.16 - 7.27 (m, 3H), 7.03 - 7.13 (m, 1H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 176.1, 172.2, 153.5, 147.3, 144.9, 144.9, 130.2, 130.2, 130.1, 130.1, 125.5, 125.5, 123.9, 123.9, 123.6, 123.6, 122.7, 122.6, 122.6, 121.8, 121.8, 119.1, 119.1, 118.1, 117.9, 114.7, 111.9, 111.1, 75.2, 62.7, 62.1, 46.3; **^{19}F NMR** (376 MHz, *DMSO-d_6*) δ -130.4, -131.8; **HRMS:** (ESI) m/z calculated for: $C_{22}H_{10}F_2N_6O_2$+H, 429.0912 found: 429.0906.



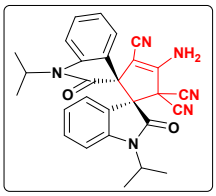
(3h) 4'-amino-1,1''-bis(2-methoxyethyl)-2,2''-dioxodispiro[indoline-3,1'-cyclopentane-2',3''-indolin]-3'-ene-3',5',5'-tricarbonitrile, the titled compound was prepared by following the optimized procedure-(B), obtained as a solid, (43.4 mg, 86% yield & d. r. 9:1), diastereomeric ratio calculated by **^{1}H NMR** of crude product, M. P. 210-212 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.5

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.44 (s, 2 H), 7.70 (d, *J*=7.8 Hz, 1 H), 7.41 (t, *J*=7.7 Hz, 1 H), 7.24 - 7.34 (m, 2 H), 7.19 (t, *J*=7.7 Hz, 1 H), 7.07 (d, *J*=5.8 Hz, 2 H), 6.93 (d, *J*=7.8 Hz, 1 H), 3.64 - 3.90 (m, 4 H), 3.36 - 3.56 (m, 4 H), 3.09 (d, *J*=5.6 Hz, 6 H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 174.6, 170.9, 153.5, 143.9, 143.8, 131.5, 130.6, 126.2, 126.1, 123.2, 122.9, 121.9, 118.2, 114.7, 111.8, 111.3, 110.4, 109.9, 75.9, 68.9, 68.8, 61.6, 61.5, 58.1, 58.1, 58.1, 46.6; **HRMS:** (ESI) m/z calculated for: $C_{28}H_{24}N_6O_4$ +H, 509.1937; found: 509.1932



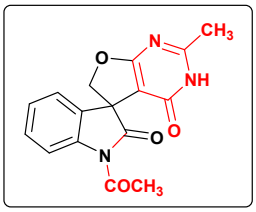
(3i) 4'-amino-1,1''-diethyl-2,2''-dioxodispiro[indoline-3,1'-cyclopentane-2',3''-indolin]-3'-ene-3',5',5'-tricarbonitrile, the titled compound was prepared by following the optimized procedure-(B), obtained as a solid, (38.7 mg, 87% yield & d. r. 9:1), diastereomeric ratio calculated by ^{1}H NMR of crude product, M. P. 234-236 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.5

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 8.45 (br. s., 2H), 7.68 - 7.77 (m,1H), 7.39 - 7.48 (m, 1H), 7.26 - 7.35 (m, 2H), 7.14 - 7.22 (m, 1H), 7.01 - 7.09 (m, 2H), 6.87 - 6.93 (m, 1H), 3.71 - 3.84 (m, 1H), 3.66 - 3.71 (m, 1H), 3.61 - 3.66 (m, 1H), 3.48 (dd, *J*=14.1, 7.1 Hz, 1H), 0.94 (q, *J*=7.3 Hz, 6H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 174.1, 170.5, 153.6, 143.2, 142.9, 131.8, 130.8, 126.5, 126.3, 123.1, 122.9, 122.1, 118.5, 114., 111.8, 111.3, 109.8, 109., 75.4, 61.6, 61.4, 46.4, 34.5, 12.2, 11.9; **HRMS:** (ESI) m/z calculated for: $C_{26}H_{20}N_6O_2$ +Na, 471.1545; found: 471.1540



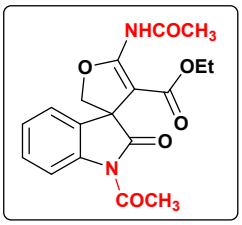
(3j) 4'-amino-1,1''-diisopropyl-2,2''-dioxodispiro[indoline-3,1'-cyclopentane-2',3''-indolin]-3'-ene-3',5',5'-tricarbonitrile, the titled compound was prepared by following the optimized procedure-(B), obtained as a solid, (41.2 mg, 87% yield d. r. 9:1), diastereomeric ratio calculated by **^{1}H NMR** of crude product, M. P. 222-224°C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.5

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 (s, 2H), 7.70 - 7.77 (m, 1H), 7.38 - 7.44 (m, 1H), 7.31 - 7.35 (m, 1H), 7.25 - 7.31 (m, 1H), 7.13 - 7.20 (m, 2H), 7.00 - 7.06 (m, 2H), 4.39 - 4.44 (m, 1H), 4.33 - 4.39 (m, 1H), 1.29 (d, *J*=6.9 Hz, 6H), 1.08 - 1.18 (m, 6H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 174.2, 170.8, 153.7, 142.7, 131.7, 130.7, 126.5, 126.5, 126.5, 122.7, 122.4, 122.2, 118.6, 114.8, 111.8, 111., 110., 110.3, 75.4, 61.7, 61.1, 46.4, 44.4, 44.2, 18.9, 18.6, 18.5, 18.2; **HRMS:** (ESI) m/z calculated for: $C_{28}H_{24}N_6O_2$ +H, 477.2039; found: 477.2034.



(4a) 1'-acetyl-2-methyl-6H-spiro[furo[2,3-d]pyrimidine-5,3'-indoline]-2',4(3H)-dione, the titled compound was prepared by following the optimized procedure-(C), obtained as a solid, (51 mg, 82% yield), M. P. 202-204 °C, Rf (Ethyl acetate/Pet. ether; 40:60) = 0.5

^{1}H NMR (400 MHz, *DMSO-d_6*) δ 11.29 (s, 1H), 8.12 (d, *J*=8.1 Hz, 1H), 7.54 (d, *J*=7.4 Hz, 1H), 7.44 (t, *J*=7.8 Hz, 1H), 7.33 (t, *J*=7.4 Hz, 1H), 4.85 (d, *J*=9.5 Hz, 1H), 4..63 (d, J=9.5 Hz, 1H), 2.60 (s, 3H), 2.10 (s, 3H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ 177.6, 170.4, 168.1, 159.0, 139.7, 129.6, 128.7, 125.8, 124.2, 115.7, 113.8, 77.3, 71.7, 58.9, 26.2, 23.3; **HRMS:** (ESI) m/z calculated for: $C_{16}H_{13}N_3O_4$+Na, 334.0806; found: 334.0798



(4b) ethyl5-acetamido-1'-acetyl-2'-oxo-2H-spiro[furan-3,3'-indoline]-4-carboxylate, the titled compound was prepared by following the optimized procedure-(C), obtained as a sticky solid, (48 mg, 67% yield), Rf (Ethyl acetate/Pet. ether; 40:60) = 0.7

^{1}H NMR (400 MHz, *CHLOROFORM-d*) δ 9.79 (br. s., 1H), 8.14 (d, *J*=8.1 Hz, 1H), 7.24 - 7.31 (m, 1H), 7.11 - 7.24 (m, 2H), 4.91 (d, *J*=9.5 Hz, 1H), 4.68 (d, *J*=9.5 Hz, 1H), 3.74 - 3.89 (m, 2H), 2.62 (s, 3H), 2.22 (s, 3H), 0.80 (t, *J*=7.1 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ 178.7, 170.5, 167.1, 165.1, 162.4, 139.6, 130.6, 129.3, 125.8, 122.9, 116.3, 88.1, 81.4, 59.9, 55.8, 26.4, 24.9, 13.5; **HRMS:** (ESI) m/z calculated for: $C_{18}H_{18}N_2O_6$+Na, 381.1063; found: 381.1057

8) References.

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2. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3.
3. P. Zhao, Y. Li, G. Gao, S. Wang, Y. Yan, X. Zhan, Z. Liu, Z. Mao, S. Chen and L. Wang, *Eur. J. Med. Chem.*, 2014, **86**, 165.
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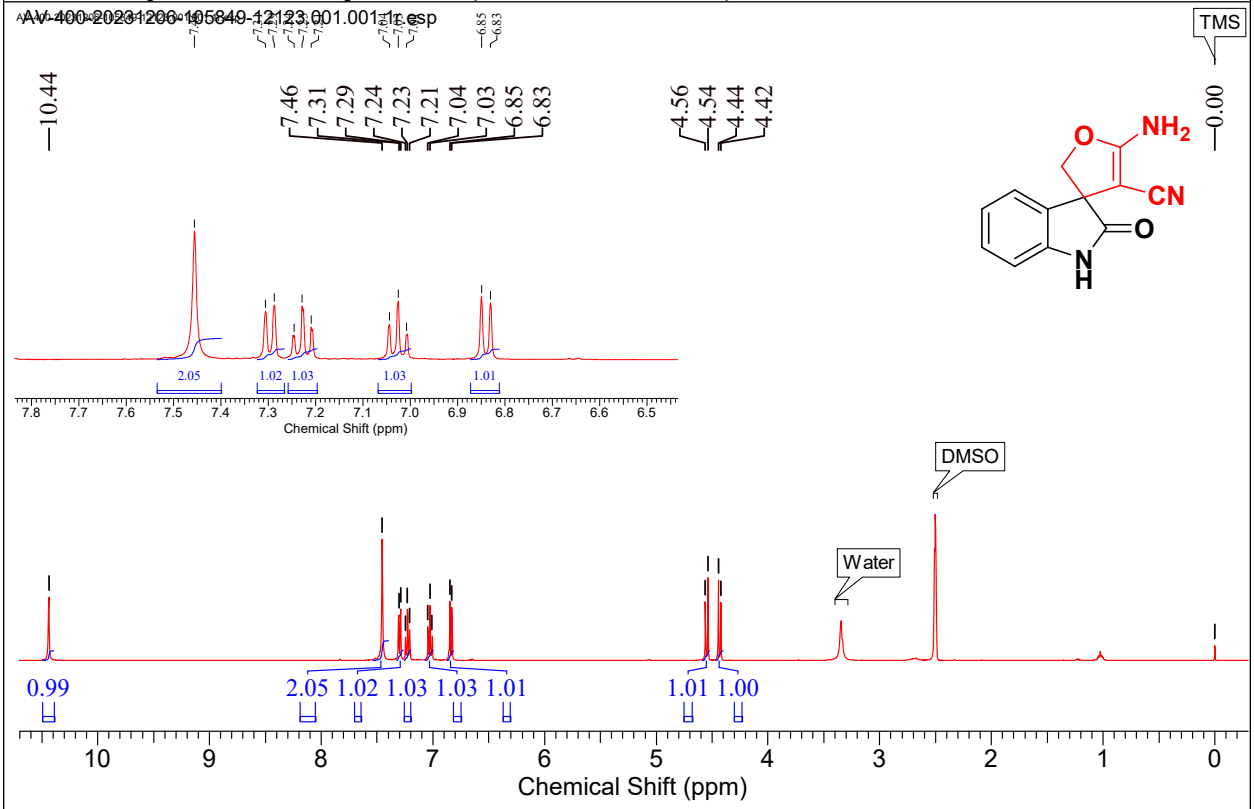
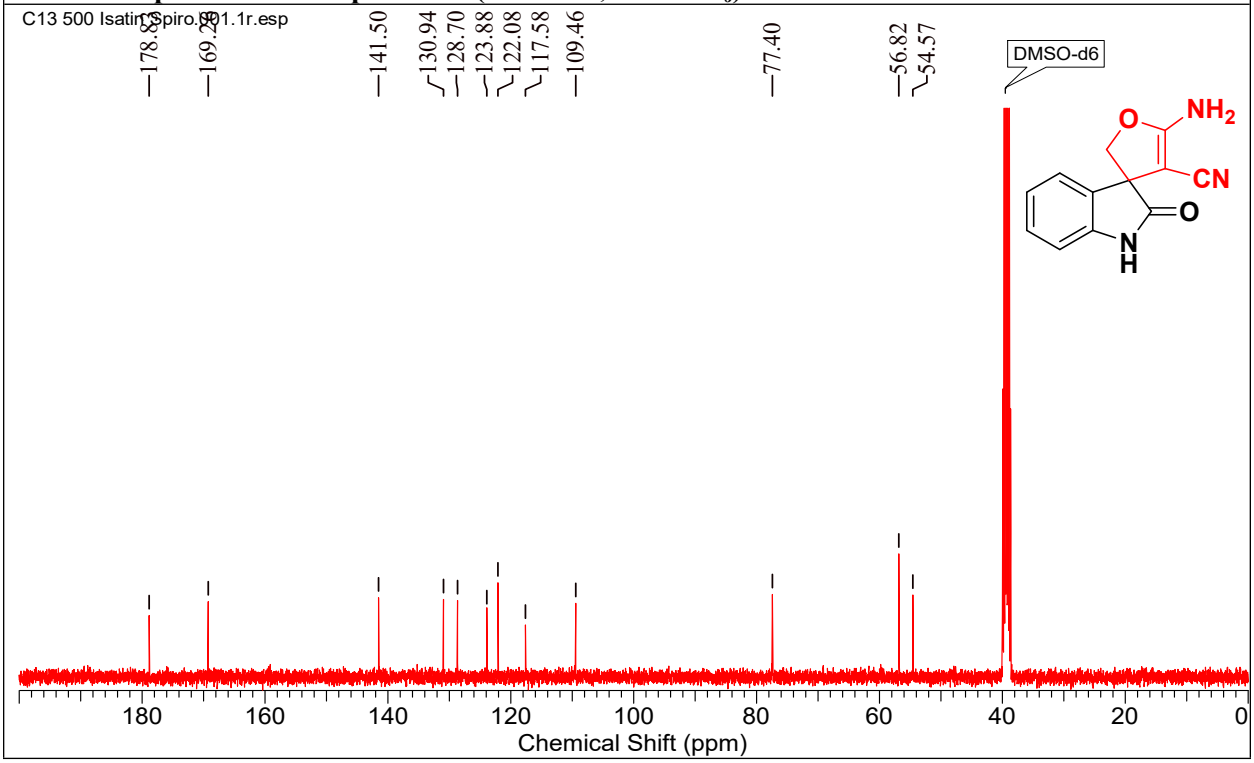
5. G.M. Coppola, *J. Heterocycl. Chem.* 1987, **24**, 1249.
6. C. B. Nichinde, B. R. Patil S. S. Chaudhari, B. P. Mali, R. G. Gonnade and A. K. Kinage, *RSC Adv*., 2023, **13**, 13206.
7. J.M.G.D.O. Ferreira, G.A. da Silva, M.C. Coelho, C.G.L. Junior and J.A. Vale, *Results Chem.* 2021, **3**, 100135.

9) NMR Spectra of Compounds.

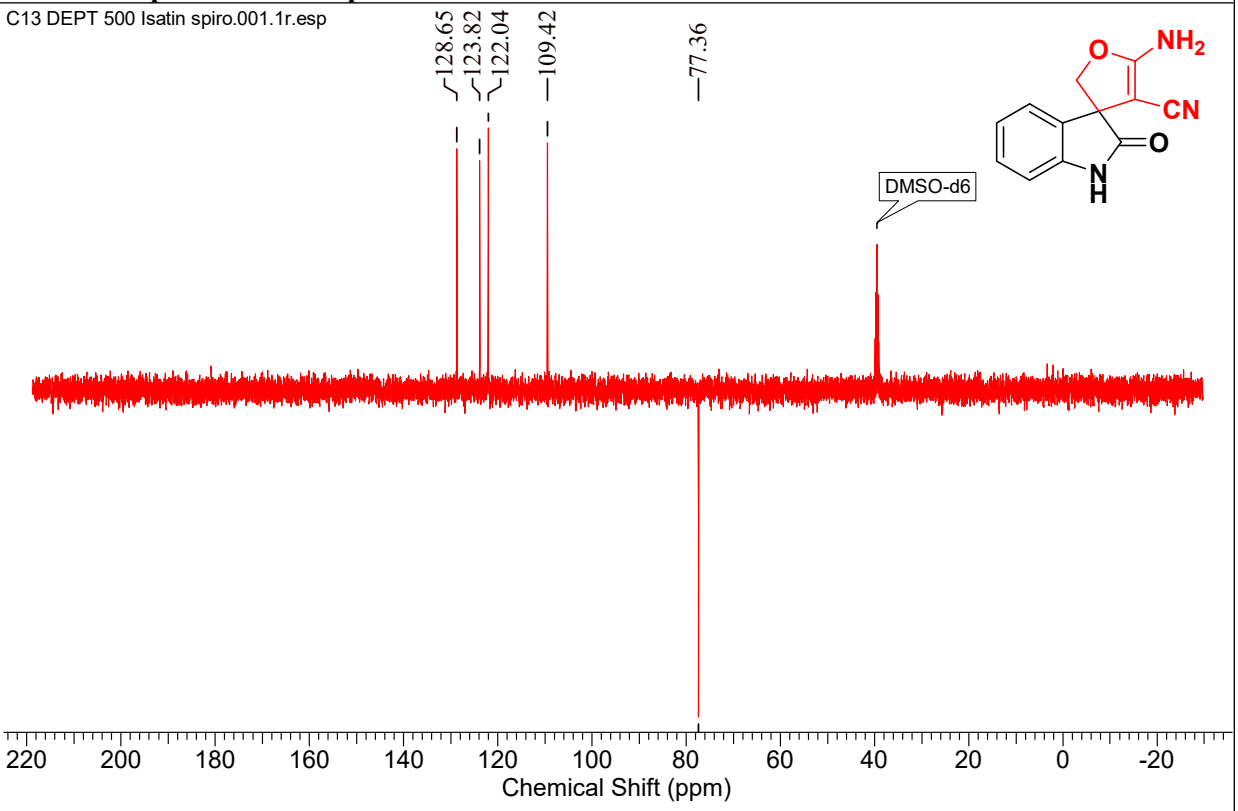
^{1}H NMR spectrum of compound 2a (400 MHz, *DMSO-d_6*)



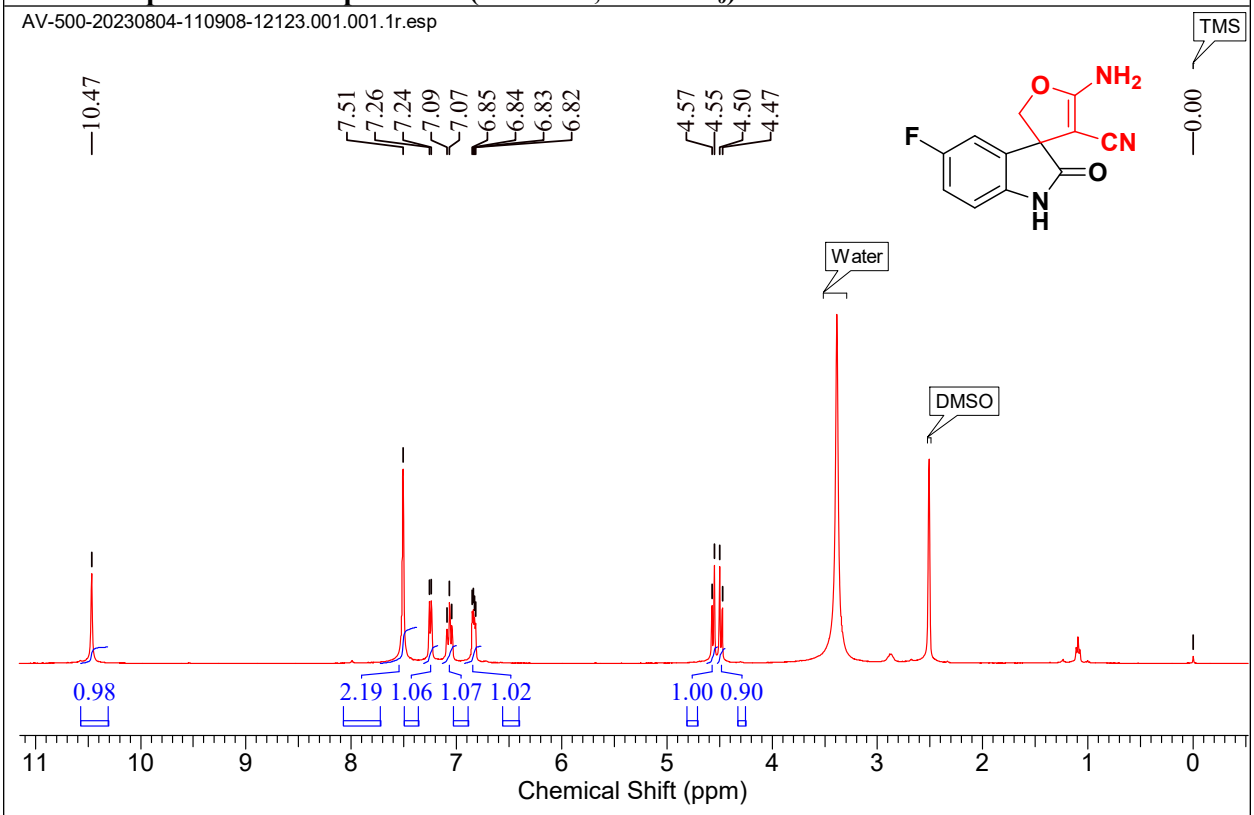
^{13}C NMR spectrum of compound 2a (101 MHz, *DMSO-d_6*)



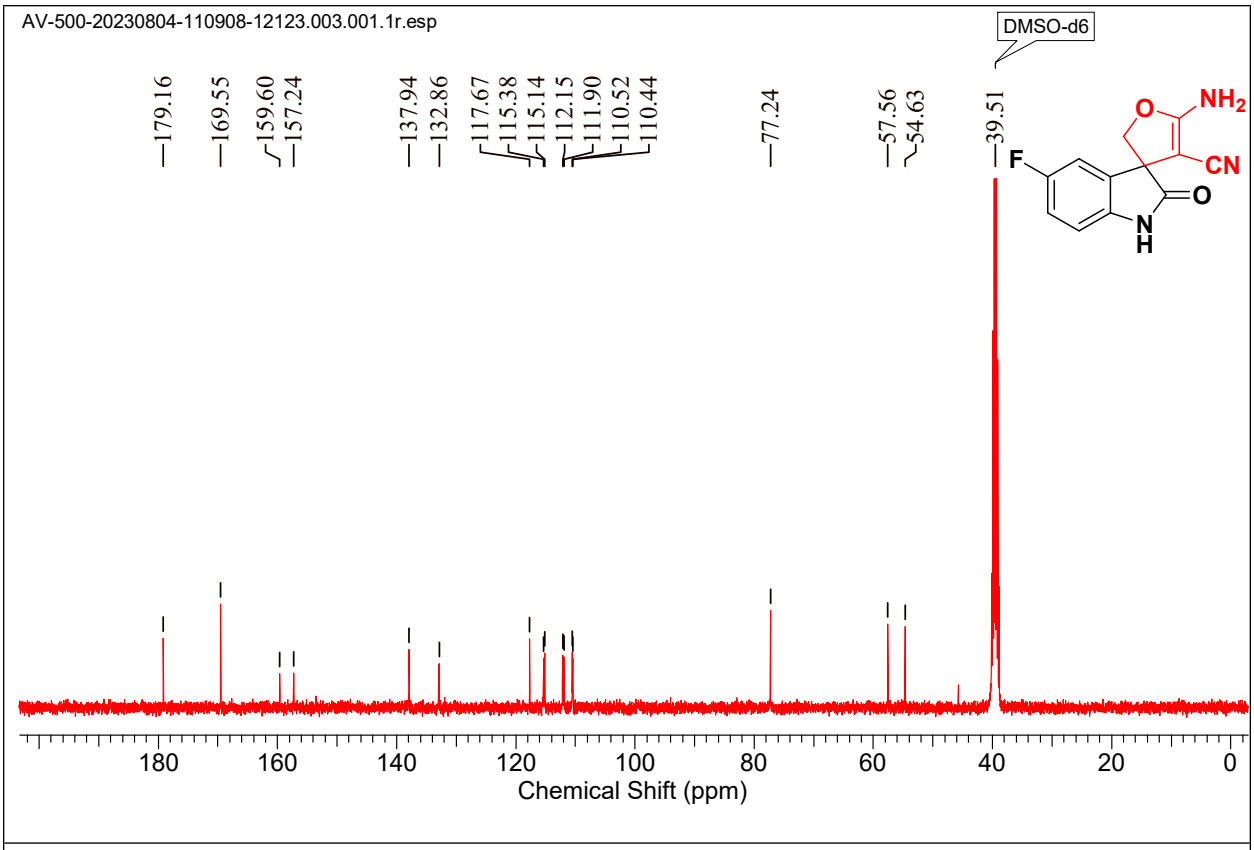
135 DEPT spectrum of compound 2a



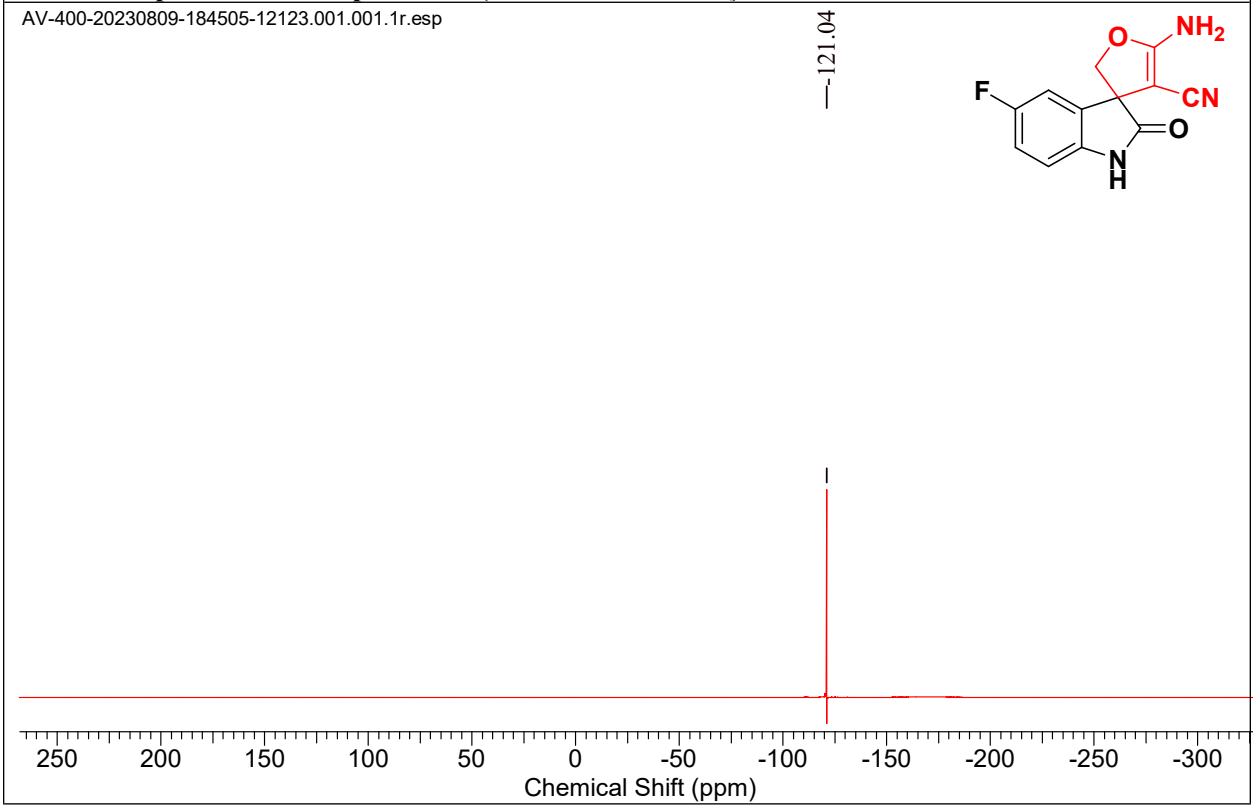
^{1}H NMR spectrum of compound 2b (400 MHz, *DMSO-d_6*)



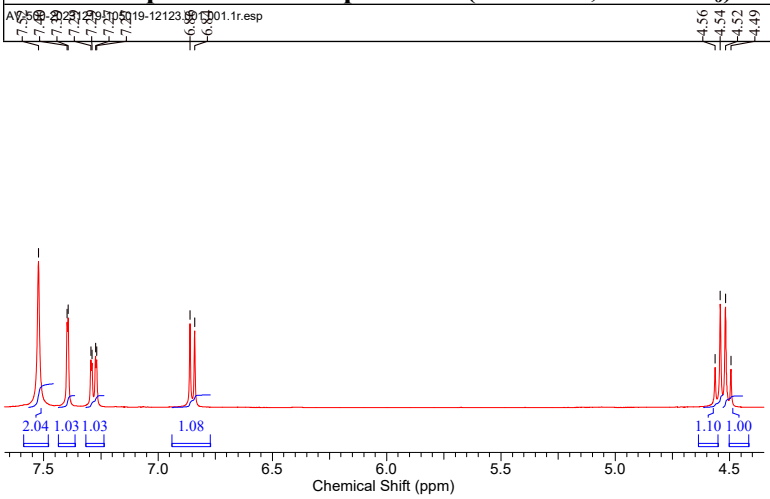
^{13}C NMR spectrum of compound 2b (101 MHz, *DMSO-d_6*)

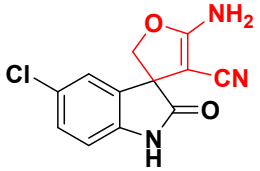


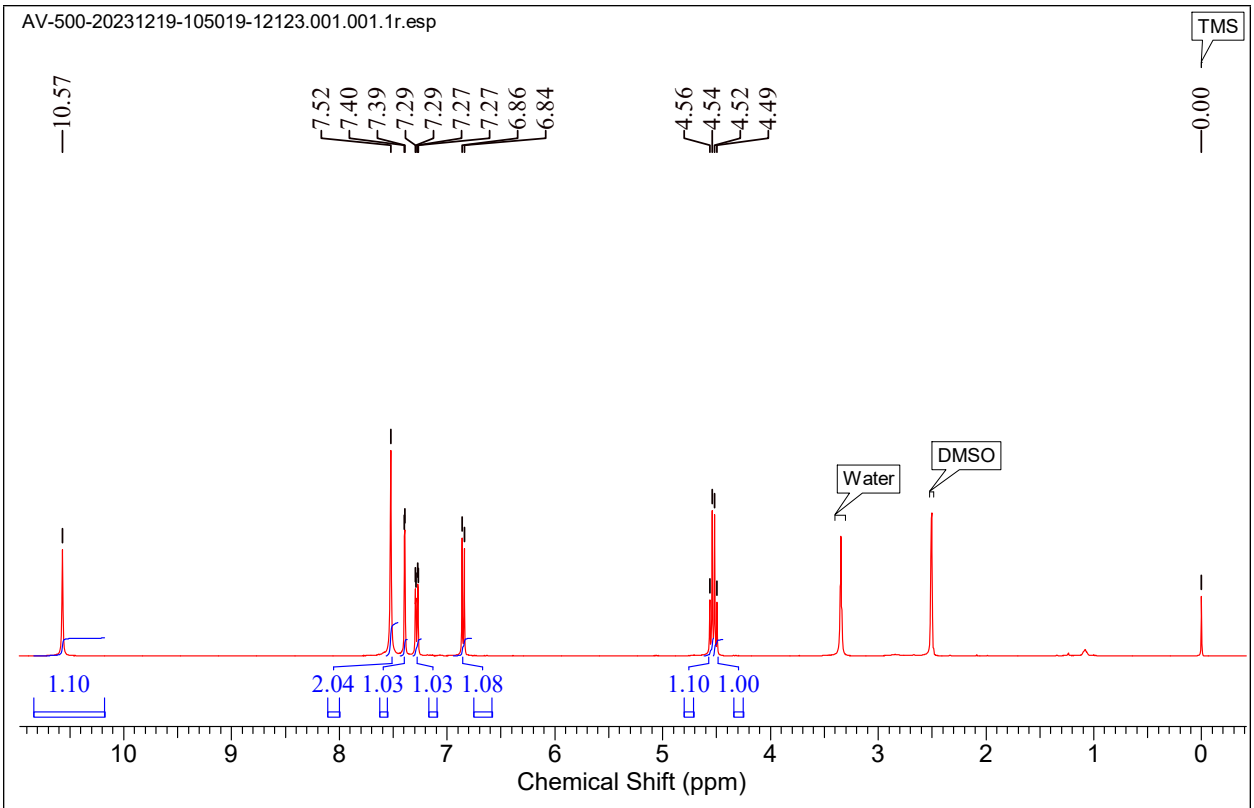
^{19}F NMR Spectrum of compound 2b (376 MHz, *DMSO-d_6*)



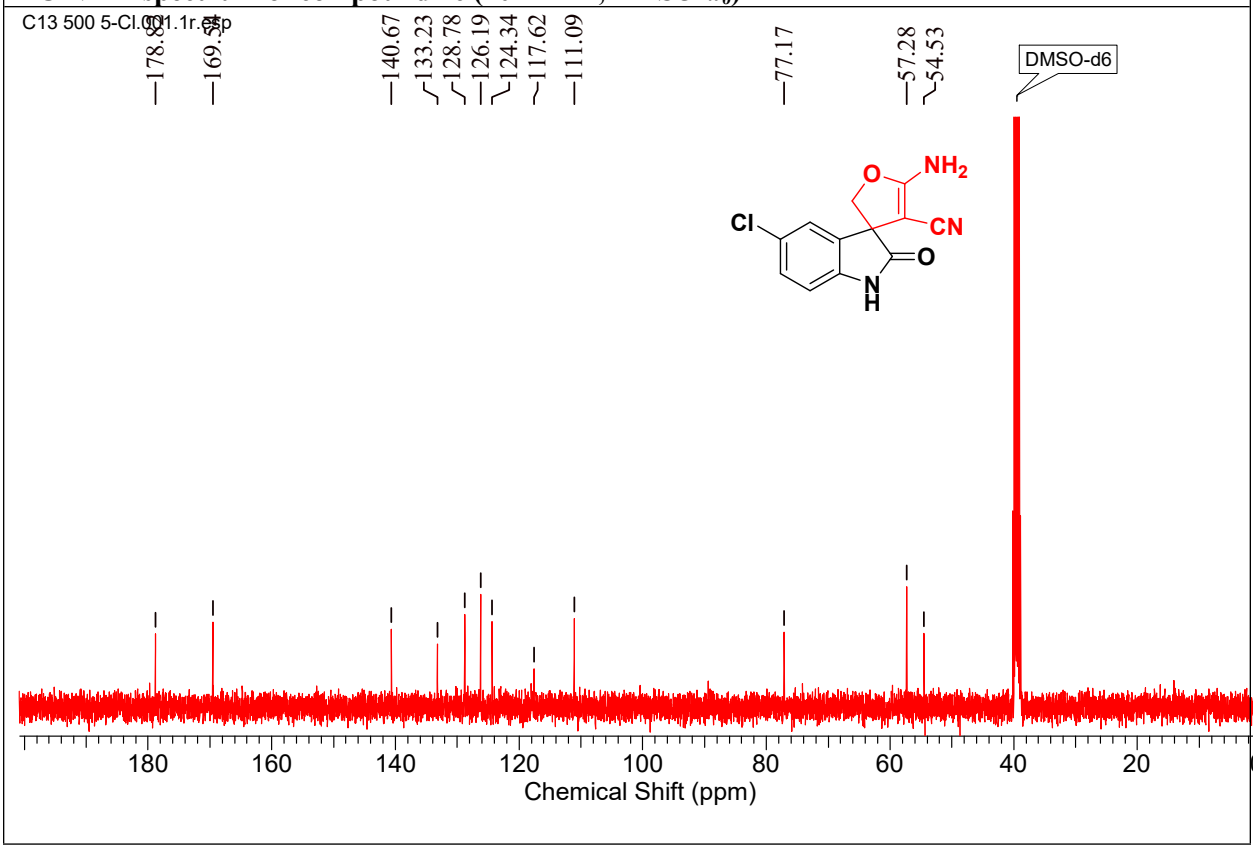
^{1}H NMR spectrum of compound 2c (400 MHz, *DMSO-d_6*)



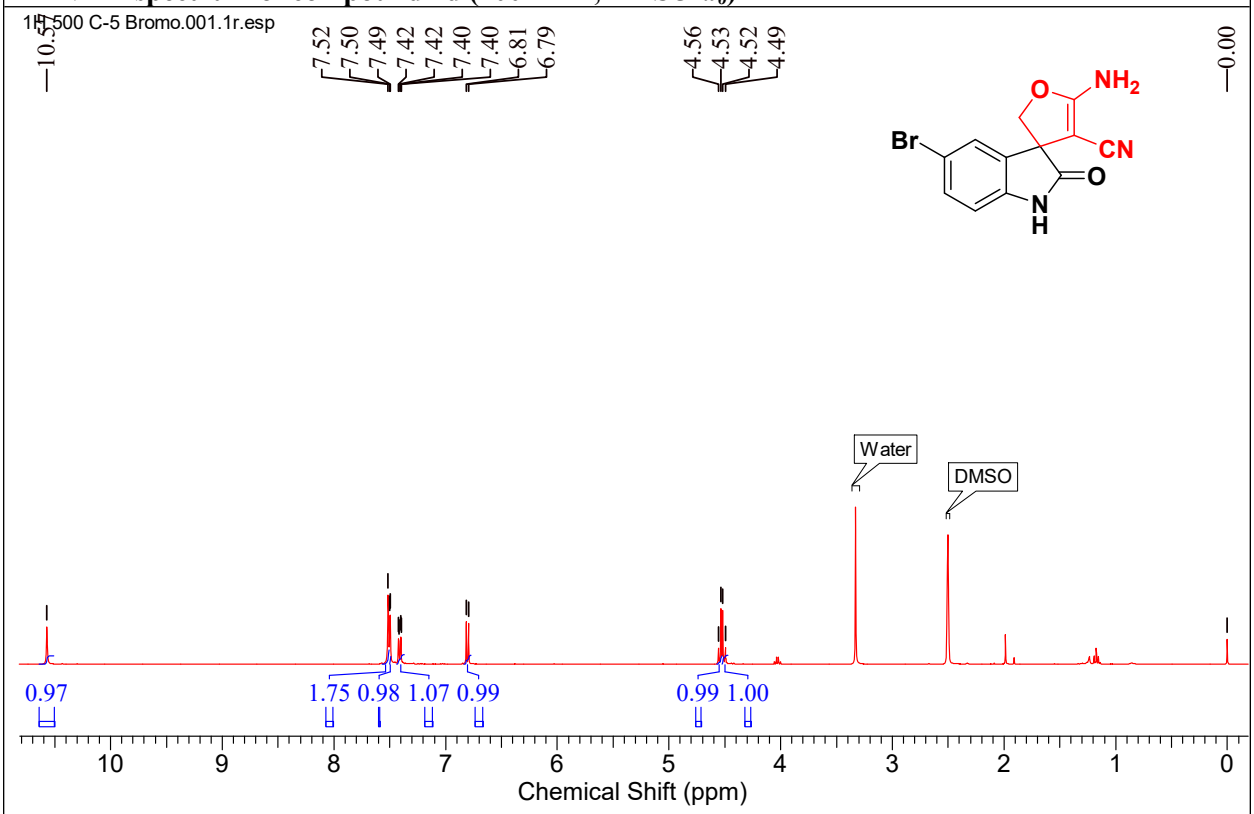




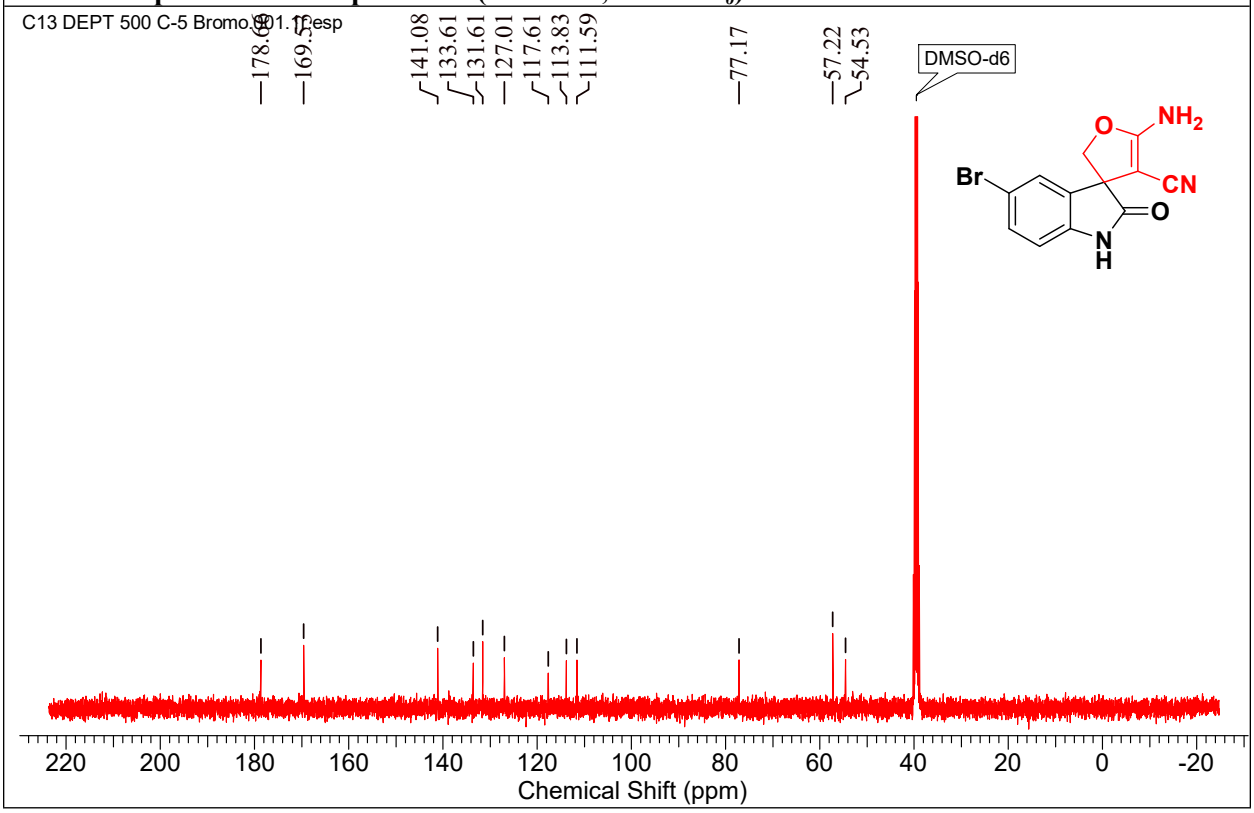
^{13}C NMR spectrum of compound 2c (101 MHz, *DMSO-d$_6$*)



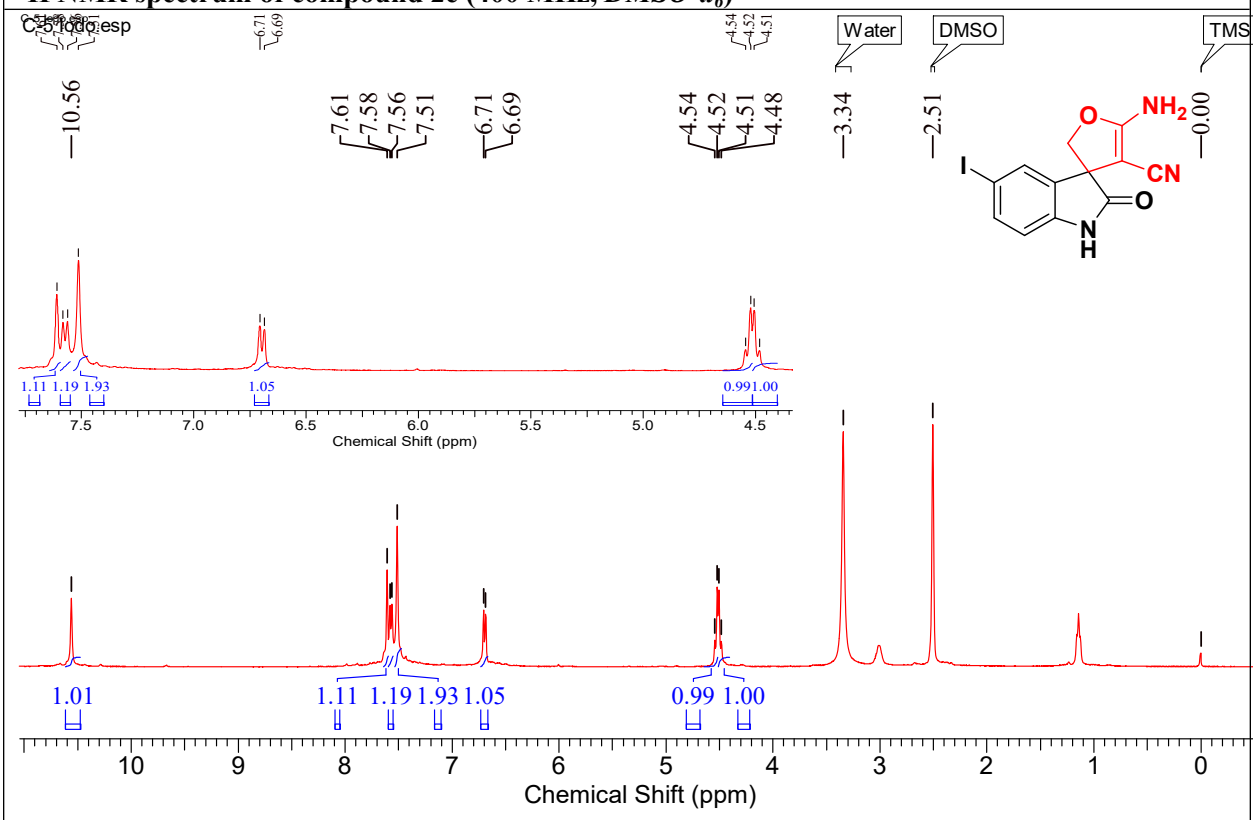
^{1}H NMR spectrum of compound 2d (400 MHz, *DMSO-d_6*)



