Conjugate addition/ cyclization of propanal with isatylidene malononitriles: An Efficient one-pot organocatalytic approach for the synthesis of 3'-methyl spiro[2H-pyran-3,4'-indoline]

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Supporting Information

Contents.

1.General information

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The one pot reactions were carried out with anhydrous solvents in reaction tube. All solvents were purchased anhydrous. The reactions were monitored by analytical thin layer chromatography (TLC) visualizing under UV light (254 nm) or I_2 staining. ^1H NMR spectra, ^{13}C NMR spectra and ^{19}F NMR spectra was acquired in appropriate deuterated solvents at room temperature on Bruker: Ultrashield AV 400 MHz, Ultrashield AV 500 MHz spectrometer. Chemical shifts (δ) are reported for ^1H NMR in ppm from TMS as internal standard solvent signals as secondary standards. ^{13}C NMR from the residual solvent peak. ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity designated as *s* (singlet), *d* (doublet), *t* (triplet), *dd* (doublet of doublet), *q* (quartet), *m* (multiplet), etc., coupling constant (Hz). Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ ppm). HRMS data was recorded on a Thermo scientific Q-Exactive, Accela 1250 pump. Single crystal x-ray diffraction measurements were carried out on Bruker D8 venture dual micro focus source diffractometer.

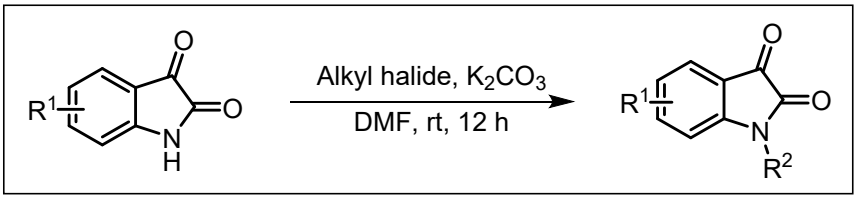
2. SINGLE CRYSTAL X-RAY DIFFRACTION STUDIES

The good quality single crystals of each compound suitable for single-crystal X-ray diffraction analysis were selected using Leica polarizing microscope (S8APO). The X-ray intensity data for all compounds were measured on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics with X-ray generator power setting at 50 kV and 1.4 mA. The intensity measurements were carried out with both Cu and Mo micro-focus sealed tube diffraction source (CuKα = 1.54178 Å; Mo K α= 0.71073 Å) at 100(2) K temperature. A preliminary set of cell constants and an orientation matrix were calculated from 36 and 40 frames for Mo and Cu radiations, respectively. The complete intensity data were collected using an optimized strategy that consisted of different sets of ω, φ and 2θ with 0.5° width keeping the sample-to-detector distance fixed at 5.00 cm with varying exposure time (10-20 sec) depending on the diffraction power of the crystals. The whole process of X-ray data acquisition (unit–cell measurements and data collection) was controlled and monitored by the APEX3 program suite of Bruker-AXS (Bruker, 2016).[1] The complete data sets were corrected for Lorentz-polarization and absorption effects (multi-scan method) using SAINT and SADABS programs with the transmission coefficients. Using the APEX3 (Bruker, 2016) program suite,[1] the structure was solved using direct methods with the ShelXS-97 (Sheldrick, 2008) structure solution program.[2] The model was refined with ShelXL-2013 (Sheldrick, 2015) using Least Squares minimization based on F^2.[3] All non-hydrogen atoms were refined anisotropically. Conversely, hydrogen atoms were refined isotropically by placing them in a geometrically idealized position (C-H = 0.95 Å for sp2 hybridized C-atoms including H atoms in phenyl and ethyne groups, C-H = 0.98 Å for the methyl H-atoms) and constrained to ride on their parent atoms [Uiso(H) = 1.2 Ueq(C) or 1.5 Ueq(methyl C)]. ORTEPs for all the compounds were plotted at the 50% probability displacement ellipsoids, and H atoms are shown as small spheres of arbitrary radii.[4] The molecular packing diagrams were generated using the Mercury program.[5] Geometrical calculations were performed using SHELXTL (Bruker, 2016)[1] and PLATON.[6] Experiment details of the single crystal X-ray diffraction analysis, including crystal data, data collection and structure refinement for all the compounds, are summarized in Table 1.

Table 1. Crystallographic data for compounds 4Ao and 4Bb.

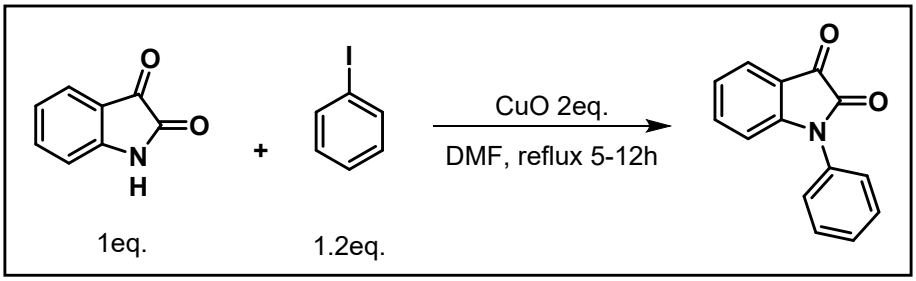
Identification code	4Ao	4Bb
Empirical formula	$C_{18}H_{18}F_3N_3O_3$	$C_{16}H_{17}N_3O_2$
Formula weight	381.35	283.32
Temperature/K	150(2)	150.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	14.564(5)	9.3030(13)
b/Å	11.352(4)	8.9537(13)
c/Å	11.354(4)	17.411(2)
α/°	90	90
β/°	96.202(9)	97.146(4)
γ/°	90	90
Volume/Å^3	1866.3(11)	1439.0(3)
Z	4	4
ρ_{calc}g/cm^3	1.357	1.308
μ/mm^{-1}	0.113	0.089
F(000)	792	600.0
Crystal size/mm^3	0.262 × 0.211 × 0.185	0.312 × 0.268 × 0.215
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.812 to 50.332	4.412 to 50.06
Index ranges	-17 ≤ h ≤ 17, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13	-11 ≤ h ≤ 11, -10 ≤ k ≤ 10, -19 ≤ l ≤ 20
Reflections collected	24235	21631
Independent reflections	3327 [R_{int} = 0.0634, R_{sigma} = 0.0416]	2546 [Rint = 0.1079, Rsigma = 0.0608]
Data/restraints/parameters	3327/13/265	2546/0/200
Goodness-of-fit on F^2	1.025	1.106
Final R indexes [I>=2σ (I)]	R_1 = 0.0518, wR_2 = 0.1195	R1 = 0.0626, wR2 = 0.1188
Final R indexes [all data]	R_1 = 0.0767, wR_2 = 0.1361	R1 = 0.1001, wR2 = 0.1334
Largest diff. peak/hole / e Å^{-3}	0.70/-0.52	0.28/-0.27
CCDC number	**2430995**	**2434923**

3.(a). General Procedure for the preparation of N- alkyl substituted isatine[7] : N-Substituted isatin derivatives were synthesized from commercially available isatins and alkyl or aryl halides in the presence of potassium carbonate as base in DMF solution. Alkyl halides (12 mmol, 1.2 equiv) was added to a stirred solution of isatin (10 mmol, 1.0 equiv) and K_2CO_3 (12 mmol, 1.2 equiv) in DMF and stirred for 12 h at room temperature. Reactions were monitored by TLC until completion. The reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The crude residue was then purified by column chromatography on silica gel with ethyl acetate-pet ether (10/90 to 20/80) to provide N-protected isatin derivatives.

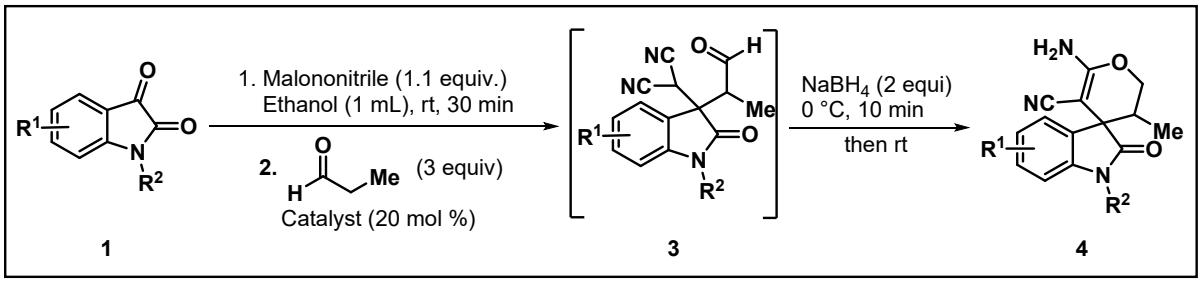


(b). General Procedure for the preparation of N-Aryl substituted isatin[8] :

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 organic and aqueous layers were separated. The organic layer dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum and resulting crude product, which was purified by
column chromatography to afford pure product.

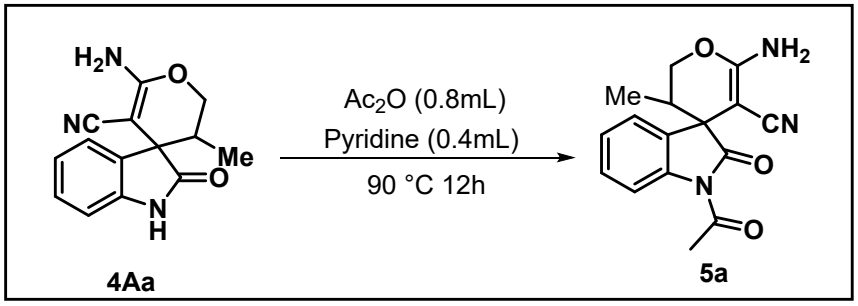


4. General Procedure for the One Pot Synthesis of 3'-alkyl spiro[2H-pyran-3,4′-indoline] : A mixture of isatin derivative (0.5 mmol, 1 equiv.), malonitrile (0.55 mmol, 1.1 equiv.) in Ethanol (mL), was stirred at room temperature for 30 minutes, followed by addition of aliphatic aldehyde (1.5 mmol, 3 equiv.) and L-proline (0.1 mmol, 20 mol%), stirred continuously for next up to 60 min, then reaction was monitored by TLC until completion. After complete formation of Michael adduct 3, added $NaBH_4$ (1 mmol) at 0 °C then stirred reaction mixture for 10 min then at rt for 1-2 h.



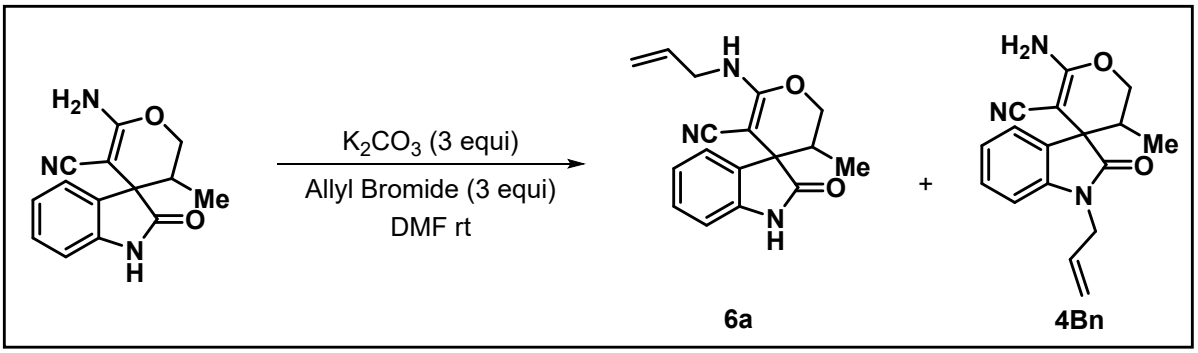
5. General Procedure for the synthetic transformation of product 5a (Procedure F1)

In 10 mL round bottom flask equipped with magnetic stirring bar, were added (4Aa, 0.5mmol), (5 mL, VAc2O / 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 Product **5a.**[9]



5. General Procedure for the synthetic transformation of product 6a (Procedure F2)

In an oven dried round bottom flask equipped with a magnetic stirring bar, product 4Aa (0.5mmol, 1 equiv.) was dissolved in DMF (5mL). to this solution, K_2CO_3 was added and the reaction mixture was stirred for 5-10 minutes. Subsequently, allyl bromide (1.5 mmol, 3 equiv.) was added and the reaction was allowed to proceed at rt with continuous stirring for 12 h. Upon completion of the reaction, as indicated by TLC, the reaction mixture was poured into cold water and extracted with ethyl acetate (3 × 10 mL). combined organic layers were concentrated under reduced pressure at 50 °C to yield the crude product, which was then purified by column chromatography on silica gel using 20-30% ethyl acetate in petroleum ether as the eluent to afford the pure product.[10]



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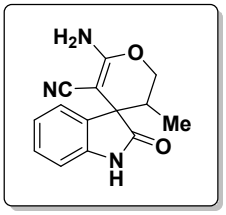
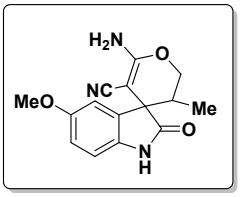
Characterization data of products

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



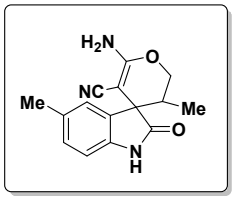
The titled compound was prepared by following the procedure, obtained as a Solid, 121 mg, 95% yield, **mp** = 220−222°C; column chromatography on silica gel (petroleum ether/EtOAc 65:35); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 9.35 (br. s., 1H), 7.03 - 7.16 (m, 2H), 6.92 (t, J=7.50 Hz, 1H), 6.80 (d, J=7.63 Hz, 1H), 5.73 (br. s., 2H), 4.45 (t, J=11.13 Hz, 1H), 4.00 (dd, J=10.69, 3.94 Hz, 1H), 2.15 (ddd, J=11.35, 7.04, 4.13 Hz, 1H), 0.51 (d, J=6.88 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 179.6, 166.7, 143.4, 132.7, 129.4, 124.2, 123.2, 119.7, 110.2, 68.5, 57.0, 50.9, 36.2, 10.7; **HRMS (ESI)** calcd for: $C_{14}H_{14}O_2N_3$, [M + H]$^{+}$ 256.1081, found: 256.1077.

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



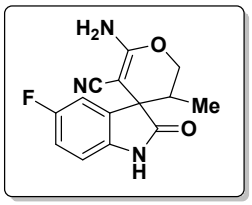
The titled compound was prepared by following the procedure, obtained as a Solid, 137 mg, 96% yield, **mp** = 182−184°C; column chromatography on silica gel (petroleum ether/EtOAc 62:38); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 9.44 (br. s., 1H), 6.96 (d, *J*=2.38 Hz, 1H), 6.88 (d, *J*=8.50 Hz, 1H), 6.82 (dd, *J*=8.38, 2.50 Hz, 1H), 5.86 (br. s., 1H), 4.31 (dd, *J*=11.19, 3.81 Hz, 1H), 4.17 (t, *J*=11.13 Hz, 1H), 3.78 (s, 3H), 2.36 (ddd, *J*=10.98, 7.04, 3.88 Hz, 1H), 0.60 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 179.9, 166.2, 156.6, 136.1, 133.3, 119.9, 114.0, 113.0, 110.9, 69.3, 57.0, 56.1, 52.9, 35.6, 11.4; **HRMS (ESI)** calcd for: $C_{15}H_{16}O_3N_3$, [M + H]$^{+}$ 286.1186, found: 286.1182.

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



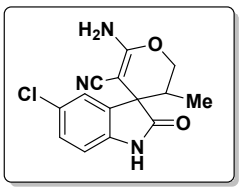
The titled compound was prepared by following the procedure, obtained as a Solid, 123 mg, 92% yield, **mp** = 236−238°C; column chromatography on silica gel (petroleum ether/EtOAc 65:35); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 9.35 (br. s., 1H), 7.03 (s, 1H), 6.92 (d, J=7.75 Hz, 1H), 6.70 (d, J=7.88 Hz, 1H), 5.72 (br. s., 2H), 4.18 (dd, J=11.07, 3.69 Hz, 1H), 4.03 (t, J=11.13 Hz, 1H), 2.10 - 2.26 (m, 4H), 0.45 (d, J=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 179.6, 165.9, 140.3, 132.0, 131.9, 129.5, 126.5, 119.7, 110.0, 69.2, 57.2, 52.2, 35.5, 21.0, 11.3; **HRMS (ESI)** calcd for: $C_{15}H_{16}O_2N_3$, [M + H]$^{+}$ 270.1237, found: 270.1230.

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



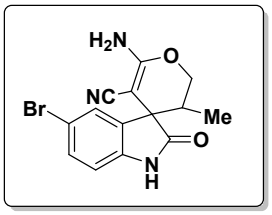
The titled compound was prepared by following the procedure, obtained as a Solid, 128 mg, 94% yield, **mp** = 280−282°C; column chromatography on silica gel (petroleum ether/EtOAc 60:40); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 9.44 (br. s., 1H), 7.08 (dd, J=8.50, 2.50 Hz, 1H), 6.86 - 6.93 (m, 1H), 6.79 - 6.85 (m, 1H), 5.79 (br. s., 2H), 4.21 (dd, J=11.26, 3.75 Hz, 1H), 4.05 (t, J=11.13 Hz, 1H), 2.24 (ddd, J=10.88, 7.07, 3.81 Hz, 1H), 0.49 (d, J=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 179.0, 165.5, 157.6, 138.1, 133.0, 118.8, 114.8, 112.8, 110.4, 68.4, 55.7, 52.1, 34.7, 10.5; ^{19}F NMR (376 MHz, *Acetone d^{6}*) δ ppm -122.7; **HRMS (ESI)** calcd for: $C_{14}H_{13}O_2N_3F$, [M + H]$^{+}$ 274.0986, found: 274.0989.