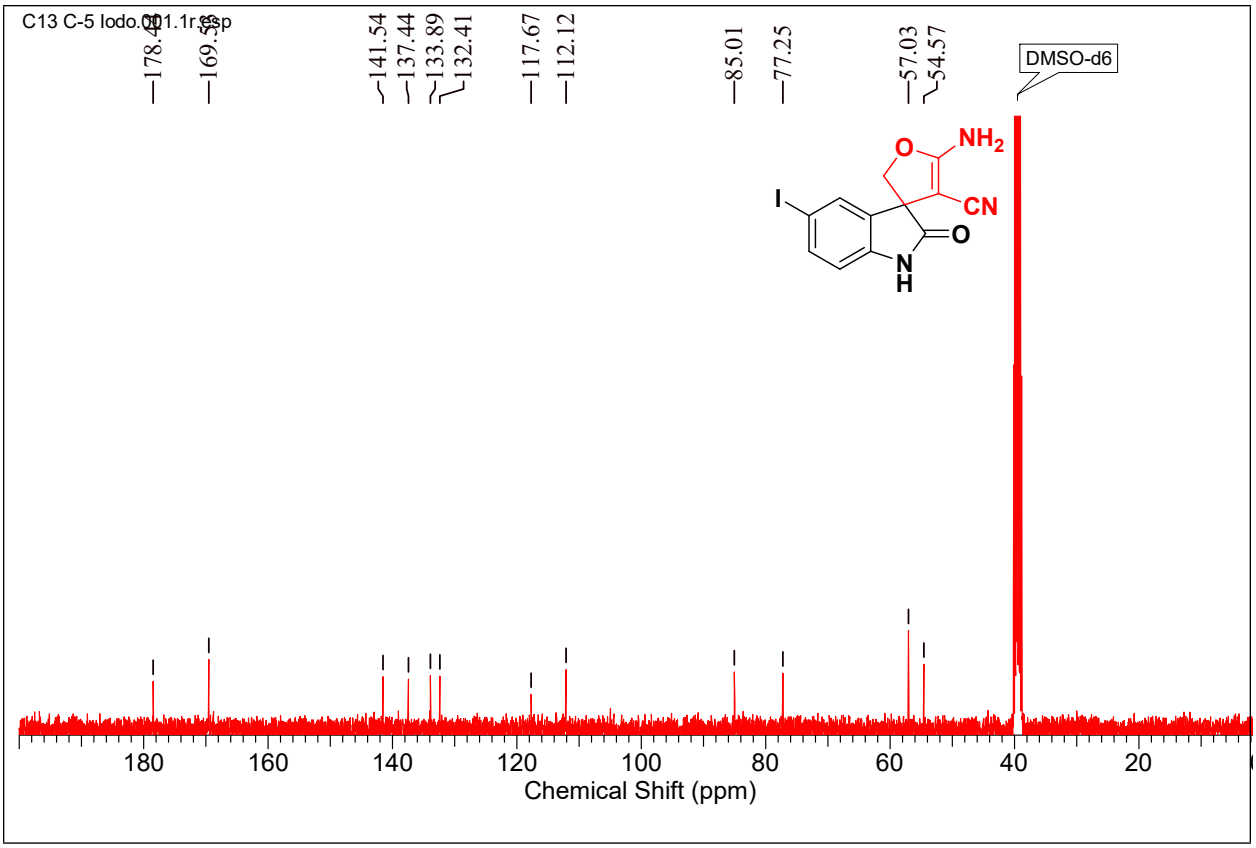
^{13}C NMR spectrum of compound 2d (101 MHz, *DMSO-d_6*)



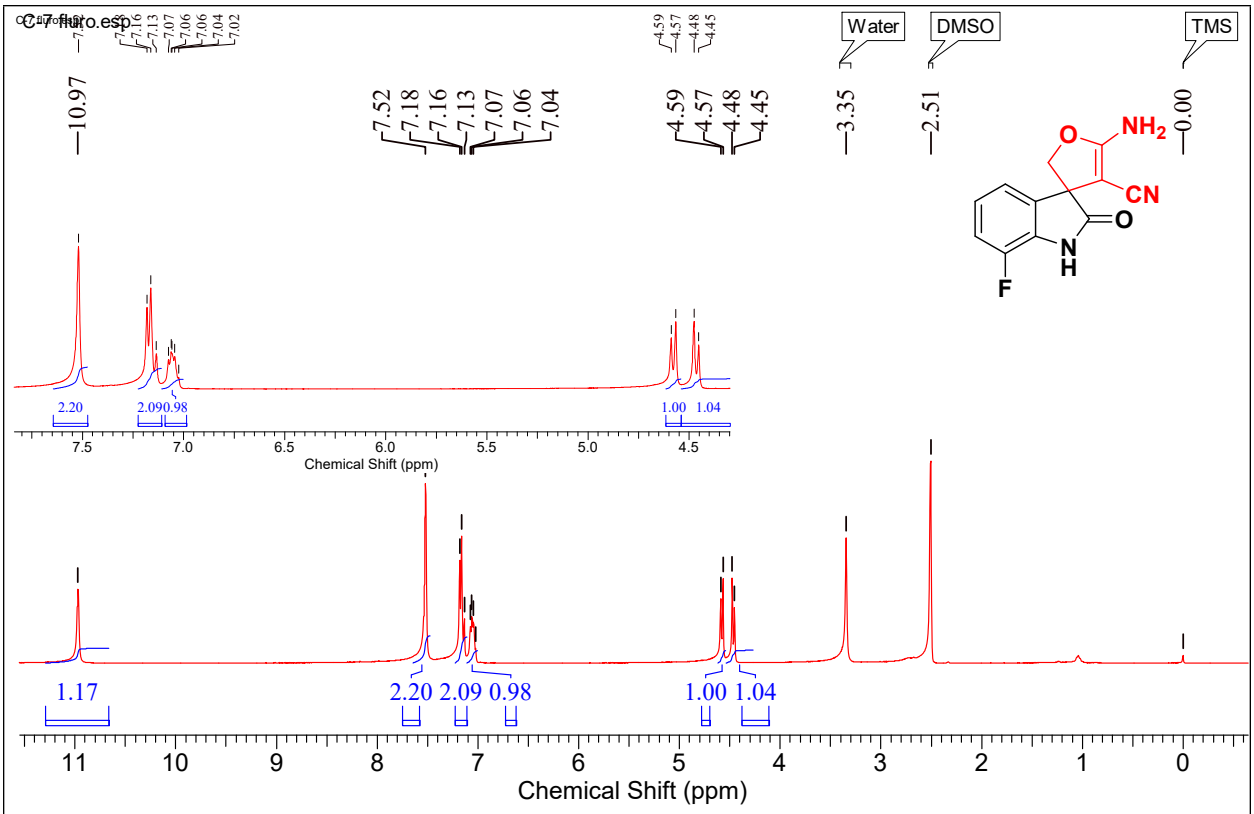
^{1}H NMR spectrum of compound 2e (400 MHz, *DMSO-d_6*)



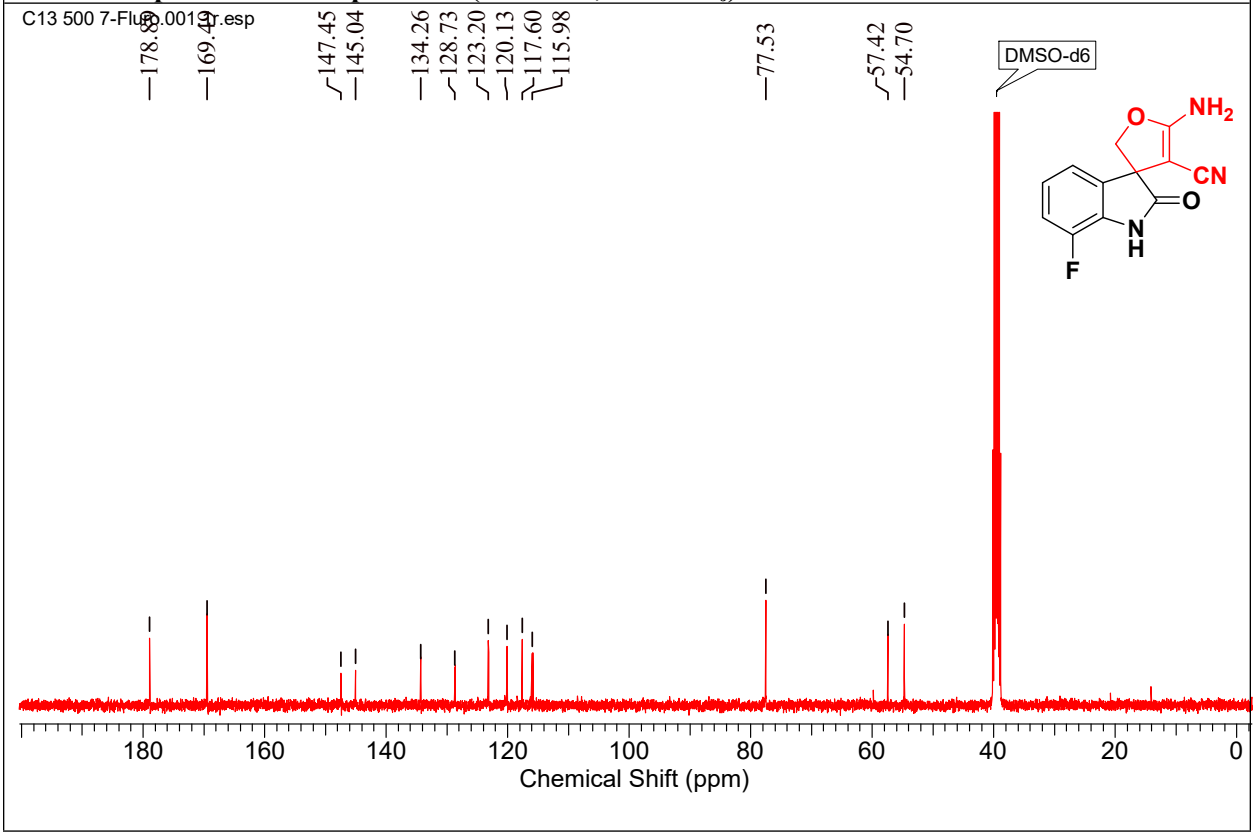
^{13}C NMR spectrum of compound 2e (101 MHz, DMSO-d_6)



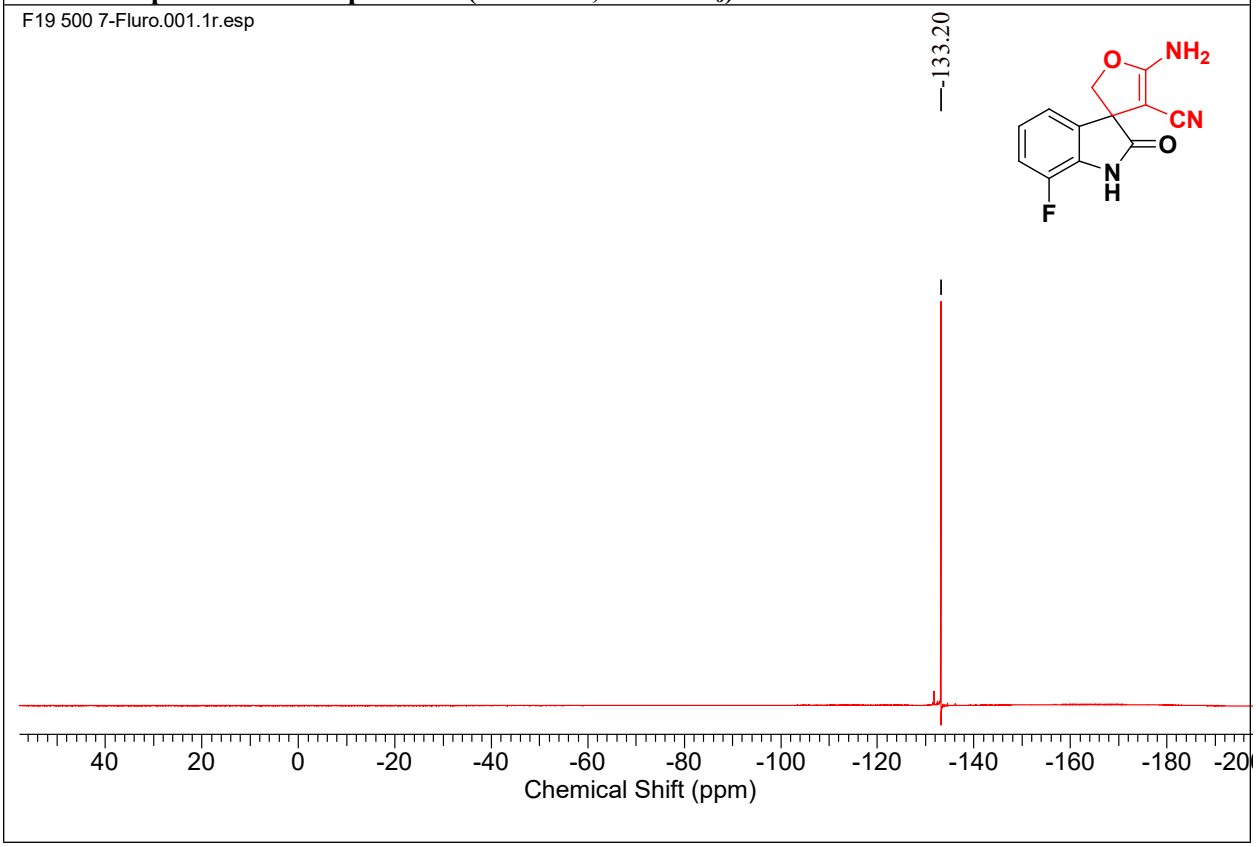
^{1}H NMR spectrum of compound 2f (400 MHz, DMSO-d_6)



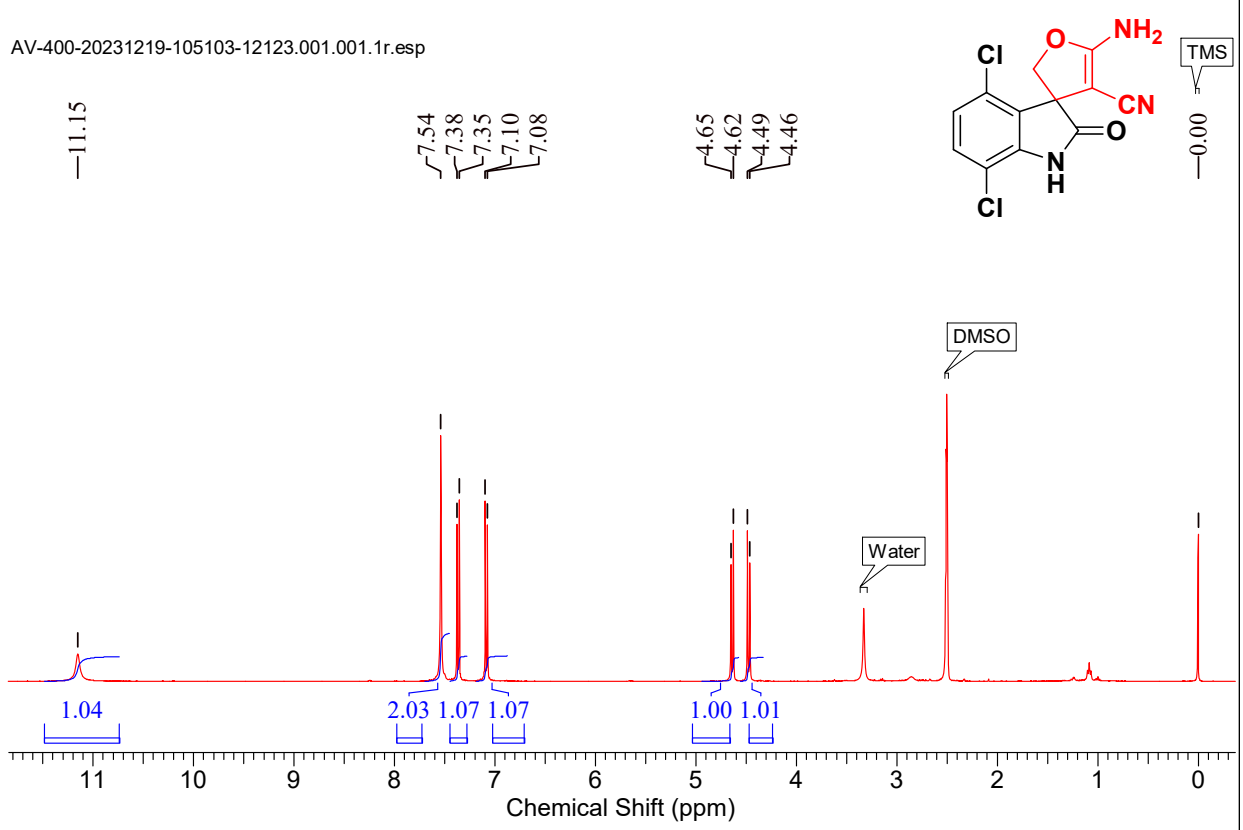
^{13}C NMR spectrum of compound 2f (101 MHz, *DMSO-d$_6$*)



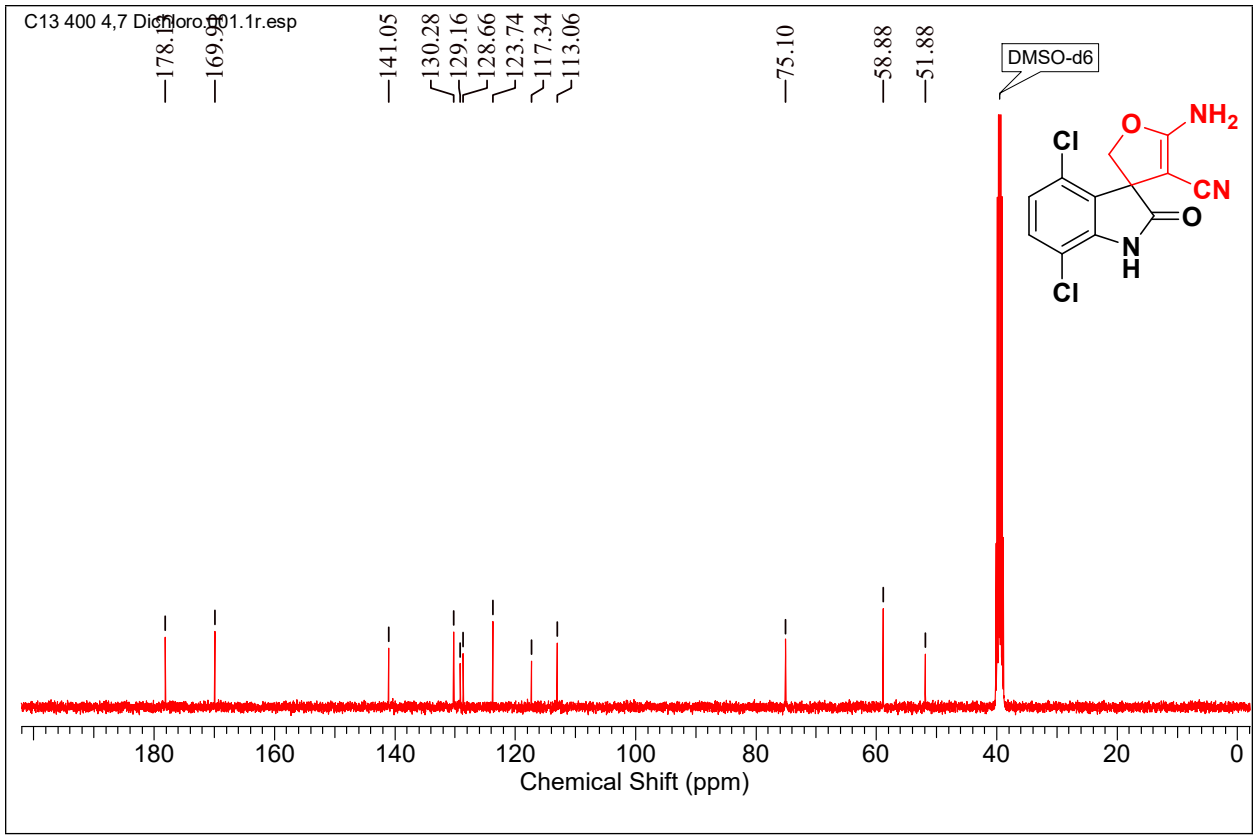
^{19}F NMR spectrum of compound 2f (376 MHz, *DMSO-d_6*)



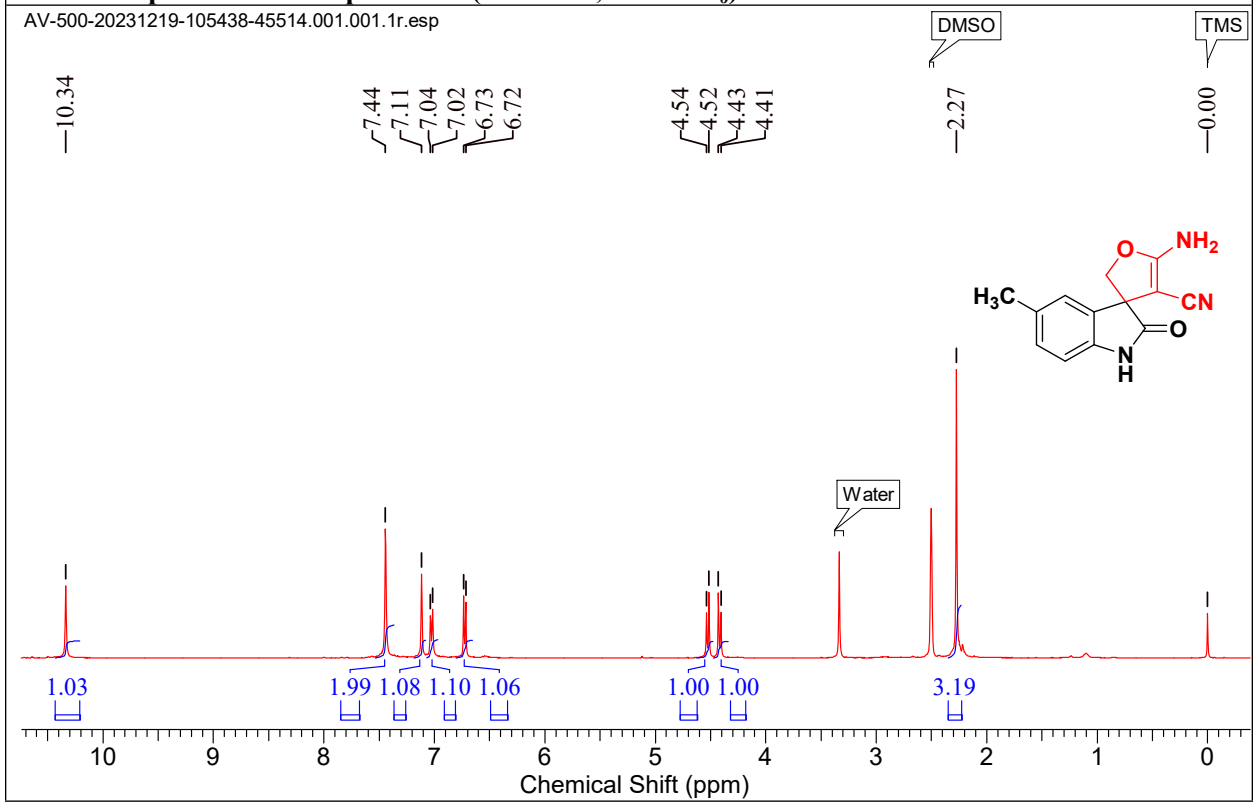
^{1}H NMR spectrum of compound 2g (400 MHz, *DMSO-d_6*)



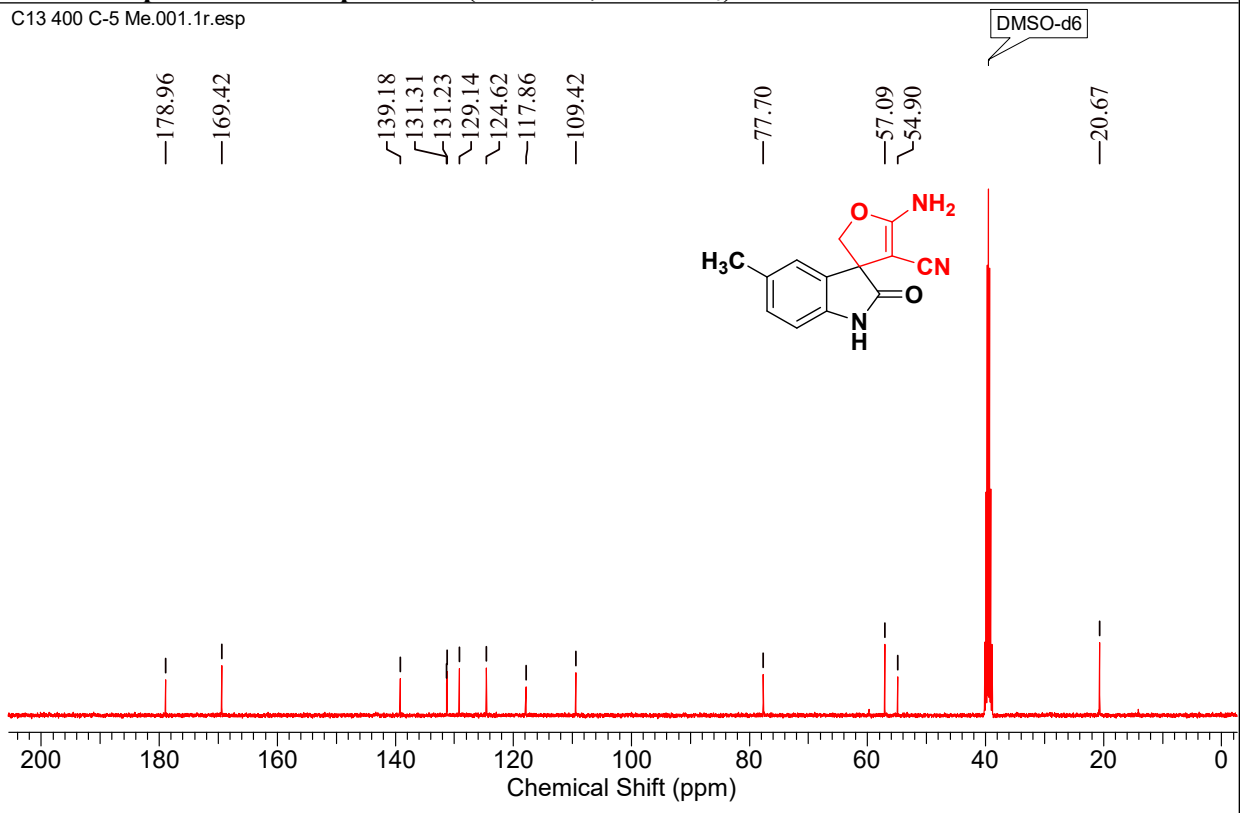
^{13}C NMR spectrum of compound 2g (101 MHz, *DMSO-d_6*)



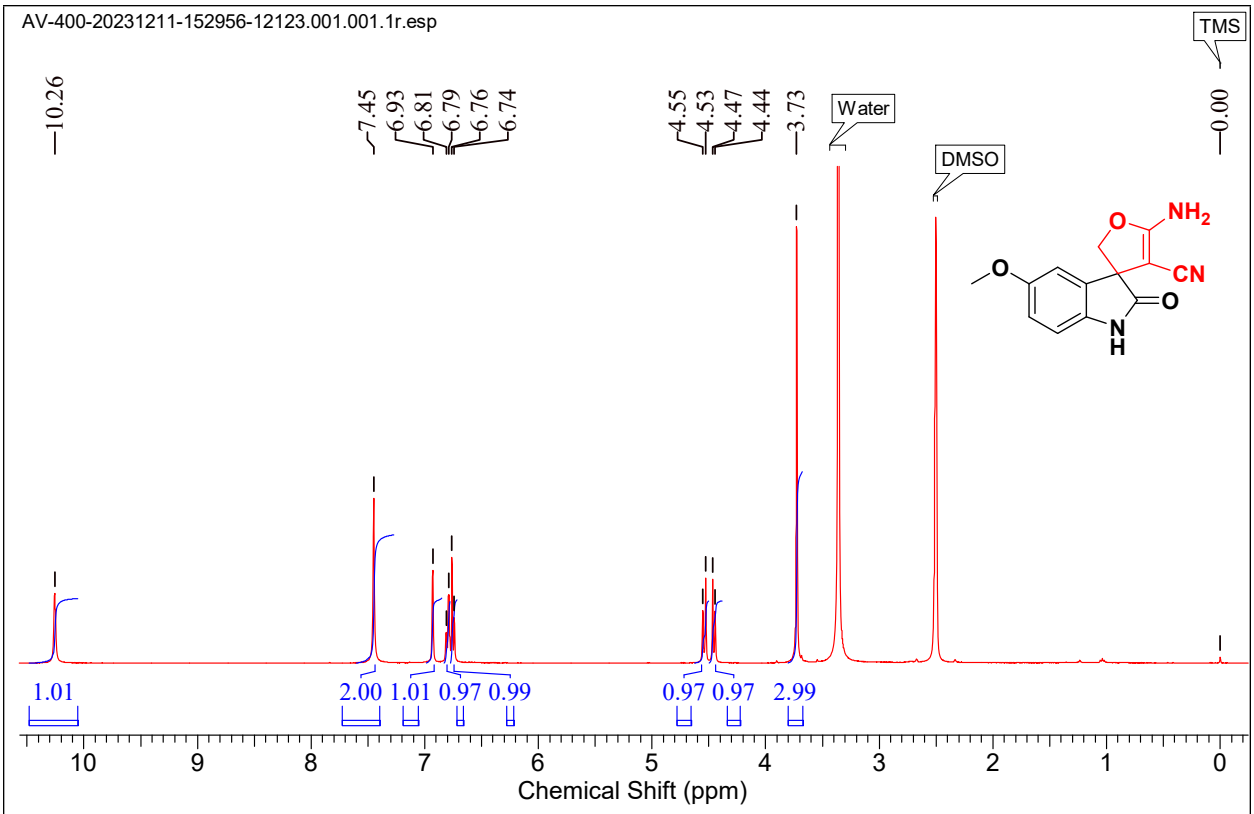
^{1}H NMR spectrum of compound 2h (400 MHz, *DMSO-d_6*)



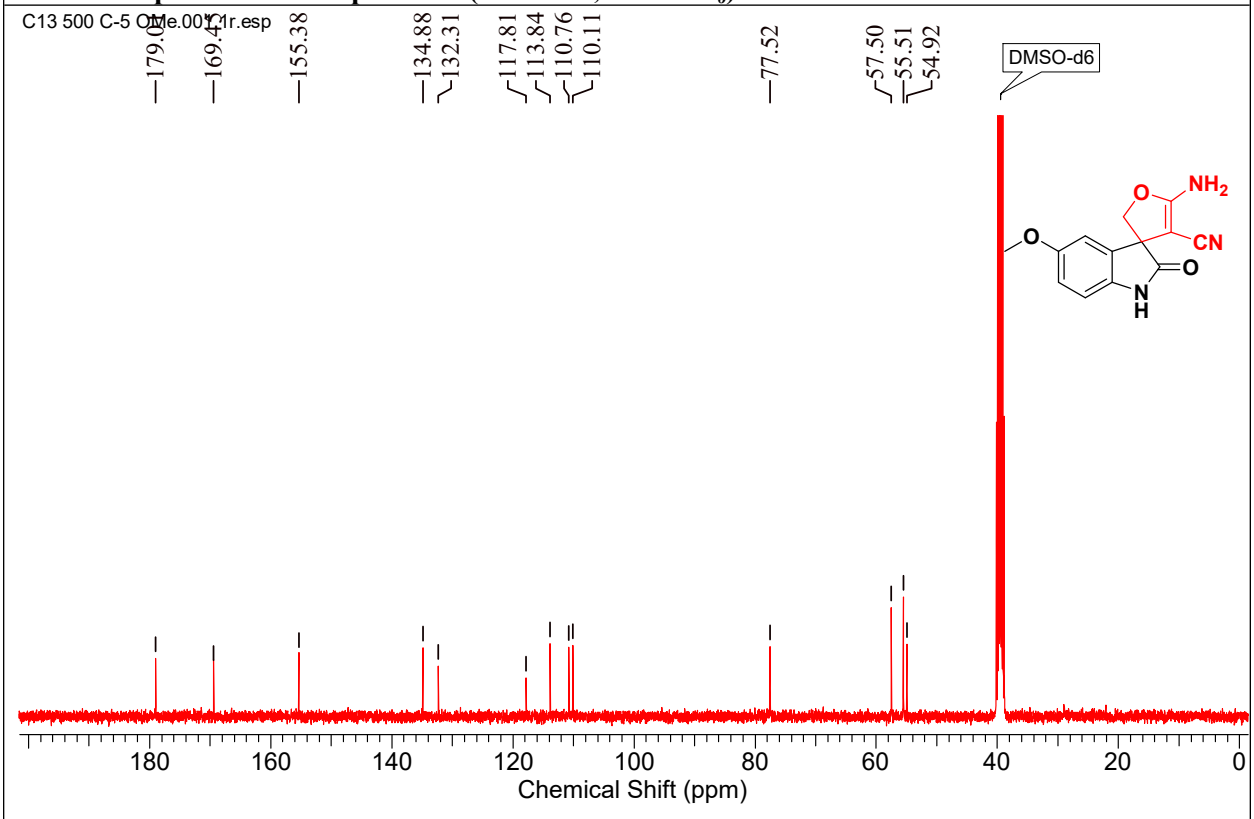
^{13}C NMR spectrum of compound 2h (101 MHz, *DMSO-d_6*)



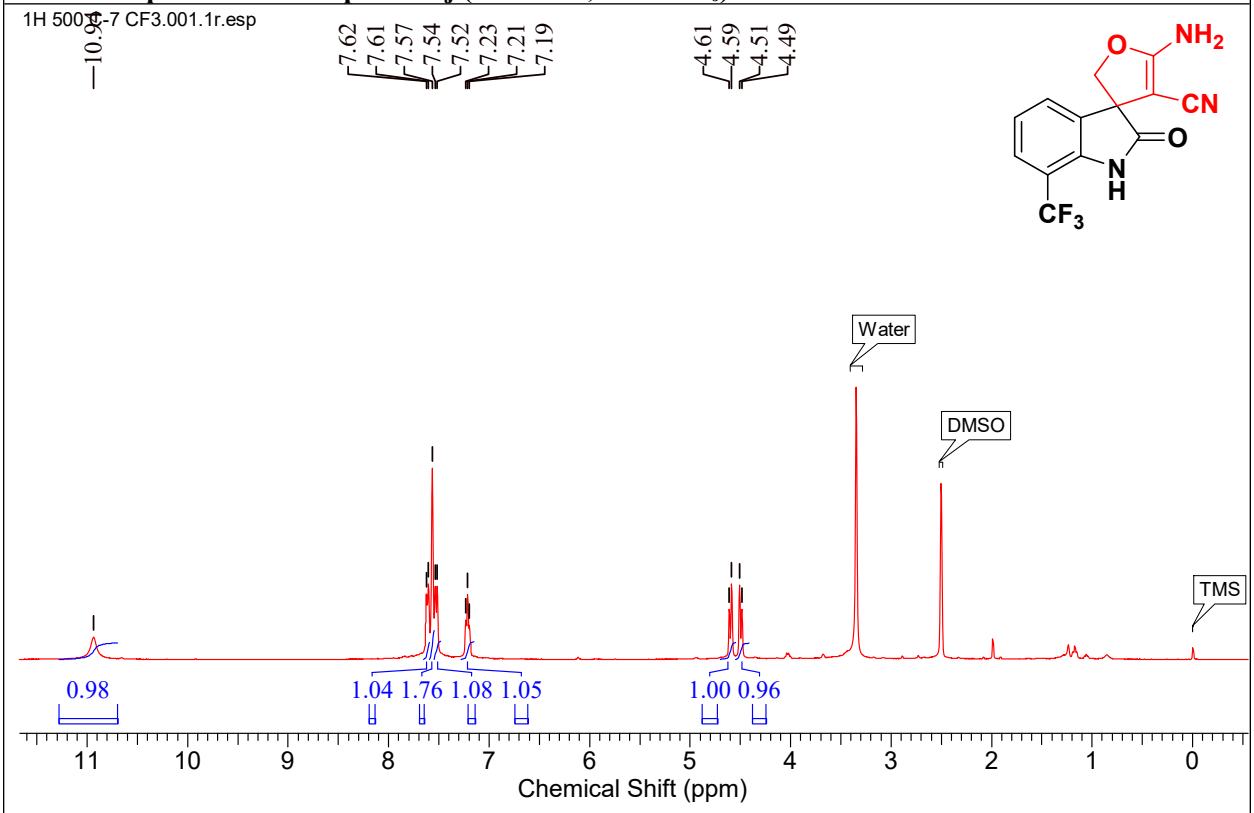
^{1}H NMR spectrum of compound 2i (400 MHz, *DMSO-d_6*)



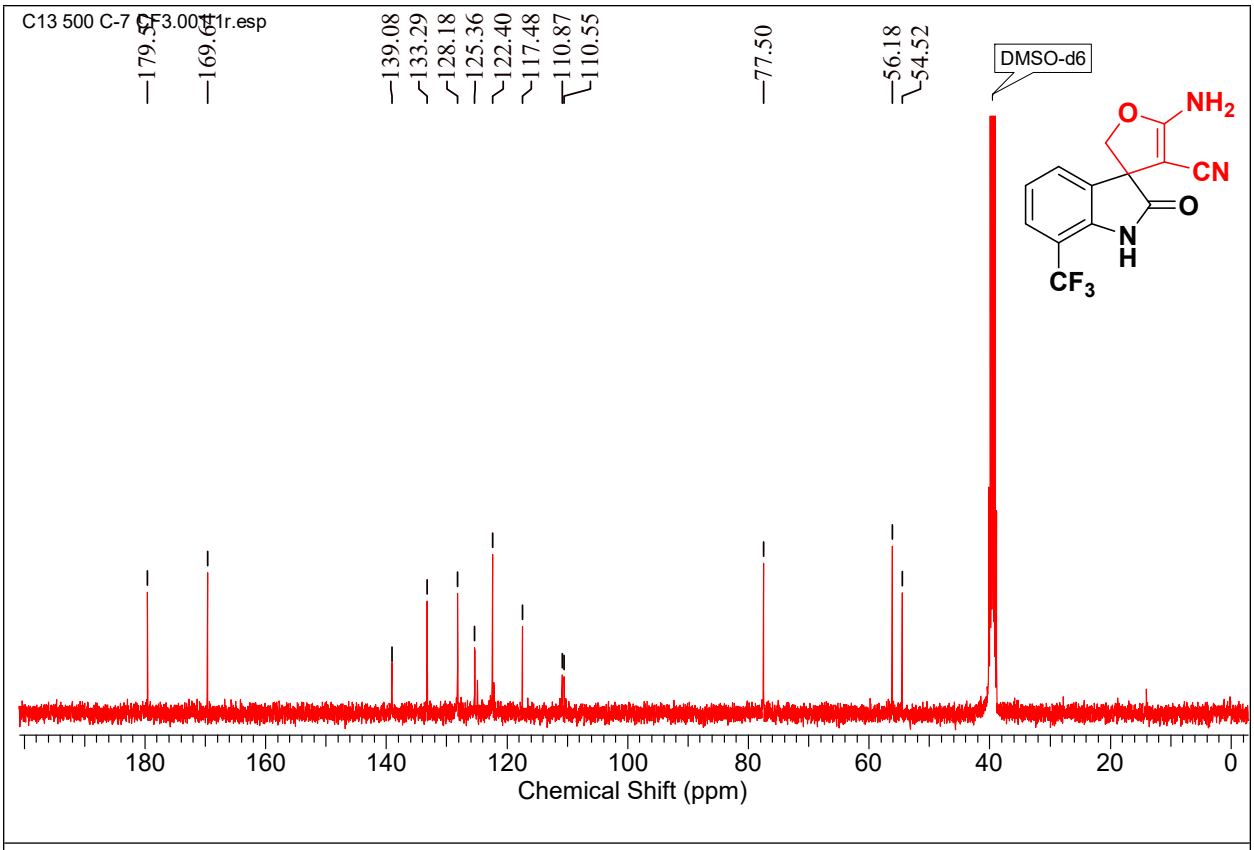
^{13}C NMR spectrum of compound 2i (101 MHz, *DMSO-d_6*)



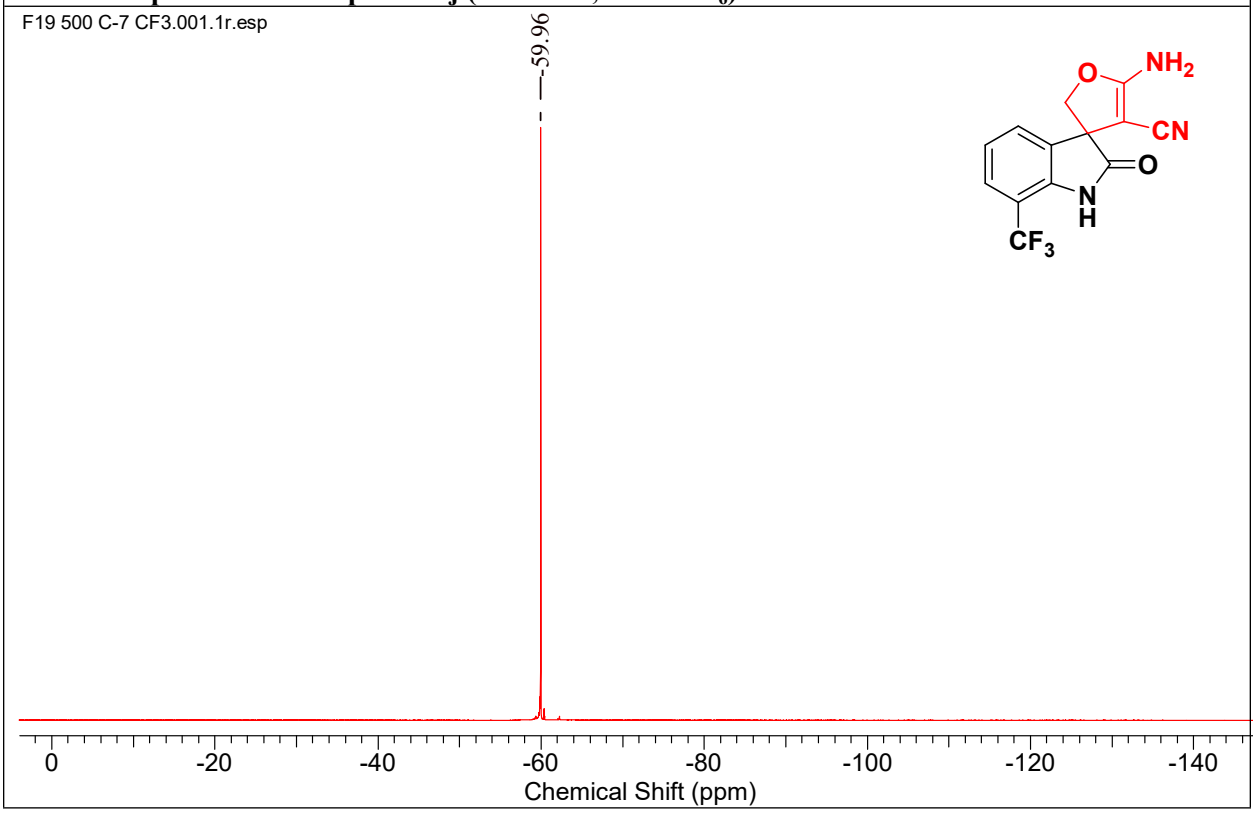
^{1}H NMR spectrum of compound 2j (400 MHz, *DMSO-d_6*)



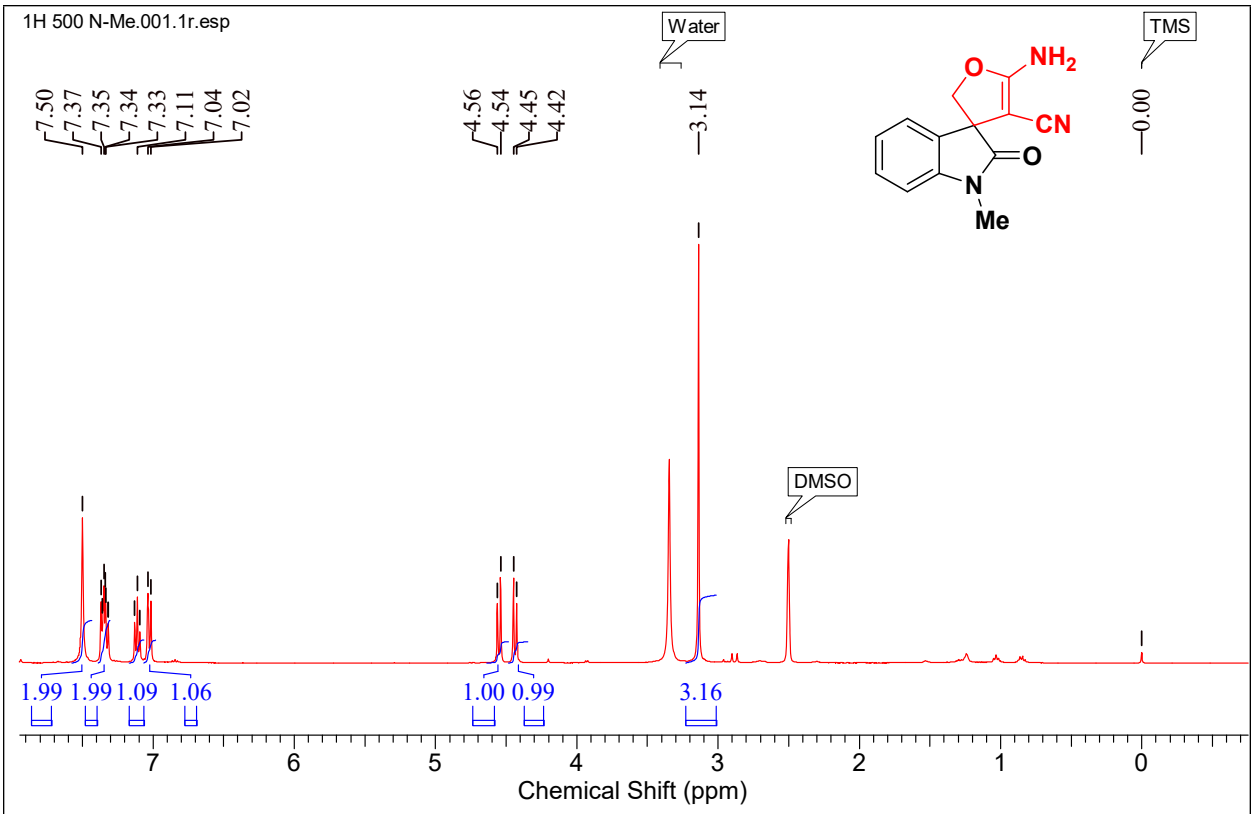
^{13}C NMR spectrum of compound 2j (101 MHz, *DMSO-d_6*)