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



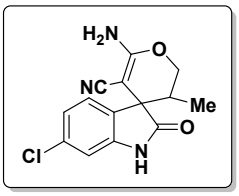
The titled compound was prepared by following the procedure, obtained as a Solid, 138 mg, 95% yield, **mp** = 262−262°C; column chromatography on silica gel (petroleum ether/EtOAc 58:42); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 9.68 (br. s., 1H), 7.42 (br. s., 2H), 6.92 (d, *J*=8.50 Hz, 1H), 5.97 (br. s., 2H), 4.56 (t, *J*=11.19 Hz, 1H), 4.15 (dd, *J*=10.51, 3.25 Hz, 1H), 2.22 - 2.42 (m, 1H), 0.68 (d, *J*=6.88 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 179.2, 166.8, 142.6, 135.2, 132.3, 127.4, 119.6, 115.2, 112.1, 68.4, 56.3, 51.3, 36.0, 10.7; **HRMS (ESI)** calcd for: $C_{14}H_{13}O_2N_3Cl$, [M + H]$^{+}$ 290.0691, found: 290.0686.

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



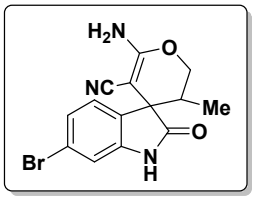
The titled compound was prepared by following the procedure, obtained as a Solid, 162 mg, 97% yield, **mp** = 244−246°C; column chromatography on silica gel (petroleum ether/EtOAc 58:42); **^{1}H NMR** (400 MHz, *Acetone d^6*) δ ppm 9.84 (br. s., 1H), 7.34 - 7.43 (m, 1H), 7.28 (dd, *J*=8.25, 2.00 Hz, 1H), 6.98 (d, *J*=8.25 Hz, 1H), 5.98 (br. s., 2H), 4.34 (dd, *J*=11.26, 3.75 Hz, 1H), 4.19 (t, *J*=11.13 Hz, 1H), 2.36 (ddd, *J*=10.91, 7.10, 3.88 Hz, 1H), 0.62 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^6*) δ ppm 179.7, 166.4, 141.8, 134.1, 129.3, 127.7, 126.2, 119.7, 111.9, 69.2, 56.3, 52.8, 35.6, 11.4**; HRMS (ESI)** calcd for: $C_{14}H_{12}O_2N_3BrNa$, $[M + Na]^+$ 356.0005, found: 356.0006.

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



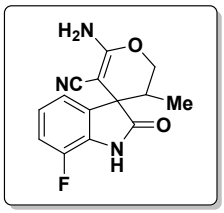
The titled compound was prepared by following the procedure, obtained as a Solid, 135 mg, 93% yield, **mp** = 258−260°C, column chromatography on silica gel (petroleum ether/EtOAc 58:42); **^{1}H NMR** (400 MHz, *Acetone d^6*) δ ppm 10.11 (br. s., 1H), 7.21 (d, J=7.95 Hz, 1H), 6.92 (dd, J=7.95, 1.96 Hz, 1H), 6.84 (d, J=1.83 Hz, 1H), 5.96 (s, 2H), 4.20 (dd, J=11.13, 3.67 Hz, 1H), 4.00 (t, J=11.07 Hz, 1H), 2.20 (ddd, J=10.85, 7.00, 3.79 Hz, 1H), 0.47 (d, J=7.09 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^6*) δ ppm 179.3, 165.5, 143.8, 133.5, 130.1, 126.5, 121.6, 119.1, 110.0, 68.4, 55.4, 51.4, 34.7, 10.7 **HRMS (ESI)** calcd for: $C_{14}H_{12}O_2N_3ClNa$, $[M + Na]^+$ 312.0510, found: 312.0505.

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



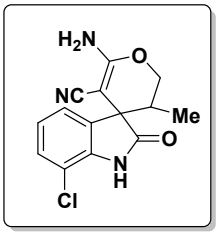
The titled compound was prepared by following the procedure, obtained as a Solid, 160 mg, 96% yield, **mp** = 238−240°C; column chromatography on silica gel (petroleum ether/EtOAc 55:45); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ 9.68 (br. s., 1H), 7.24 (dd, J = 1.8, 8.0 Hz, 1H), 7.19 (d, J = 8.1 Hz, 1H), 7.13 (d, J = 1.6 Hz, 1H), 5.95 (br. s., 2H), 4.56 (t, *J*=11.13 Hz, 1H), 4.14 (dd, *J*=10.76, 4.00 Hz, 1H), 2.30 (ddd, *J*=11.41, 7.10, 4.00 Hz, 1H), 0.67 (d, *J*=6.88 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 179.4, 166.7, 144.9, 132.0, 126.0, 125.9, 122.2, 119.5, 113.4, 68.3, 56.3, 50.8, 35.9, 10.7; **HRMS (ESI)** calcd for: $C_{14}H_{13}O_2N_3Br$, $[M + H]^+$ 334.0191, found: 334.0186.

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



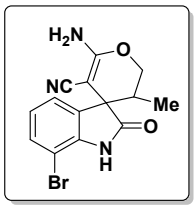
The titled compound was prepared by following the procedure, obtained as a Solid, 134 mg, 98% yield, **mp** = 260−262°C; column chromatography on silica gel (petroleum ether/EtOAc 58:42); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 10.56 (br. s., 1H), 7.19 (d, *J*=7.13 Hz, 1H), 7.08 - 7.15 (m, 1H), 7.01 - 7.08 (m, 1H), 6.13 (br. s., 2H), 4.33 (dd, *J*=11.19, 3.69 Hz, 1H), 4.15 (t, *J*=11.13 Hz, 1H), 2.36 (ddd, *J*=10.79, 7.04, 3.81 Hz, 1H), 0.59 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 179.7, 166.2, 146.6, 135.1, 130.0, 123.4, 121.8, 119.9, 116.3, 69.1, 56.2, 52.8, 35.6, 11.4; **^{19}F NMR** (376 MHz, *Acetone d^{6}*) δ ppm -134.52 **HRMS (ESI)** calcd for: $C_{14}H_{13}O_2N_3F$, $[M + H]^+$ 274.0986, found: 274.0989.

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



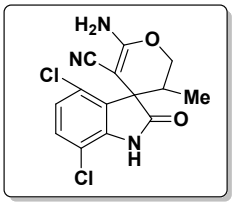
The titled compound was prepared by following the procedure, obtained as a Solid, 137 mg, 95% yield, **mp** = 230−232°C; column chromatography on silica gel (petroleum ether/EtOAc 55:45); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 10.39 (s, 1H), 7.15 - 7.23 (m, 2H), 6.95 (dd, J=8.25, 7.40 Hz, 1H), 6.07 (br. s., 2H), 4.21 (dd, J=11.13, 3.79 Hz, 1H), 4.03 (t, J=11.13 Hz, 1H), 2.23 (ddd, J=10.94, 7.03, 3.79 Hz, 1H), 0.47 (d, J=6.97 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 179.2, 165.7, 140.1, 134.4, 128.8, 123.9, 123.1, 119.3, 114.7, 68.4, 55.4, 52.7, 35.0, 10.8**;** **HRMS (ESI)** calcd for: $C_{14}H_{13}O_2N_3Cl$, $[M + H]^+$ 290.0691, found: 290.0686.

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



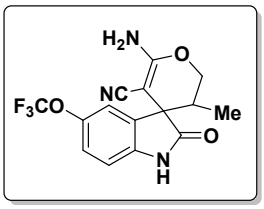
The titled compound was prepared by following the procedure, obtained as a Solid, 164 mg, 98% yield, **mp** = 232−234°C; column chromatography on silica gel (petroleum ether/EtOAc 56:44); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 10.30 (br. s., 1H), 7.43 (dd, J=8.19, 0.94 Hz, 1H), 7.35 (d, J=7.38 Hz, 1H), 6.96 - 7.07 (m, 1H), 6.17 (s, 2H), 4.33 (dd, J=11.19, 3.81 Hz, 1H), 4.14 (t, J=11.13 Hz, 1H), 2.35 (ddd, J=10.88, 7.07, 3.81 Hz, 1H), 0.59 (d, J=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 178.7, 165.2, 141.3, 132.9, 131.2, 124.0, 123.1, 118.9, 102.2, 68.0, 55.1, 52.6, 34.7, 10.4**; HRMS (ESI)** calcd for: $C_{14}H_{13}O_2N_3Br$, $[M + H]^+$ 334.0186, found: 334.0182.

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



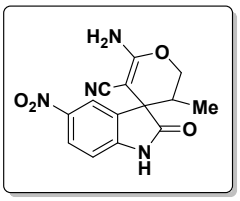
The titled compound was prepared by following the procedure, obtained as a Solid, 151 mg, 94% yield, **mp** = 228−230°C; column chromatography on silica gel (petroleum ether/EtOAc 52:48); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 10.77 (br. s., 1H), 7.19 (d, J=8.63 Hz, 1H), 6.94 (d, J=8.63 Hz, 1H), 5.96 (s, 2H), 4.59 (t, J=11.26 Hz, 1H), 4.07 (dd, J=10.69, 3.94 Hz, 1H), 2.78 (ddd, J=11.29, 7.04, 4.19 Hz, 1H), 0.71 (d, J=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 177.9, 165.8, 141.4, 129.5, 128.2, 127.6, 123.6, 119.1, 113.1, 66.8, 52.4, 51.9, 29.9, 10.2; **HRMS (ESI)** calcd for: $C_{14}H_{12}O_2N_3Cl_2$, [M + H]$^+$ 324.0307, found: 324.0302.