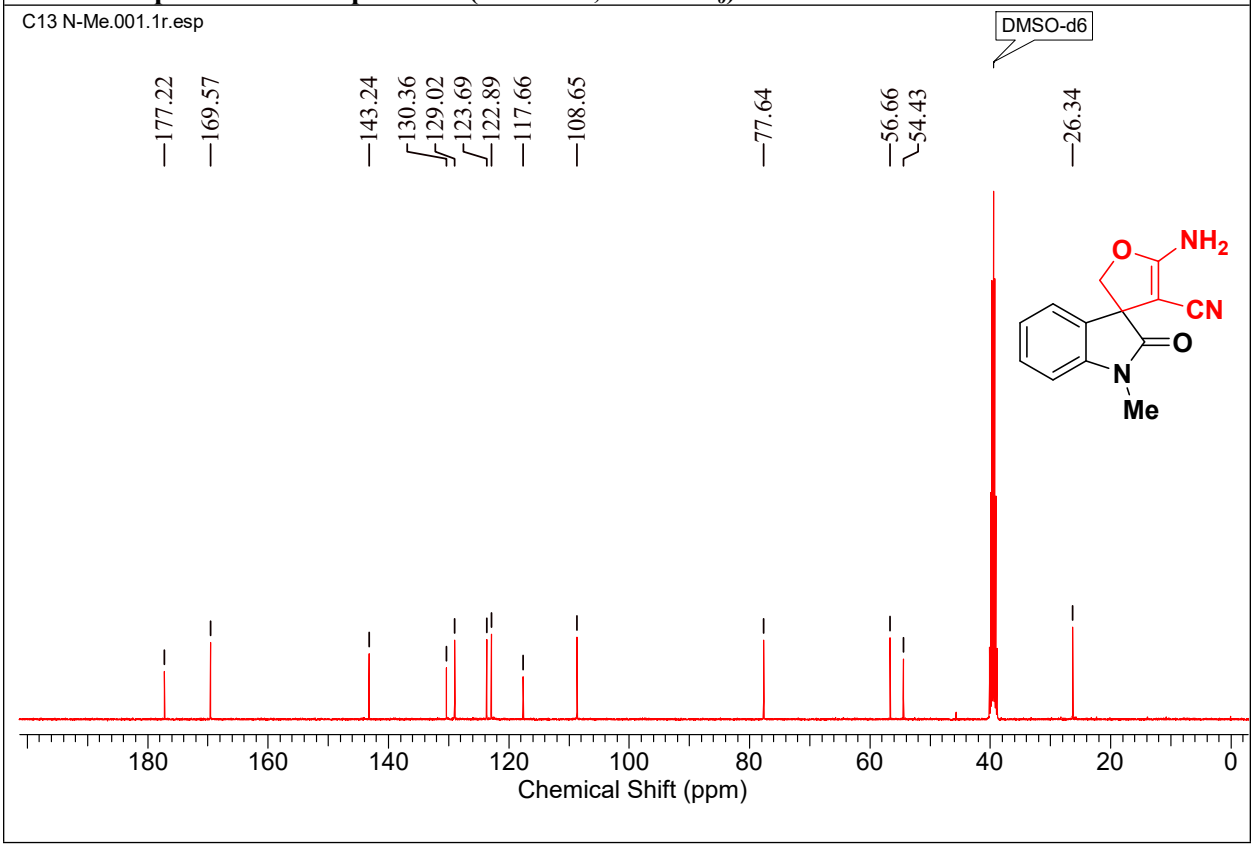
^{19}F NMR spectrum of compound 2j (376 MHz, DMSO-d_6)



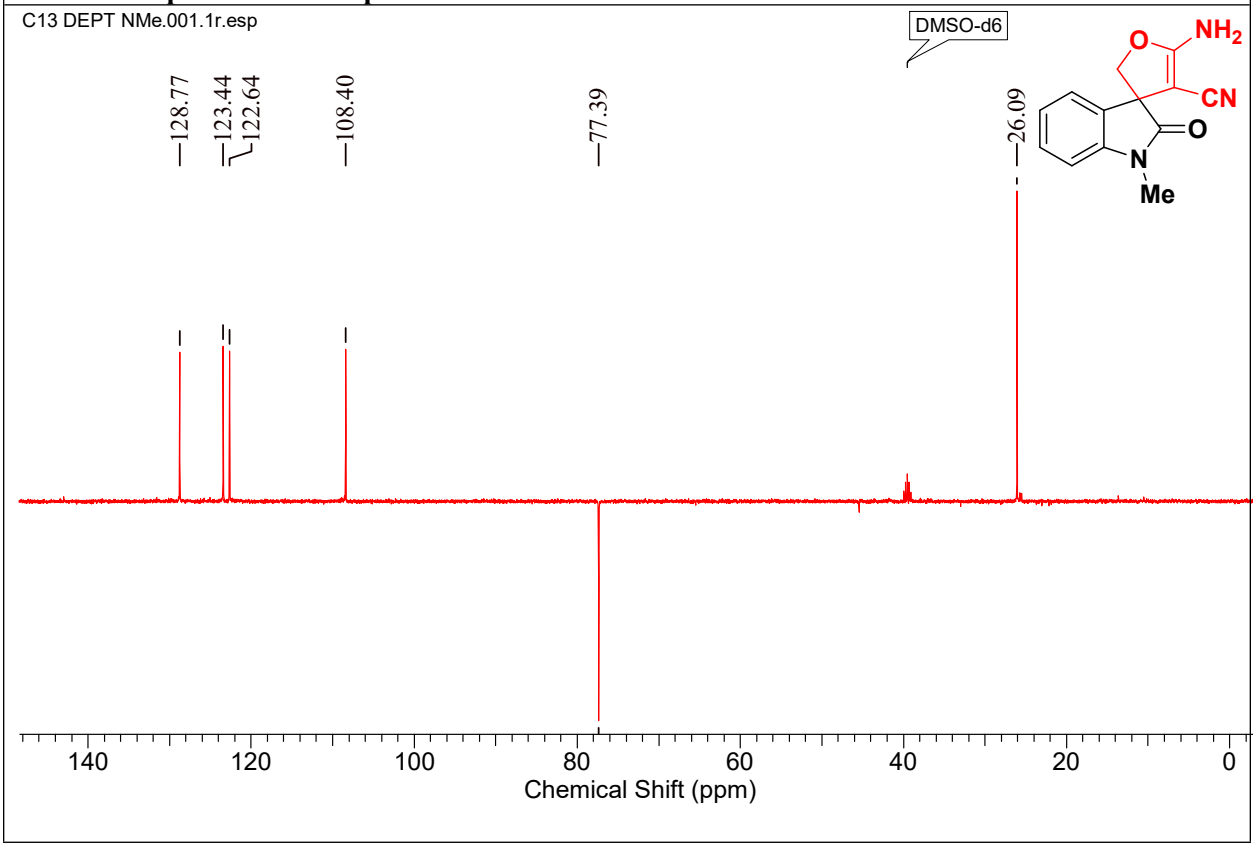
^{1}H NMR spectrum of compound 2l (400 MHz, *DMSO-d_6*)



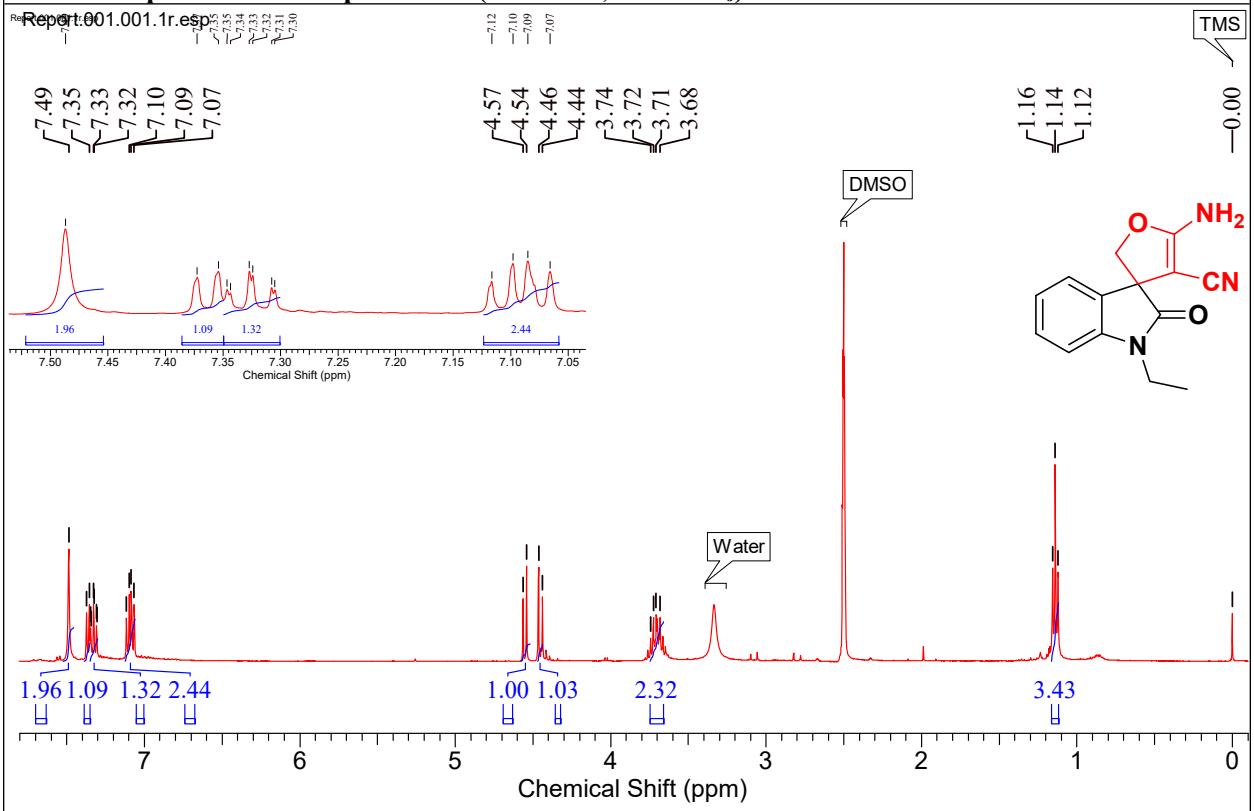
^{13}C NMR spectrum of compound 2l (101 MHz, *DMSO-d_6*)



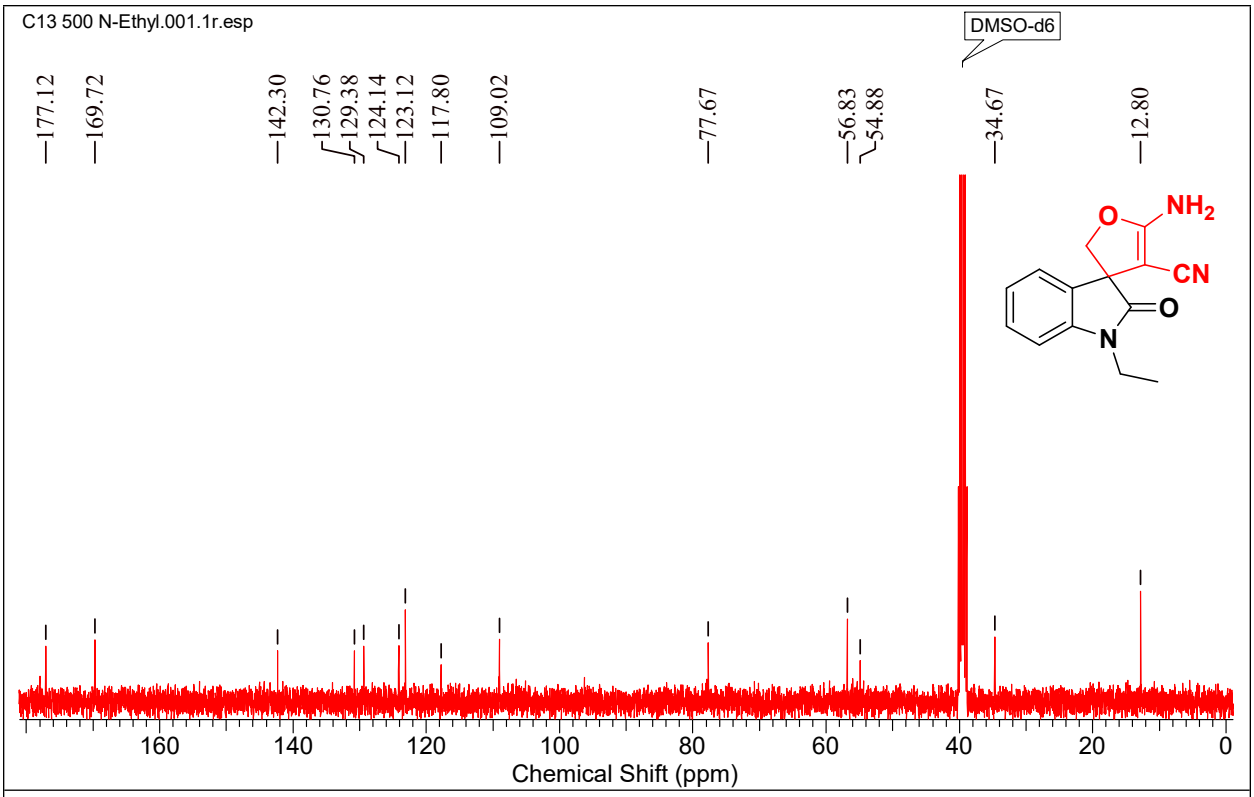
135 DEPT spectrum of compound 2l



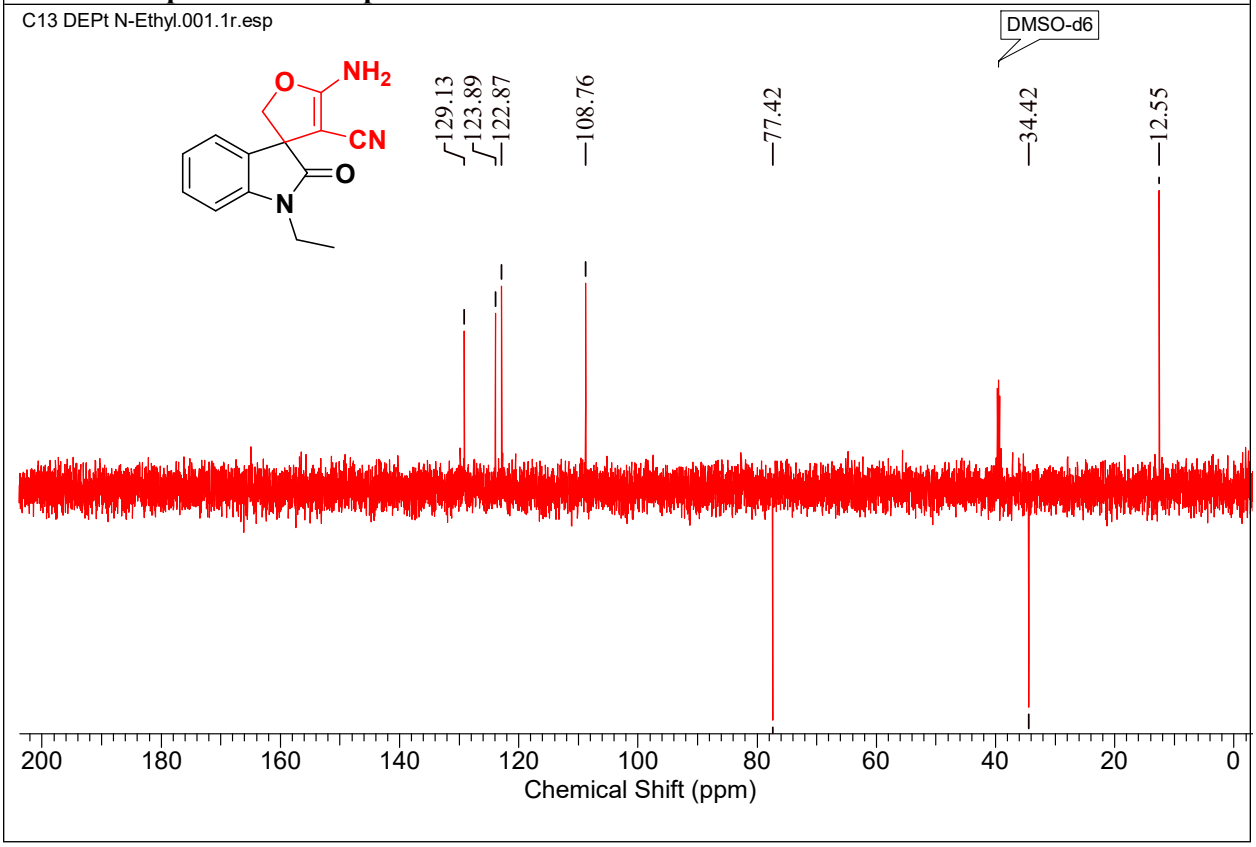
^{1}H NMR spectrum of compound 2m (400 MHz, *DMSO-d_6*)



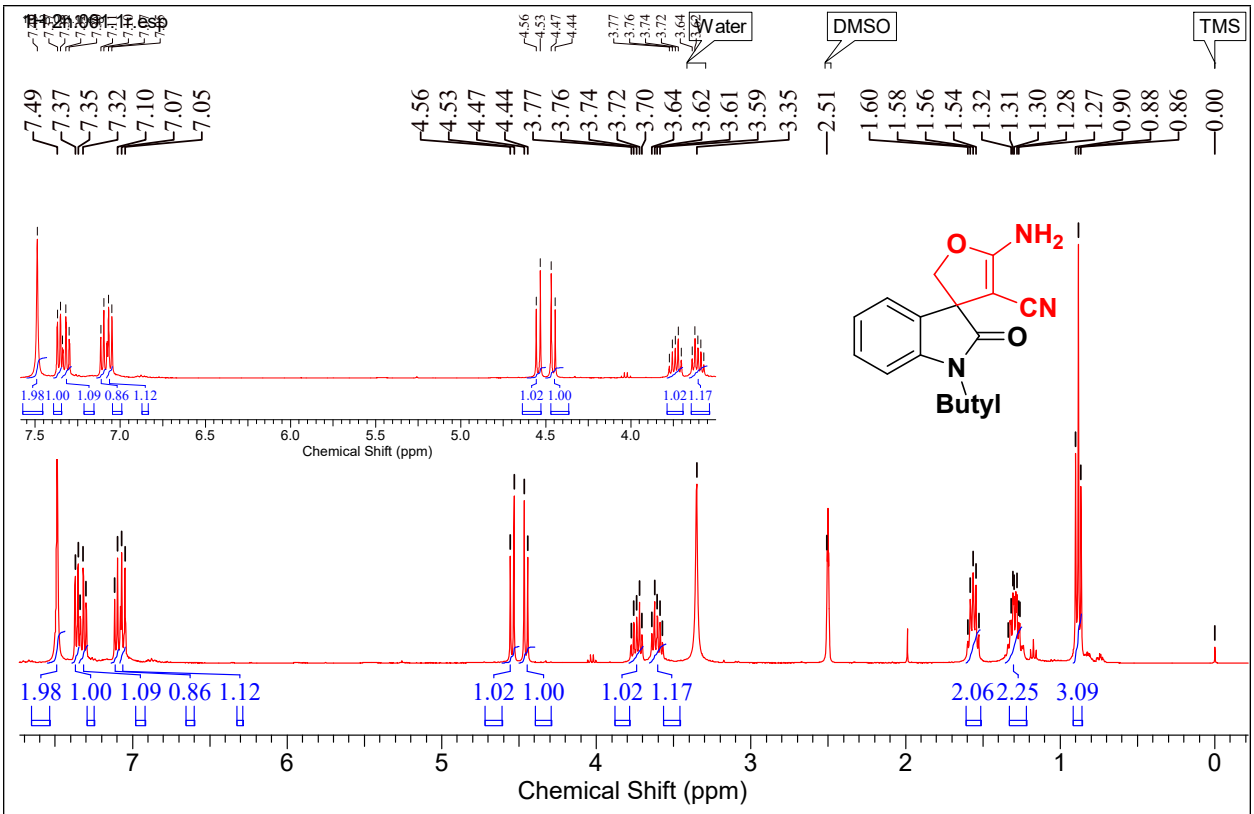
^{13}C NMR spectrum of compound 2m (101 MHz, *DMSO-d_6*)



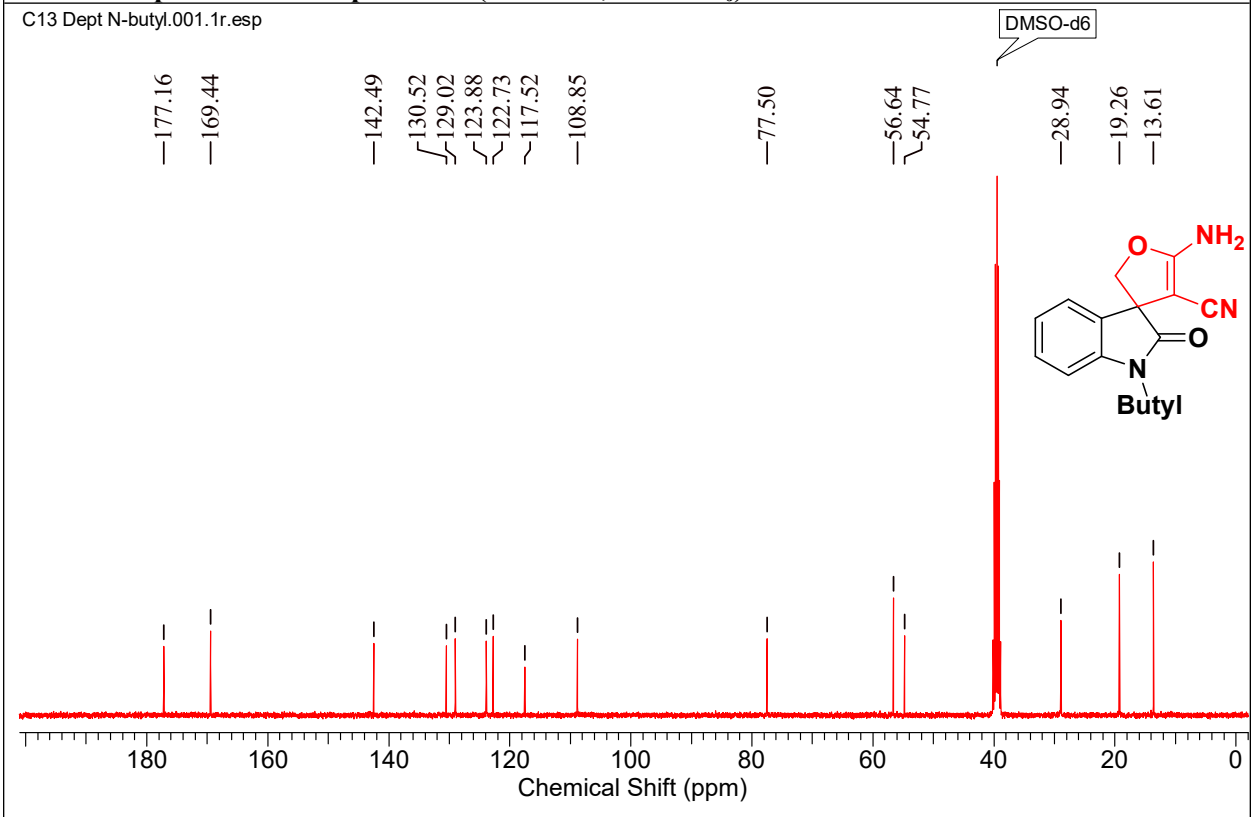
135 DEPT spectrum of compound 2m



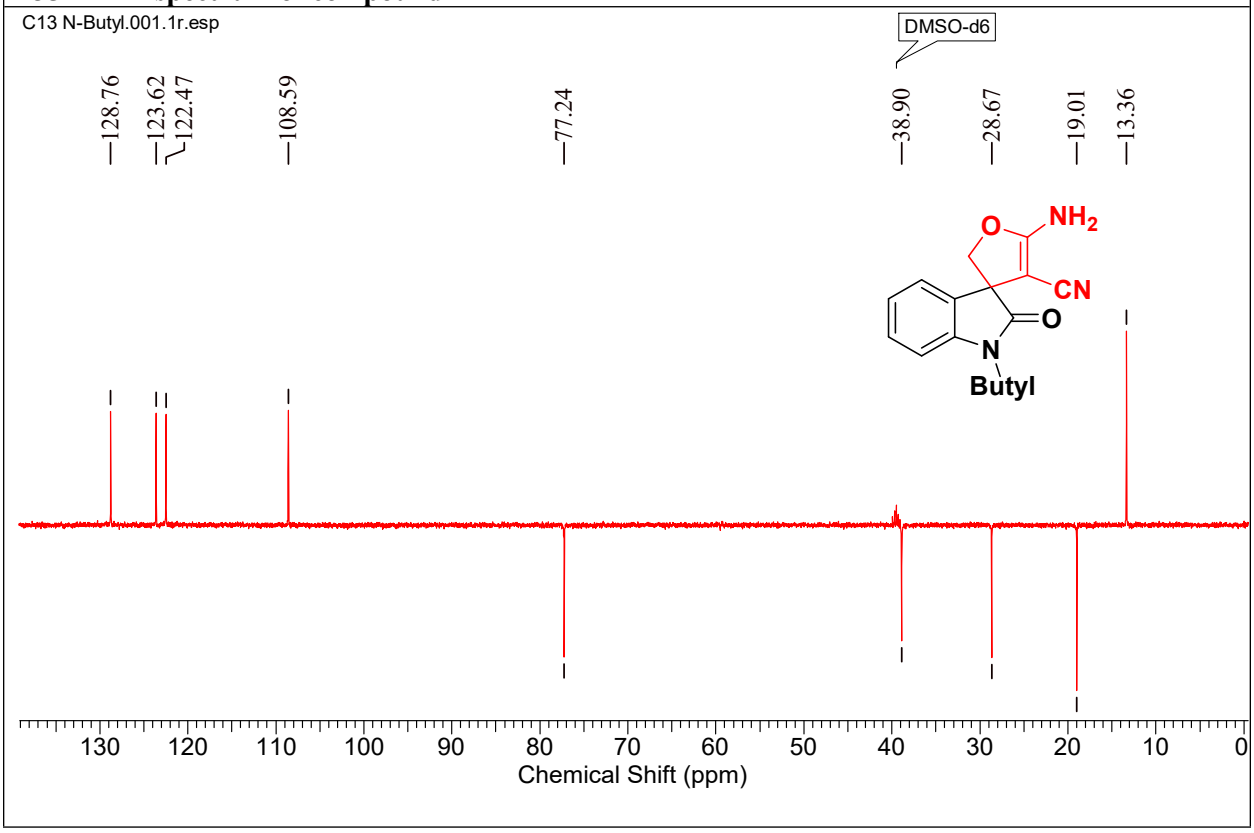
^{1}H NMR spectrum of compound 2n (400 MHz, *DMSO-d_6*)



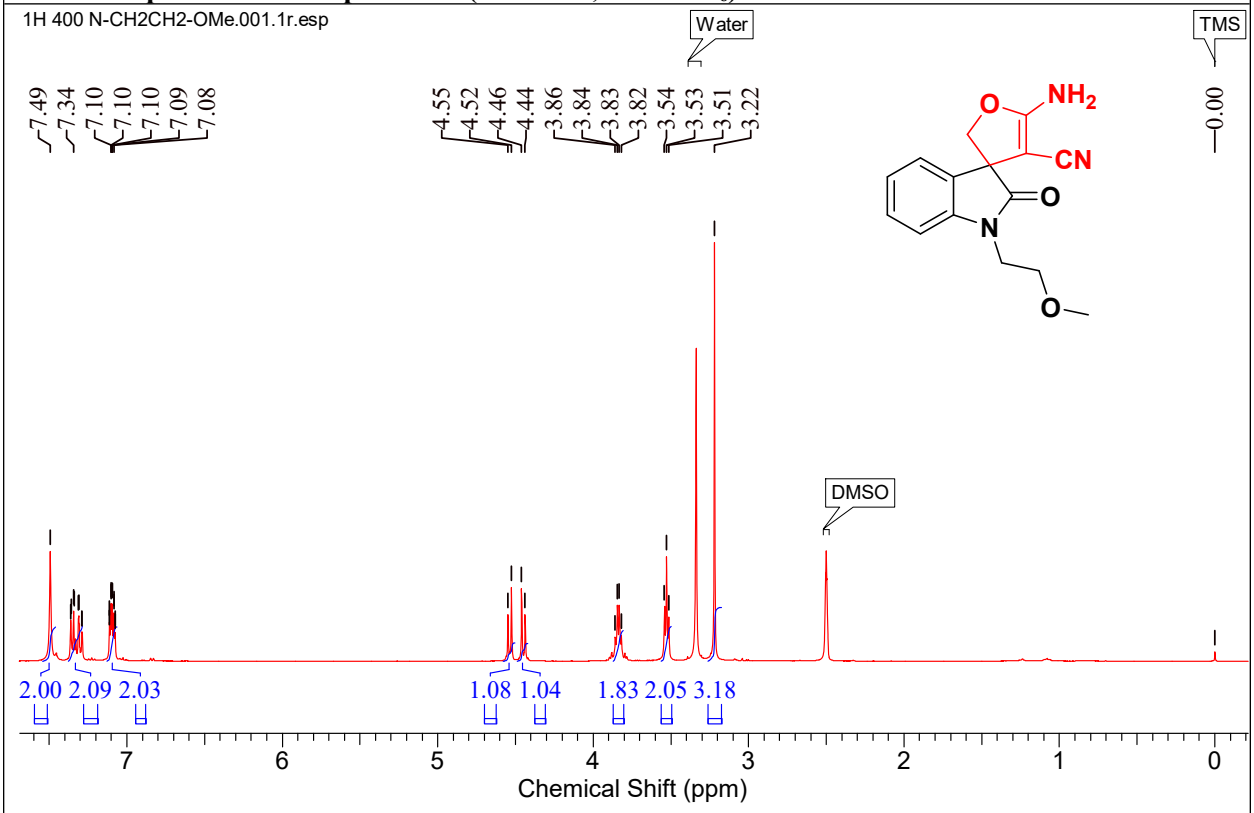
^{13}C NMR spectrum of compound 2n (101 MHz, *DMSO-d_6*)



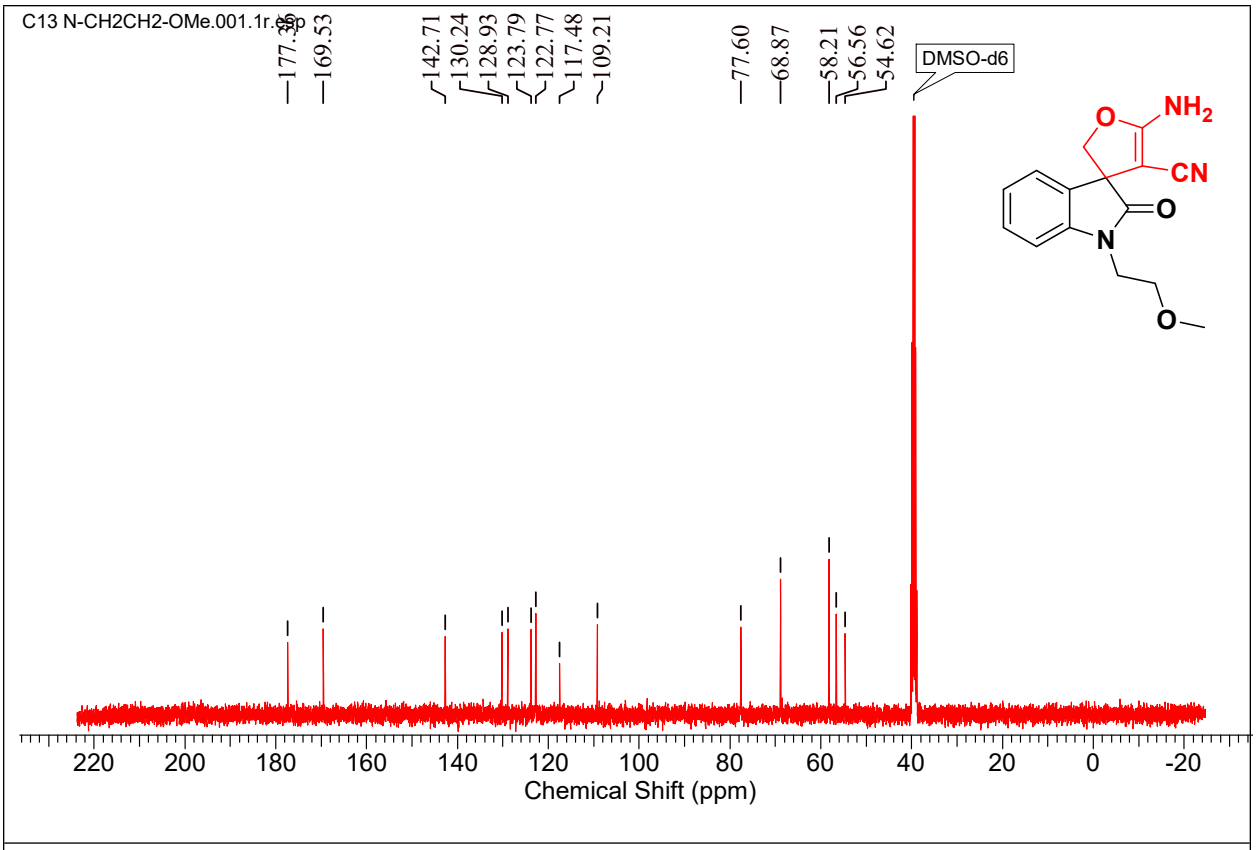
135 DEPT spectrum of compound 2n



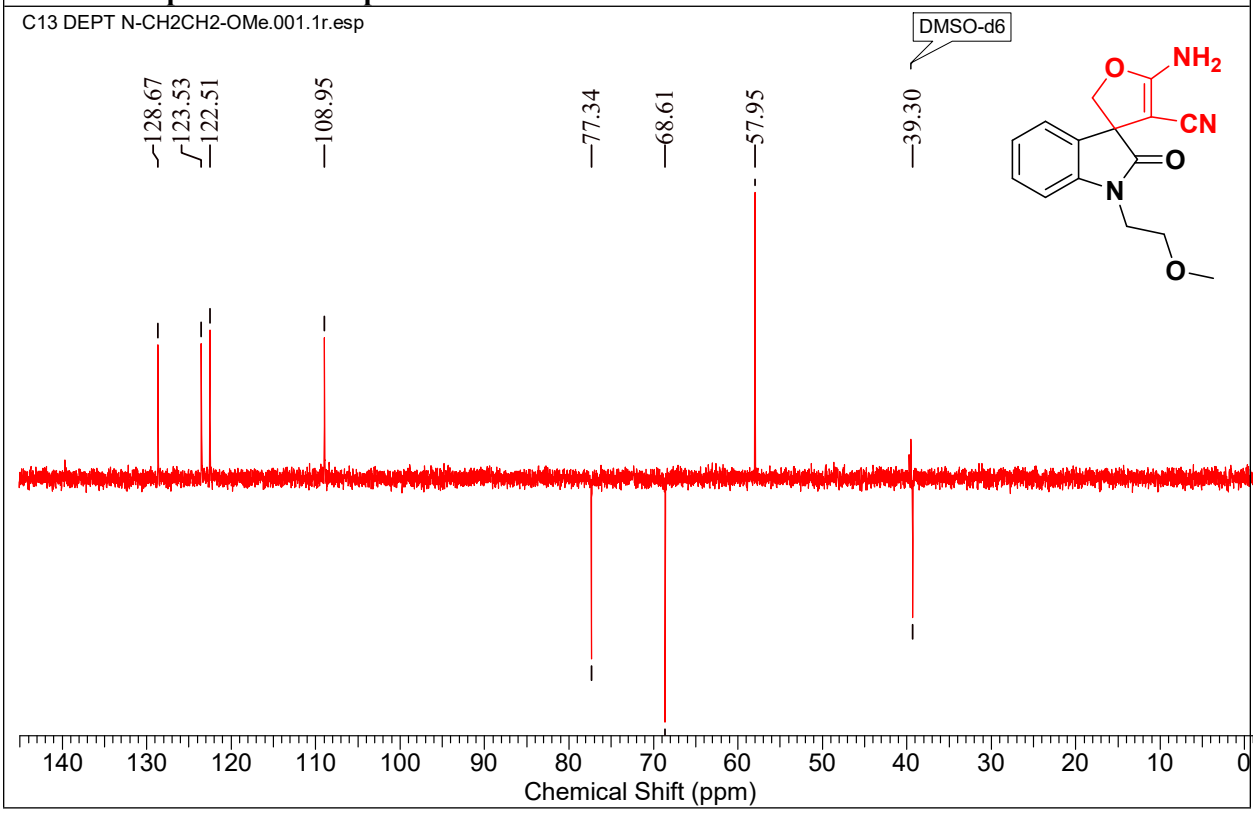
^{1}H NMR spectrum of compound 2o (400 MHz, DMSO-d_6)



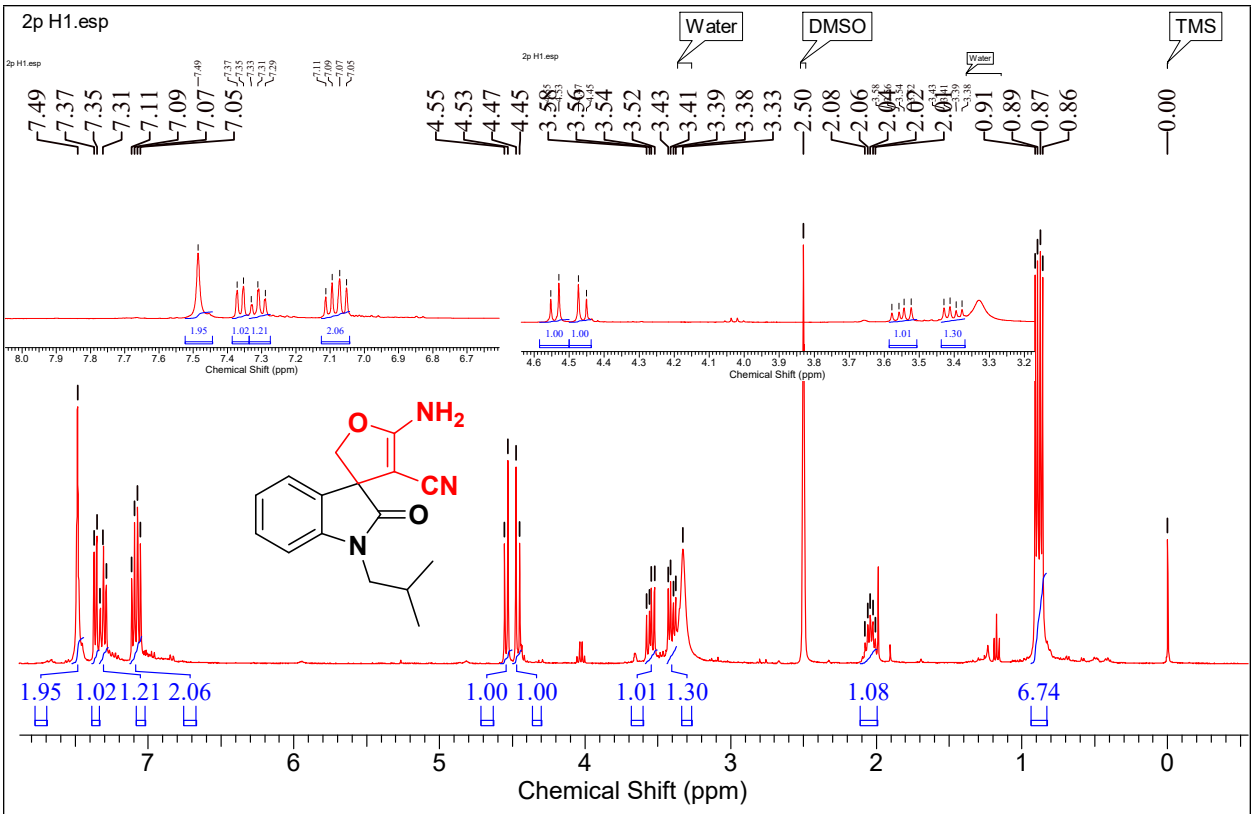
^{13}C NMR spectrum of compound 2o (101 MHz, *DMSO-d_6*)



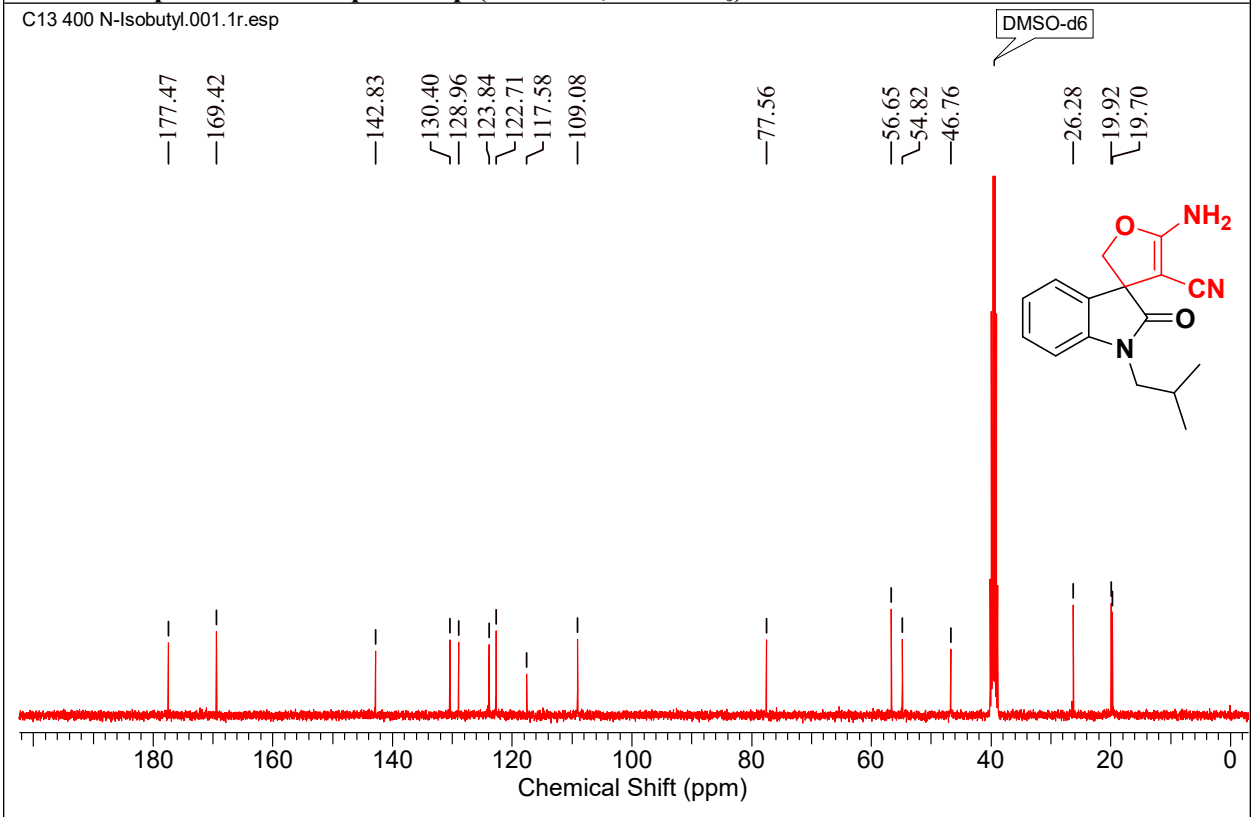
135 DEPT spectrum of compound 2o



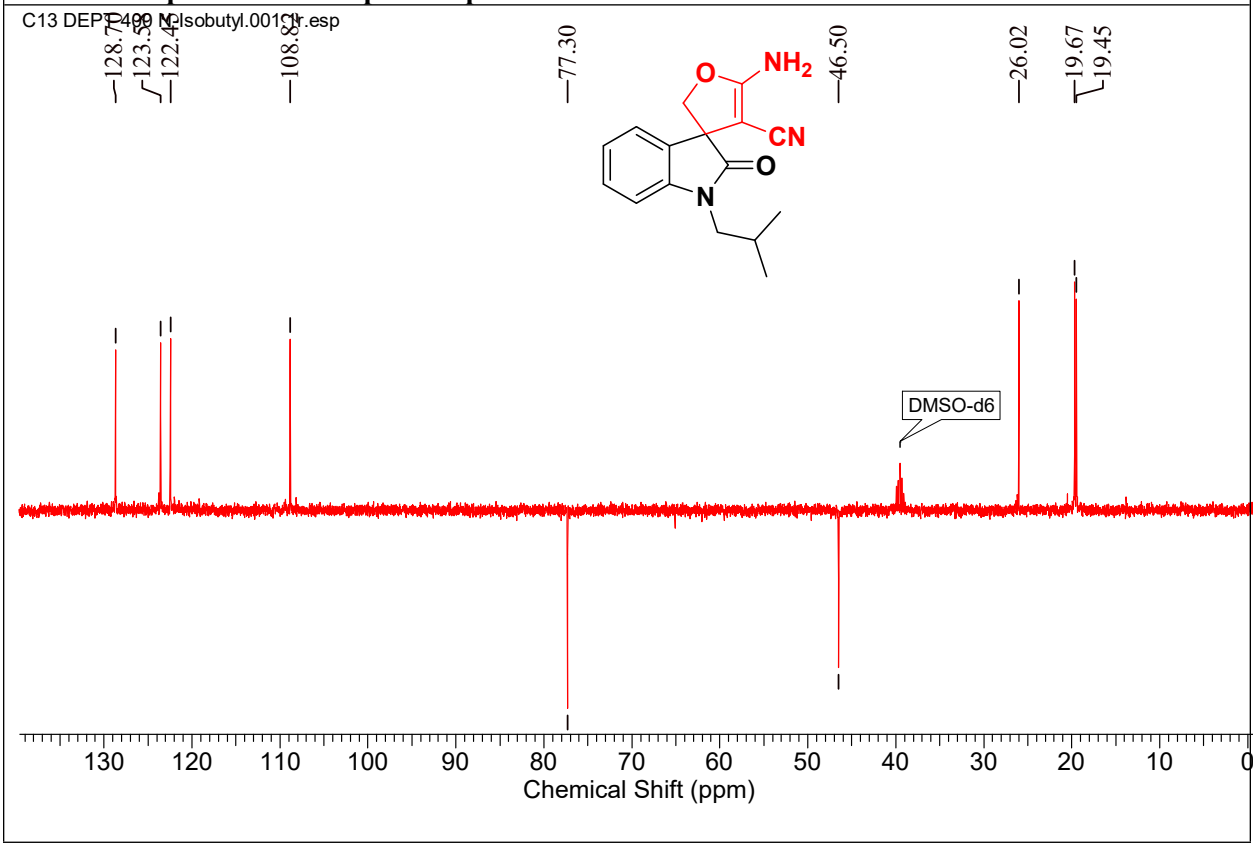
^{1}H NMR spectrum of compound 2p (400 MHz, DMSO-d_6)



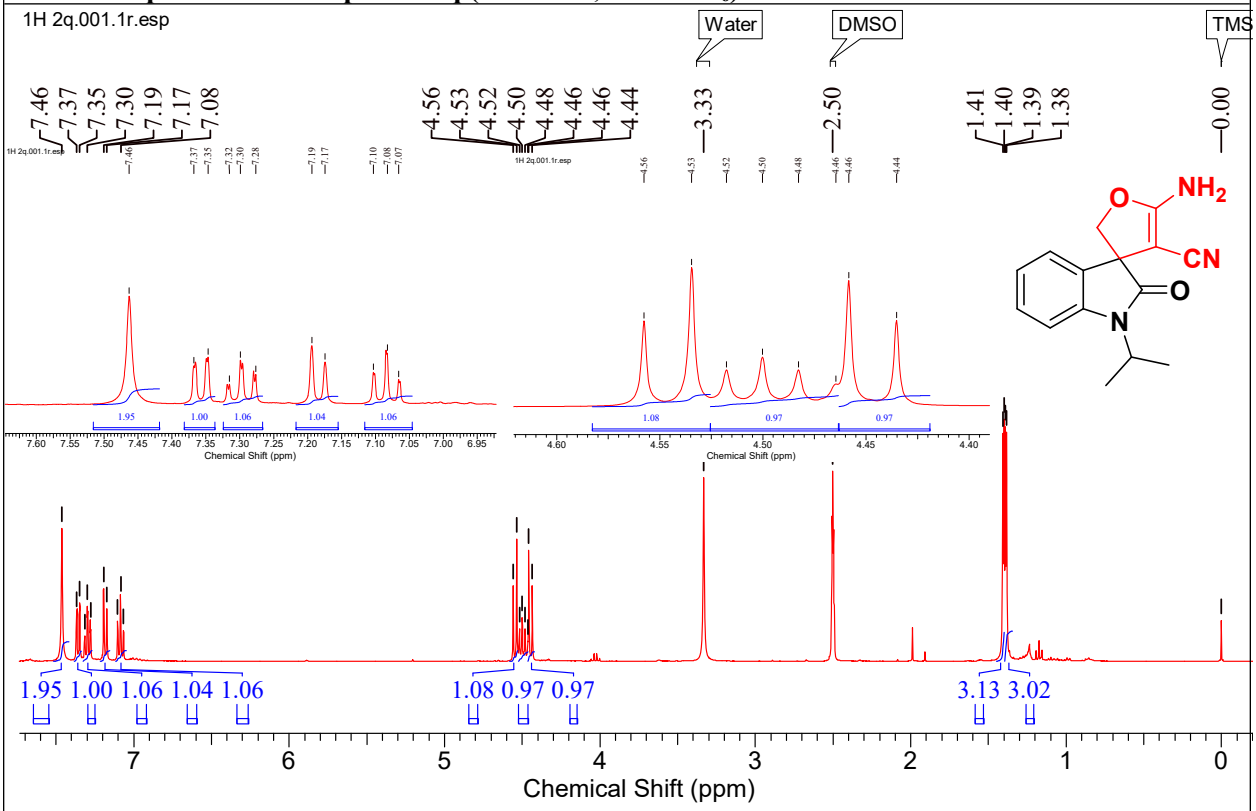
^{13}C NMR spectrum of compound 2p (101 MHz, *DMSO-d_6*)



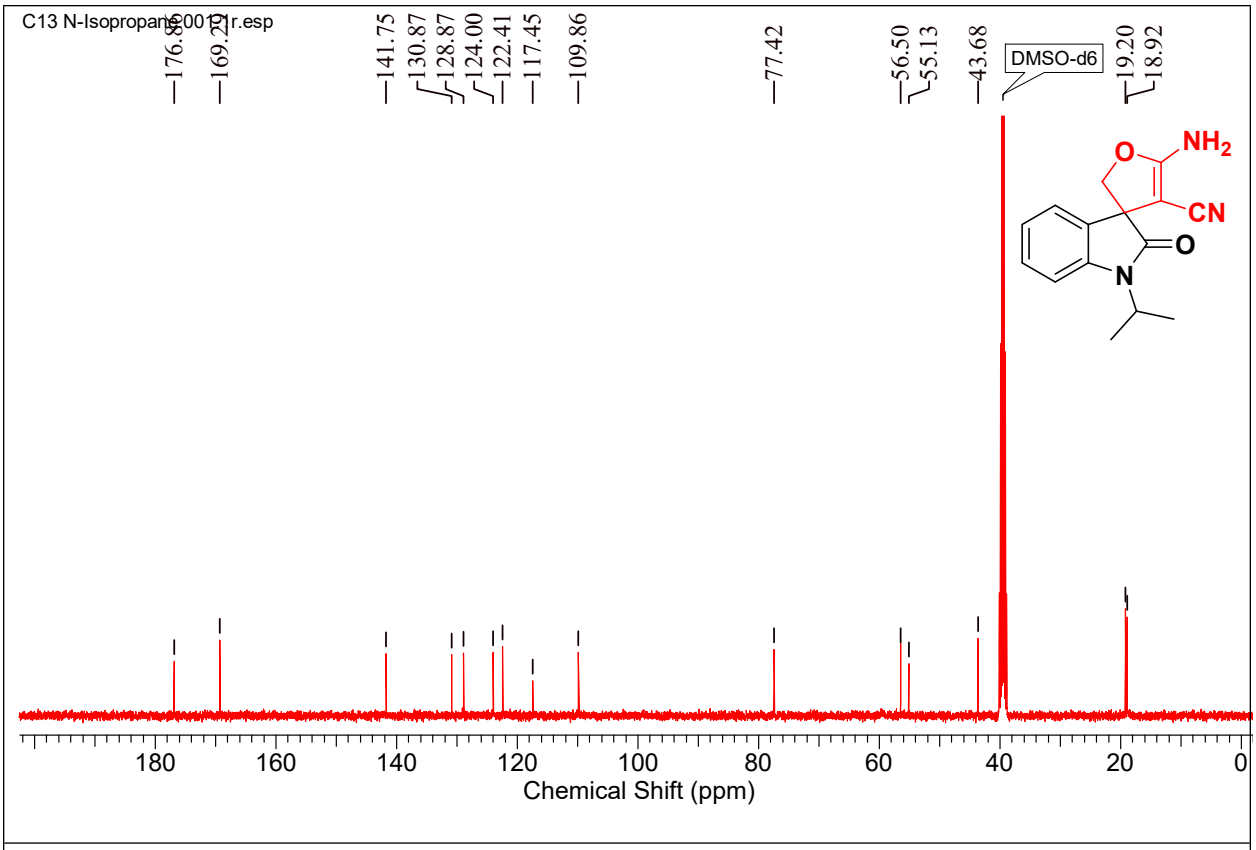
135 DEPT spectrum of compound 2p



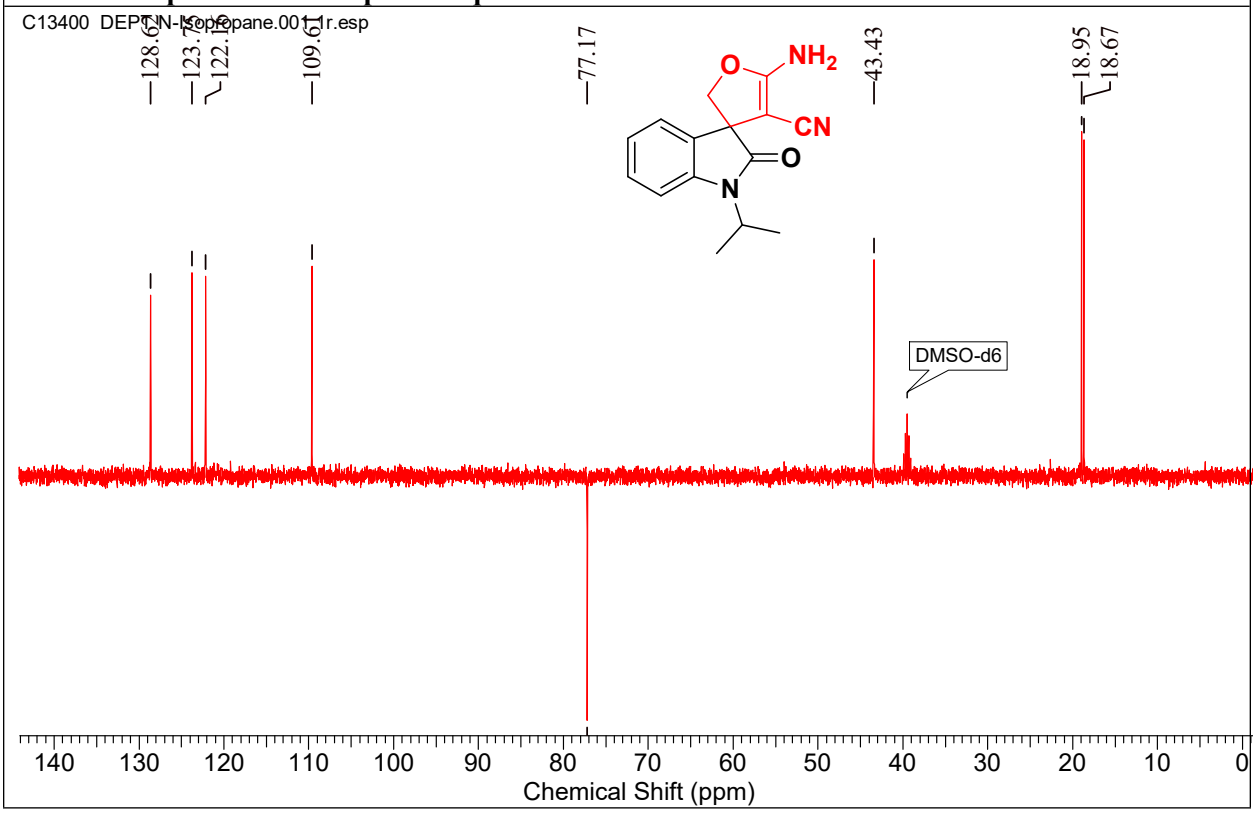
^{1}H NMR spectrum of compound 2q (400 MHz, DMSO-d_6)



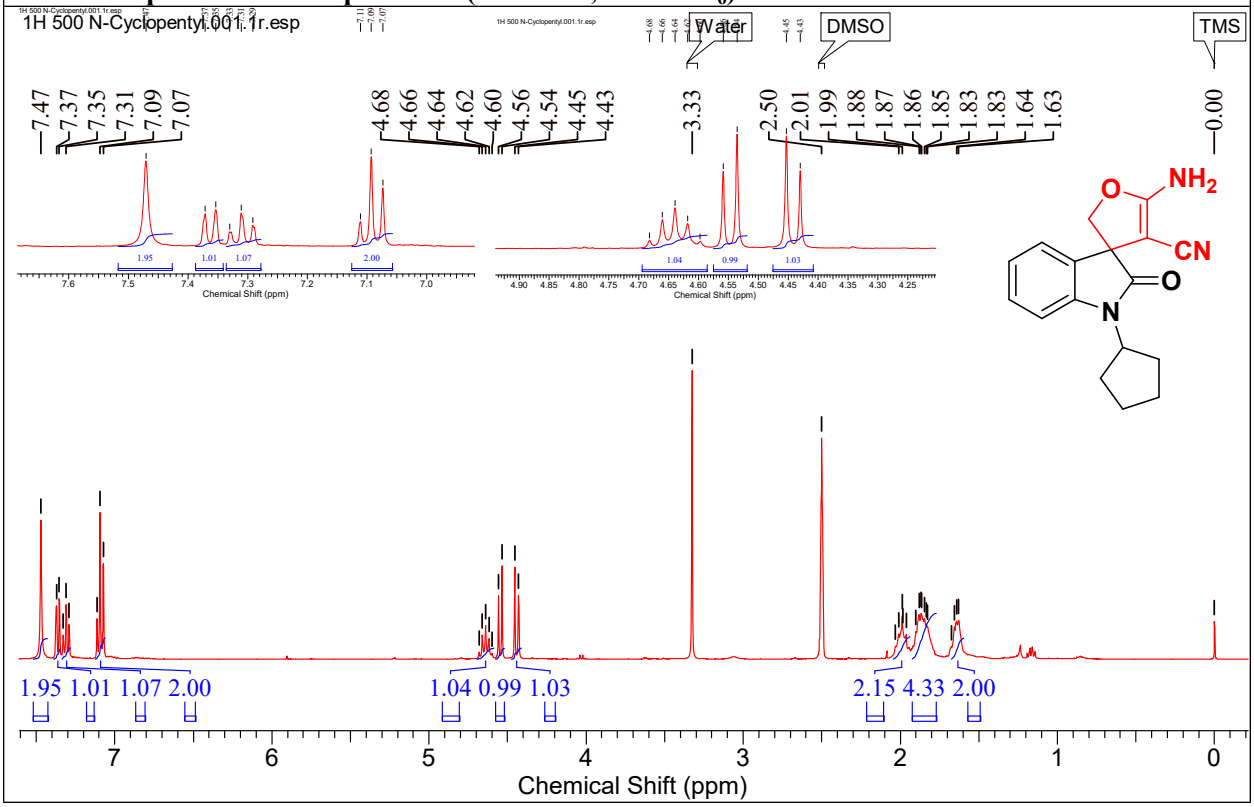
^{13}C NMR spectrum of compound 2q (101 MHz, *DMSO-d_6*)



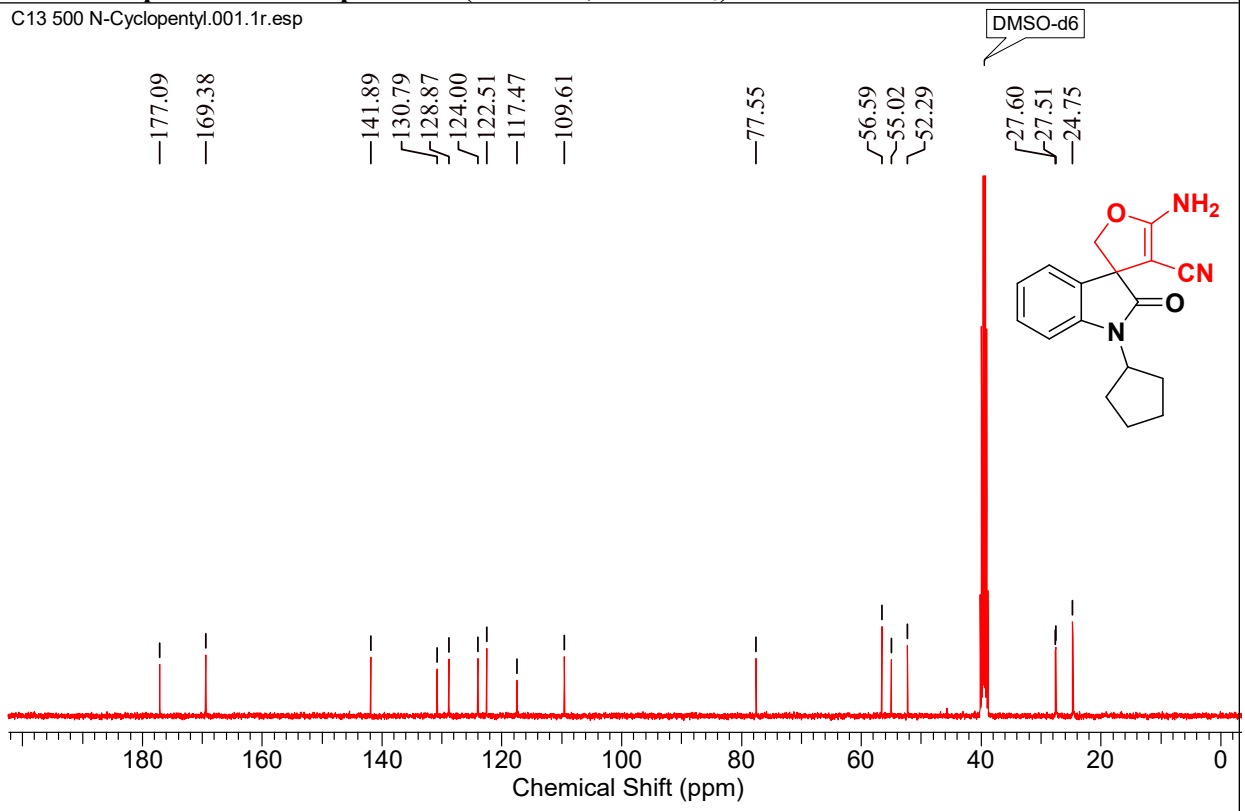
135 DEPT spectrum of compound 2q



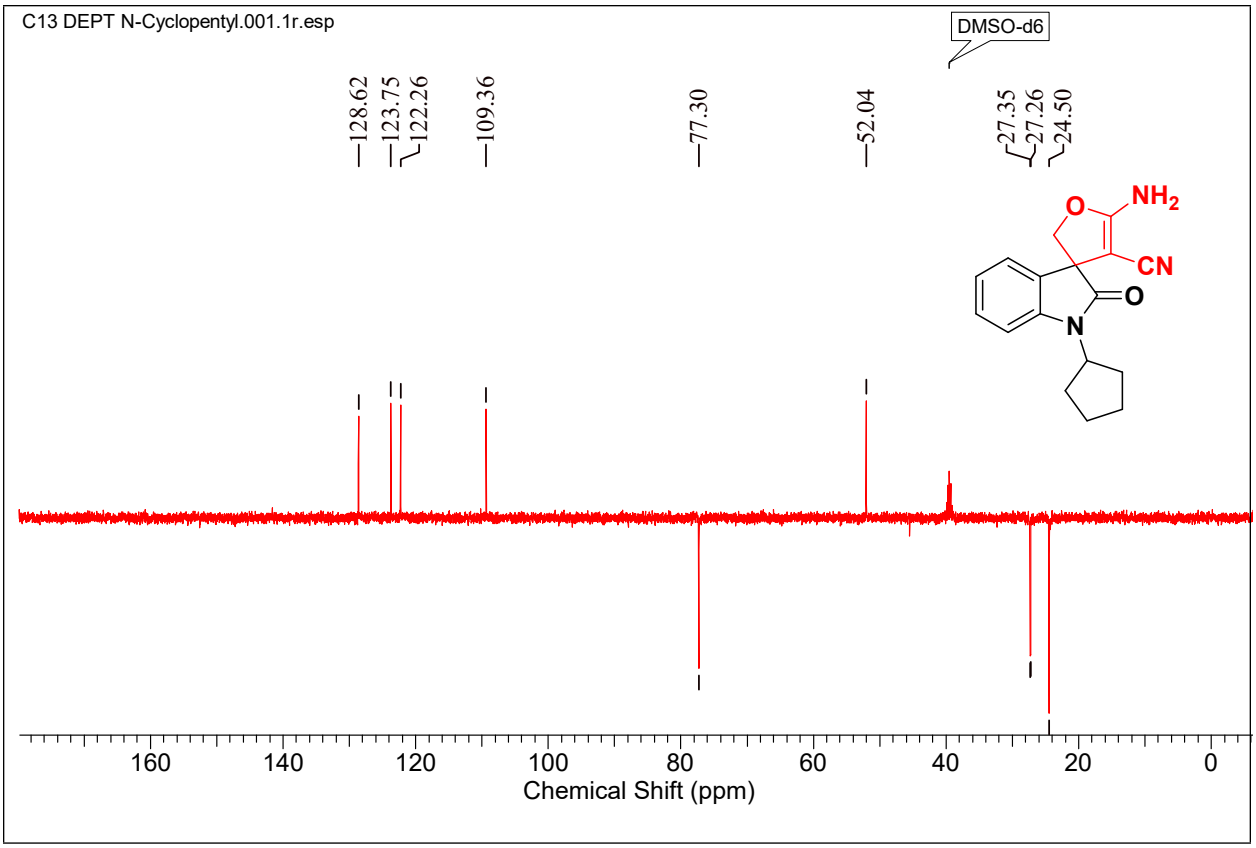
^{1}H NMR spectrum of compound 2r (400 MHz, DMSO-d_6)



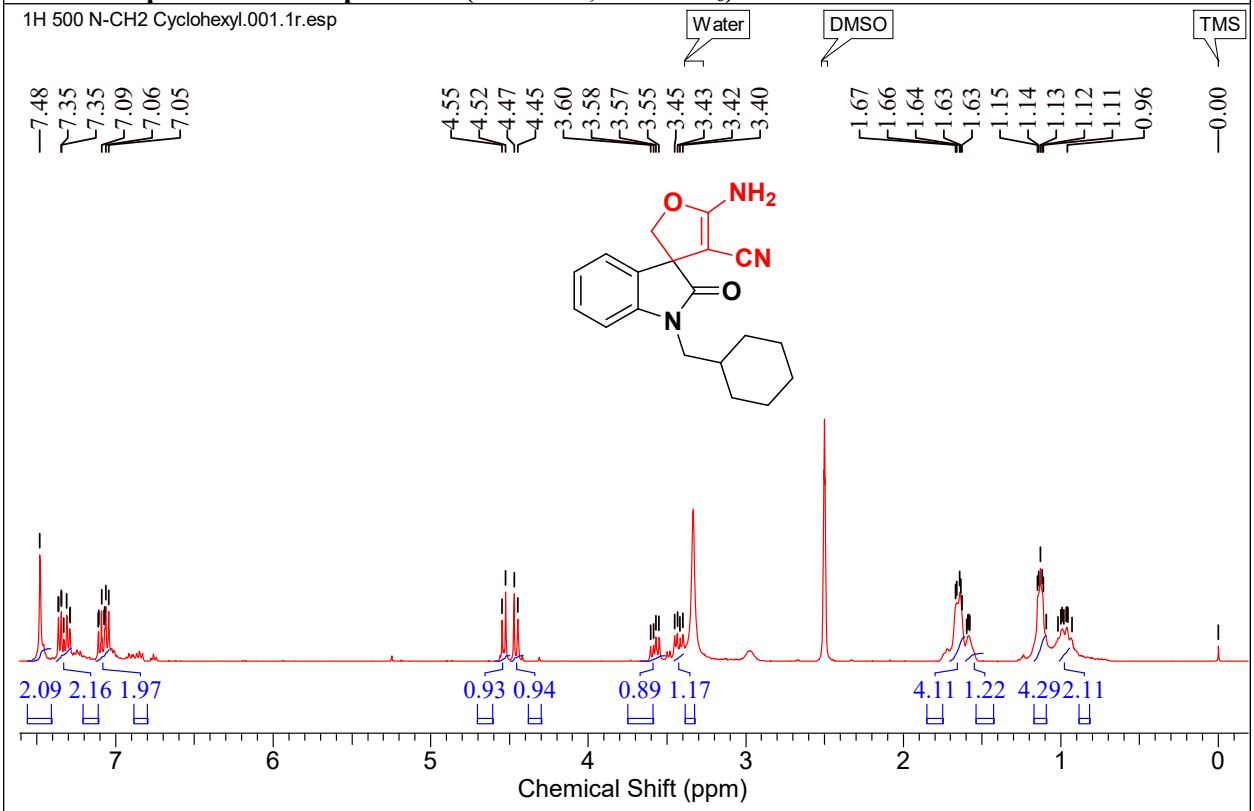
^{13}C NMR spectrum of compound 2r (101 MHz, *DMSO-d_6*)



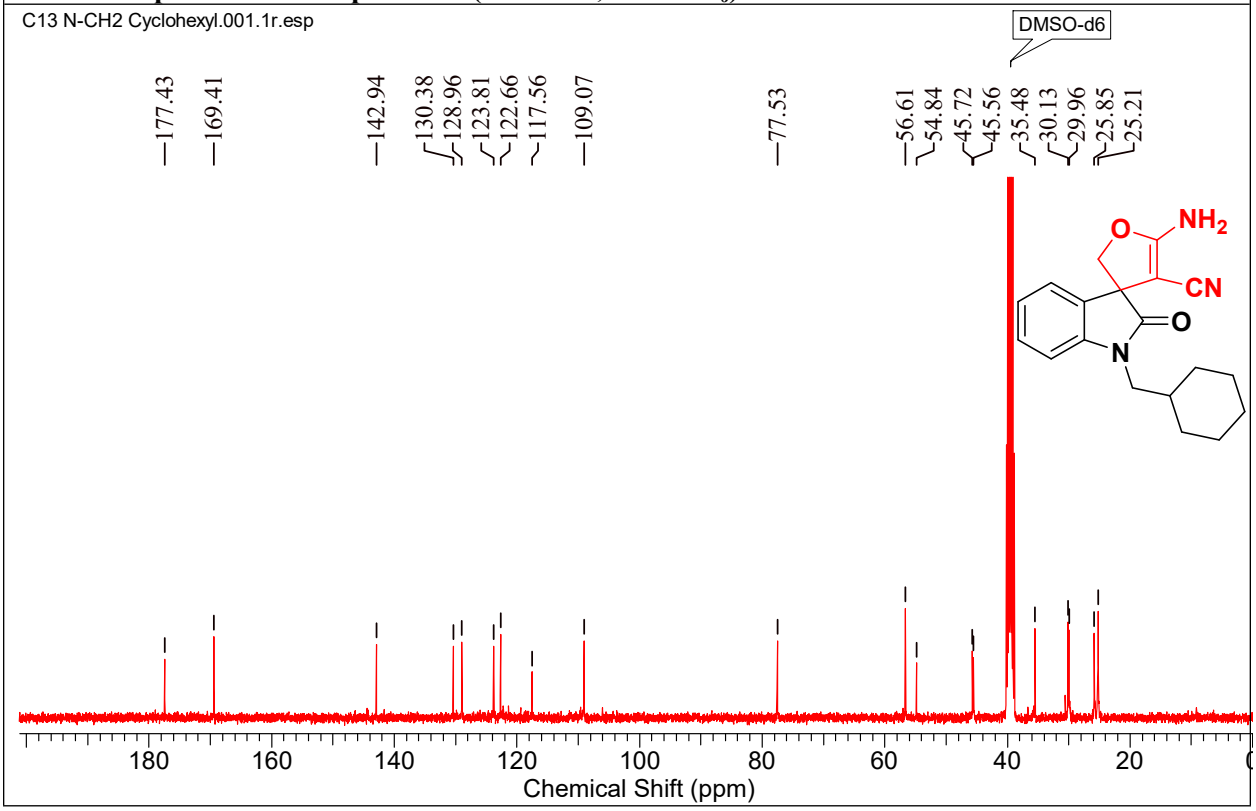
135 DEPT spectrum of compound 2r


C13 DEPT N-Cyclopentyl.001.1r.esp
DMSO-d6
128.62
123.75
122.26
109.36
77.30
52.04
27.35
27.26
24.50
O
NH2
CN
O
N
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

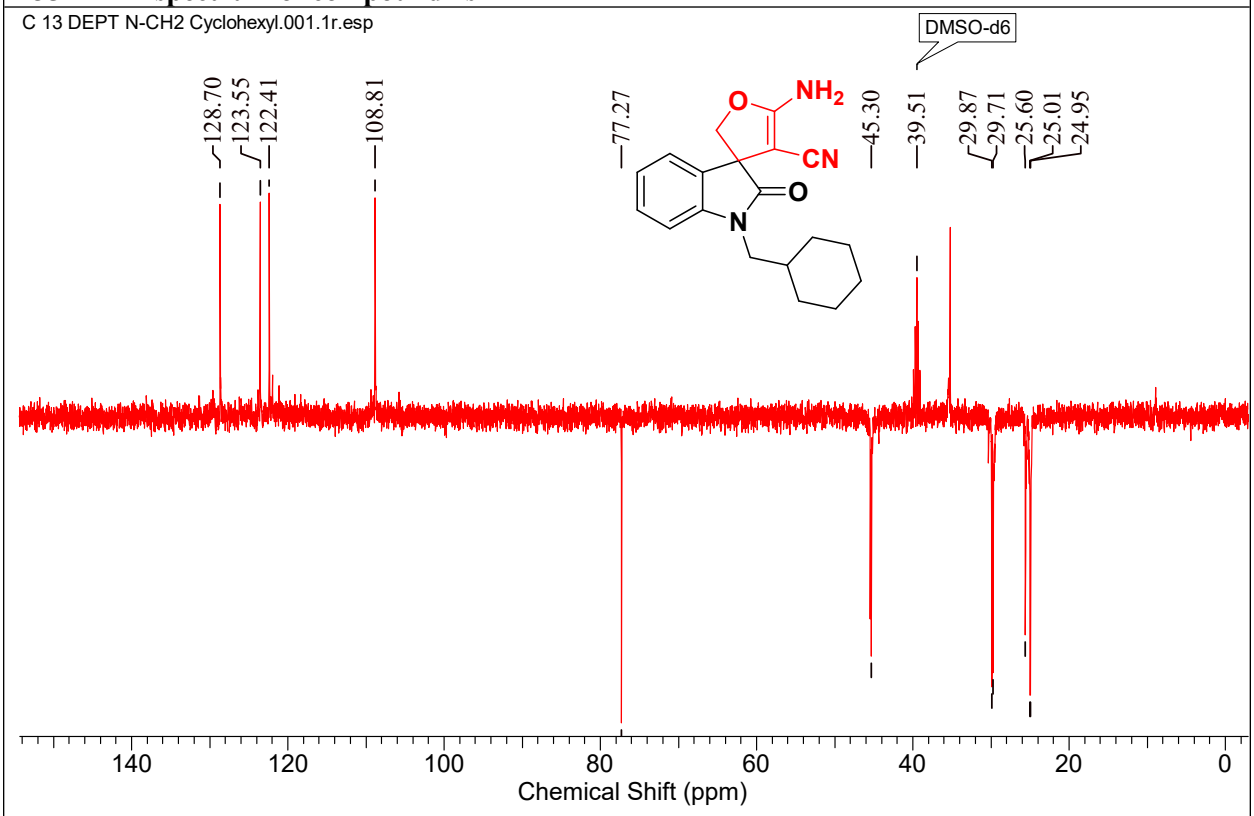
^{1}H NMR spectrum of compound 2s (400 MHz, DMSO-d_6)



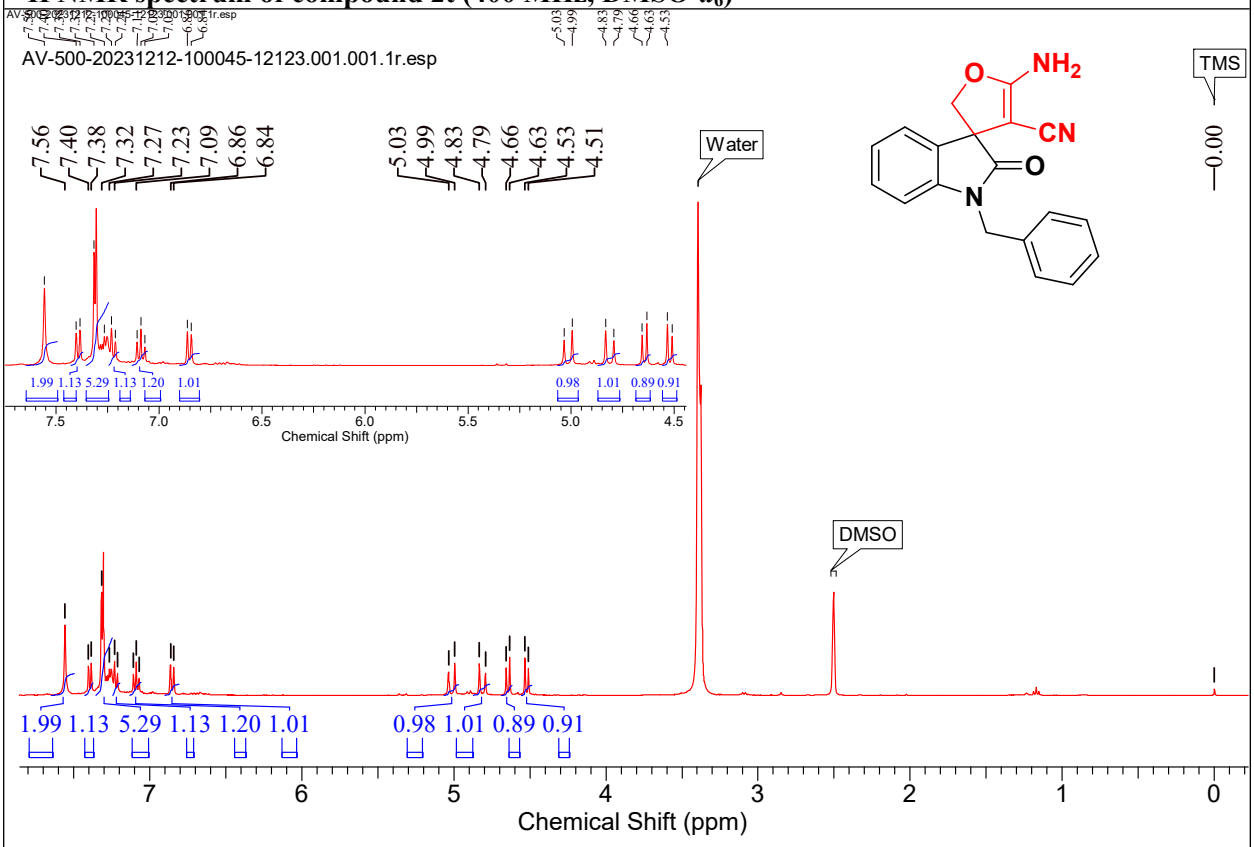
^{13}C NMR spectrum of compound 2s (101 MHz, *DMSO-d_6*)



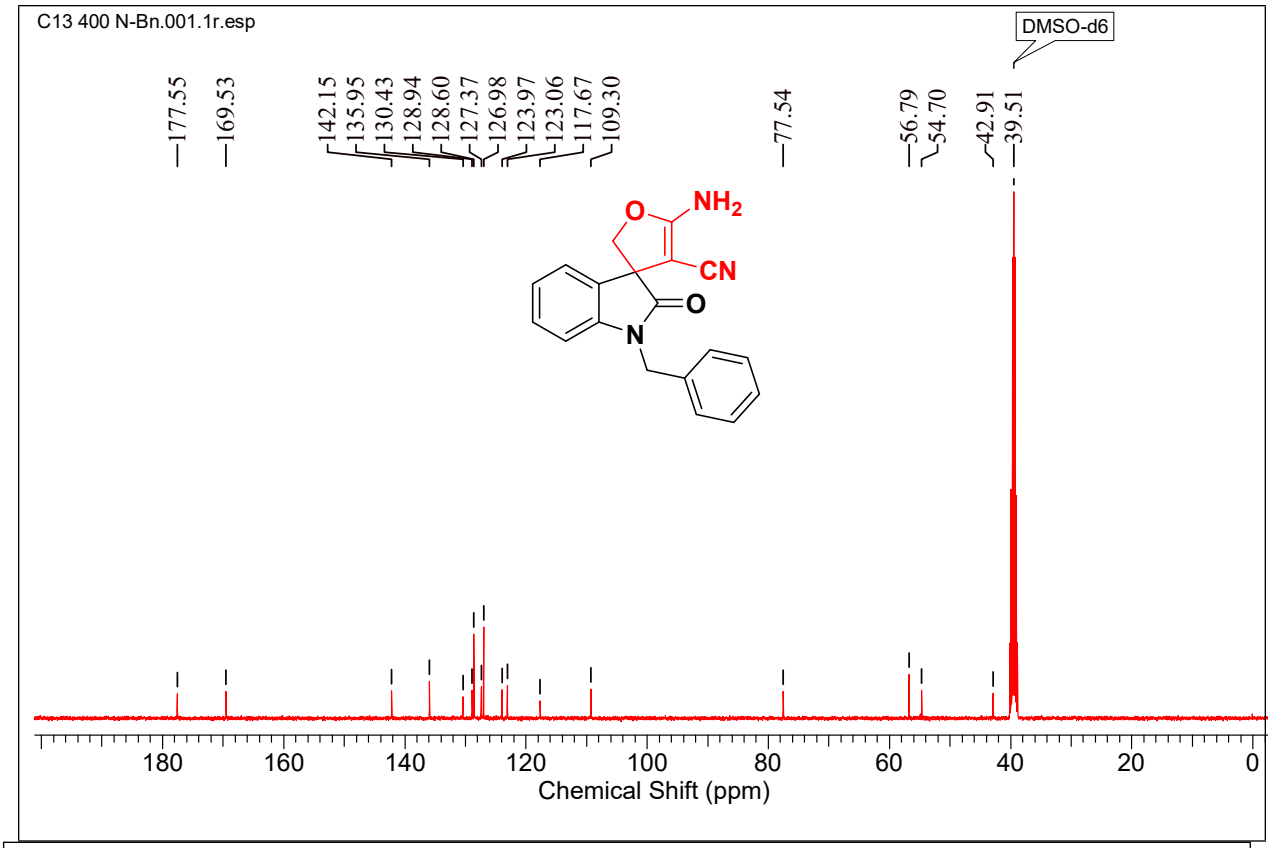
135 DEPT spectrum of compound 2s



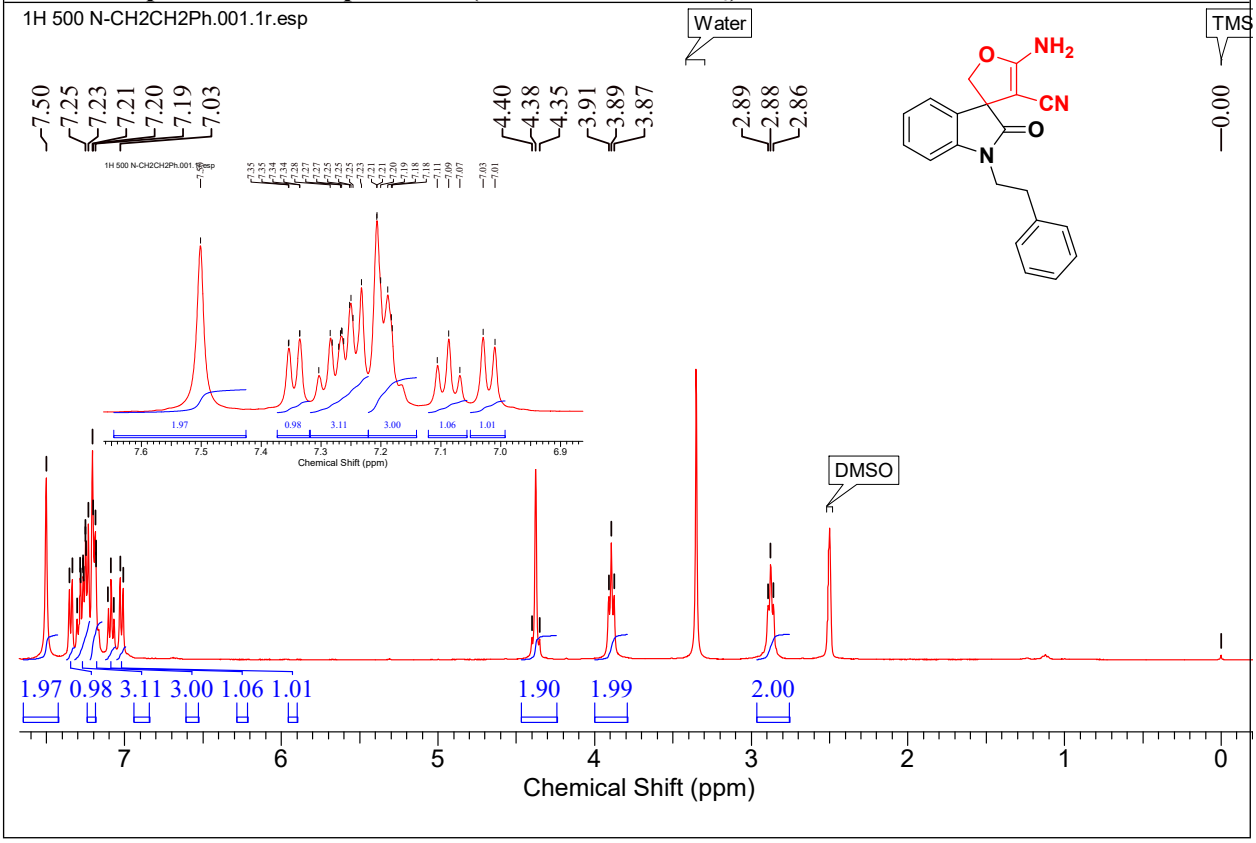
^{1}H NMR spectrum of compound 2t (400 MHz, DMSO-d_6)



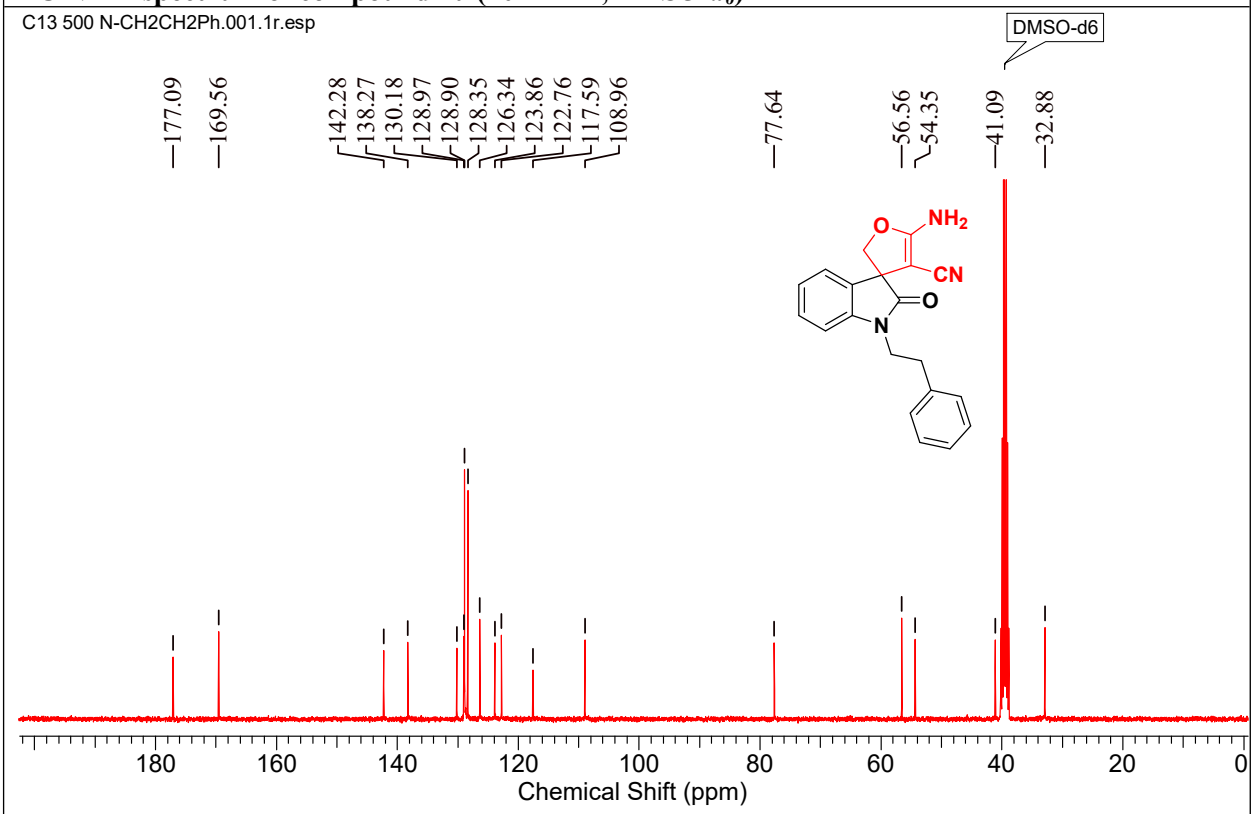
^{13}C NMR spectrum of compound 2t (101 MHz, *DMSO-d_6*)



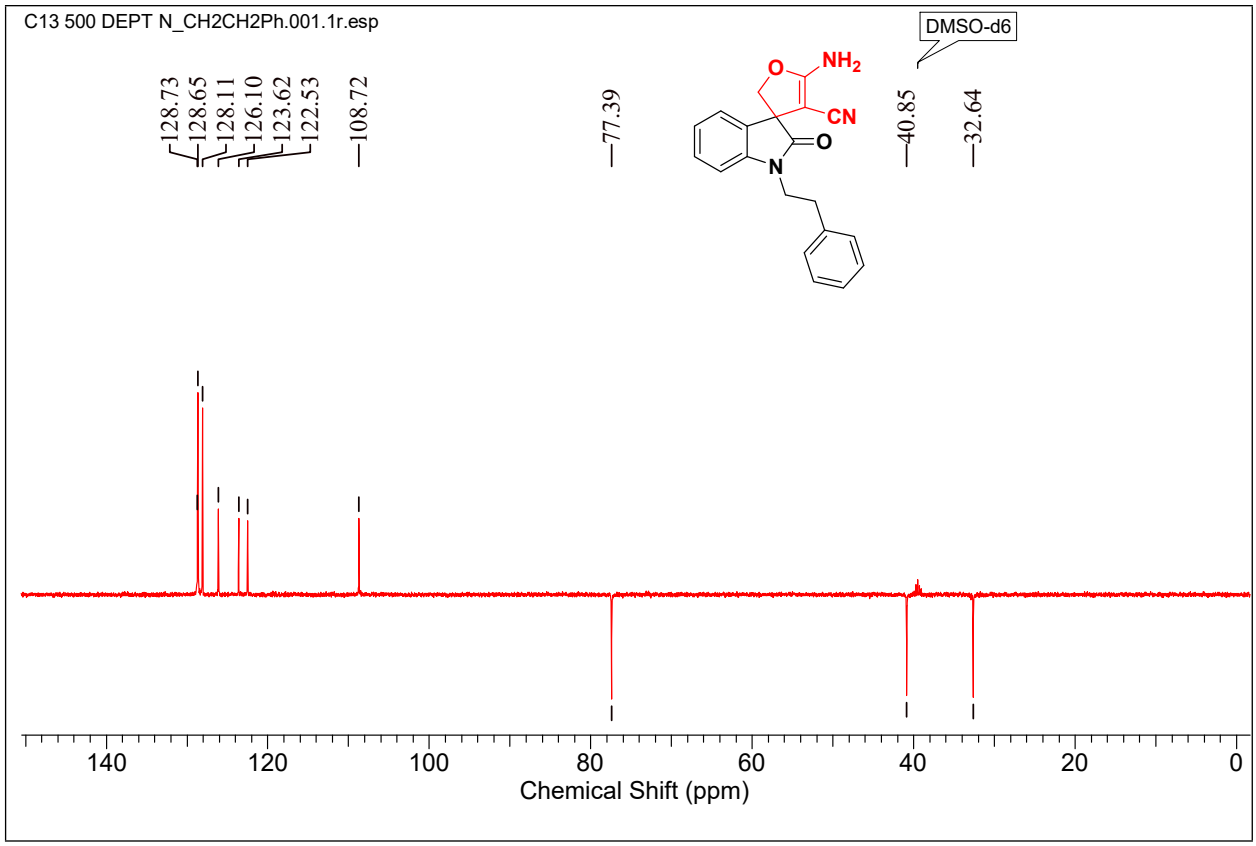
^{1}H NMR spectrum of compound 2u (400 MHz, DMSO-d_6)



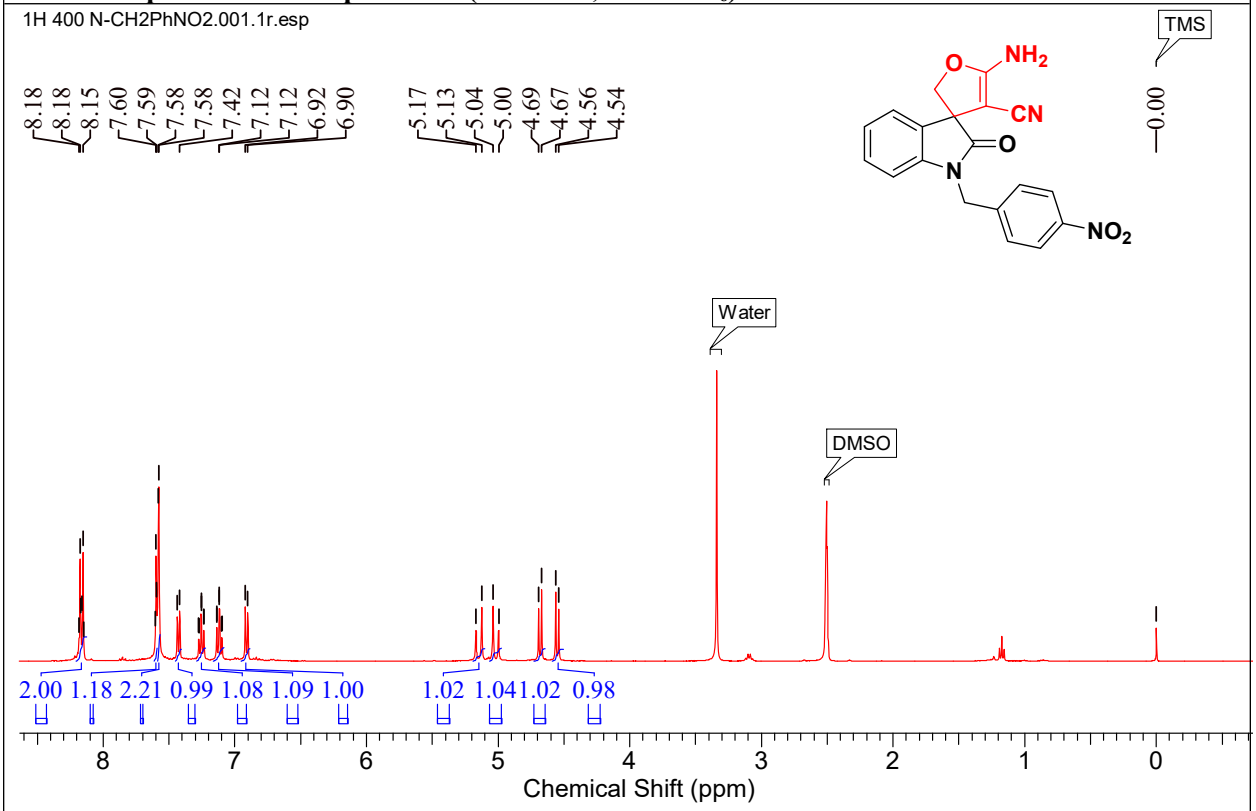
^{13}C NMR spectrum of compound 2u (101 MHz, *DMSO-d_6*)