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



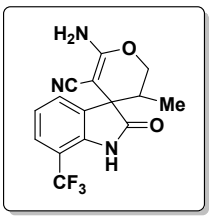
The titled compound was prepared by following the procedure, obtained as a Solid, 163 mg, 96% yield, **mp** = 192−194°C; column chromatography on silica gel (petroleum ether/EtOAc 52:48); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 9.70 (br. s., 1H), 7.27 (s, 1H), 7.20 - 7.25 (m, 1H), 7.04 (d, J=8.38 Hz, 1H), 5.98 (br. s., 2H), 4.58 (t, J=11.19 Hz, 1H), 4.16 (dd, J=10.76, 4.00 Hz, 1H), 0.68 (d, J=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 179.6, 166.8, 145.3, 142.4, 134.5, 122.7, 120.3, 119.4, 118.2, 111.1, 68.3, 56.2, 51.5, 36.0, 10.7; ^{19}F NMR (376 MHz, *Acetone d^{6}*) δ ppm -58.96; **HRMS (ESI)** calcd for: $C_{15}H_{12}O_3N_3F_3Na$, [M + Na]$^{+}$ 362.0728, found: 362.0722.

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



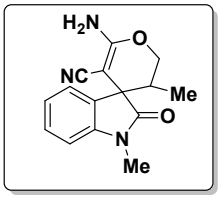
The titled compound was prepared by following the procedure, obtained as a Solid, 136 mg, 91% yield, **mp** = 230−232°C; column chromatography on silica gel (petroleum ether/EtOAc 50:50); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 10.08 (br. s., 1H), 8.12 (dd, *J*=8.57, 2.19 Hz, 1H), 8.09 (d, *J*=2.00 Hz, 1H), 7.07 (d, *J*=8.50 Hz, 1H), 5.94 (br. s., 2H), 4.28 (dd, *J*=11.38, 3.75 Hz, 1H), 4.16 (t, *J*=11.07 Hz, 1H), 2.29 (ddd, *J*=10.69, 7.07, 3.75 Hz, 1H), 0.55 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 178.8, 165.2, 147.6, 142.7, 131.7, 125.2, 120.3, 118.0, 109.2, 67.8, 57.3, 51.3, 34.3, 10.0; **HRMS (ESI)** calcd for: $C_{14}H_{12}O_4N_4Na$, [M + Na]$^{+}$ 323.0756, found: 323.0751.

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



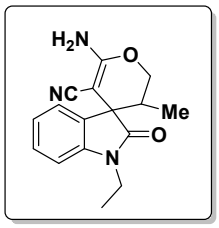
The titled compound was prepared by following the procedure, obtained as a Solid, 151 mg, 94% yield, **mp** = 190−192°C; column chromatography on silica gel (petroleum ether/EtOAc 50:50); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 9.78 (br. s., 1H), 7.52 (d, J=7.50 Hz, 1H), 7.43 (d, J=8.13 Hz, 1H), 7.12 (t, J=7.75 Hz, 1H), 5.88 (br. s., 2H), 4.24 (dd, J=11.26, 3.75 Hz, 1H), 4.06 (t, J=11.01 Hz, 1H), 2.25 (ddd, J=10.79, 7.10, 3.75 Hz, 1H), 0.48 (d, J=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 180.0, 166.5, 140.1, 134.1, 130.0, 126.1, 126.0, 123.0, 119.5, 112.2, 69.2, 56.2, 51.7, 35.8, 11.5; **^{19}F NMR** (376 MHz, *Acetone d^{6}*) δ ppm -61.65 **HRMS (ESI)** calcd for: $C_{15}H_{13}O_2N_3F_3$ [M + H]$^{+}$ 324.0954, found: 324.0953.

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



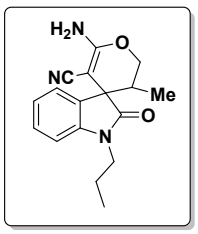
The titled compound was prepared by following the procedure, obtained as a Solid, 126 mg, 94% yield, **mp** = 218−220°C; column chromatography on silica gel (petroleum ether/EtOAc 65:35 **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 7.29 - 7.42 (m, 2H), 7.10 (t, *J*=7.50 Hz, 1H), 7.04 (d, *J*=7.75 Hz, 1H), 6.14 (br. s., 2H), 4.32 (dd, *J*=11.13, 3.75 Hz, 1H), 4.15 (t, *J*=11.07 Hz, 1H), 3.23 (s, 3H), 2.34 (ddd, *J*=10.79, 7.04, 3.81 Hz, 1H), 0.49 (d, *J*=6.88 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 177.8, 165.7, 144.1, 130.8, 128.8, 125.0, 122.6, 119.4, 108.5, 68.6, 55.6, 51.4, 35.0, 26.0, 10.8; **HRMS (ESI)** calcd for: $C_{15}H_{16}O_2N_3$ [M + H]$^{+}$ 270.1237, found: 270.1236.

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



The titled compound was prepared by following the procedure, obtained as a Solid, 132 mg, 93% yield, **mp** = 208−210°C; column chromatography on silica gel (petroleum ether/EtOAc 75:25); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 7.28 - 7.34 (m, 1H), 7.19 - 7.24 (m, 1H), 7.05 - 7.11 (m, 1H), 6.89 (d, *J*=7.75 Hz, 1H), 4.80 (br. s., 2H), 4.30 (dd, *J*=11.26, 3.63 Hz, 1H), 4.02 - 4.14 (m, 1H), 3.72 - 3.88 (m, 2H), 2.36 - 2.51 (m, 1H), 1.28 (t, *J*=7.25 Hz, 3H), 0.55 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 177.2, 164.7, 142.4, 130.0, 128.8, 124.8, 122.6, 118.9, 108.5, 68.9, 56.9, 50.5, 35.0, 34.3, 12.6, 11.2; **HRMS (ESI)** calcd for: $C_{16}H_{18}O_2N_3$ [M + H]$^{+}$ 284.1394, found: 284.1391.

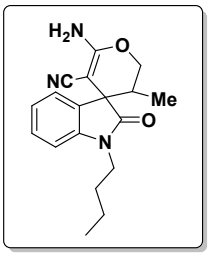
6'-amino-3'-methyl-2-oxo-1-propyl-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (4Bc):



The titled compound was prepared by following the procedure, obtained as a Solid, 138 mg, 93% yield, **mp** = 204−206°C; column chromatography on silica gel (petroleum ether/EtOAc 66:34); **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 7.37 (d, *J*=7.38 Hz, 1H), 7.33 (td, *J*=7.72, 1.19 Hz, 1H), 7.04 - 7.12 (m, 2H), 6.14 (s, 2H), 4.32 (dd, *J*=11.13, 3.88 Hz, 1H), 4.16 (t, *J*=11.13 Hz,

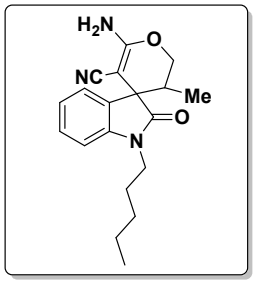
1H), 3.73 (t, *J*=7.13 Hz, 2H), 2.36 (ddd, *J*=11.07, 7.07, 3.88 Hz, 1H), 1.70 (sxt, J=7.10 Hz, 2H), 0.96 (t, *J*=7.44 Hz, 3H), 0.50 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 177.7, 165.5, 143.3, 130.8, 128.7, 125.0, 122.3, 119.3, 108.7, 68.5, 55.7, 51.1, 41.5, 34.9, 20.7, 11.0, 10.7; **HRMS (ESI)** calcd for: $C_{17}H_{20}O_2N_3$ [M + H]$^+$ 298.1550, found: 298.1550.

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



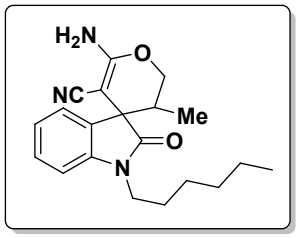
The titled compound was prepared by following the procedure, obtained as a Solid, 143 mg, 92% yield, **mp** = 190−192°C; column chromatography on silica gel (petroleum ether/EtOAc 68:32 **^{1}H NMR** (400 MHz, *Acetone d^{6}*) δ ppm 7.33 - 7.39 (m, 1H), 7.28 - 7.33 (m, 1H), 7.07 - 7.11 (m, 1H), 7.06 (d, J=7.50 Hz, 1H), 5.86 (br. s., 2H), 4.33 (dd, J=11.07, 3.69 Hz, 1H), 4.17 (t, J=11.13 Hz, 1H), 3.77 (t, J=7.13 Hz, 2H), 2.37 (ddd, J=10.79, 7.10, 3.88 Hz, 1H), 1.66 (td, J=7.38, 3.88 Hz, 2H), 1.42 (dq, J=14.96, 7.39 Hz, 2H), 0.94 (t, J=7.38 Hz, 3H), 0.52 (d, J=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone d^{6}*) δ ppm 178.2, 166.1, 144.2, 131.5, 129.5, 125.8, 123.0, 119.7, 109.4, 69.4, 57.1, 51.8, 40.4, 35.7, 30.4, 20.7, 14.1, 11.4; **HRMS (ESI)** calcd for: $C_{18}H_{22}O_2N_3$ [M + H]$^+$ 312.1707, found: 312.1704.