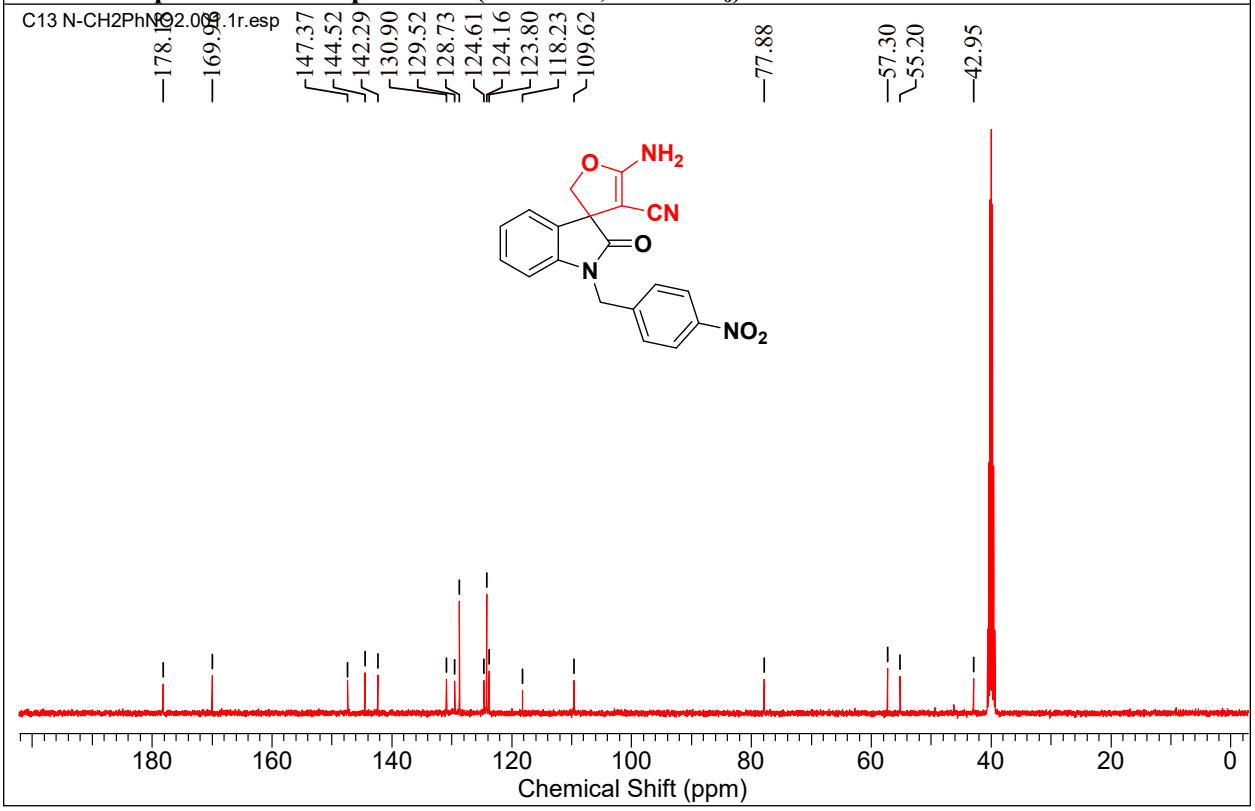
135 DEPT spectrum of compound 2u


C13 500 DEPT N_CH2CH2Ph.001.1r.esp
DMSO-d6
128.73
128.65
128.11
126.10
123.62
122.53
108.72
77.39
40.85
32.64
O
NH2
CN
O
N
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

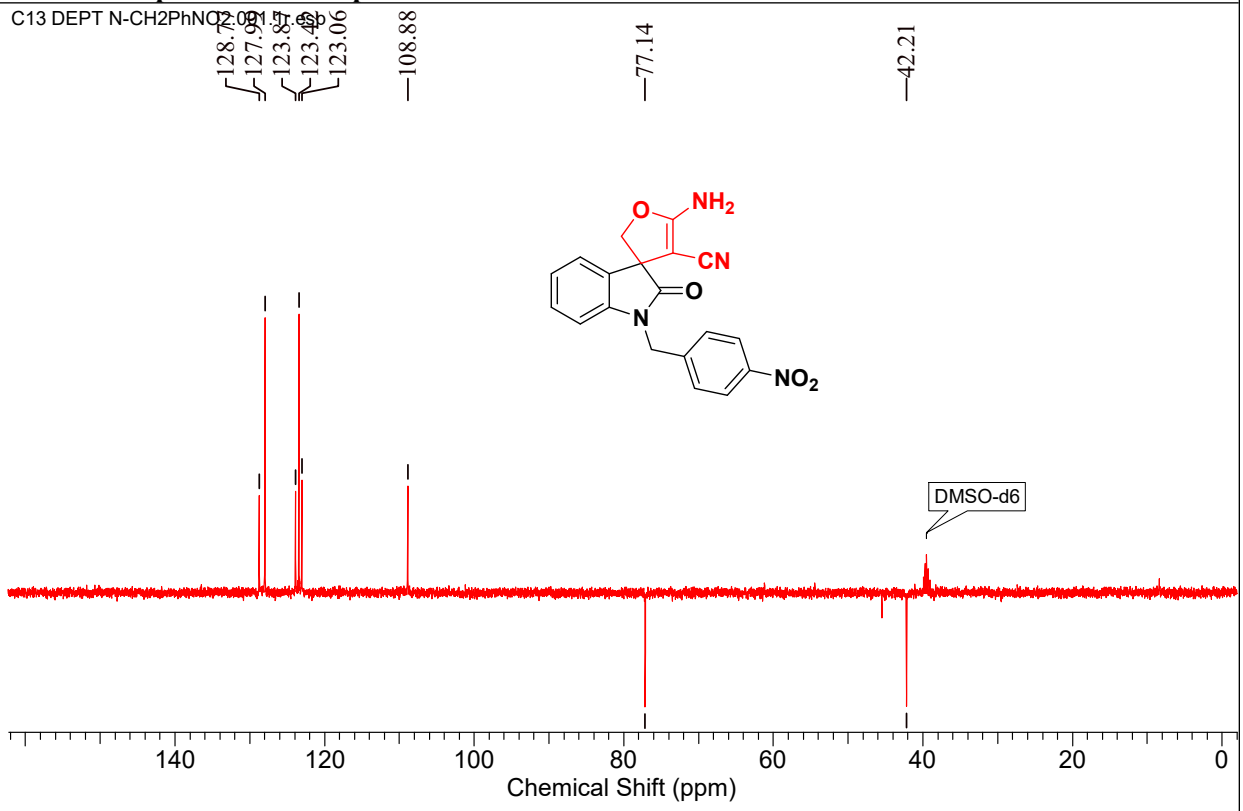
^{1}H NMR spectrum of compound 2v (400 MHz, DMSO-d_6)



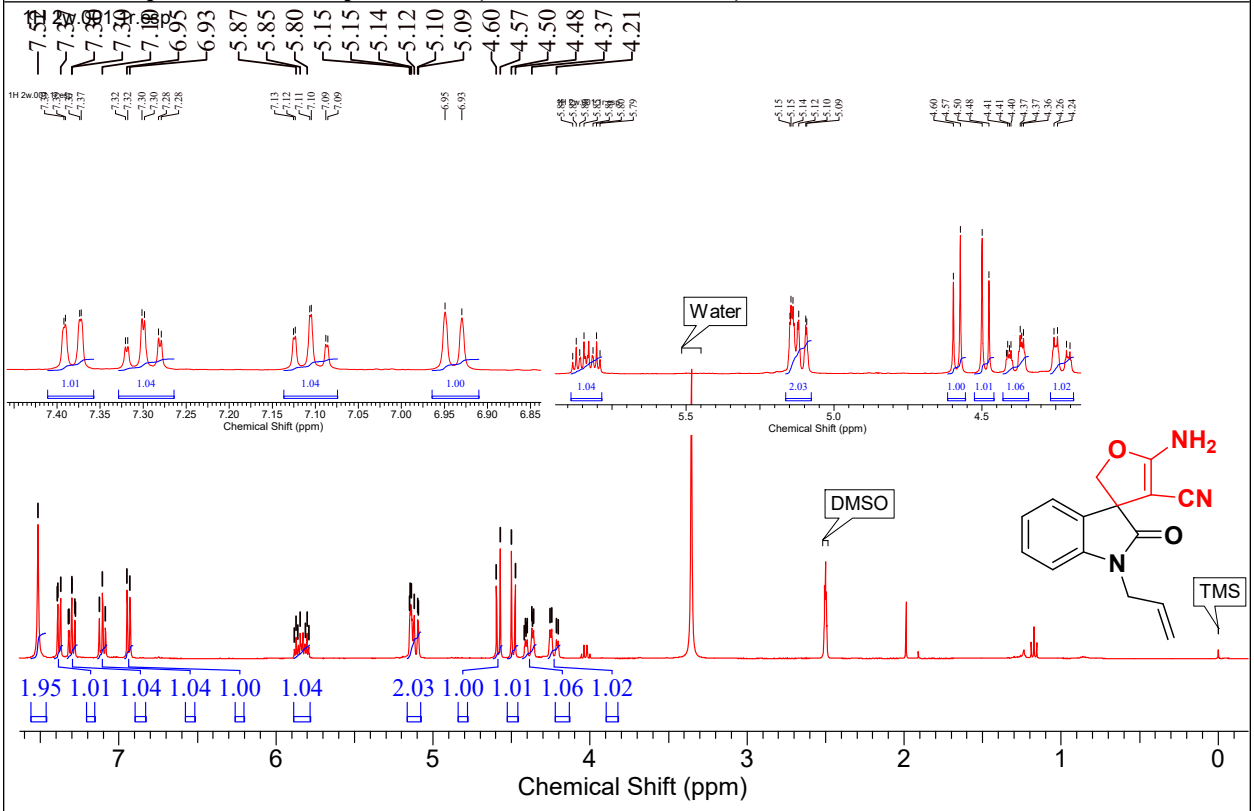
^{13}C NMR spectrum of compound 2v (101 MHz, *DMSO-d_6*)



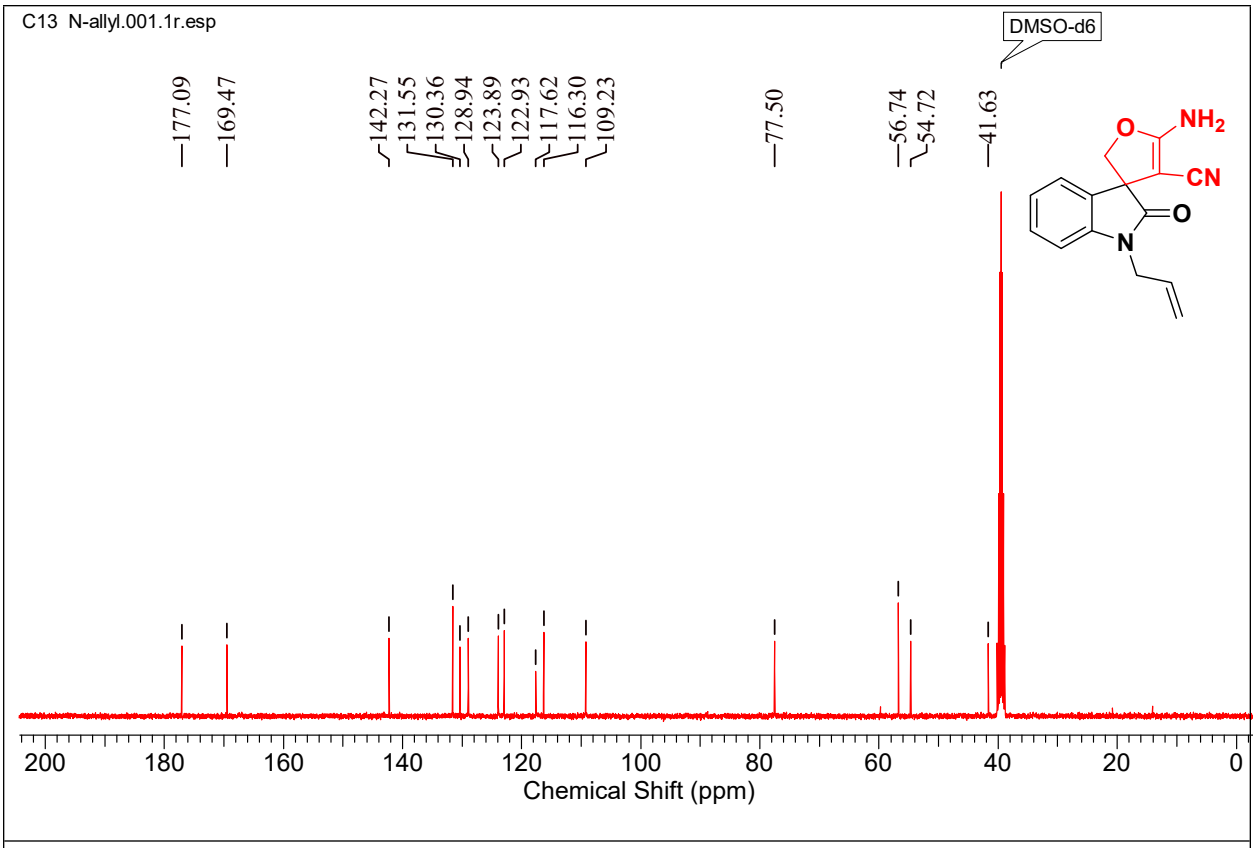
135 DEPT spectrum of compound 2v



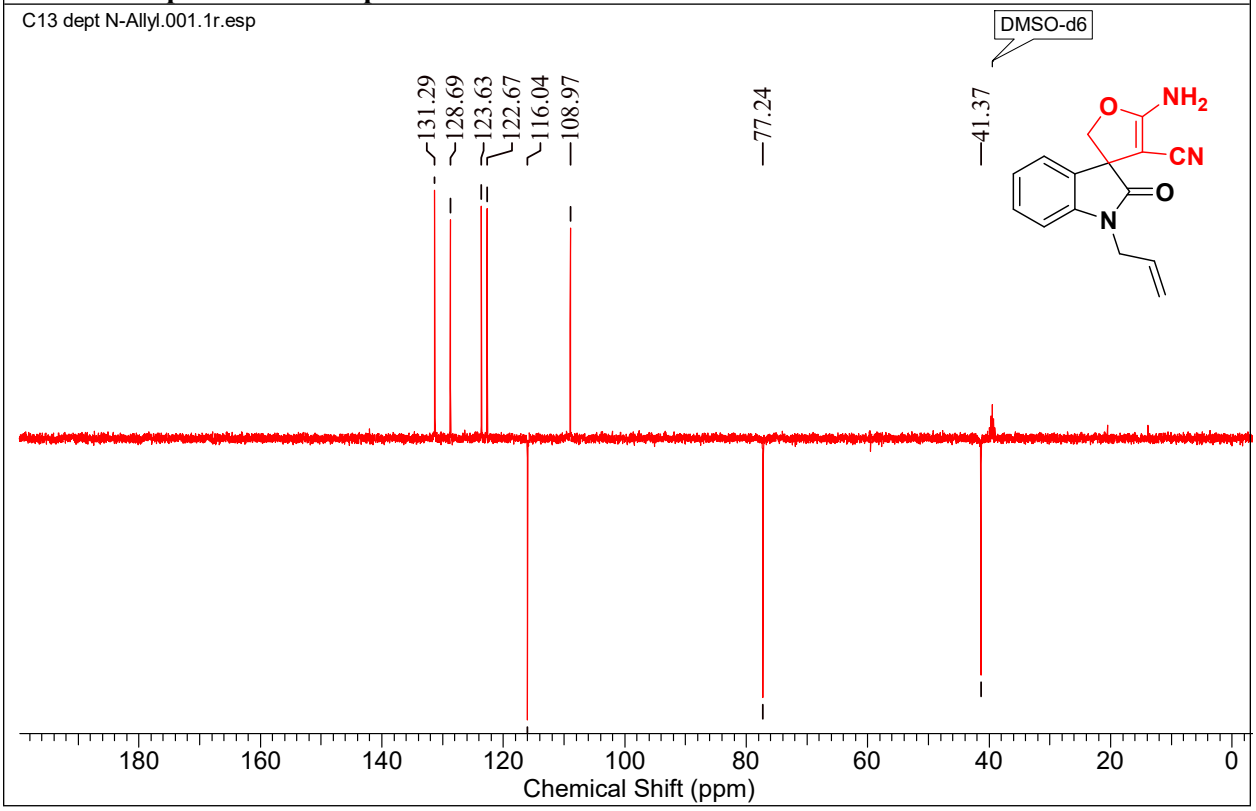
^{1}H NMR spectrum of compound 2w (400 MHz, DMSO-d_6)



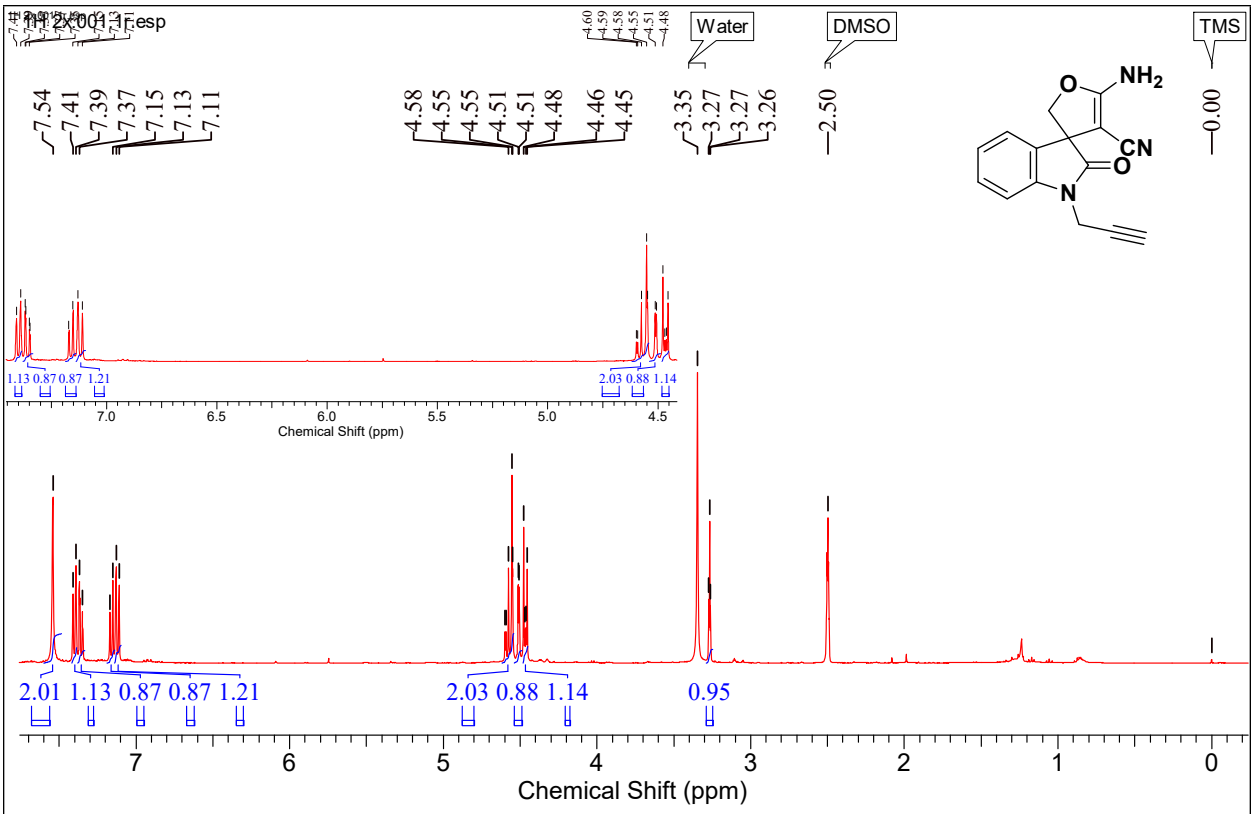
^{13}C NMR spectrum of compound 2w (101 MHz, *DMSO-d_6*)



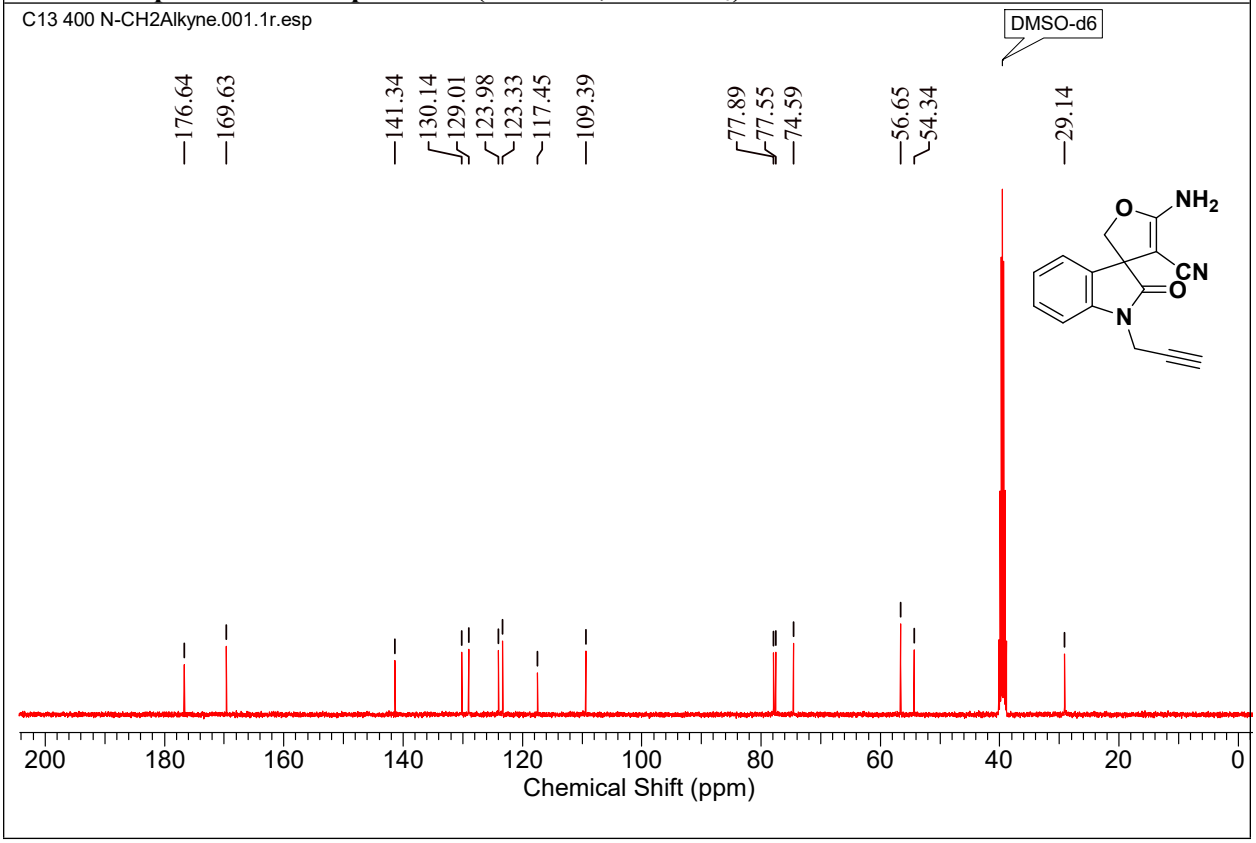
135 DEPT spectrum of compound 2w



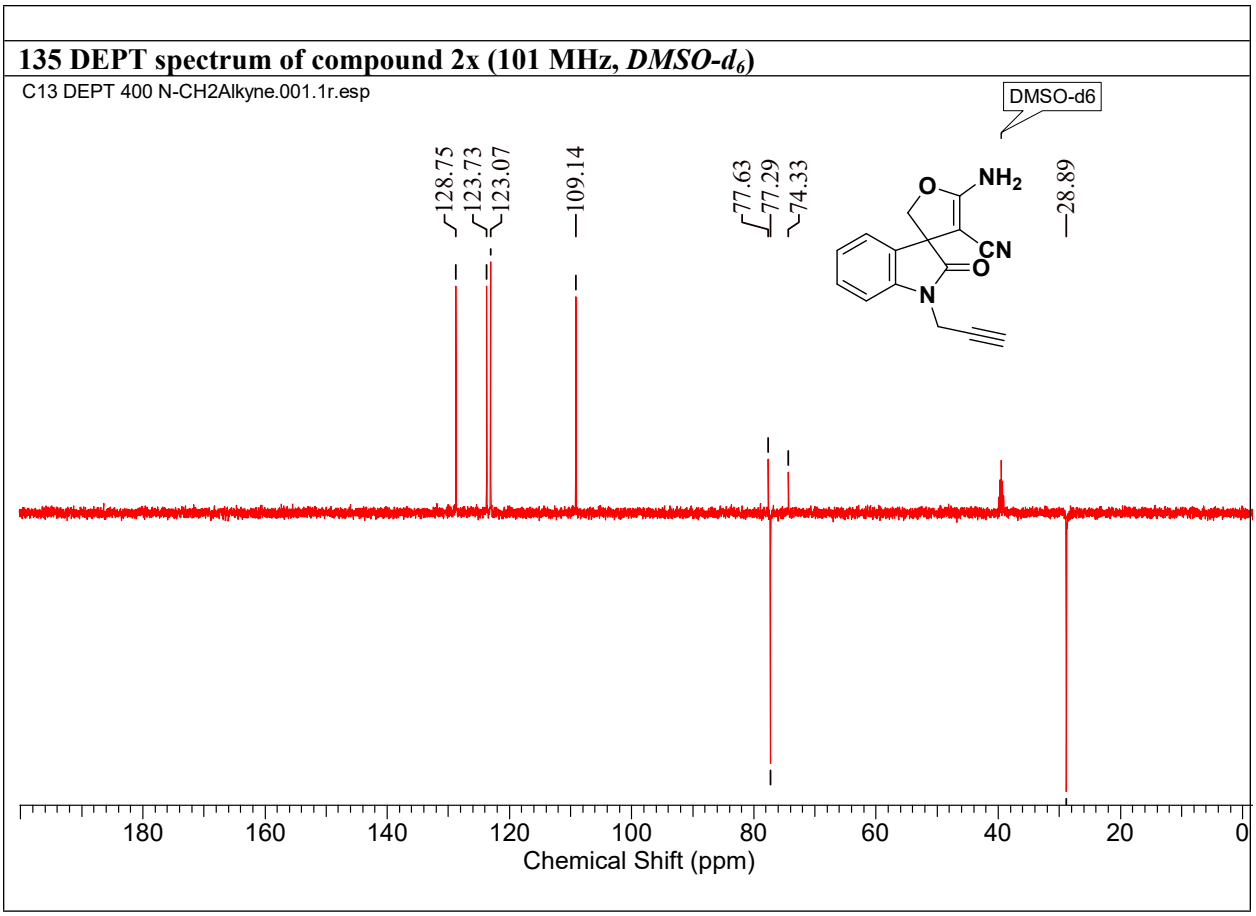
^{1}H NMR spectrum of compound 2x (400 MHz, DMSO-d_6)



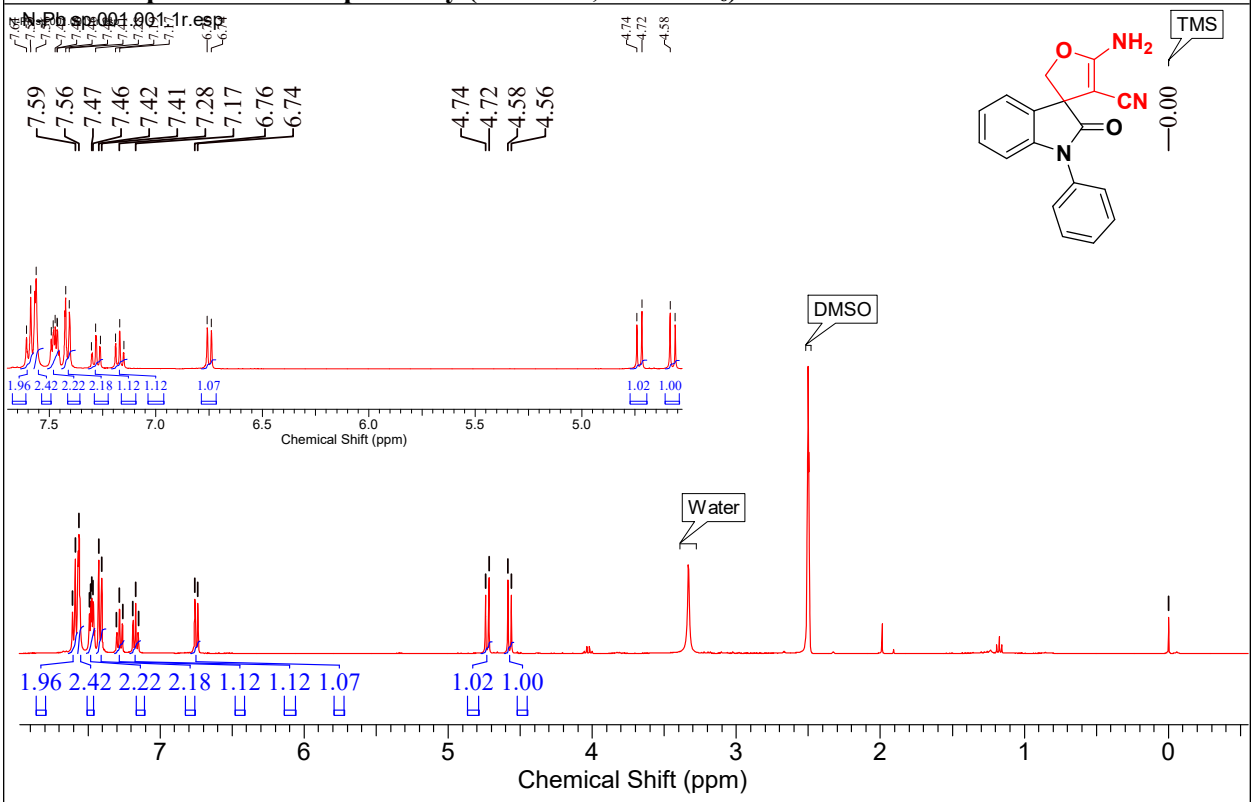
^{13}C NMR spectrum of compound 2x (101 MHz, *DMSO-d$_6$*)



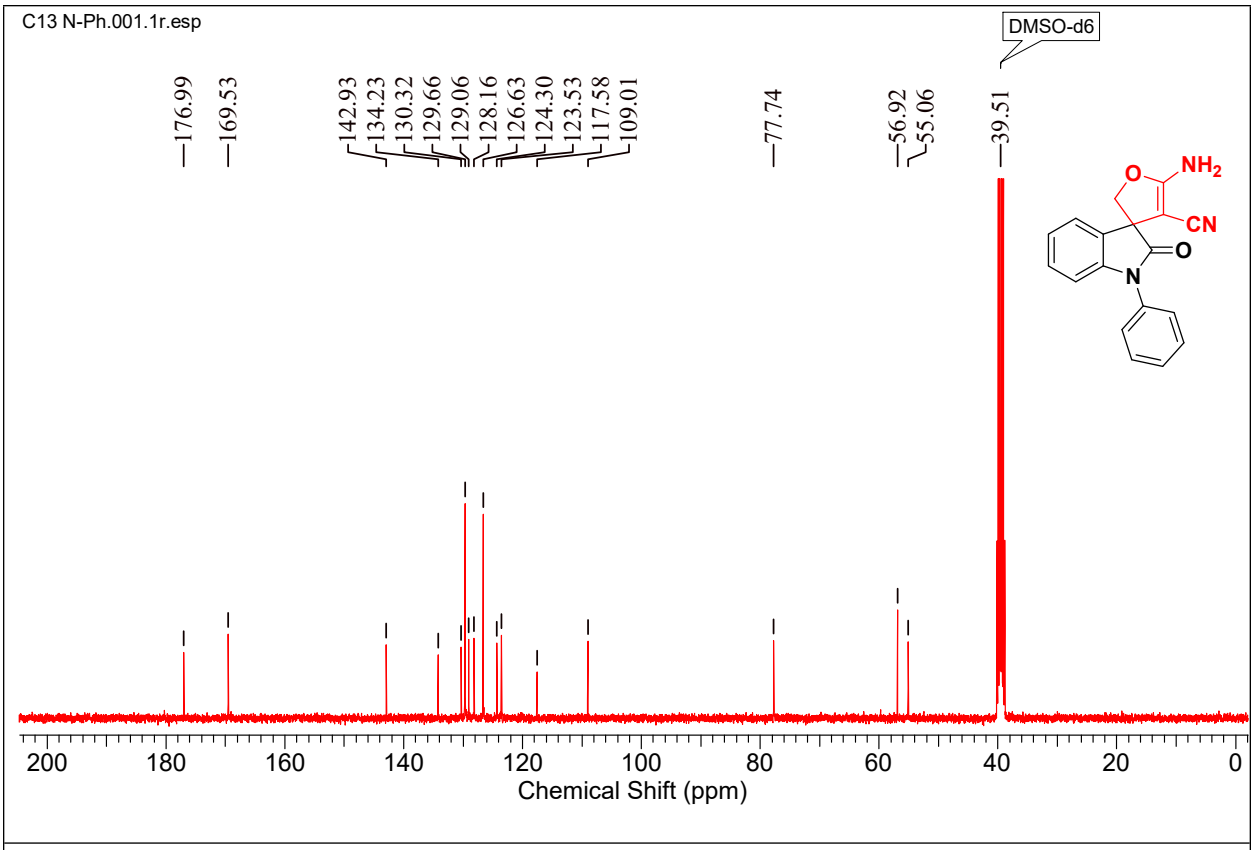
135 DEPT spectrum of compound 2x (101 MHz, *DMSO-d_6*)



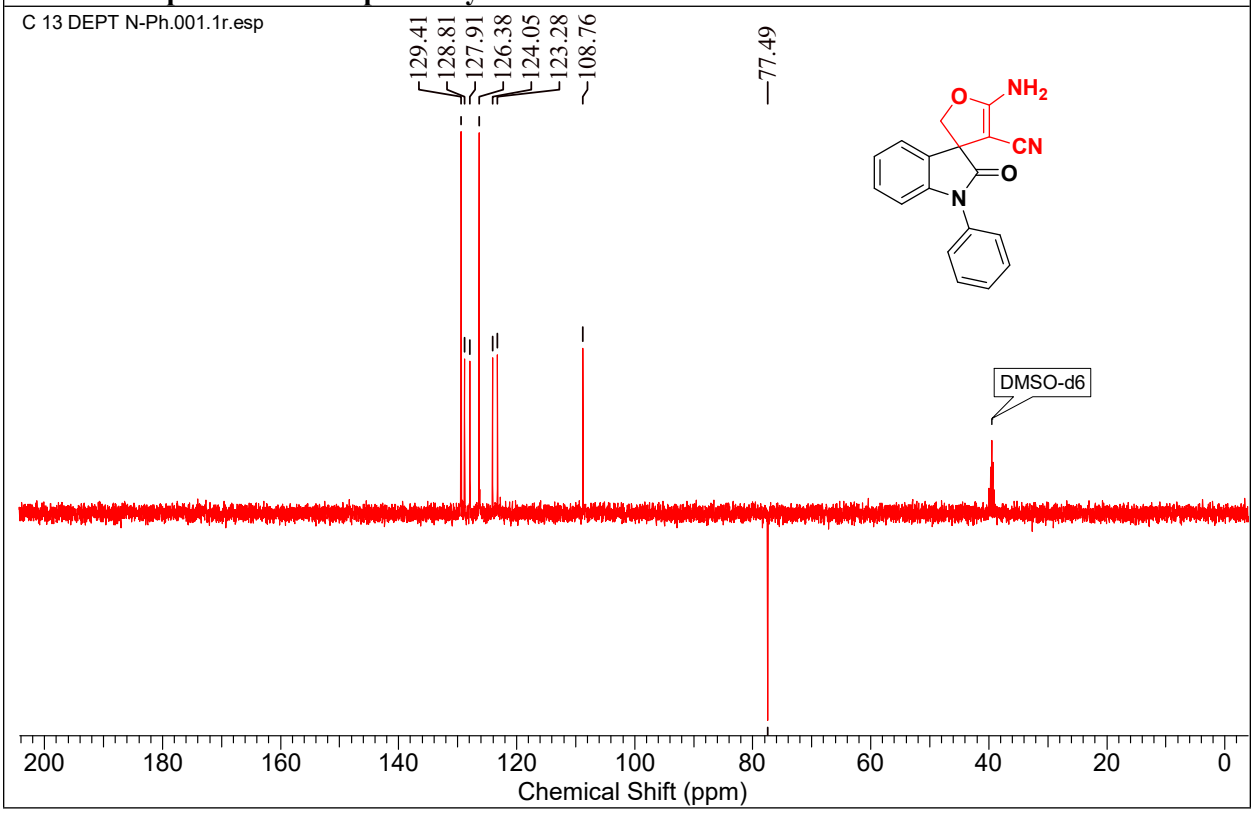
^{1}H NMR spectrum of compound 2y (400 MHz, DMSO-d_6)



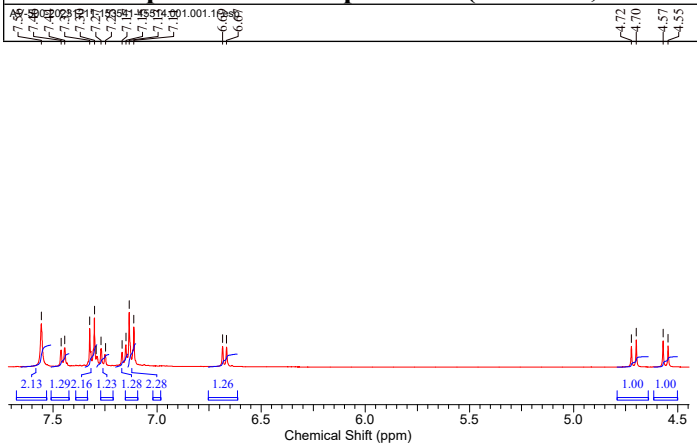
^{13}C NMR spectrum of compound 2y (101 MHz, *DMSO-d_6*)

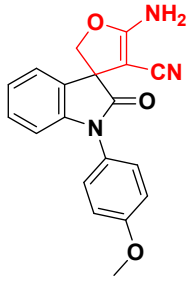


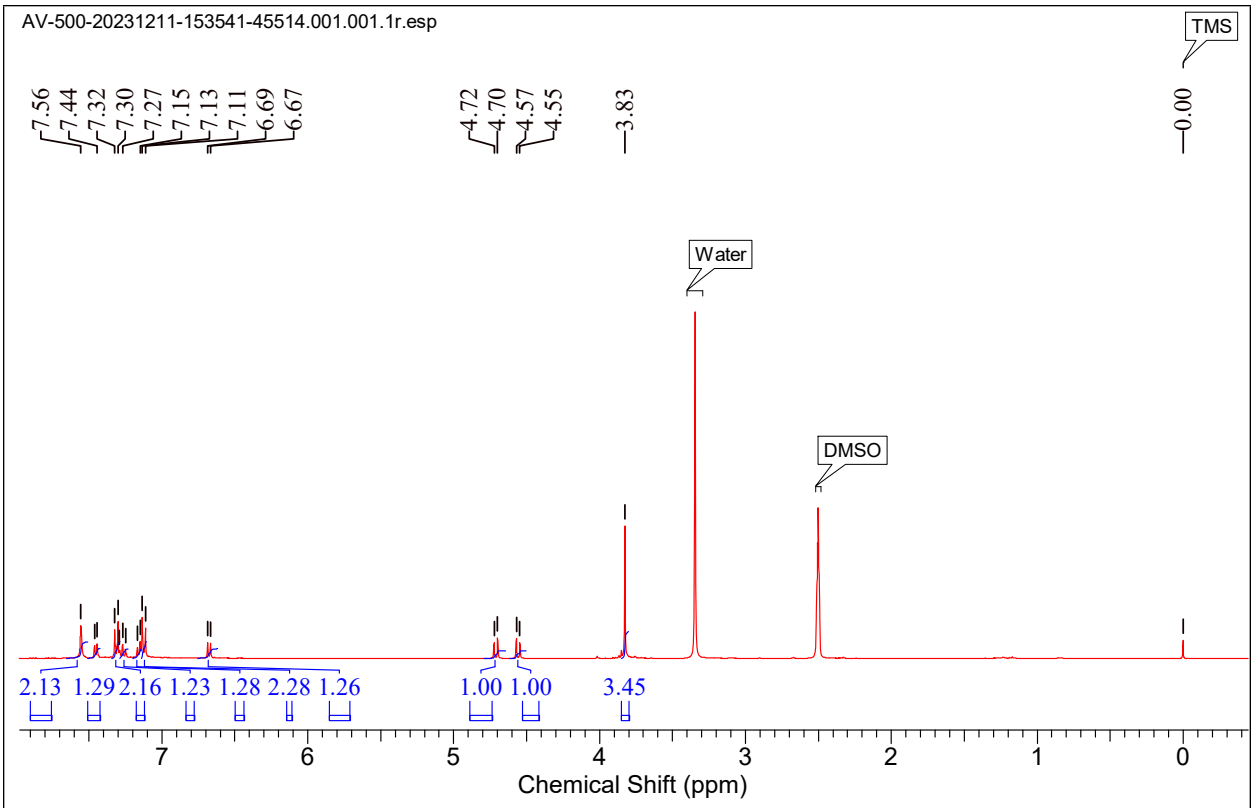
135 DEPT spectrum of compound 2y



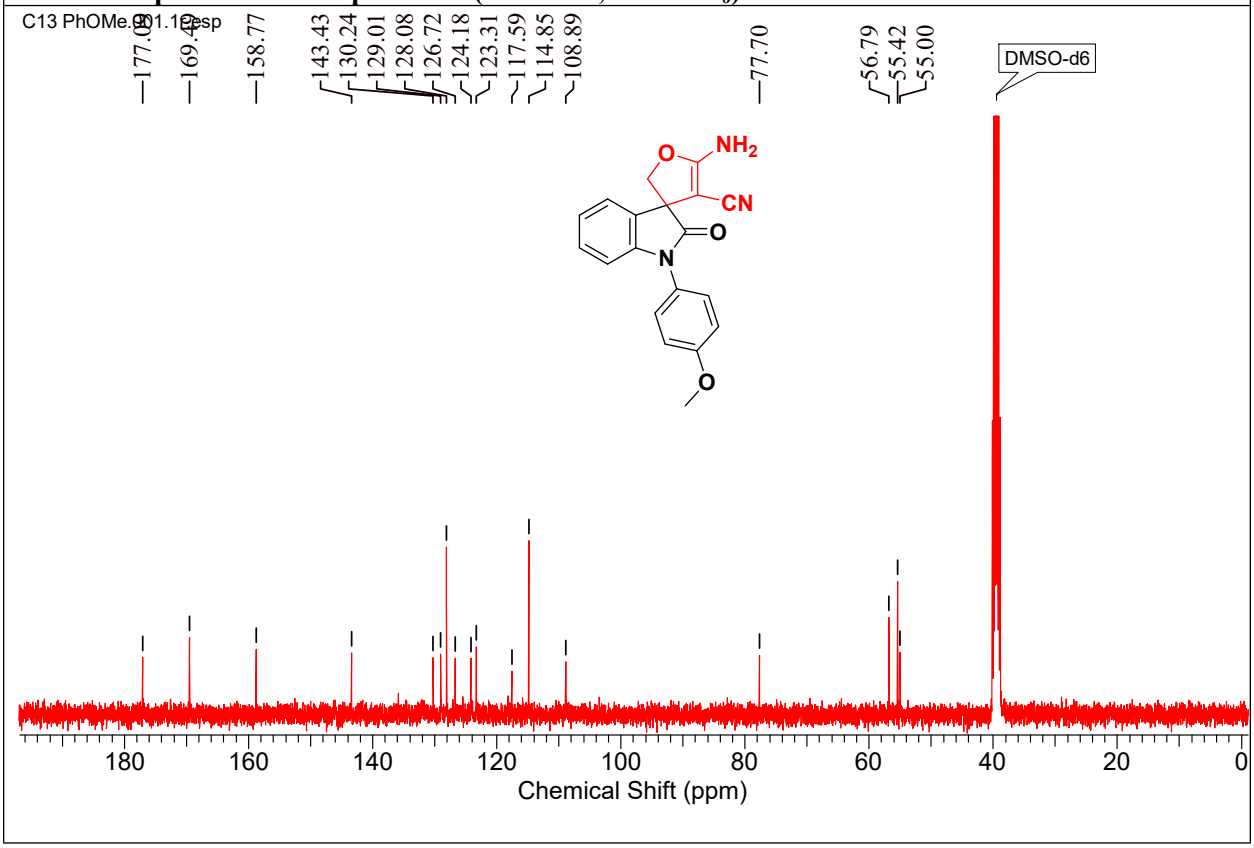
^{1}H NMR spectrum of compound 2z (400 MHz, DMSO-d_6)



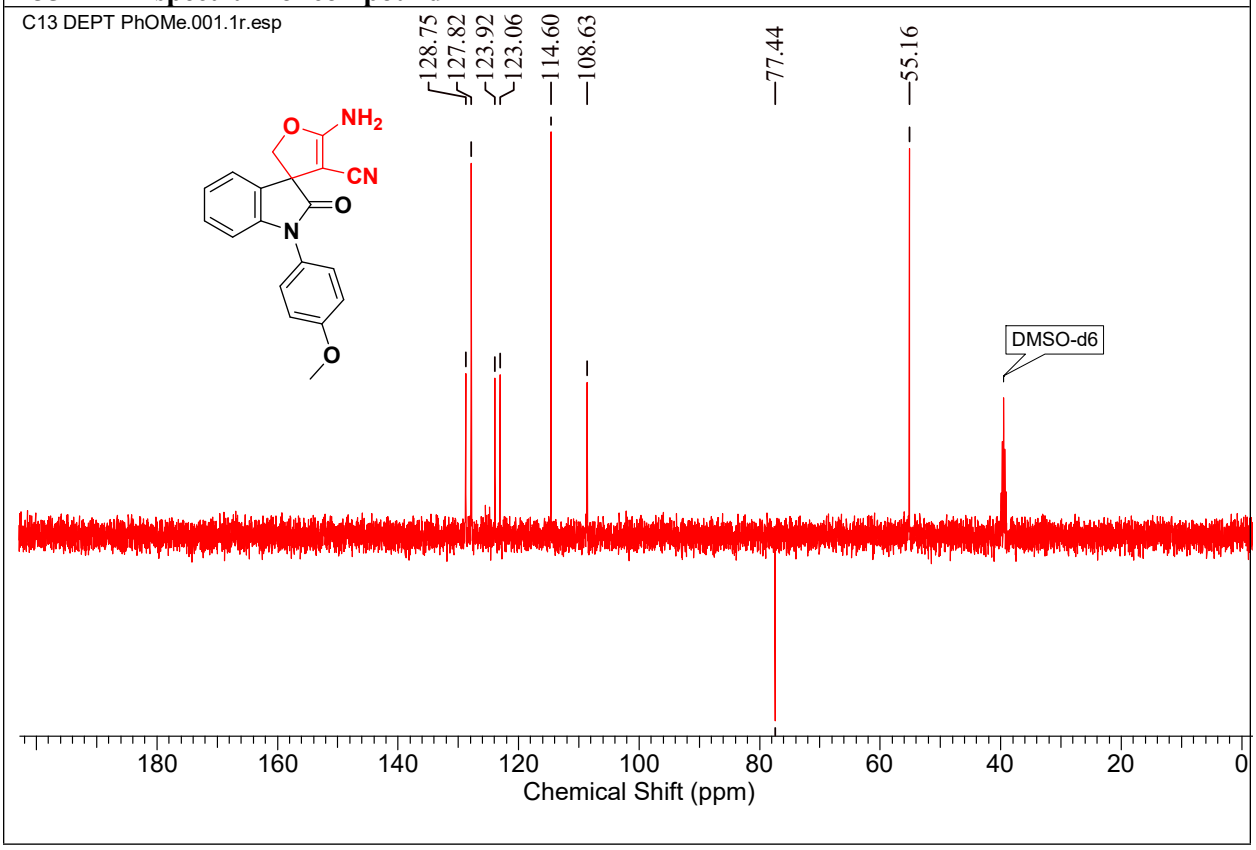




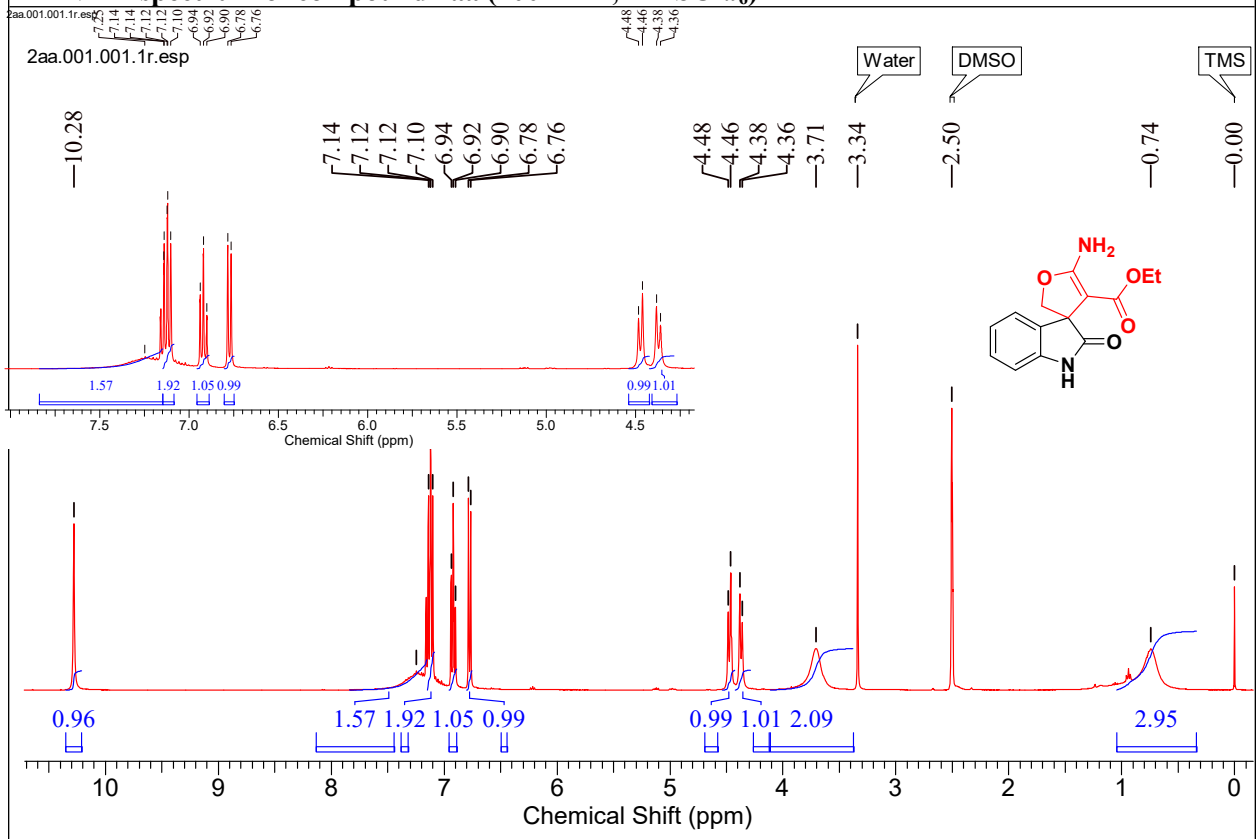
^{13}C NMR spectrum of compound 2z (101 MHz, *DMSO-d$_6$*)



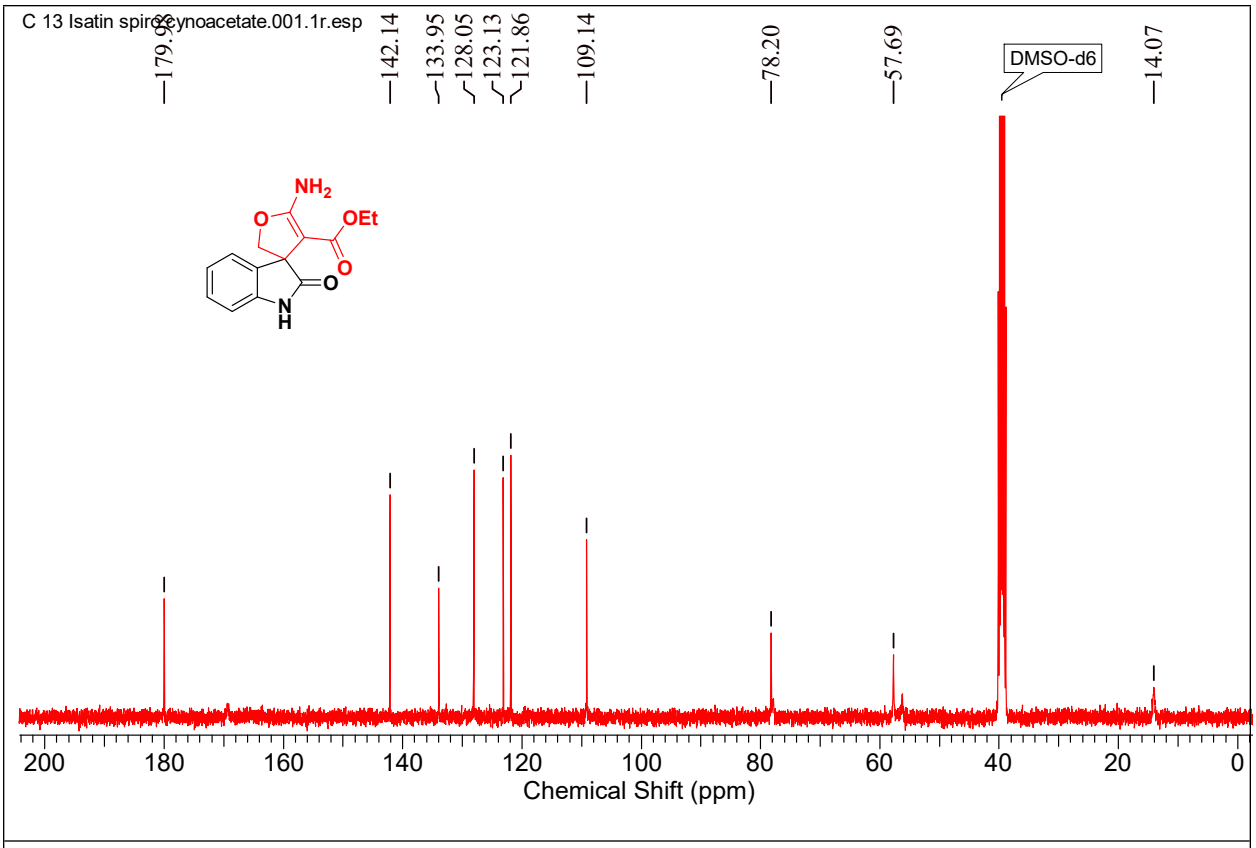
135 DEPT spectrum of compound 2z



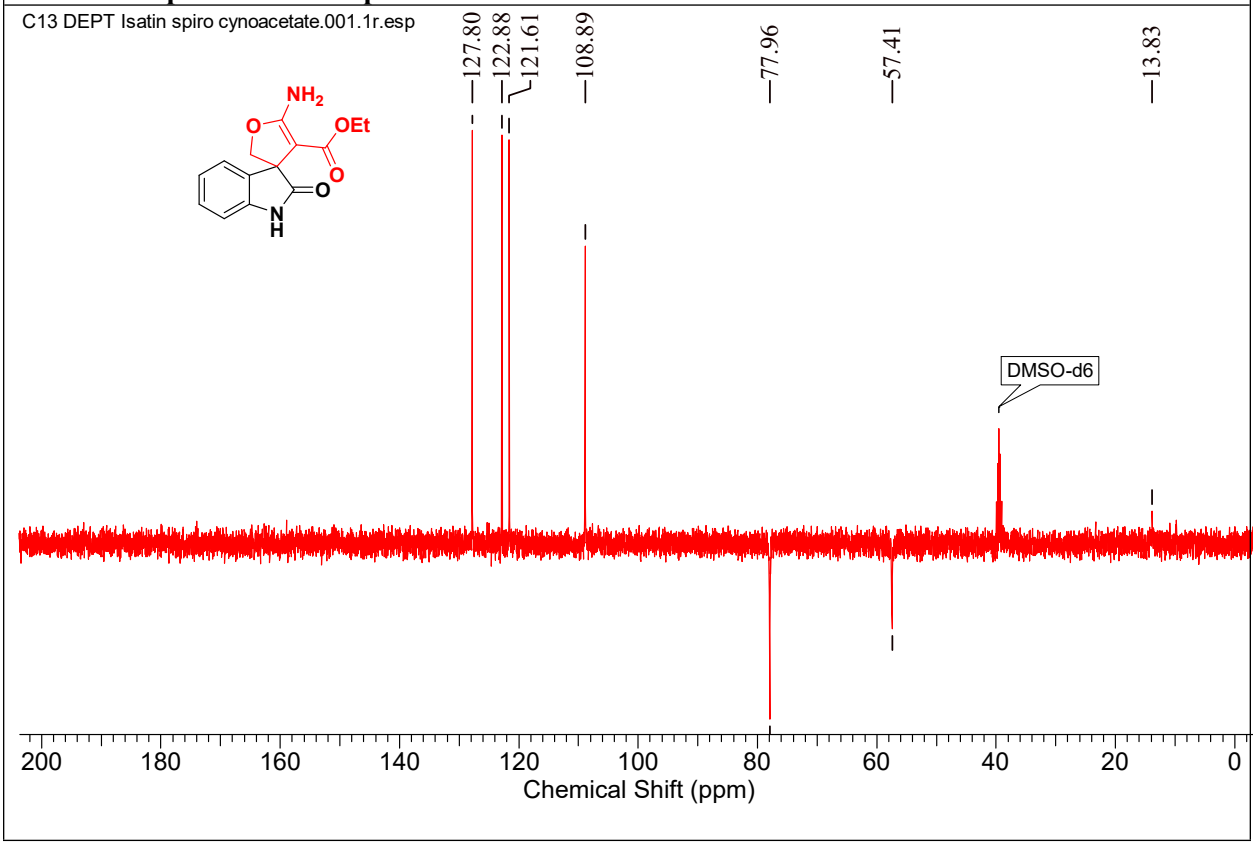
^{1}H NMR spectrum of compound 2aa (400 MHz, DMSO-d_6)



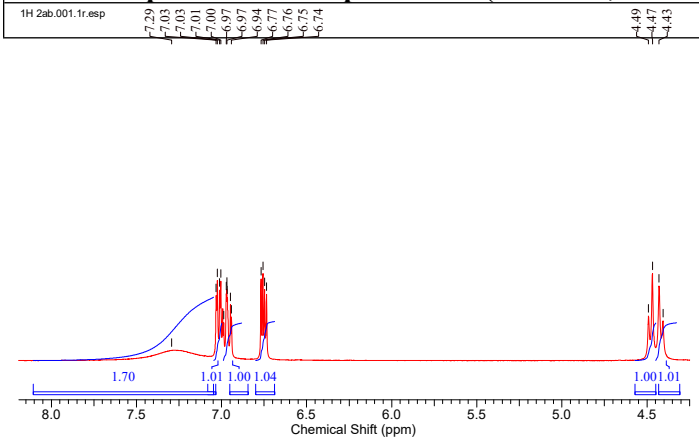
^{13}C NMR spectrum of compound 2aa (101 MHz, DMSO-d_6)

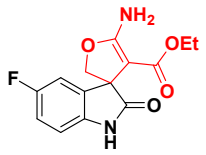


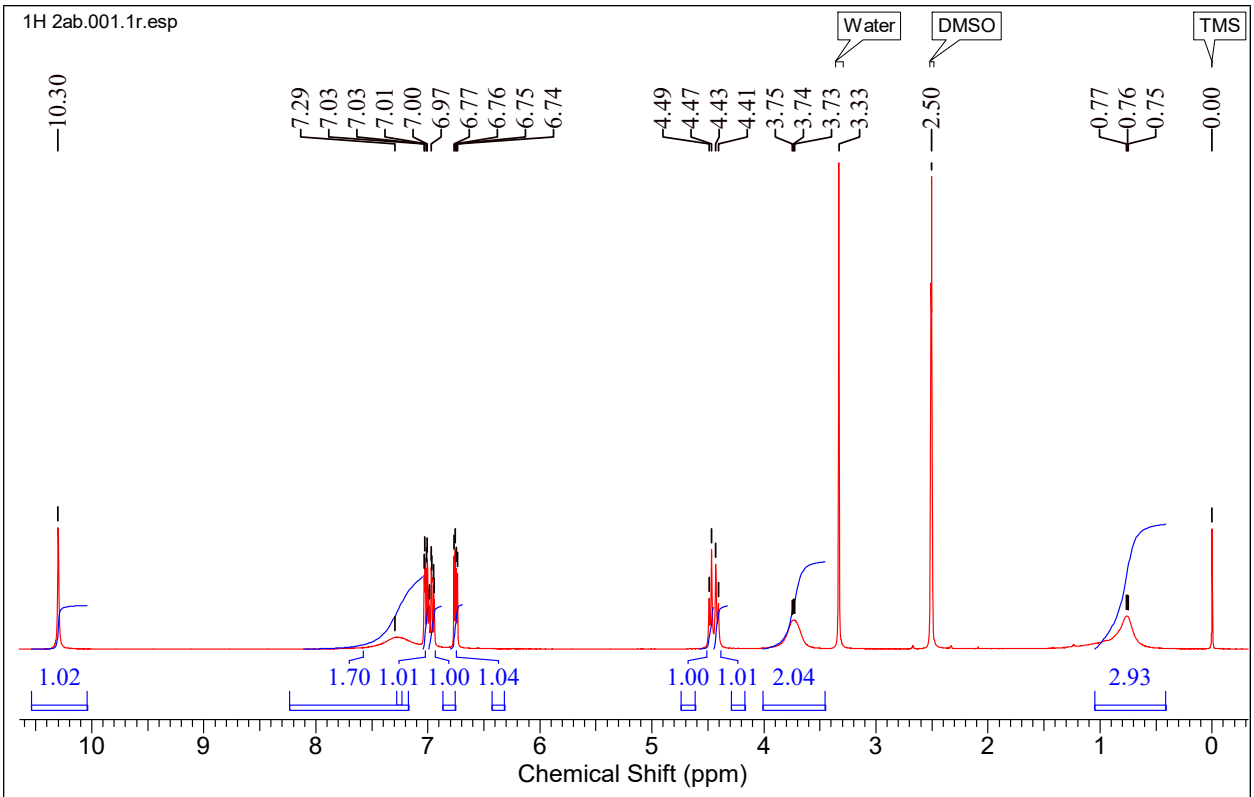
135 DEPT spectrum of compound 2aa



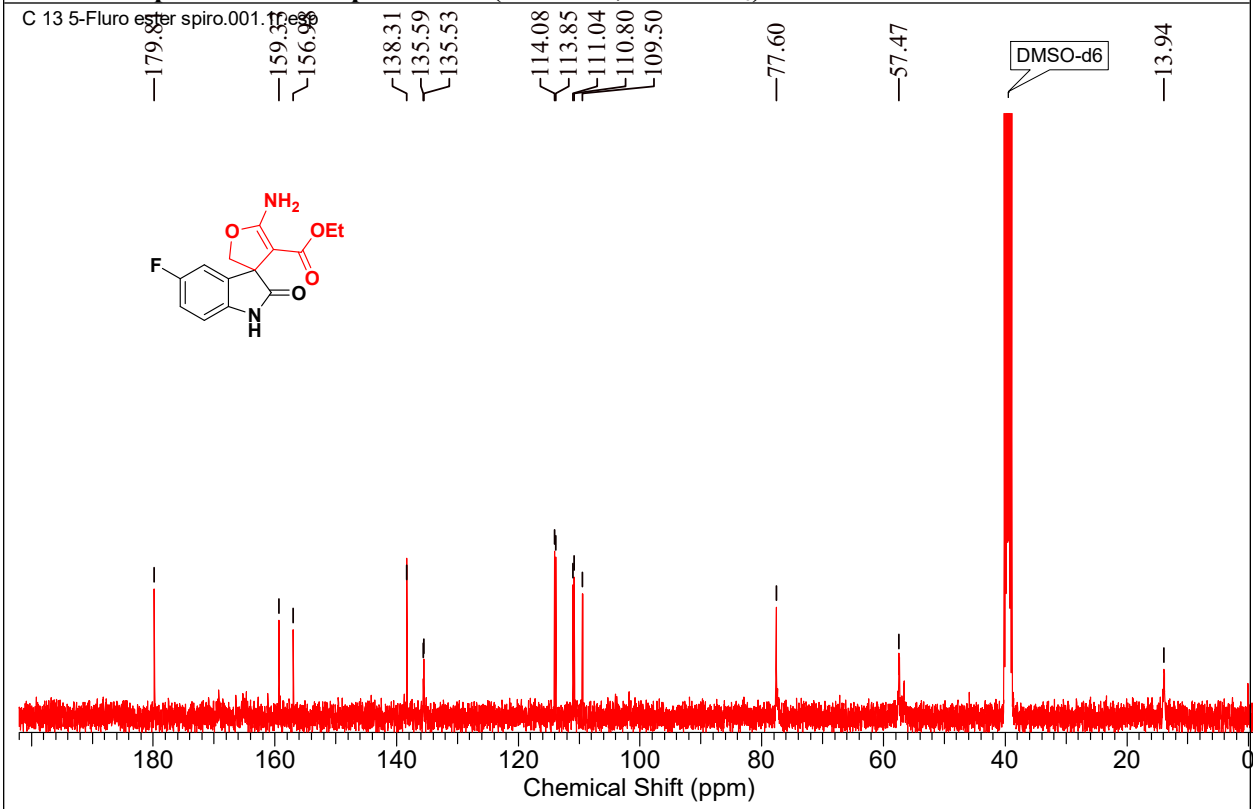
^{1}H NMR spectrum of compound 2ab (400 MHz, DMSO-d_6)



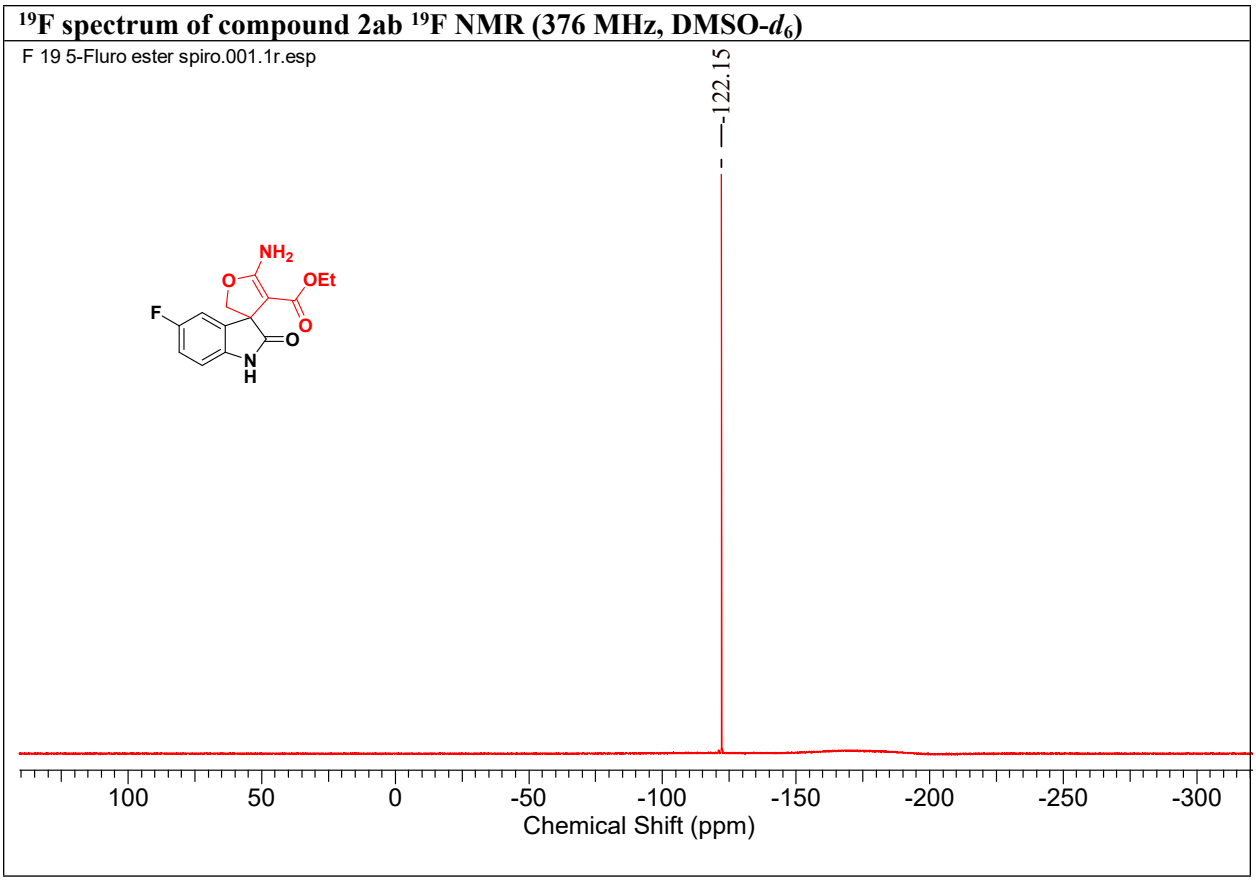




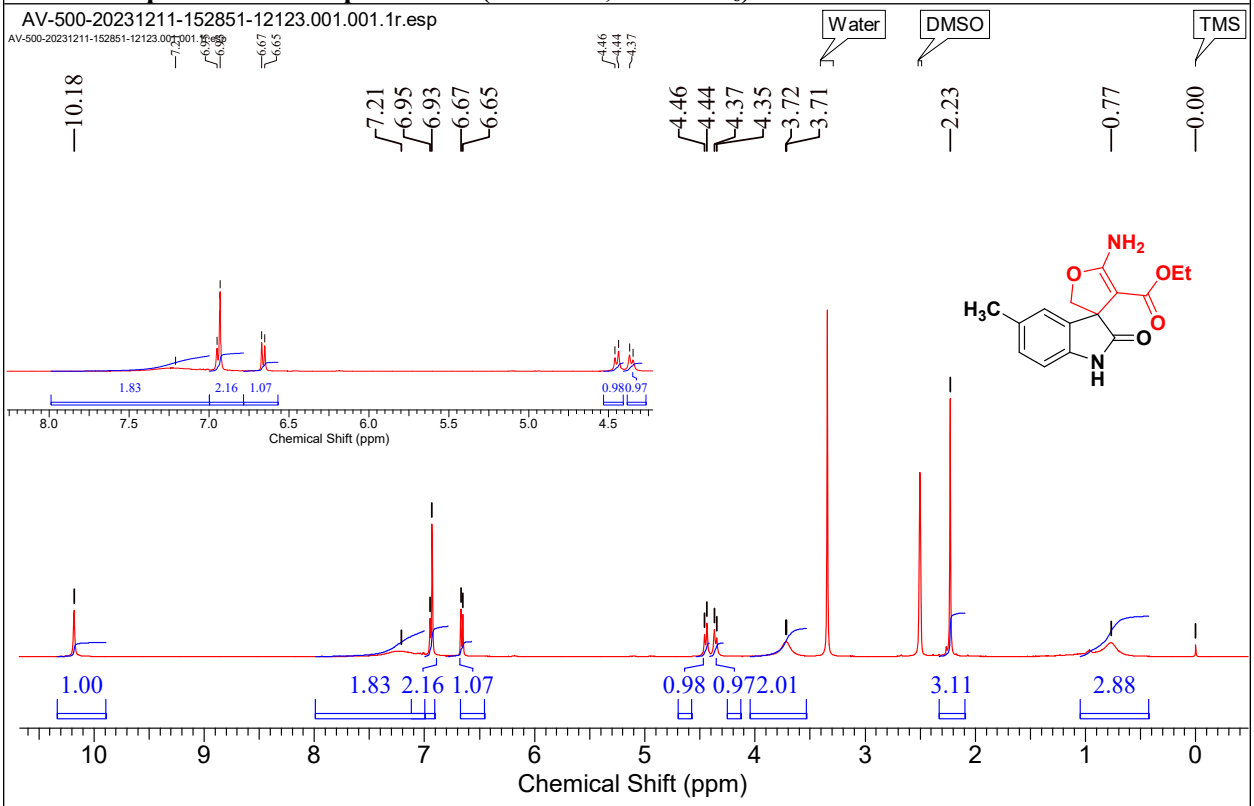
^{13}C NMR spectrum of compound 2ab (101 MHz, DMSO-d_6)



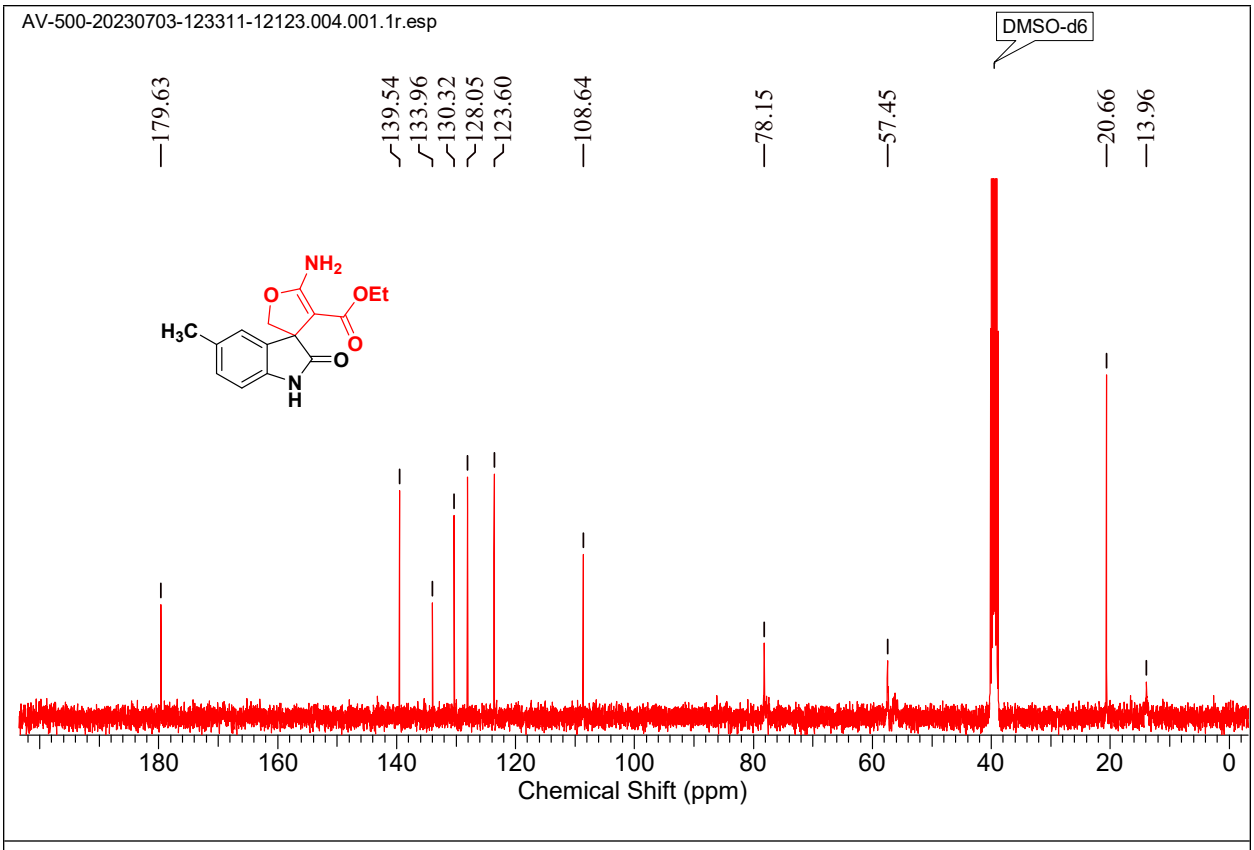
^{19}F spectrum of compound 2ab ^{19}F NMR (376 MHz, DMSO-d_6)



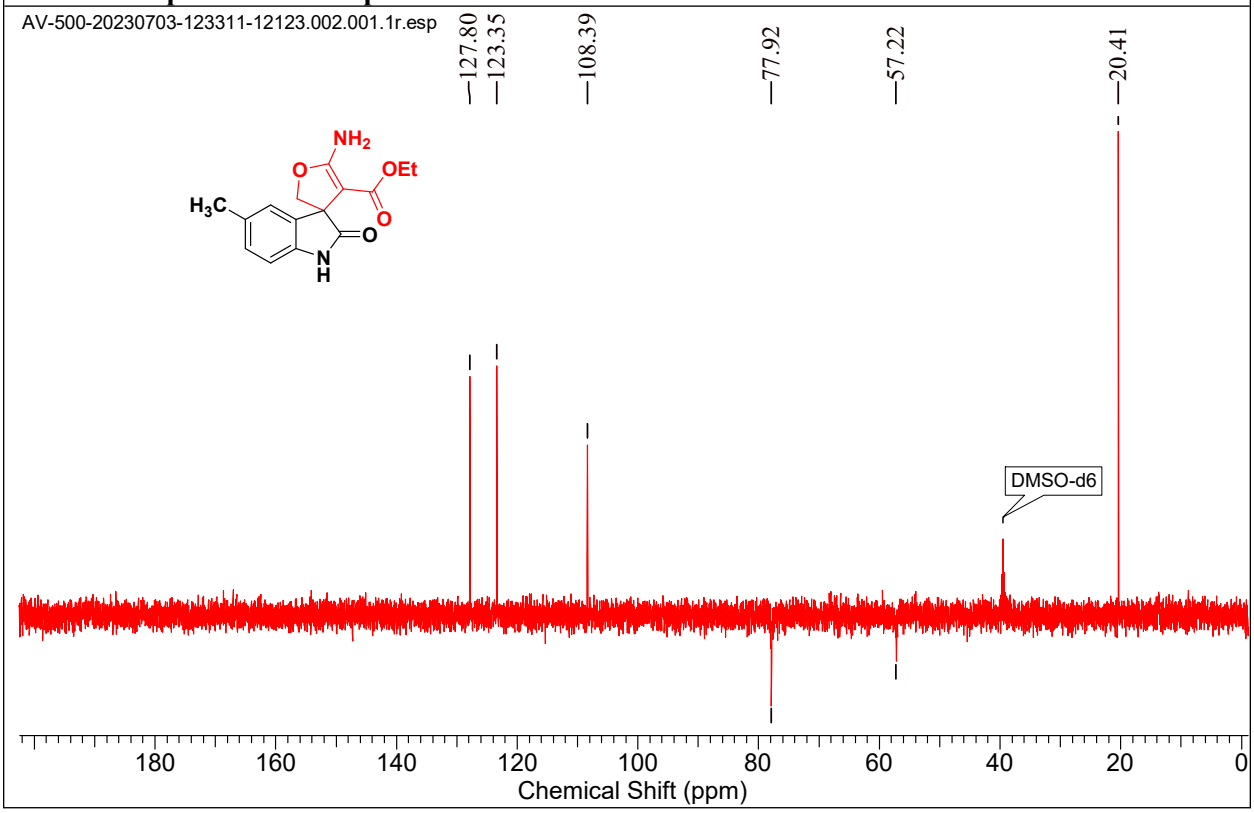
^{1}H NMR spectrum of compound 2ac (400 MHz, DMSO-d_6)



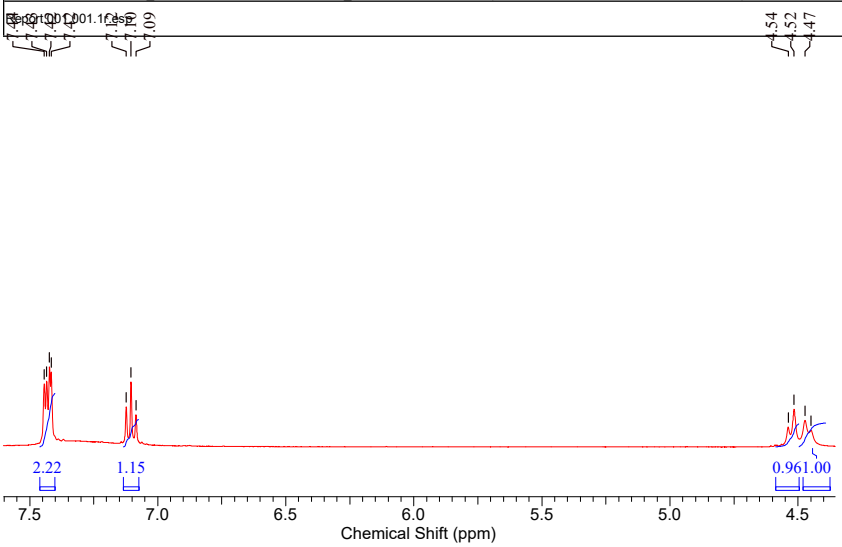
^{13}CNMR spectrum of compound 2ac (101 MHz, DMSO-d_6)

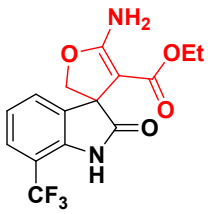


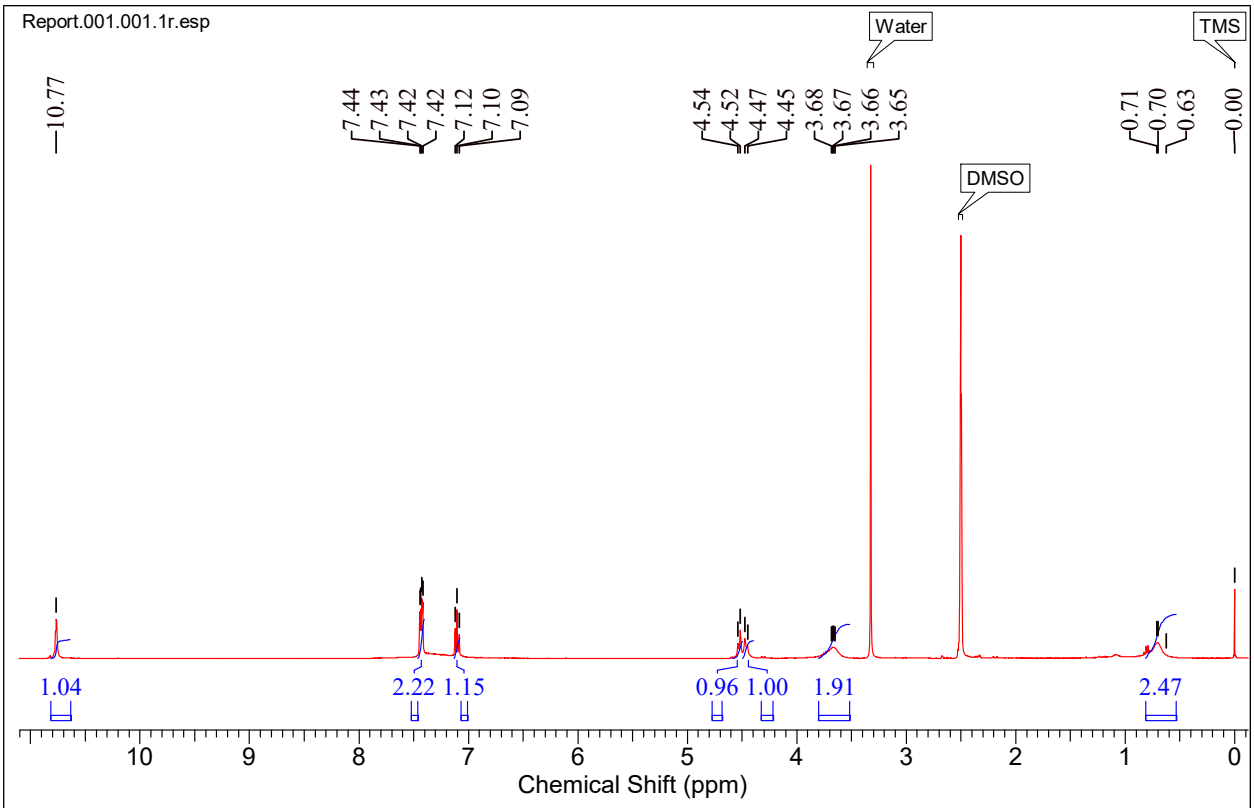
135 DEPT spectrum of compound 2ac



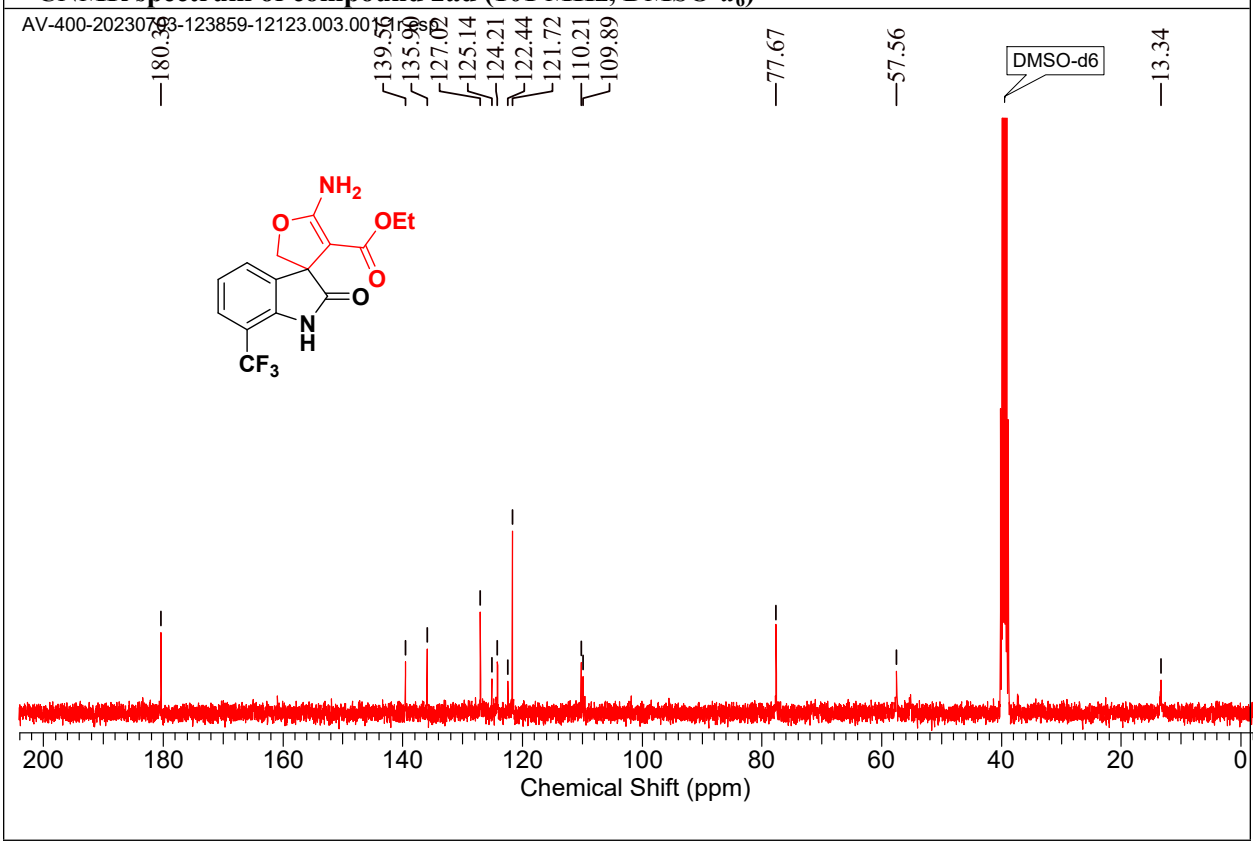
^{1}H NMR spectrum of compound 2ad (400 MHz, *DMSO-d_6*)



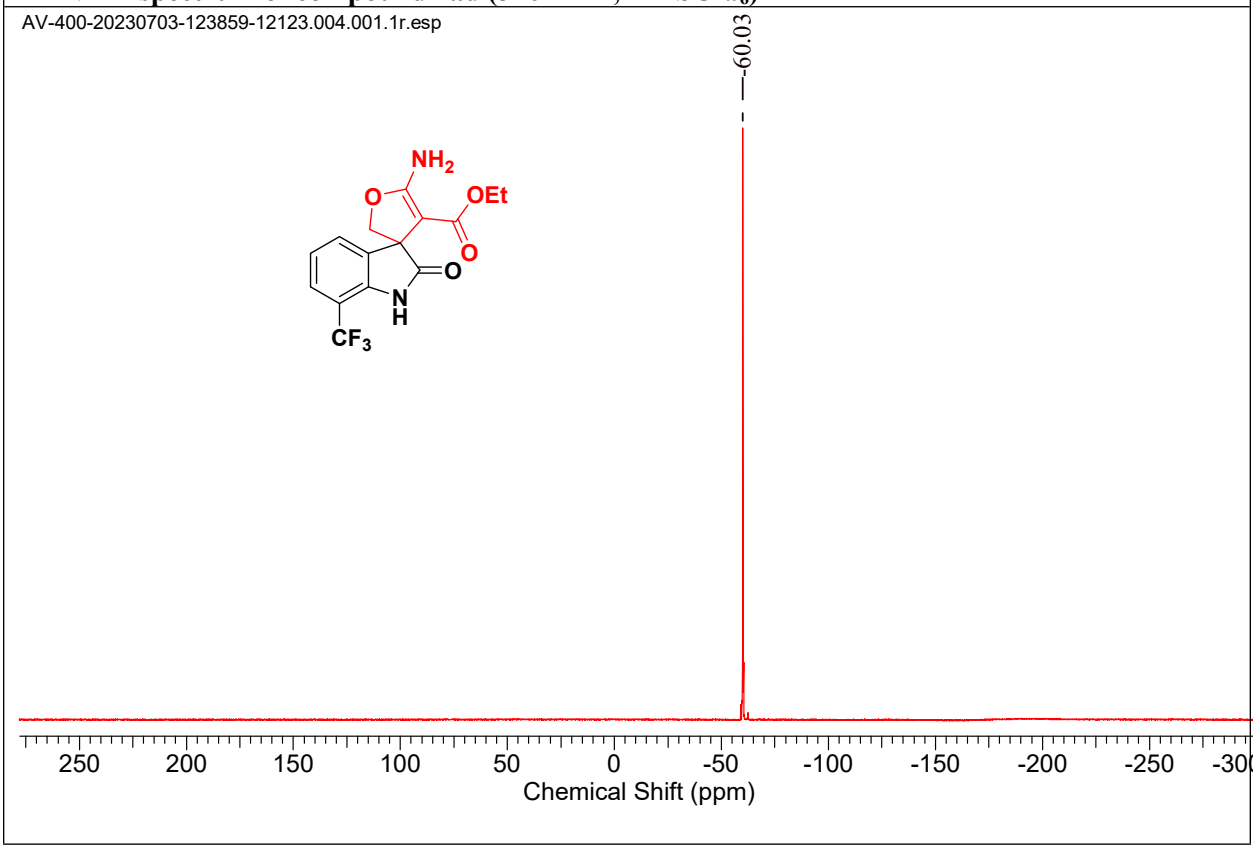




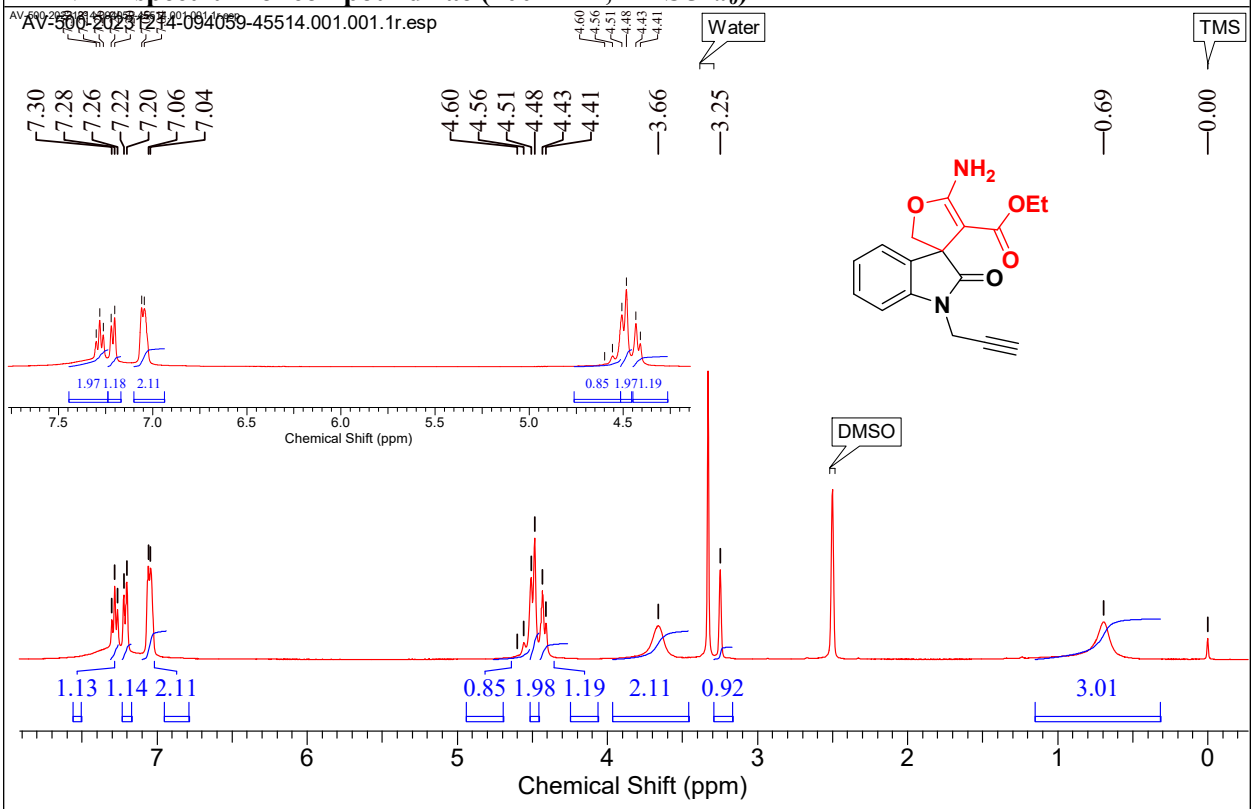
^{13}CNMR spectrum of compound 2ad (101 MHz, DMSO-d_6)