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



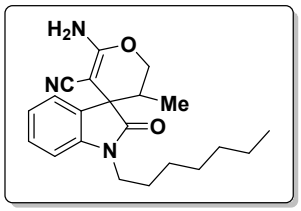
The titled compound was prepared by following the procedure, obtained as a Solid, 150 mg, 92% yield, **mp** = 182−182°C; column chromatography on silica gel (petroleum ether/EtOAc 70:30); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 7 7.27 - 7.33 (m, 1H), 7.21 (d, J=7.38 Hz, 1H), 7.04 - 7.10 (m, 1H), 6.88 (d, J=7.75 Hz, 1H), 4.81 (br. s., 2H), 4.32 (dd, J=11.13, 3.63 Hz, 1H), 4.08 (t, J=10.88 Hz, 1H), 3.66 - 3.81 (m, 2H), 2.43 (ddd, J=10.60, 6.97, 3.69 Hz, 1H), 1.69 (d, J=5.25 Hz, 2H), 1.37 (d, J=3.63 Hz, 4H), 0.90 (t, J=6.94 Hz, 3H), 0.56 (d, J=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 177.2, 164.4, 142.5, 129.5, 128.4, 124.4, 122.2, 118.6, 108.3, 68.6, 56.6, 50.2, 40.0, 34.0, 28.6, 26.6, 21.9, 13.5, 10.9; **HRMS (ESI)** calcd for: $C_{19}H_{24}O_2N_3$, [M + H]$^+$ 326.1863, found: 326.1861.

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



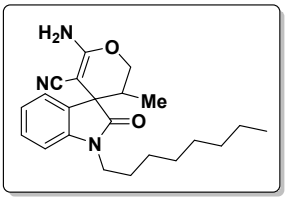
The titled compound was prepared by following the procedure, obtained as a Solid, 153 mg, 90% yield, **mp** = 178−180°C; column chromatography on silica gel (petroleum ether/EtOAc 72:28); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 7.19 - 7.26 (m, 1H), 7.14 (d, *J*=7.13 Hz, 1H), 7.00 (t, *J*=7.50 Hz, 1H), 6.80 (d, *J*=7.75 Hz, 1H), 4.68 (br. s., 2H), 4.25 (dd, *J*=11.13, 3.63 Hz, 1H), 4.00 (t, *J*=10.94 Hz, 1H), 3.66 (tt, *J*=14.62, 7.21 Hz, 2H), 2.36 (ddd, *J*=10.63, 7.00, 3.75 Hz, 1H), 1.61 (dq, *J*=13.45, 6.77 Hz, 2H), 1.21 - 1.31 (m, 6H), 0.80 (t, *J*=6.75 Hz, 3H), 0.49 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 177.5, 164.7, 142.8, 129.9, 128.7, 124.8, 122.5, 118.9, 108.6, 69.0, 57.0, 50.5, 40.4, 34.3, 31.3, 27.2, 26.5, 22.4, 13.9, 11.3; **HRMS (ESI)** calcd for: $C_{20}H_{26}O_2N_3$, $[M + H]^+$ 340.2020, found: 340.2032.

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



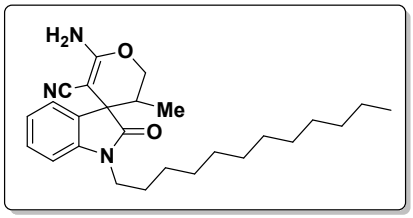
The titled compound was prepared by following the procedure, obtained as a Solid, 162 mg, 91% yield, **mp** = 175−177°C; column chromatography on silica gel (petroleum ether/EtOAc 75:25); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 7.28 - 7.33 (m, 1H), 7.21 (d, *J*=7.38 Hz, 1H), 7.07 (t, *J*=7.50 Hz, 1H), 6.88 (d, *J*=7.75 Hz, 1H), 4.72 (s, 2H), 4.33 (dd, *J*=11.07, 3.69 Hz, 1H), 4.08 (t, *J*=10.88 Hz, 1H), 3.65 - 3.81 (m, 2H), 2.43 (ddd, *J*=10.57, 7.00, 3.69 Hz, 1H), 1.69 (dq, *J*=12.91, 6.70 Hz, 2H), 1.26 - 1.37 (m, 8H), 0.87 (t, *J*=6.63 Hz, 3H), 0.57 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 177.5, 164.7, 142.9, 129.9, 128.8, 124.8, 122.5, 118.9, 108.6, 69.0, 57.2, 50.5, 40.4, 34.3, 31.6, 28.8, 27.3, 26.8, 22.5, 14.0, 11.3; **HRMS (ESI)** calcd for: $C_{21}H_{28}O_2N_3$, $[M + H]^+$ 354.2182, found: 354.2178.

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



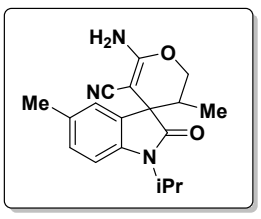
The titled compound was prepared by following the procedure, obtained as a Solid, 165 mg, 90% yield, **mp** = 172-174°C; column chromatography on silica gel (petroleum ether/EtOAc 76:24); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 7.27 - 7.32 (m, 1H), 7.21 (d, *J*=7.25 Hz, 1H), 7.07 (t, *J*=7.50 Hz, 1H), 6.88 (d, *J*=7.88 Hz, 1H), 4.74 (br. s., 2H), 4.23 - 4.39 (m, 1H), 4.08 (t, *J*=10.88 Hz, 1H), 3.66 - 3.80 (m, 2H), 2.43 (ddd, *J*=10.38, 6.88, 3.38 Hz, 1H), 1.63 - 1.73 (m, 2H), 1.25 - 1.35 (m, 10H), 0.87 (t, *J*=6.57 Hz, 3H), 0.56 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 177.8, 165.0, 143.2, 130.2, 129.1, 125.1, 122.8, 119.2, 108.9, 69.3, 50.8, 40.7, 34.6, 32.0, 29.5, 29.4, 29.4, 27.6, 27.1, 22.8, 14.3, 11.6; **HRMS (ESI)** calcd for: $C_{22}H_{30}O_2N_3$, $[M + H]^+$ 368.2338, found: 368.2335.

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



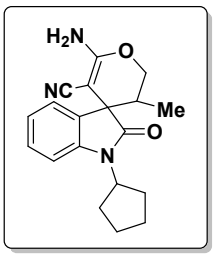
The titled compound was prepared by following the procedure, obtained as a Solid, 186 mg, 88% yield, **mp** = 160−162°C; column chromatography on silica gel (petroleum ether/EtOAc 80:20); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 7.27 - 7.32 (m, 1H), 7.21 (m, *J*=7.13 Hz, 1H), 7.07 (t, *J*=7.57 Hz, 1H), 6.88 (m, *J*=7.75 Hz, 1H), 4.75 (br. s., 2H), 4.32 (dd, *J*=11.13, 3.63 Hz, 1H), 4.08 (t, *J*=10.88 Hz, 1H), 3.64 - 3.81 (m, 2H), 2.43 (ddd, *J*=10.60, 6.97, 3.69 Hz, 1H), 1.64 - 1.73 (m, 2H), 1.21 - 1.36 (m, 18H), 0.88 (t, *J*=6.75 Hz, 3H), 0.56 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 177.5, 164.7, 142.8, 129.9, 128.7, 124.8, 122.5, 118.9, 108.6, 69.0, 57.0, 50.5, 40.4, 34.3, 31.8, 29.6, 29.5, 29.4, 29.2, 29.1, 27.3, 26.8, 22.6, 14.0, 11.2; **HRMS (ESI)** calcd for: $C_{26}H_{38}O_2N_3$ $[M + H]^+$ 424.2959, found: 424.2965.

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



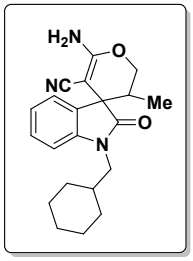
The titled compound was prepared by following the procedure, obtained as a Solid, 142 mg, 92% yield, **mp** = 228−230°C; column chromatography on silica gel (petroleum ether/EtOAc 70:30); **^{1}H NMR** (400 MHz, *Acetone*) δ ppm 7.07 (s, 1H), 6.97 (d, J=8.00 Hz, 1H), 6.91 (d, J=8.00 Hz, 1H), 5.69 (br. s., 2H), 4.38 - 4.53 (m, 1H), 4.15 (dd, J=11.13, 4.00 Hz, 1H), 4.04 (t, J=11.26 Hz, 1H), 2.17 - 2.27 (m, 4H), 1.33 (t, J=6.57 Hz, 6H), 0.36 (d, J=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone*) δ ppm 177.0, 165.0, 140.2, 131.1, 128.7, 125.7, 124.5, 118.6, 109.3, 68.5, 56.8, 50.7, 44.1, 34.8, 20.1, 18.7, 18.6, 10.4 **HRMS (ESI)** calcd for: $C_{18}H_{22}O_2N_3$ $[M + H]^+$ 312.1707, found: 312.1725.