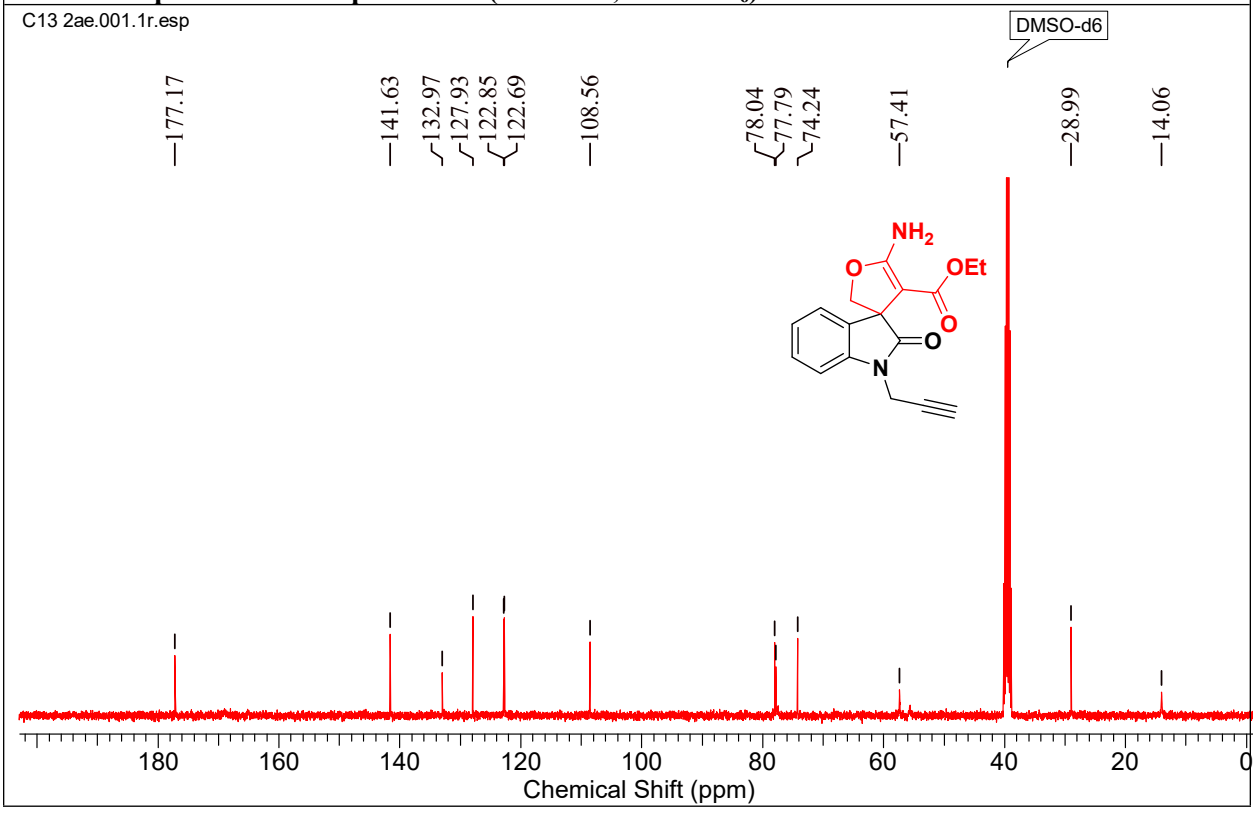
^{19}F NMR spectrum of compound 2ad (376 MHz, DMSO-d_6)



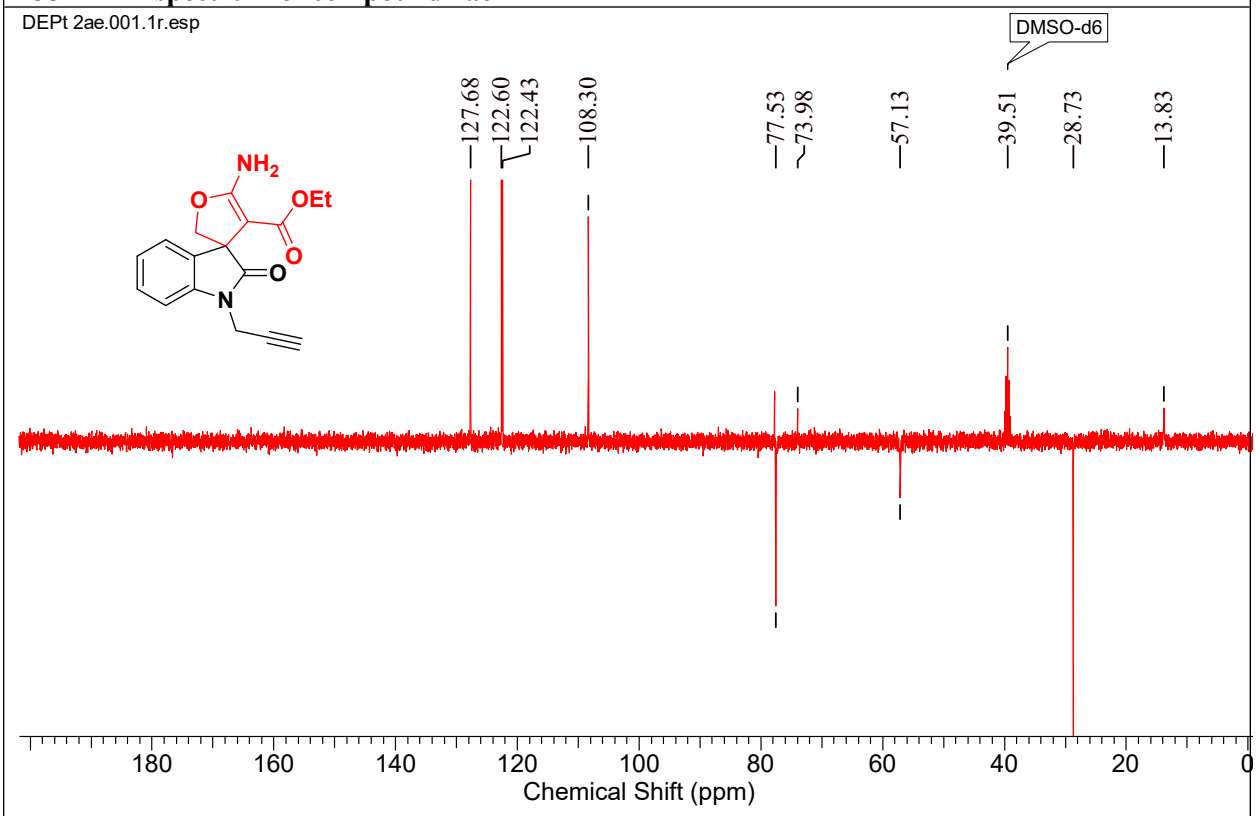
^{1}H NMR spectrum of compound 2ae (400 MHz, *DMSO-d_6*)



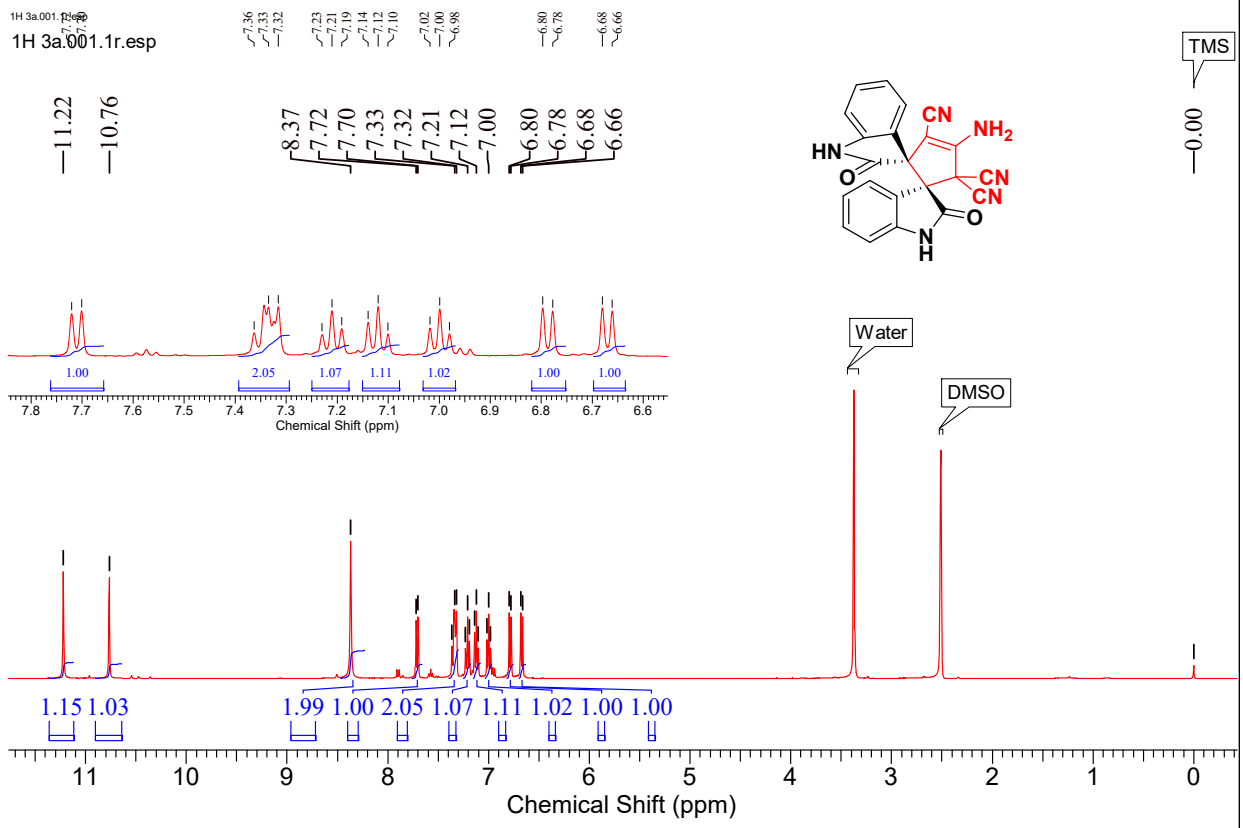
^{13}C NMR spectrum of compound 2ae (101 MHz, DMSO-*d_6*)



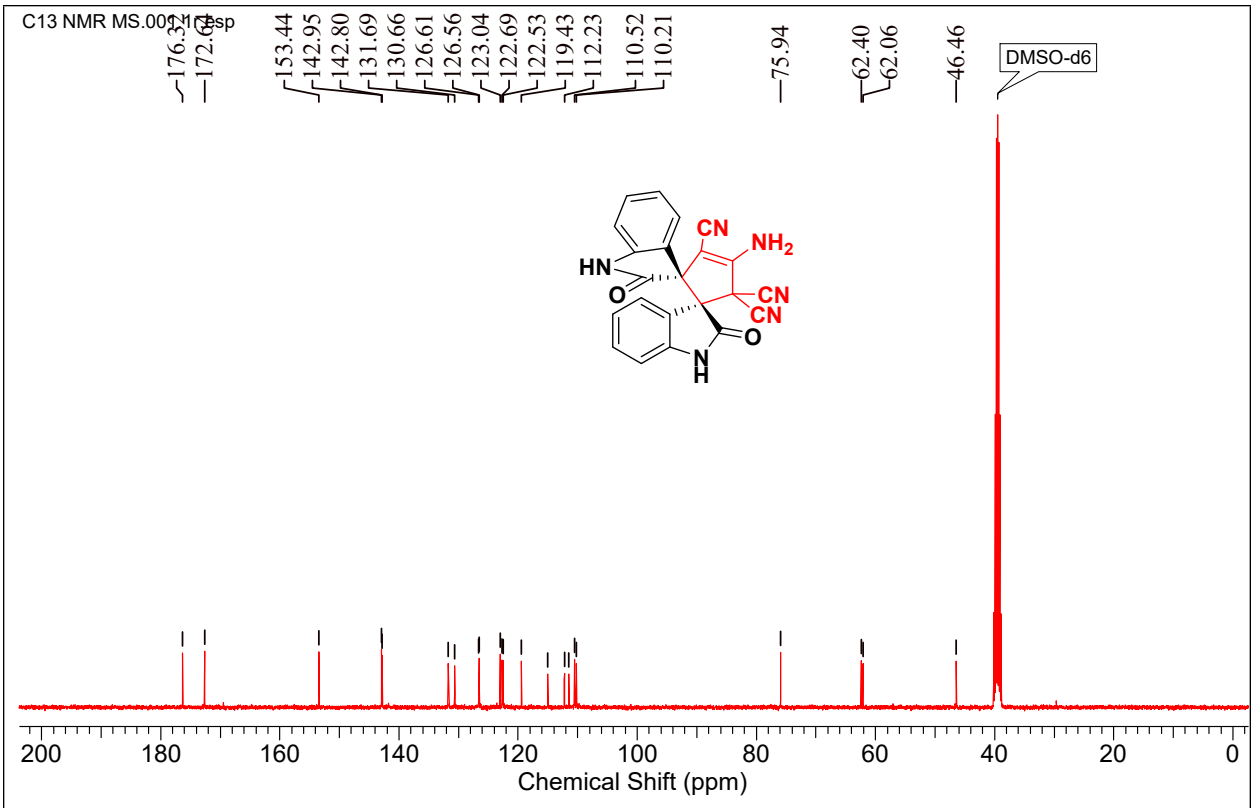
135 DEPT spectrum of compound 2ae



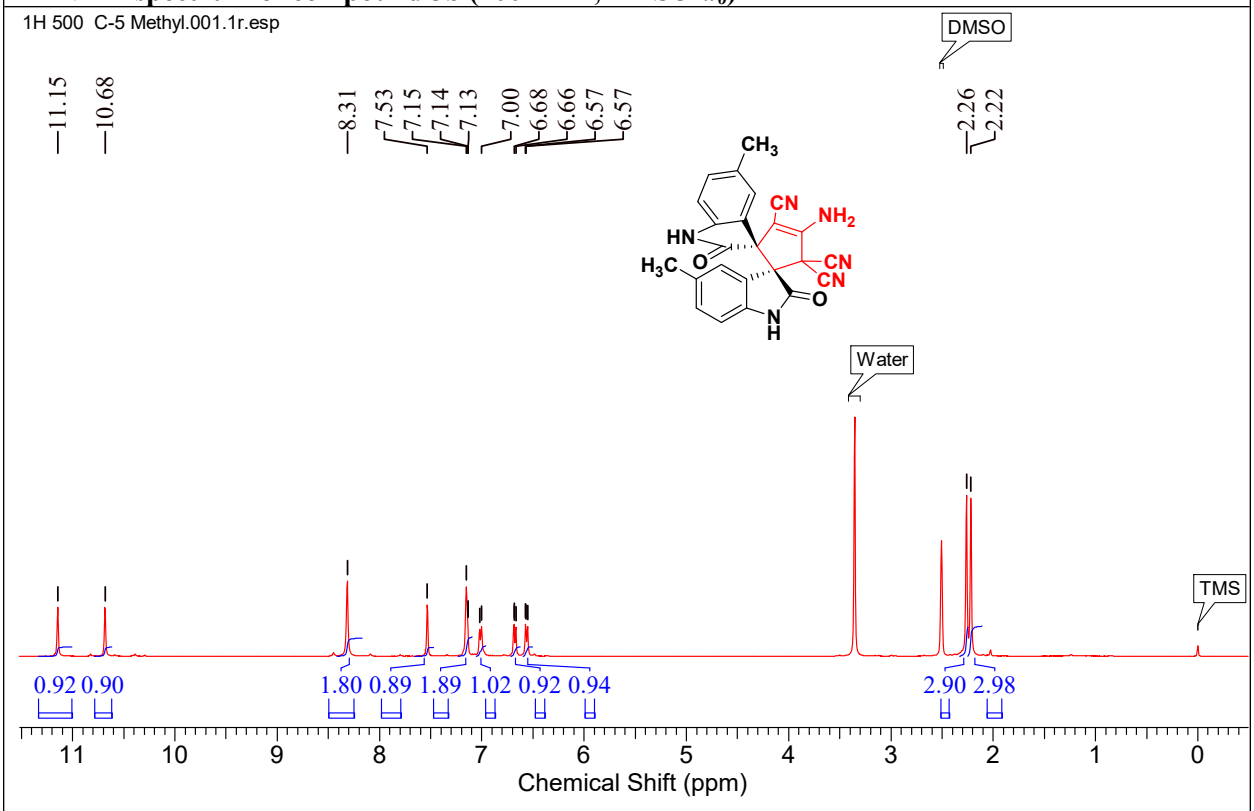
^{1}H NMR spectrum of compound 3a (400 MHz, *DMSO-d_6*)



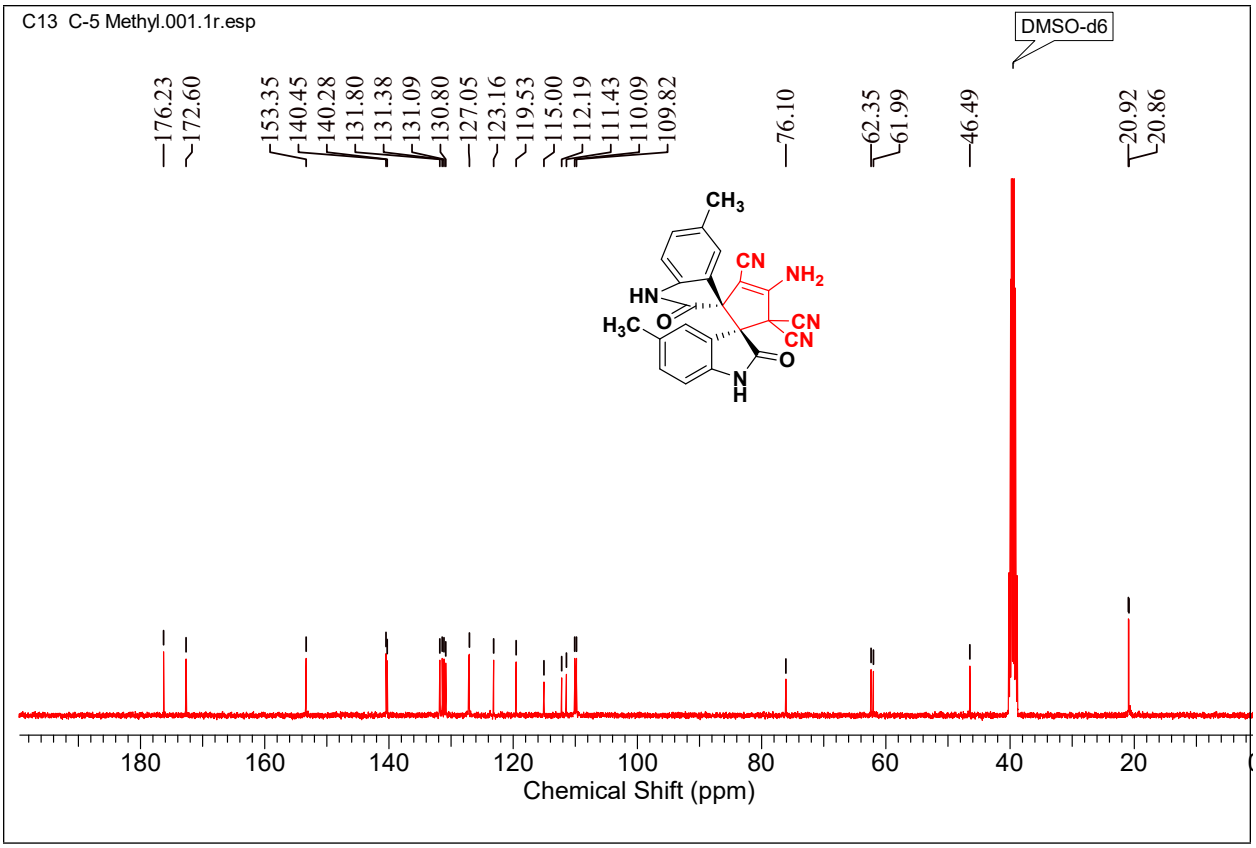
^{13}C NMR spectrum of compound 3a (101 MHz, *DMSO-d_6*)



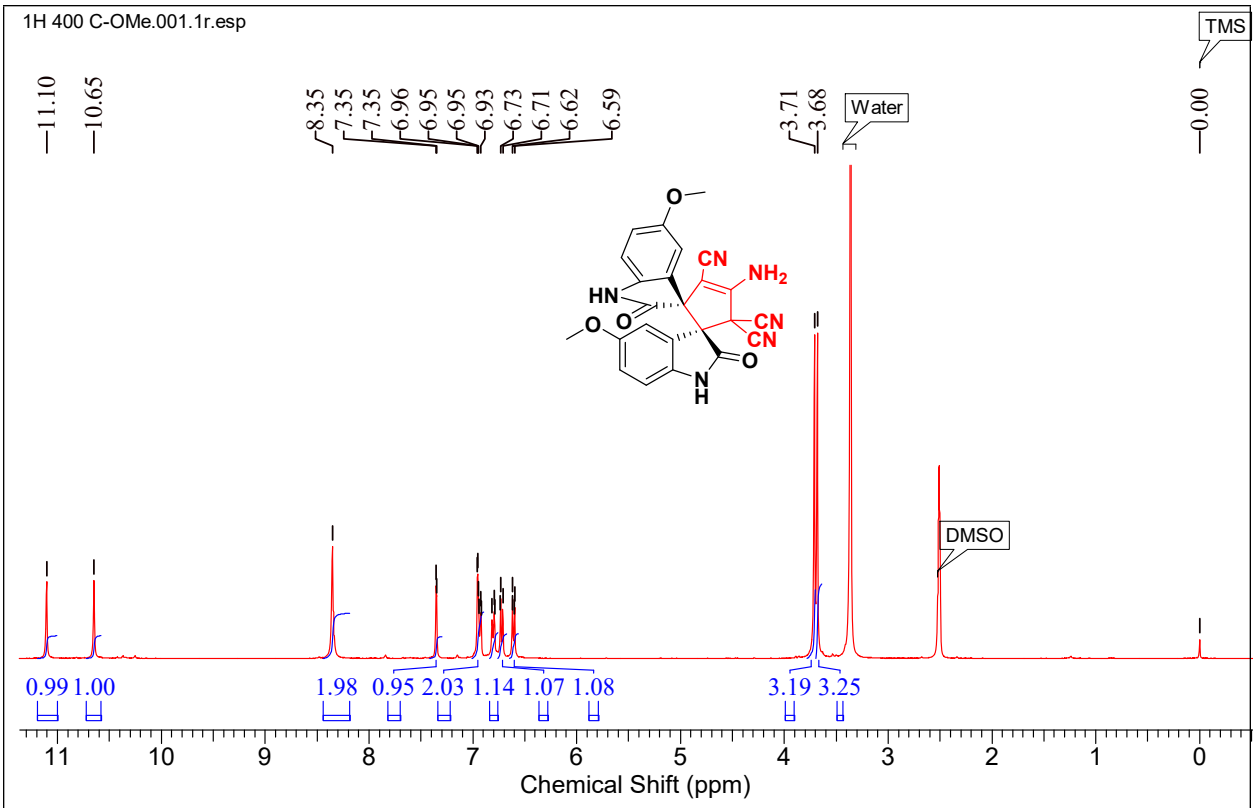
^{1}H NMR spectrum of compound 3b (400 MHz, *DMSO-d_6*)



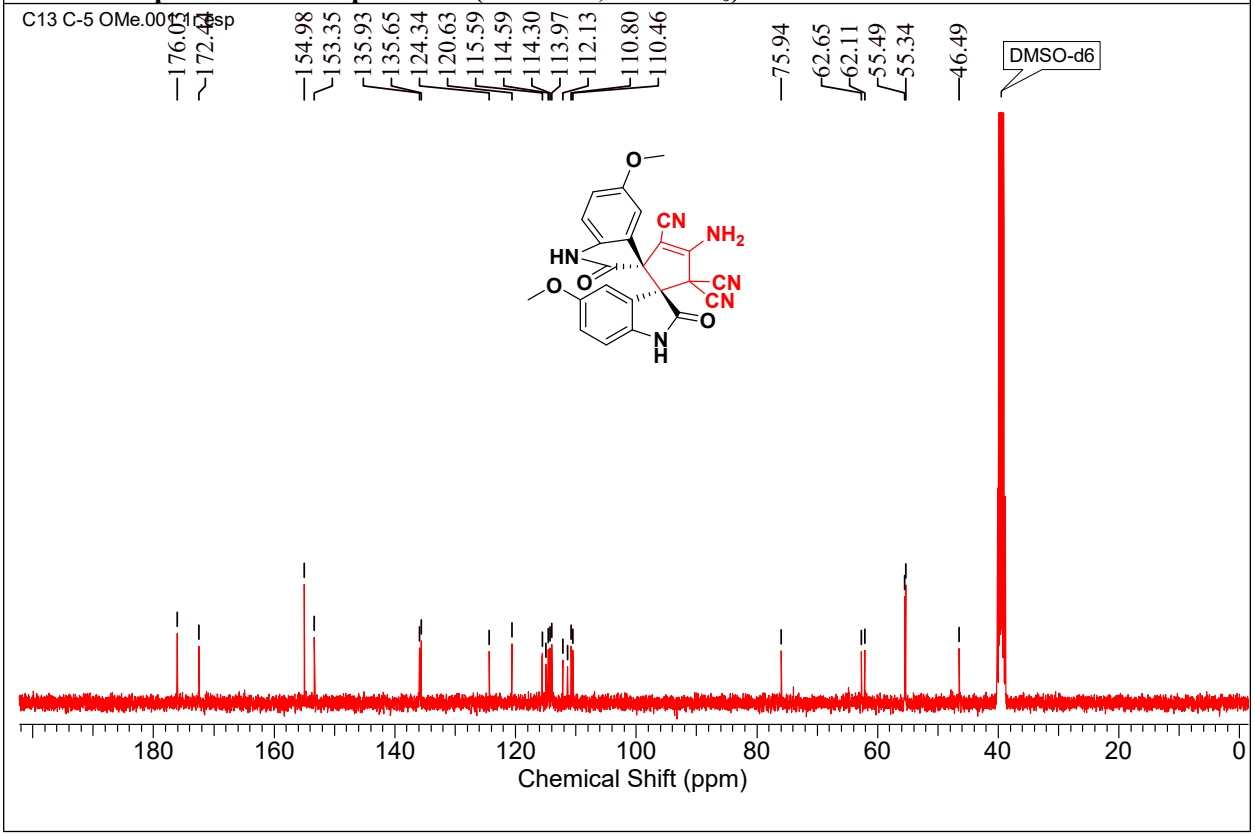
^{13}C NMR spectrum of compound 3b (101 MHz, *DMSO-d_6*)



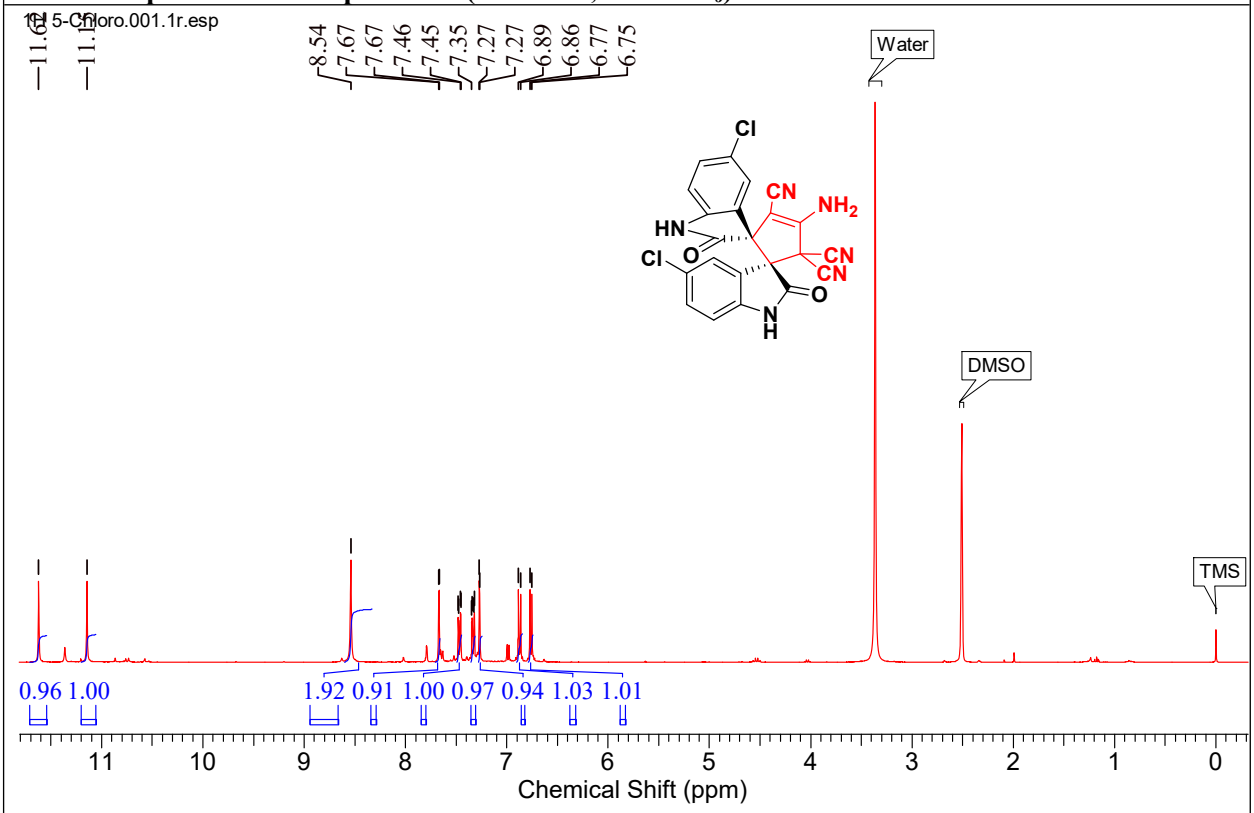
^{1}H NMR spectrum of compound 3c (400 MHz, *DMSO-d_6*)



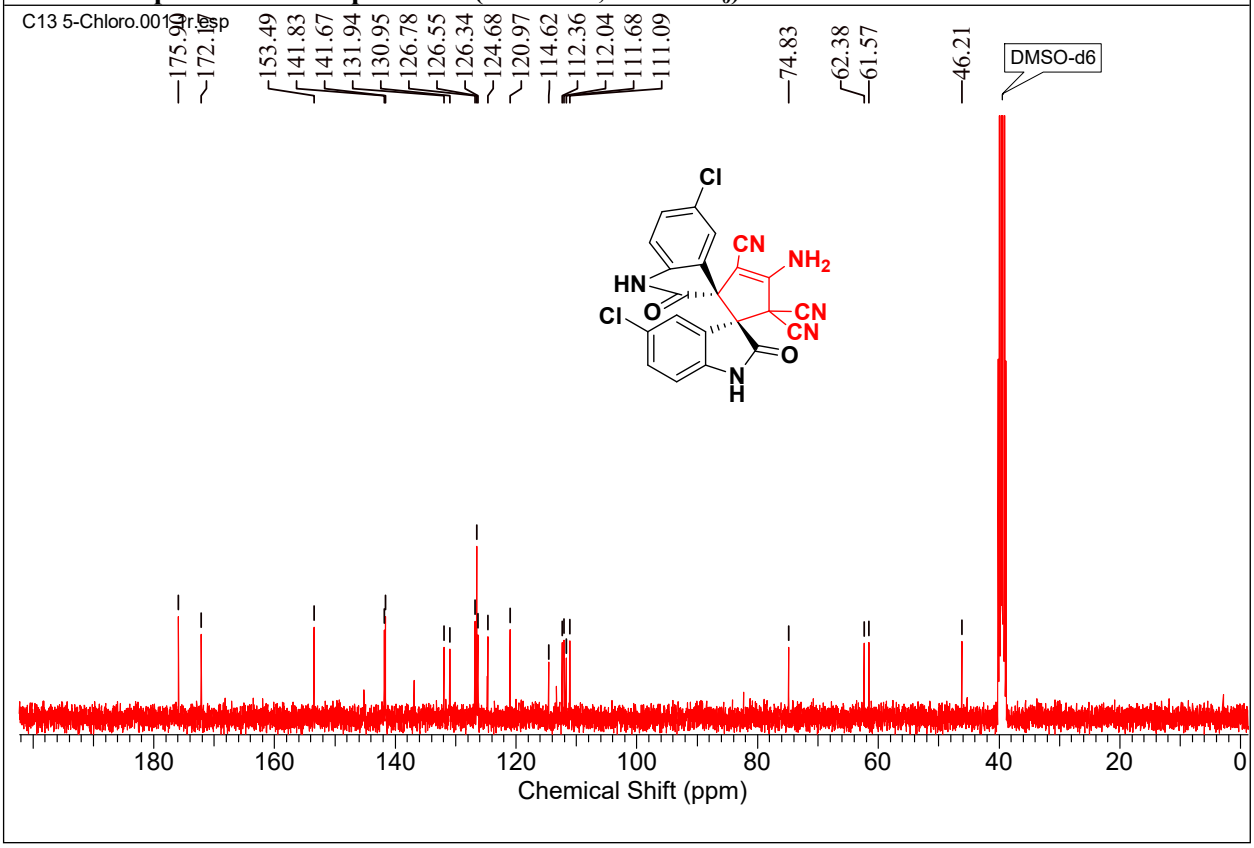
^{13}C NMR spectrum of compound 3c (101 MHz, *DMSO-d$_6$*)



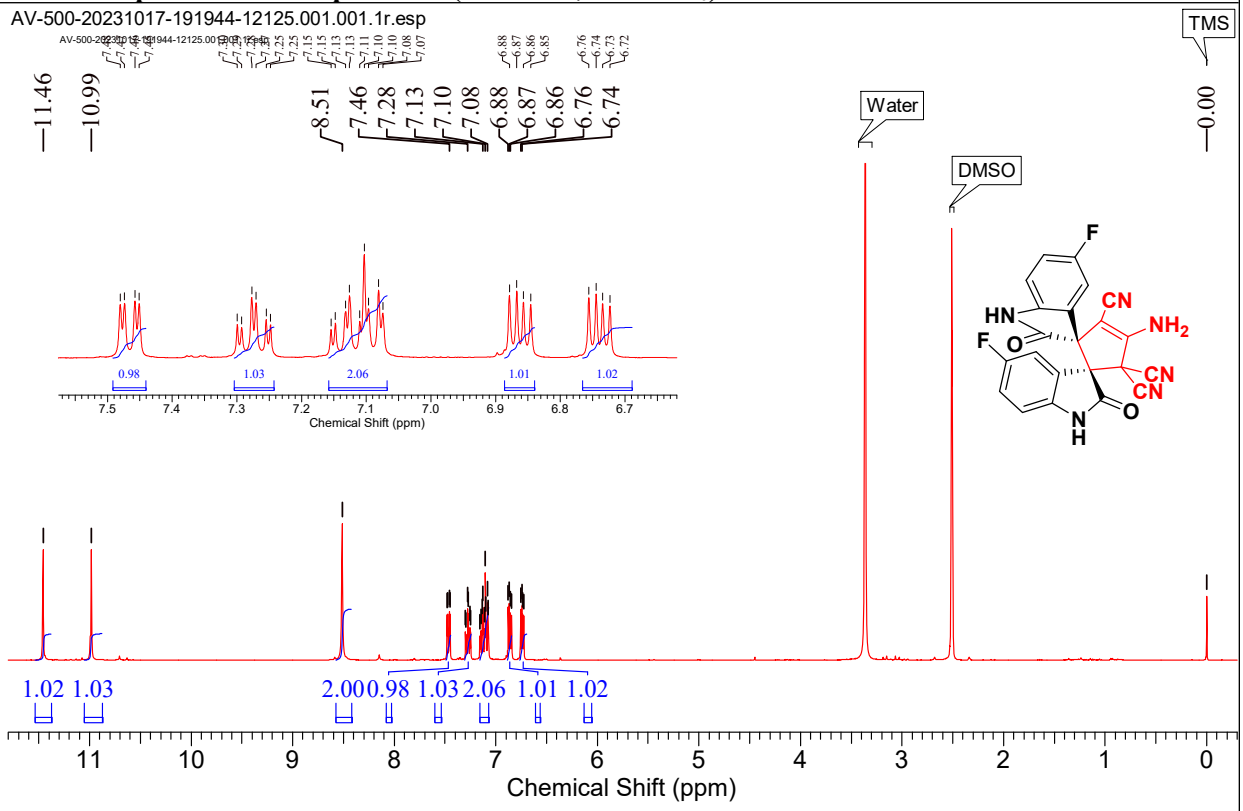
^{1}H NMR spectrum of compound 3e (400 MHz, *DMSO-d_6*)



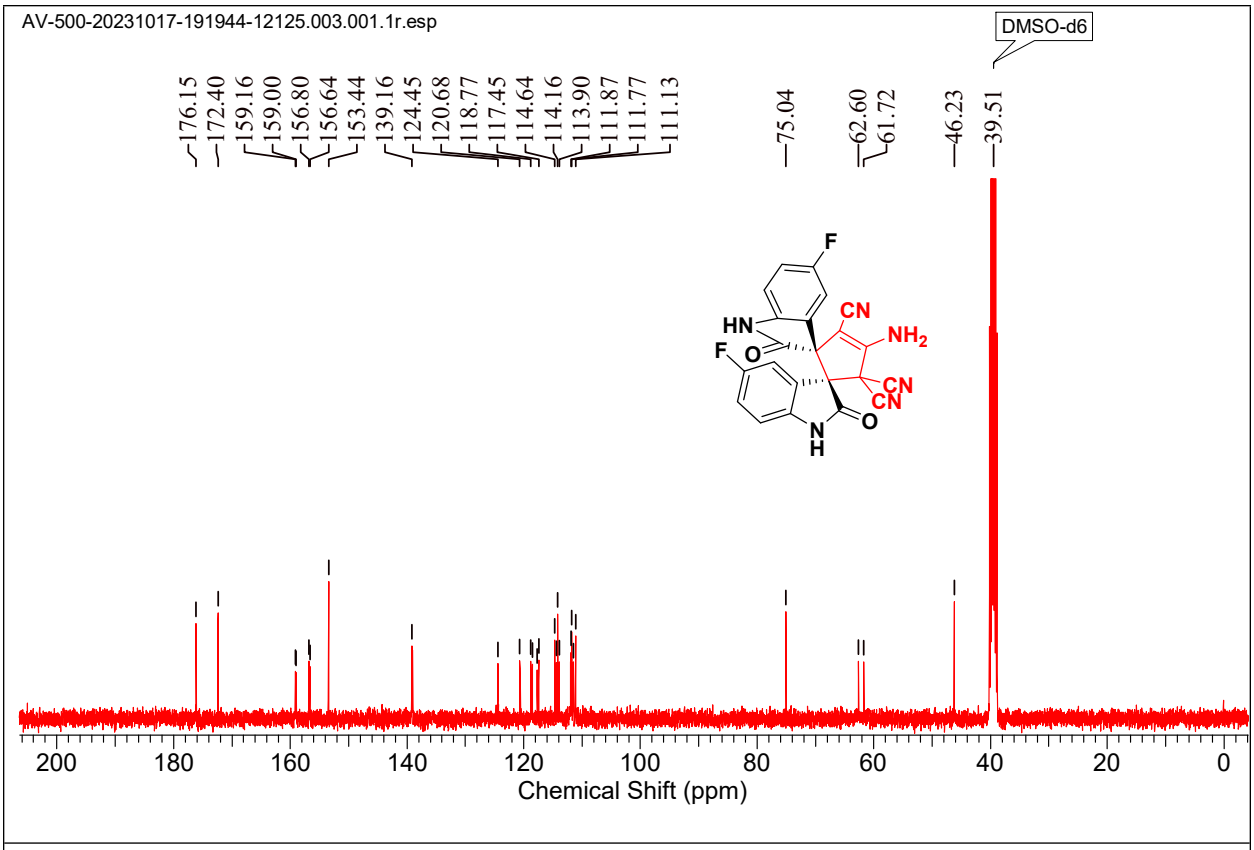
^{13}C NMR spectrum of compound 3e (101 MHz, *DMSO-d_6*)



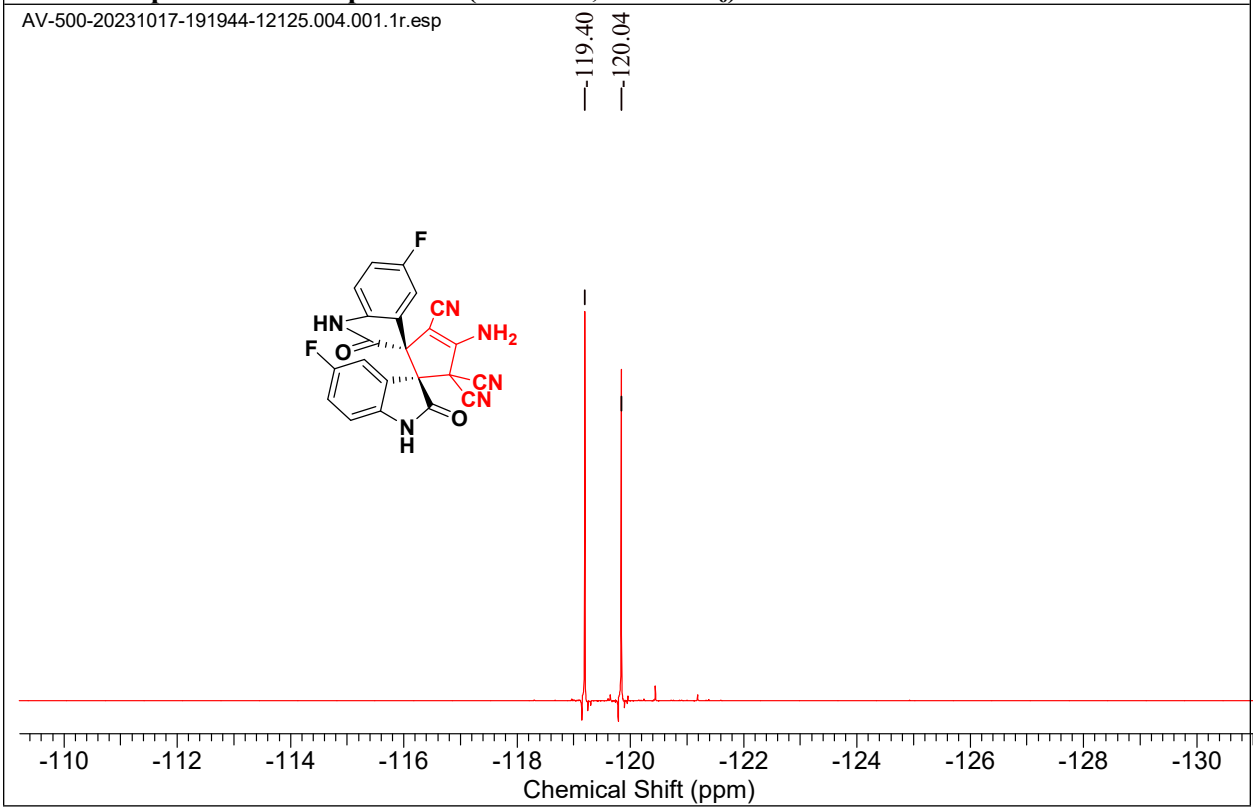
^{1}H NMR spectrum of compound 3f (400 MHz, *DMSO-d_6*)



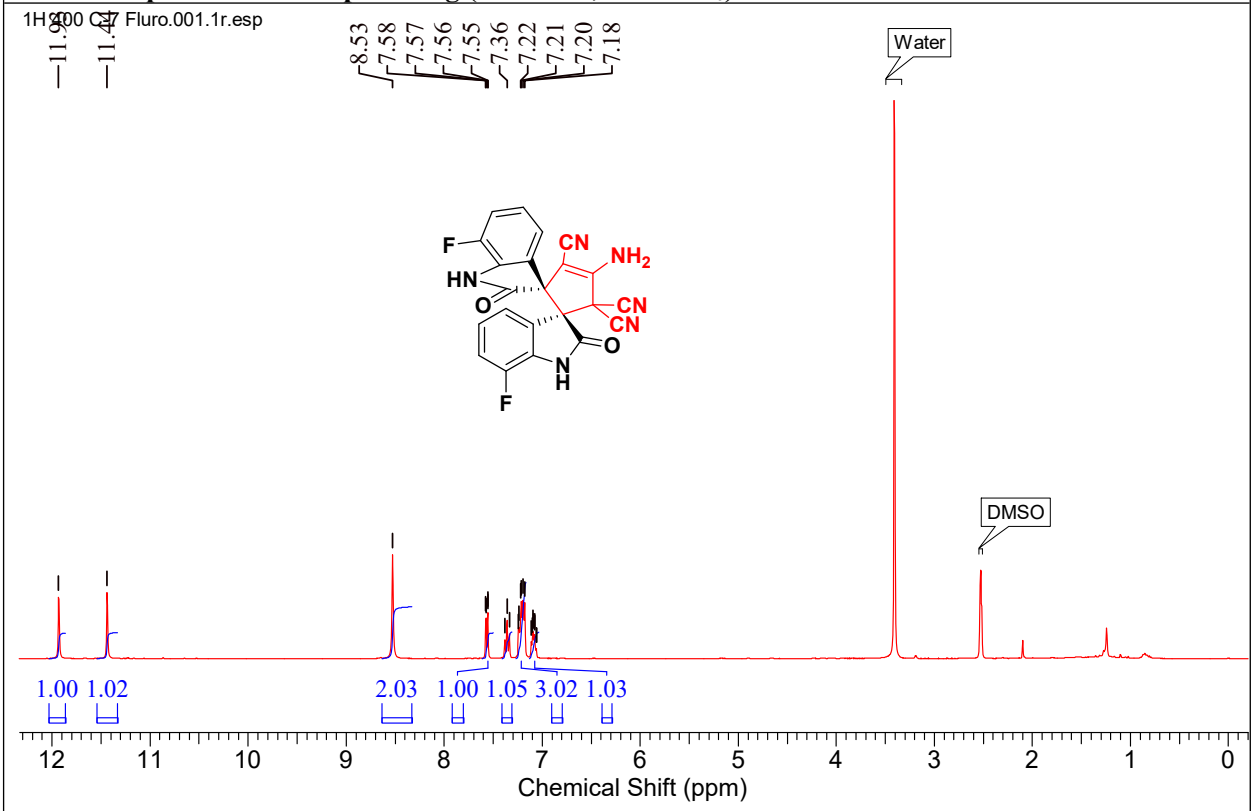
^{13}C NMR spectrum of compound 3f (101 MHz, *DMSO-d_6*)



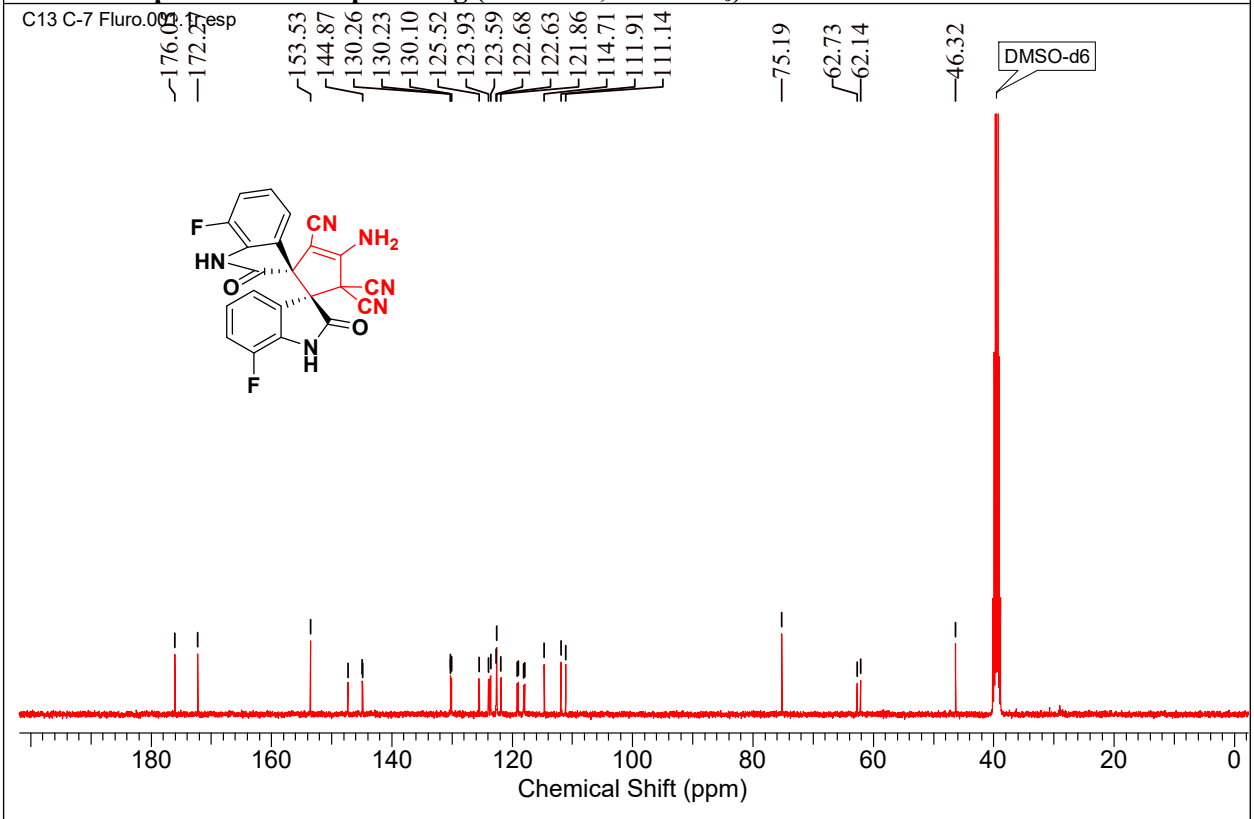
^{19}F NMR spectrum of compound 3f (376 MHz, DMSO-d_6)



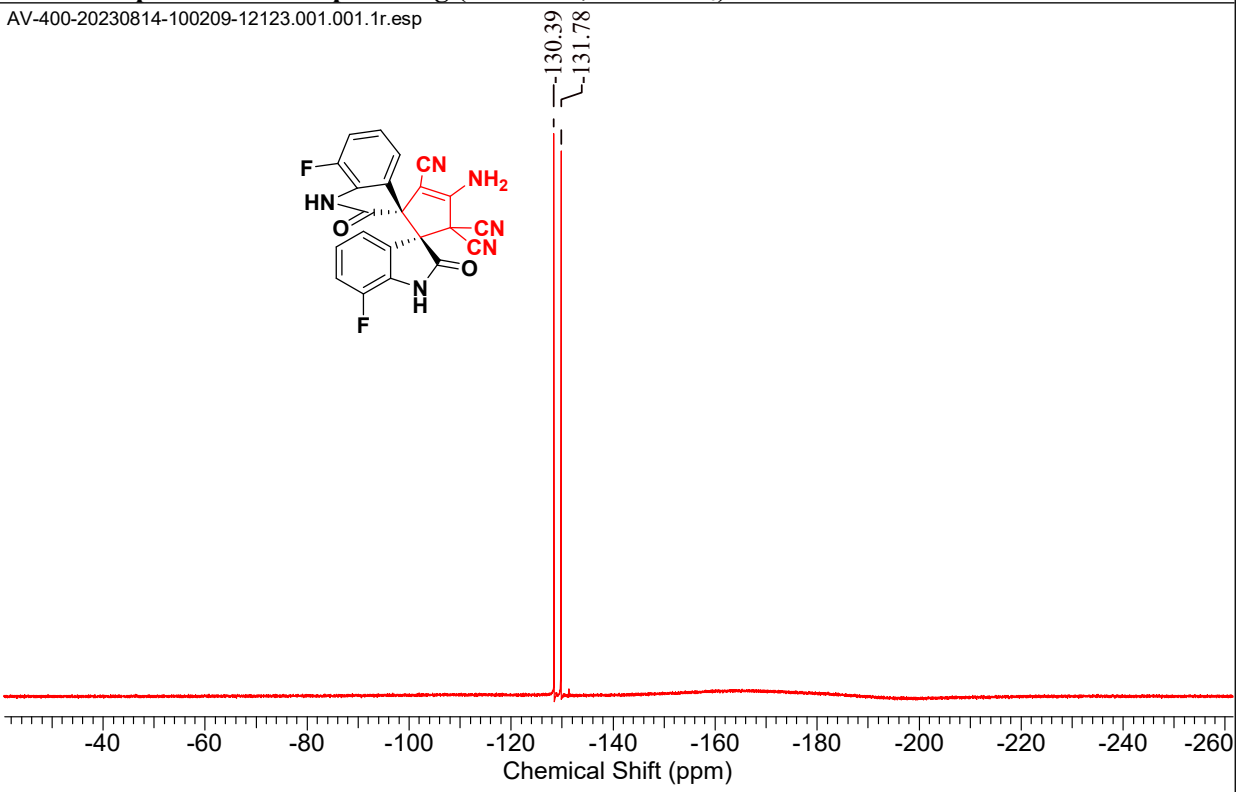
^{1}H NMR spectrum of compound 3g (400 MHz, *DMSO-d_6*)



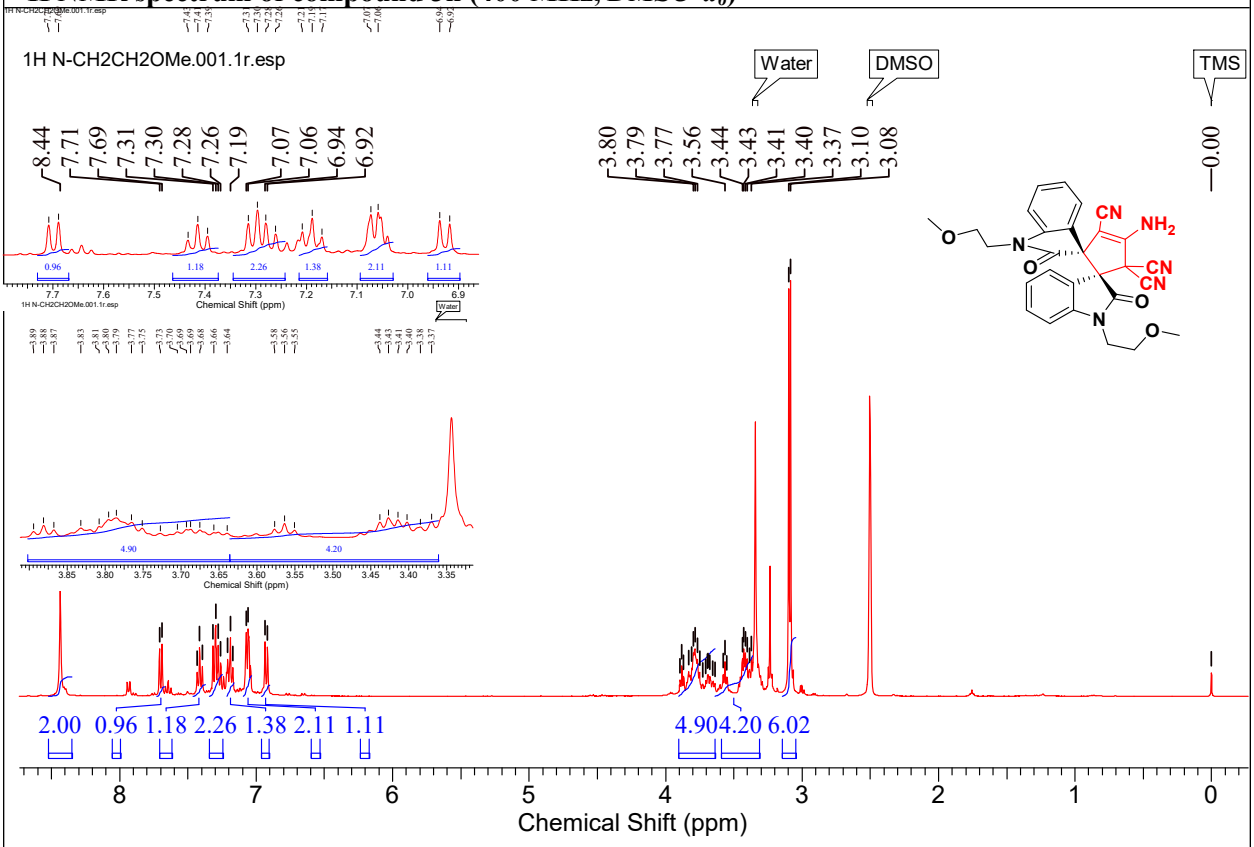
^{13}C NMR spectrum of compound 3g (101 MHz, *DMSO-d_6*)



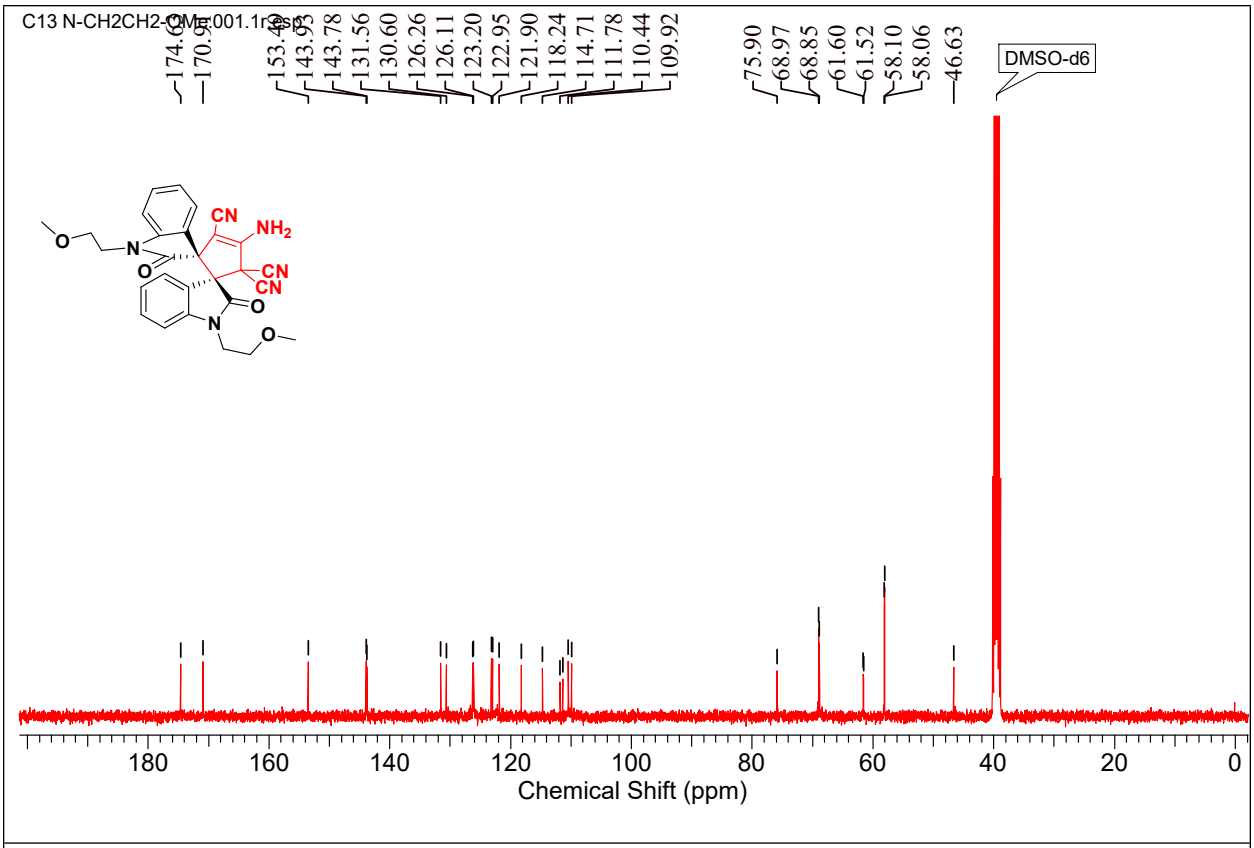
^{19}F NMR spectrum of compound 3g (376 MHz, DMSO-d_6)



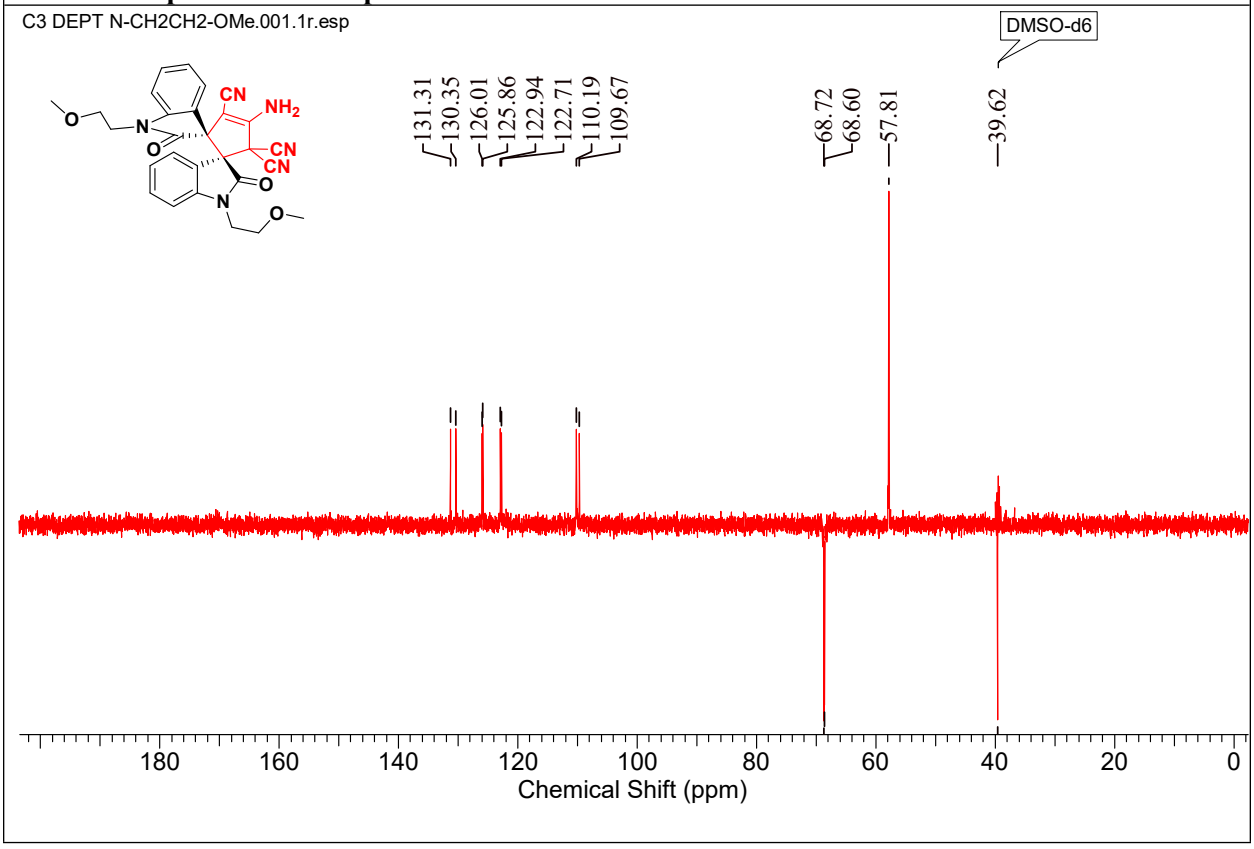
^{1}H NMR spectrum of compound 3h (400 MHz, *DMSO-d_6*)



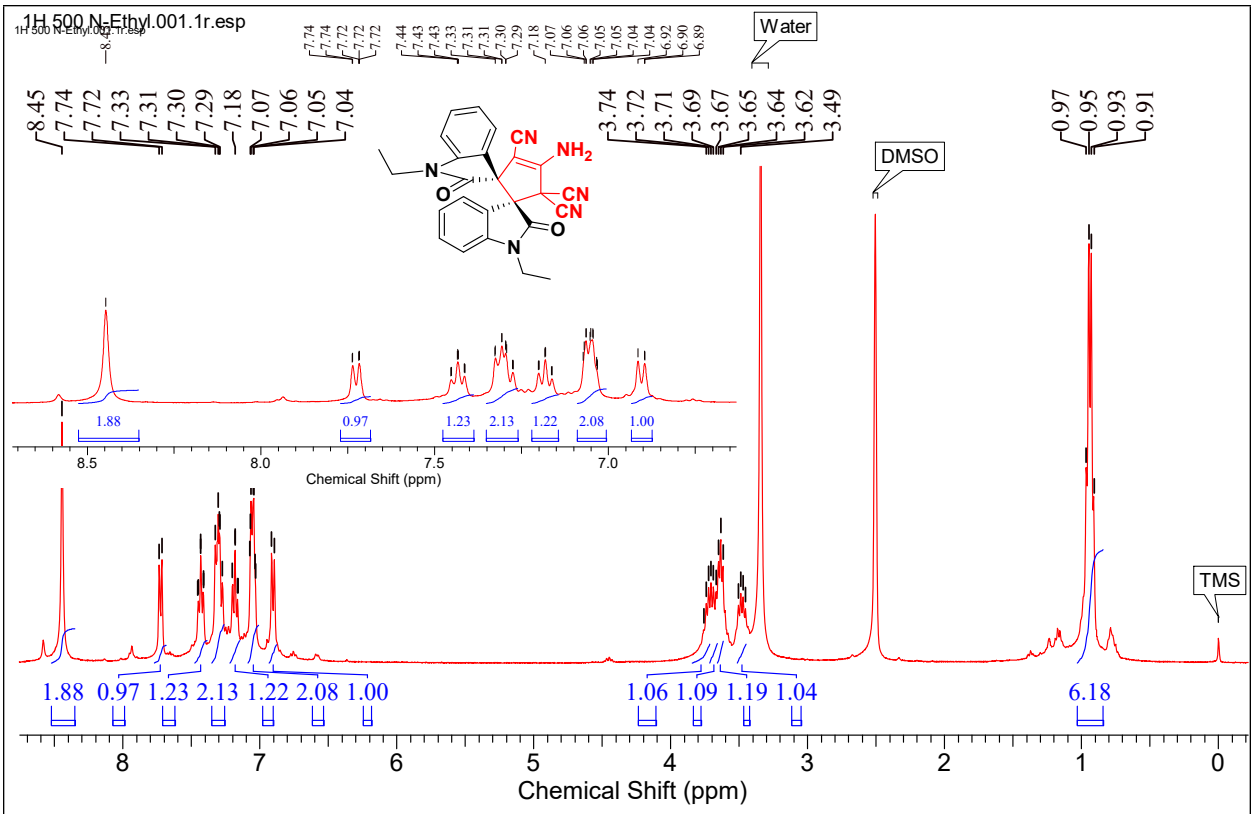
^{13}C NMR spectrum of compound 3h (101 MHz, *DMSO-d_6*)



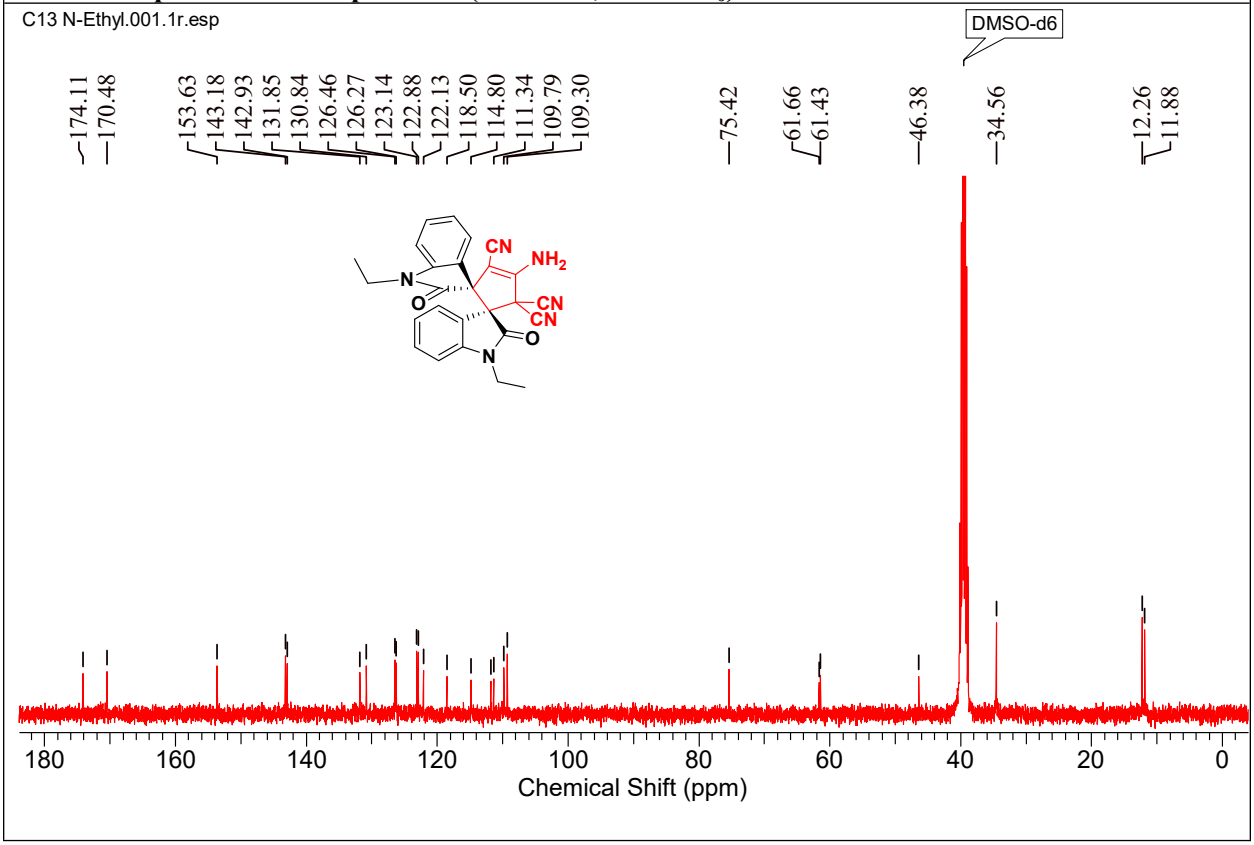
135 DEPT spectrum of compound 3h



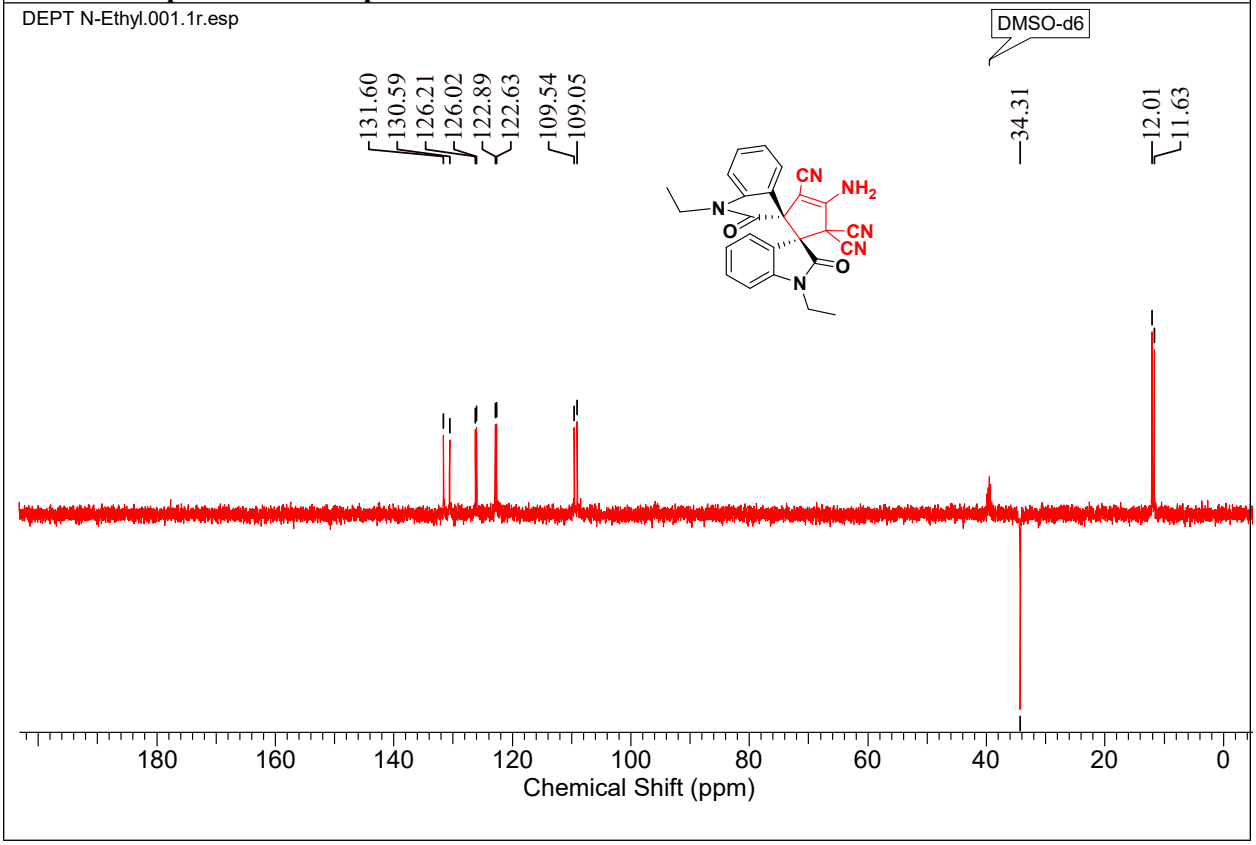
^{1}H NMR spectrum of compound 3i (400 MHz, *DMSO-d_6*)



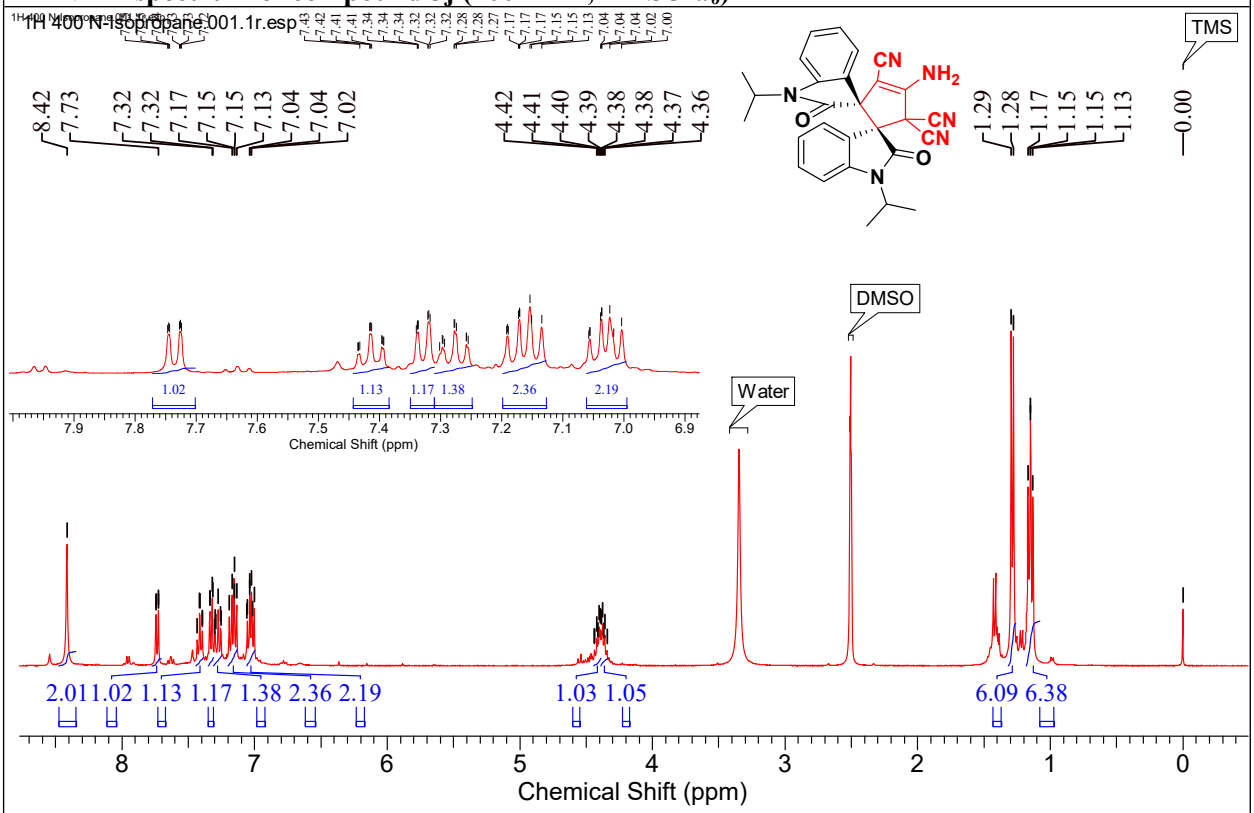
^{13}C NMR spectrum of compound 3i (101 MHz, *DMSO-d_6*)



135 DEPT spectrum of compound 3i

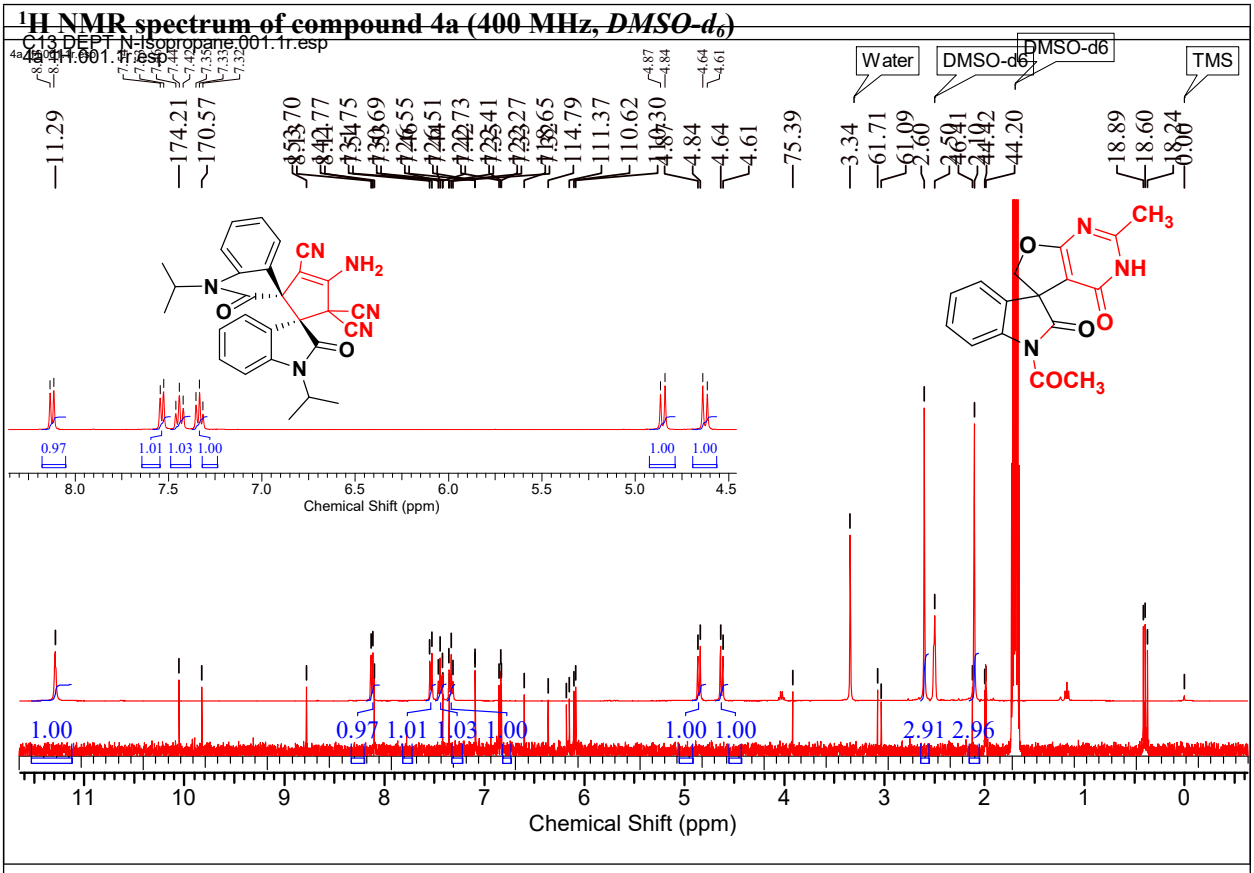


^{1}H NMR spectrum of compound 3j (400 MHz, *DMSO-d_6*)

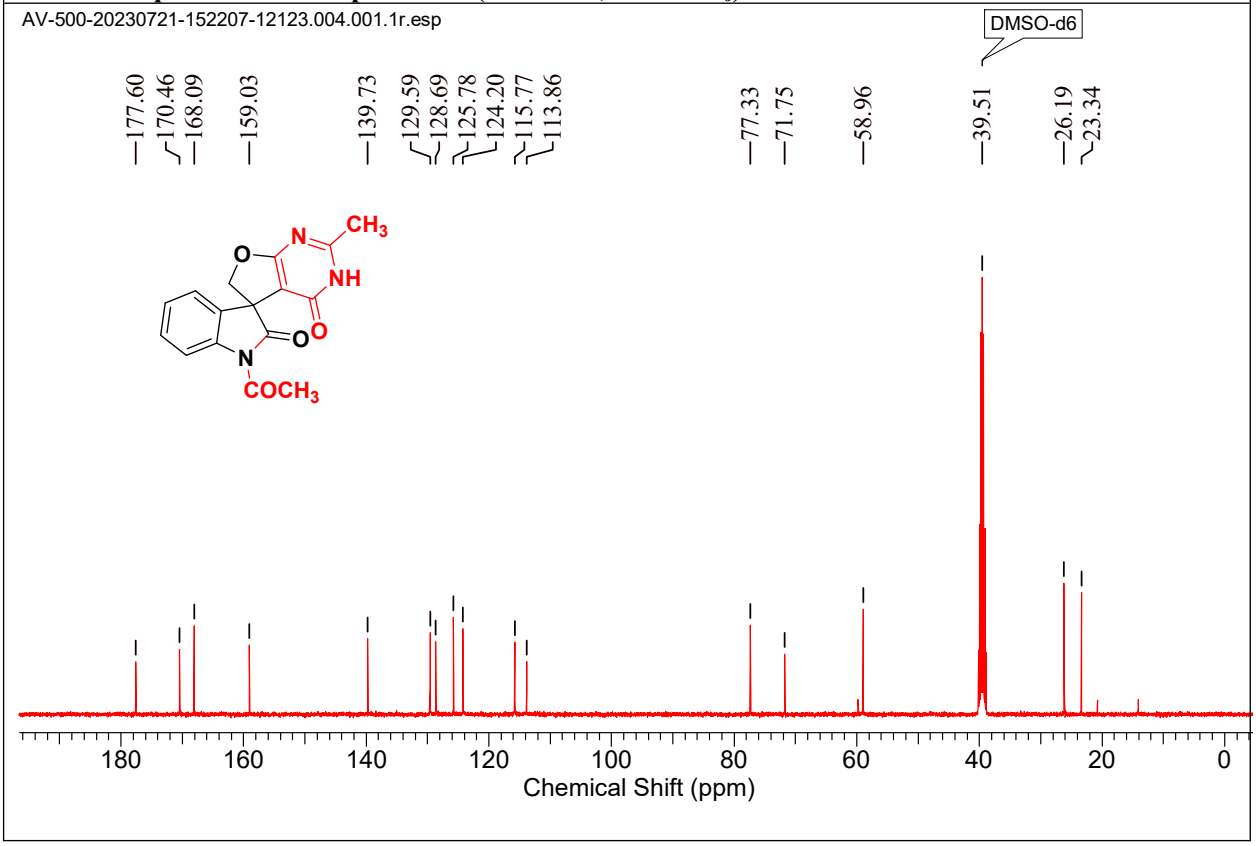


^{13}C NMR spectrum of compound 3j (101 MHz, *DMSO-d_6*)

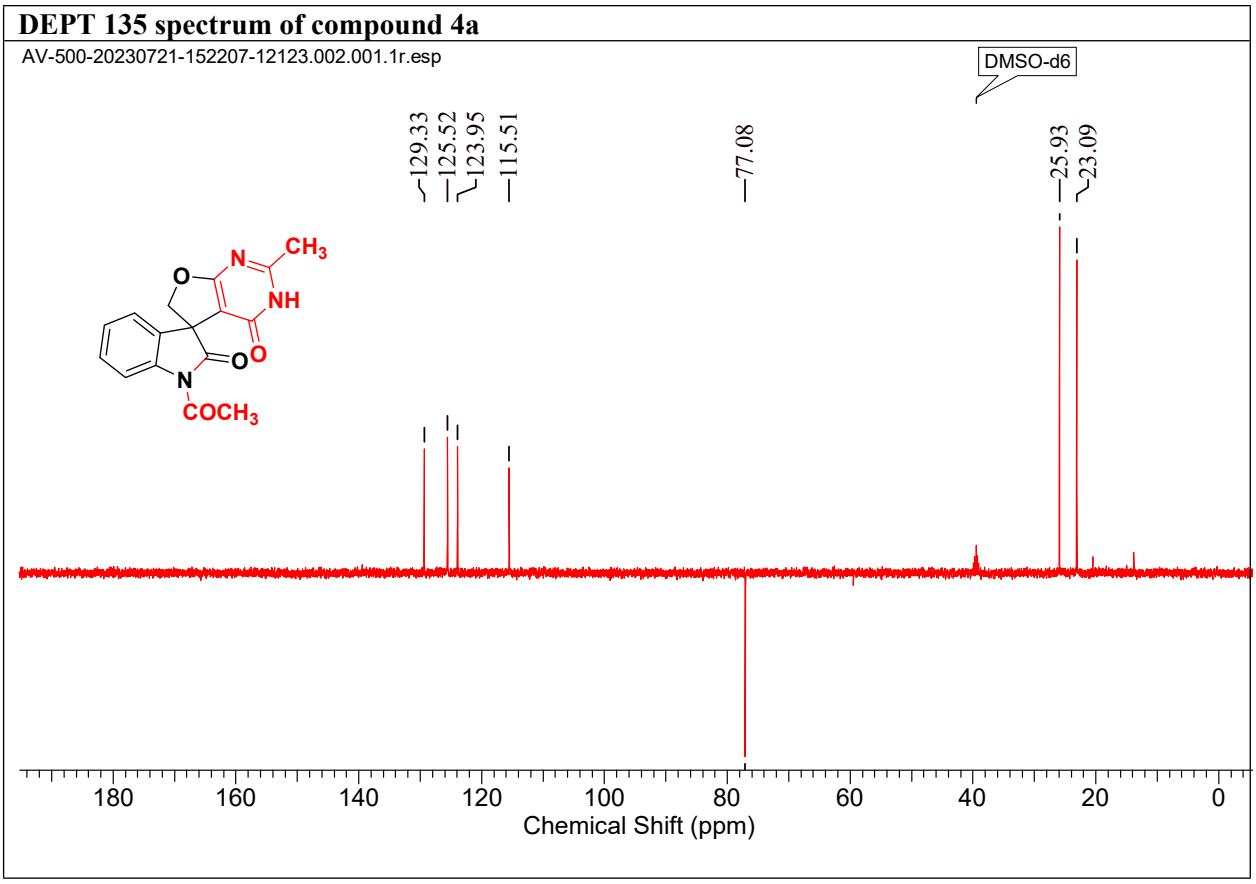
^{1}H NMR spectrum of compound 4a (400 MHz, *DMSO-d_6*)



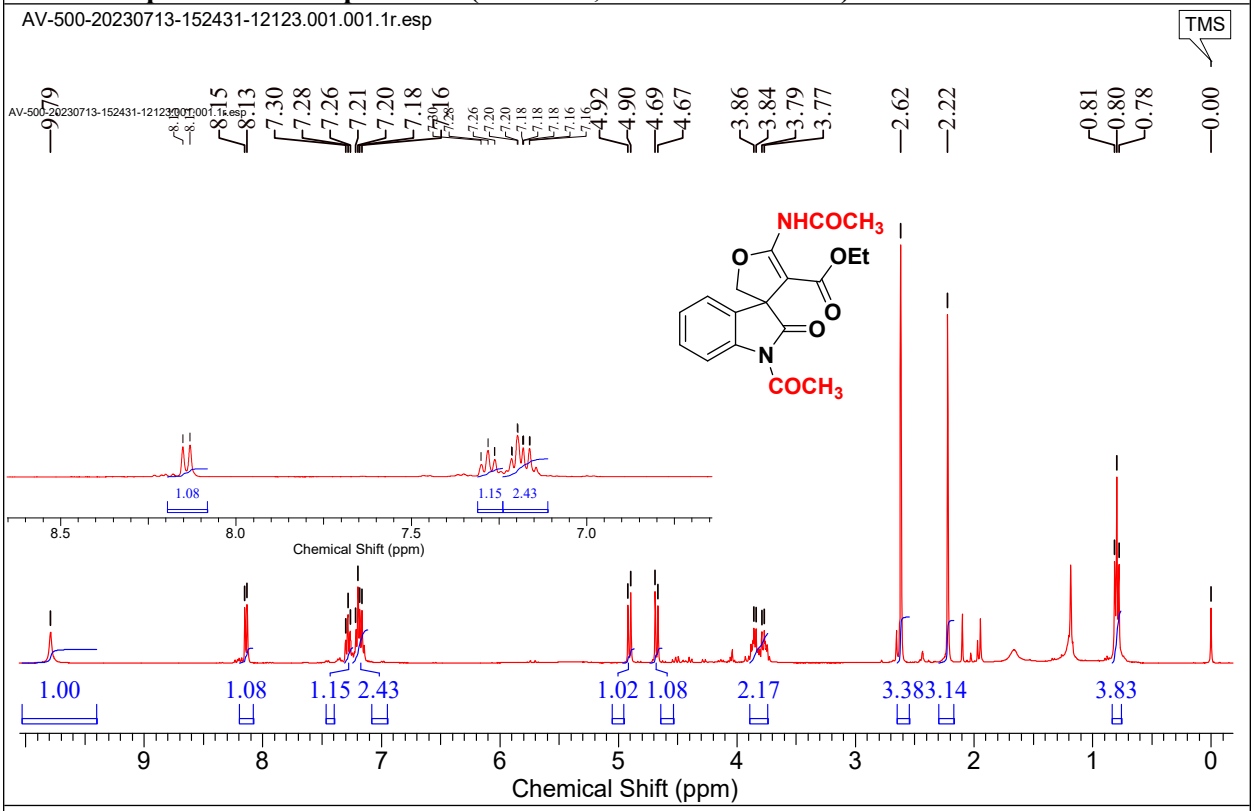
^{13}C NMR spectrum of compound 4a (101 MHz, *DMSO-d_6*)



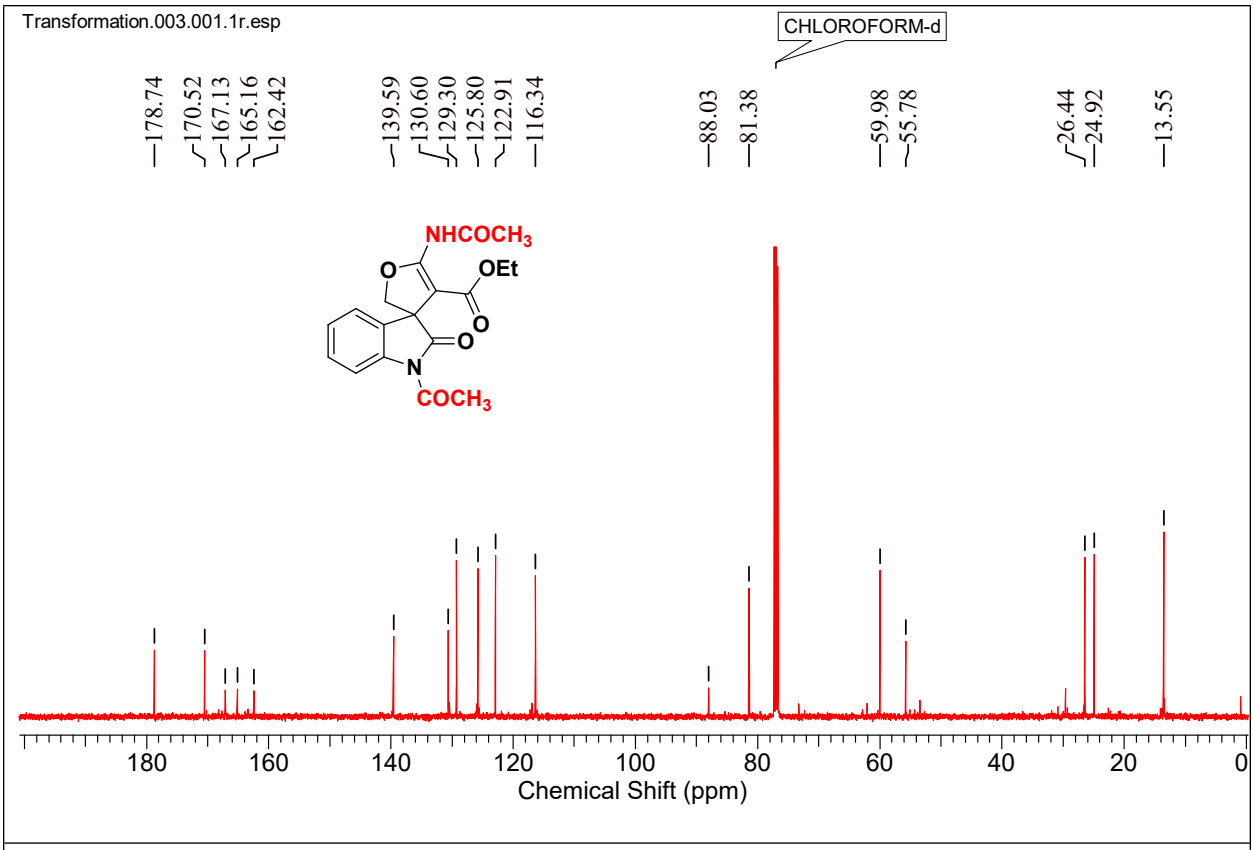
DEPT 135 spectrum of compound 4a



^{1}H NMR spectrum of compound 4b (400 MHz, *CHLOROFORM-d*)



^{13}C NMR spectrum of compound 4b (101 MHz, *CHLOROFORM-d*)



DEPT 135 spectrum of compound 4b