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



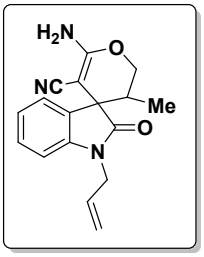
The titled compound was prepared by following the procedure, obtained as a Solid, 146 mg, 91% yield, **mp** = 226−228°C; column chromatography on silica gel (petroleum ether/EtOAc 65:35); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 7.25 (d, J=7.38 Hz, 1H), 7.16 - 7.23 (m, 1H), 7.00 (d, J=7.88 Hz, 1H), 6.93 - 6.98 (m, 1H), 6.07 (br. s., 2H), 4.62 (quin, J=8.57 Hz, 1H), 4.17 (dd, J=11.13, 3.75 Hz, 1H), 4.02 (t, J=11.19 Hz, 1H), 2.22 (ddd, J=11.13, 7.07, 3.94 Hz, 1H), 1.97 - 2.05 (m, 2H), 1.72 - 1.86 (m, 4H), 1.50 - 1.64 (m, 2H), 0.35 (d, J=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 177.4, 165.3, 142.7, 131.0, 128.3, 125.0, 121.9, 119.1, 109.3, 68.2, 55.6, 52.7, 50.8, 34.9, 27.8, 27.6, 24.9, 10.4; **HRMS (ESI)** calcd for: $C_{19}H_{22}O_2N_3$ [M + H]$^+$ 324.1707, found: 324.1696.

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



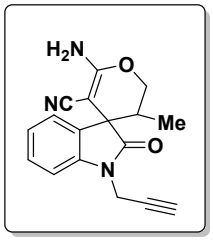
The titled compound was prepared by following the procedure, obtained as a Solid, 161 mg, 92% yield, **mp** = 206−208°C; column chromatography on silica gel (petroleum ether/EtOAc 70:30); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 7.26 - 7.32 (m, 1H), 7.21 (d, J=7.38 Hz, 1H), 7.04 - 7.10 (m, 1H), 6.88 (d, J=7.75 Hz, 1H), 4.66 (s, 2H), 4.37 (dd, J=11.07, 3.69 Hz, 1H), 4.08 (t, J=10.69 Hz, 1H), 3.57 (d, J=7.13 Hz, 2H), 2.42 (ddd, J=10.41, 6.91, 3.56 Hz, 1H), 1.84 (dt, J=7.22, 3.46 Hz, 1H), 1.66 - 1.81 (m, 5H), 1.16 - 1.29 (m, 5H), 0.60 (d, J=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 177.6, 164.4, 143.2, 129.4, 128.4, 124.5, 122.1, 118.7, 108.7, 68.8, 57.2, 50.2, 46.5, 36.0, 34.0, 30.7, 30.5, 26.0, 25.4, 25.3, 11.3; **HRMS (ESI)** calcd for: $C_{21}H_{25}O_2N_3Na$, [M + Na]$^+$ 374.1844, found: 374.1840.

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



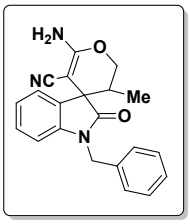
The titled compound was prepared by following the procedure, obtained as a Solid, 140 mg, 95% yield, **mp** = 170−172°C; column chromatography on silica gel (petroleum ether/EtOAc 60:40); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 7.25 - 7.31 (m, 1H), 7.23 (d, J=7.38 Hz, 1H), 7.08 (td, J=7.54, 0.81 Hz, 1H), 6.86 (d, J=7.88 Hz, 1H), 5.84 (ddt, J=17.20, 10.38, 5.16, 5.16 Hz, 1H), 5.19 - 5.31 (m, 2H), 4.80 (s, 2H), 4.36 - 4.46 (m, 2H), 4.33 (dd, *J*=10.11, 3.85 Hz, 1H), 4.03 - 4.15 (m, 1H), 2.37 - 2.52 (m, 1H), 0.59 (d, J=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 177.5, 164.8, 142.5, 130.9, 129.7, 128.7, 124.7, 122.8, 117.7, 109.3, 69.0, 56.9, 50.6, 42.6, 34.3, 11.4; **HRMS (ESI)** calcd for: $C_{17}H_{18}O_2N_3$, [M + H]$^+$ 296.1394, found: 296.1393.

6'-amino-3'-methyl-2-oxo-1-(prop-2-yn-1-yl)-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (4Bn):



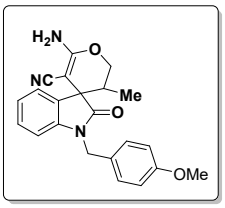
The titled compound was prepared by following the procedure, obtained as a Solid, 128 mg, 88% yield**,** **mp** = 182−284°C; column chromatography on silica gel (petroleum ether/EtOAc 70:30); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 7.27 (d, J=6.36 Hz, 1H), 7.22 - 7.25 (m, 1H), 7.04 (d, J=6.85 Hz, 1H), 6.98 - 7.02 (m, 1H), 5.78 (br. s., 2H), 4.59 (dd, J=17.85, 2.57 Hz, 1H), 4.36 (dd, J=17.79, 2.51 Hz, 1H), 4.19 (dd, *J*=11.16, 3.66 Hz, 1H), 4.04 (t, J=11.07 Hz, 1H), 2.64 (t, J=2.57 Hz, 1H), 2.24 (ddd, J=10.88, 7.03, 3.85 Hz, 1H), 0.39 (d, J=6.97 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 176.8, 165.4, 142.0, 130.5, 128.6, 124.9, 122.8, 118.6, 109.2, 77.5, 72.5, 68.4, 55.6, 51.1, 38.0, 35.3, 10.4; **HRMS (ESI)** calcd for: $C_{17}H_{16}O_2N_3$, [M + H]$^+$ 294.1243, found: 294.1240.

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



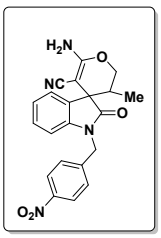
The titled compound was prepared by following the procedure, obtained as a Solid, 147 mg, 89% yield, **mp** = 222−224°C; column chromatography on silica gel (petroleum ether/EtOAc 62:38); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 7.25 - 7.35 (m, 3H), 7.18 - 7.23 (m, 2H), 7.13 - 7.17 (m, 1H), 7.10 (td, J=7.73, 1.28 Hz, 1H), 6.95 (td, J=7.55, 1.04 Hz, 1H), 6.77 (d, J=7.58 Hz, 1H), 6.03 (s, 2H), 4.92 (d, *J*=15.14 Hz, 1H), 4.81 (d, *J*=15.14 Hz, 1H), 4.23 (dd, J=11.25, 3.79 Hz, 1H), 4.06 (t, J=11.13 Hz, 1H), 2.31 (ddd, J=10.94, 7.03, 3.79 Hz, 1H), 0.40 (d, J=7.09 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 178.2, 165.8, 143.2, 136.8, 131.0, 129.0, 128.8, 127.8, 125.3, 122.8, 119.7, 109.6, 68.8, 56.0, 51.6, 43.8, 35.4, 11.0; **HRMS (ESI)** calcd for: $C_{21}H_{19}O_2N_3Na$, $[M + Na]^+$ 368.1375, found: 368.1371.

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



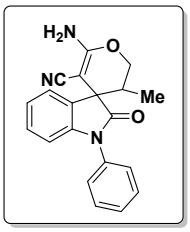
The titled compound was prepared by following the procedure, obtained as a Solid, 167 mg, 91% yield, **mp** = 272−274°C; column chromatography on silica gel (petroleum ether/EtOAc 60:40); **^{1}H NMR** (400 MHz, *Acetone*) δ ppm 7.95 (d, *J*=8.38 Hz, 2H), 7.58 (d, *J*=8.38 Hz, 2H), 7.43 (d, *J*=7.13 Hz, 1H), 7.24 (td, *J*=7.72, 1.06 Hz, 1H), 7.09 (t, *J*=7.50 Hz, 1H), 6.90 (d, *J*=7.75 Hz, 1H), 6.40 (s, 2H), 5.18 (d, *J*=16.13 Hz, 1H), 5.01 (d, *J*=16.13 Hz, 1H), 4.35 (dd, *J*=11.19, 3.81 Hz, 1H), 4.19 (t, *J*=11.13 Hz, 1H), 3.86 (s, 3H), 2.43 (ddd, *J*=10.94, 7.07, 3.75 Hz, 1H), 0.52 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 176.9, 165.0, 164.2, 140.9, 139.8, 129.1, 128.6, 128.1, 127.4, 126.0, 123.7, 121.7, 107.9, 67.3, 53.6, 50.8, 49.9, 42.3, 33.5, 10.0; **HRMS (ESI)** calcd for: $C_{22}H_{21}O_3N_3Na$, $[M + Na]^+$ 398.1481, found: 398.1478.

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



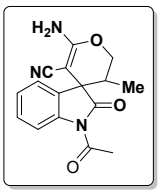
The titled compound was prepared by following the procedure, obtained as a Solid, 171 mg, 88% yield, **mp** = 266−268°C; column chromatography on silica gel (petroleum ether/EtOAc 55:45); **^{1}H NMR** (400 MHz, *Acetone*) δ ppm 8.06 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J*=8.88 Hz, 2H), 7.30 (d, *J*=6.88 Hz, 1H), 7.11 (td, *J*=7.75, 1.13 Hz, 1H), 6.97 (td, *J*=7.57, 0.88 Hz, 1H), 6.78 (d, *J*=7.75 Hz, 1H), 5.85 (br. s., 2H), 5.15 (d, *J*=16.51 Hz, 1H), 4.94 (d, *J*=16.51 Hz, 1H), 4.24 (dd, *J*=11.19, 3.81 Hz, 1H), 4.08 (t, *J*=11.13 Hz, 1H), 2.33 (ddd, *J*=10.94, 7.07, 3.88 Hz, 1H), 0.43 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm 178.7, 166.1, 148.2, 145.0, 143.1, 131.3, 129.3, 129.2, 125.9, 124.4, 123.6, 119.9, 109.8, 69.3, 56.7, 52.0, 43.6, 35.7, 11.4 **HRMS (ESI)** calcd for: $C_{21}H_{19}O_4N_4$, [M + H]$^+$ 391.1406, found: 391.1402.

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



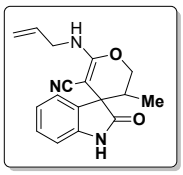
The titled compound was prepared by following the procedure, obtained as a Solid, 152 mg, 92% yield**,** **mp** = 270−272°C; column chromatography on silica gel (petroleum ether/EtOAc 55:45); **^{1}H NMR** (400 MHz, *Acetone*) δ ppm 7.55 - 7.66 (m, 2H), 7.38 - 7.53 (m, 4H), 7.29 (td, *J*=7.75, 1.13 Hz, 1H), 7.15 (td, *J*=7.54, 0.94 Hz, 1H), 6.80 (d, *J*=7.88 Hz, 1H), 5.95 (br. s., 2H), 4.37 (dd, *J*=11.18, 3.68 Hz, 1H), 4.25 (t, *J*=11.24 Hz, 1H), 2.40 - 2.57 (m, 1H), 0.68 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101 MHz, *Acetone*) δ ppm 178.0, 166.1, 144.7, 135.9, 131.2, 130.5, 129.5, 129.0, 127.8, 126.1, 123.8, 119.6, 109.9, 69.4, 57.2, 52.1, 35.9, 11.6 **HRMS (ESI)** calcd for: $C_{20}H_{18}O_2N_3$, [M + H]$^+$ 332.1399, found: 332.1395.

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



The titled compound was prepared by following procedure F1, obtained as a Solid, 105 mg, 72% yield**,** **mp** = 212−214°C; column chromatography on silica gel (petroleum ether/EtOAc 60:40); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 8.17 (d, *J*=8.13 Hz, 1H), 7.27 - 7.33 (m, 1H), 7.19 - 7.24 (m, 1H), 7.12 - 7.18 (m, 1H), 4.70 (br. s., 2H), 4.52 (t, *J*=11.44 Hz, 1H), 4.06 (dd, *J*=11.13, 4.00 Hz, 1H), 2.60 (s, 3H), 2.18 (ddd, *J*=11.51, 7.13, 4.13 Hz, 1H), 0.58 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101MHz ,CHLOROFORM-d) δ ppm 177.7, 169.6, 164.5, 139.4, 128.4, 128.2, 125.0, 121.8, 117.8, 115.6, 67.1, 56.3, 49.2, 35.5, 25.8, 9.3; 6 **HRMS (ESI)** calcd for: $C_{16}H_{16}O_3N_3$, [M + H]$^+$ 298.1192, found: 298.1187.

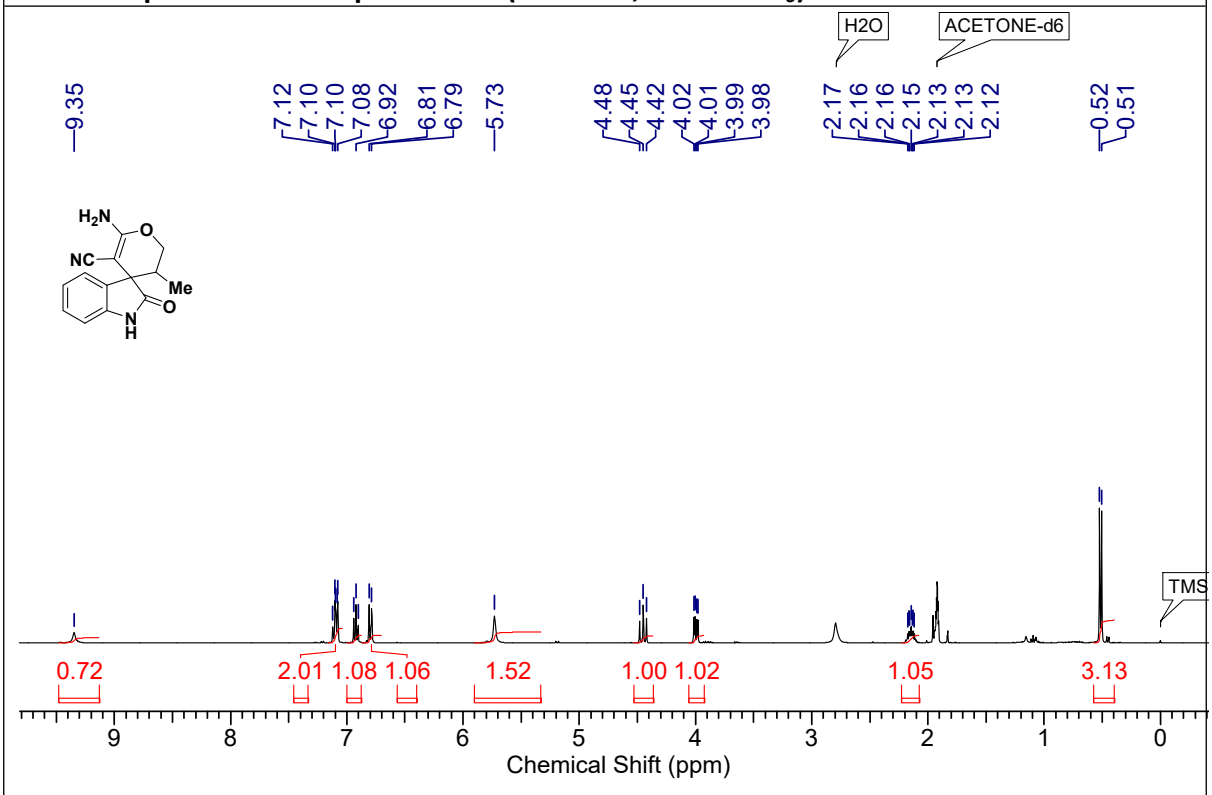
6'-(allylamino)-3'-methyl-2-oxo-2',3'-dihydrospiro[indoline-3,4'-pyran]-5'-carbonitrile (6a):



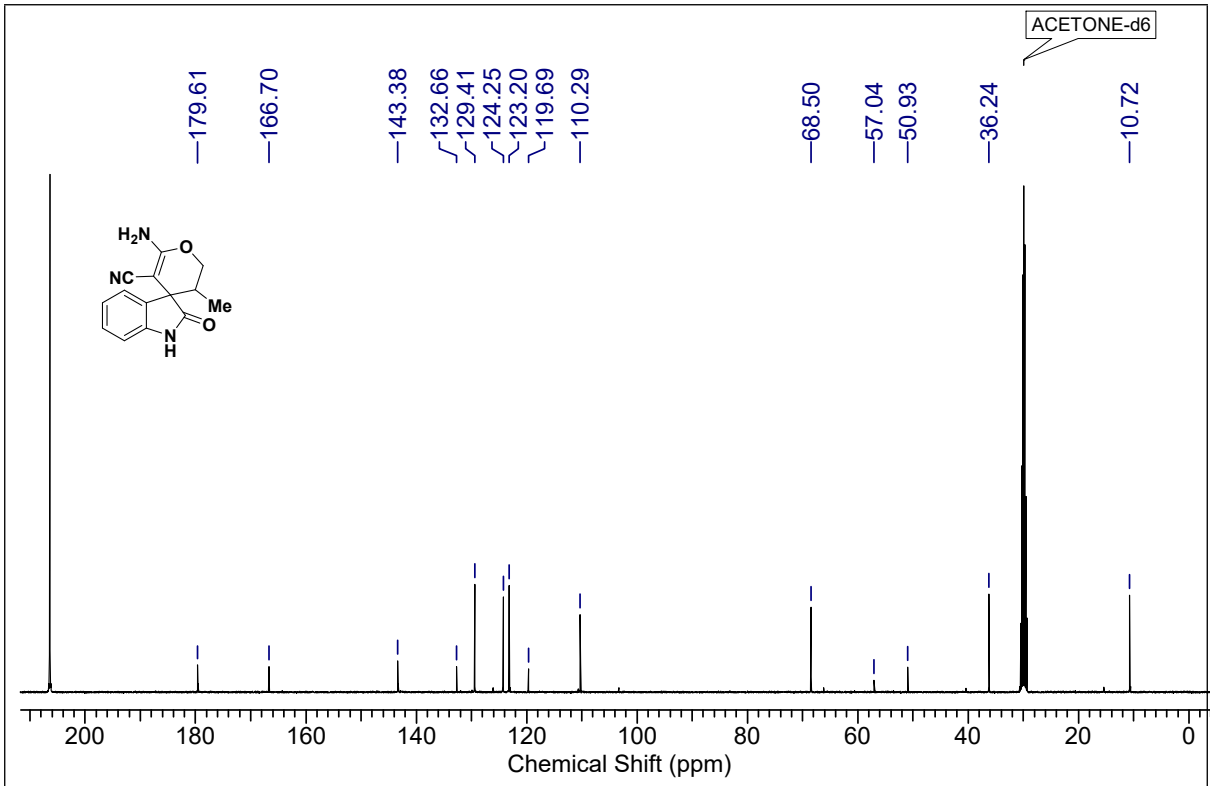
The titled compound was prepared by following the procedure F2, obtained as a Solid, 103 mg, 70% yield**,** **mp** = 228−230°C; column chromatography on silica gel (petroleum ether/EtOAc 60:40); **^{1}H NMR** (400 MHz, *CHLOROFORM-d*) δ ppm 7.19 - 7.23 (m, 1H), 7.16 (d, *J*=7.38 Hz, 1H), 6.92 - 7.05 (m, 1H), 6.78 (d, *J*=7.75 Hz, 1H), 5.67 - 5.89 (m, 1H), 5.23 (d, *J*=17.13 Hz, 1H), 5.16 (d, *J*=10.38 Hz, 1H), 4.34 - 4.43 (m, 1H), 4.22 - 4.34 (m, 2H), 4.05 (t, *J*=10.88 Hz, 1H), 2.42 (ddd, *J*=10.54, 6.97, 3.63 Hz, 1H), 0.54 (d, *J*=7.00 Hz, 3H); **^{13}C NMR** (101MHz ,CHLOROFORM-d) δ ppm 176.3, 165.3, 141.8, 130.1, 128.7, 127.7, 124.0, 121.6, 118.2, 116.8, 108.3, 68.1, 51.4, 41.7, 39.8, 33.7, 10.6. **HRMS (ESI)** calcd for: $C_{17}H_{17}O_2N_3Na$, [M + Na]$^{+}$ 318.1218, found: 318.1214.

NMR Spectra of Compounds:

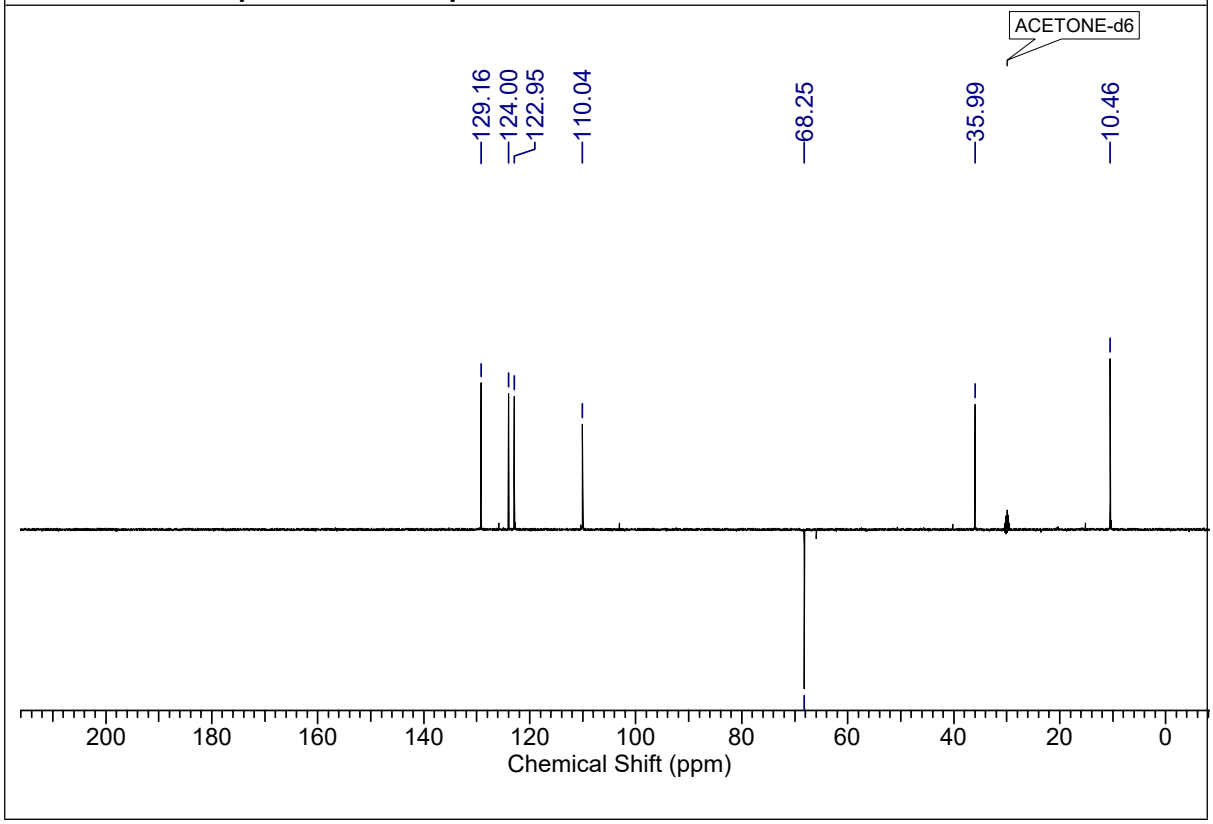
^{1}H NMR spectrum of compound 4Aa (400 MHz, Acetone-d_6)



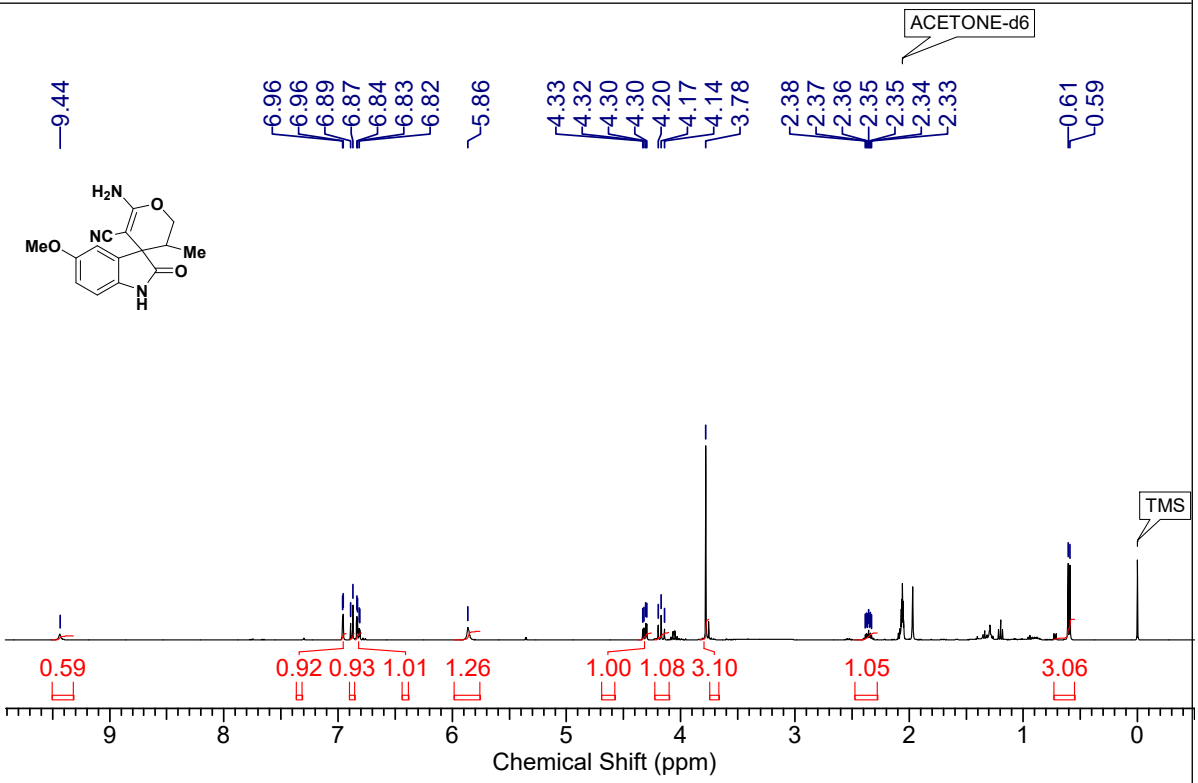
^{13}C NMR spectrum of compound 4Aa (101 MHz, Acetone-d_6)



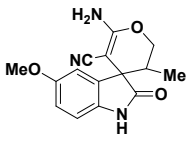
135 DEPT NMR spectrum of compound 4Aa

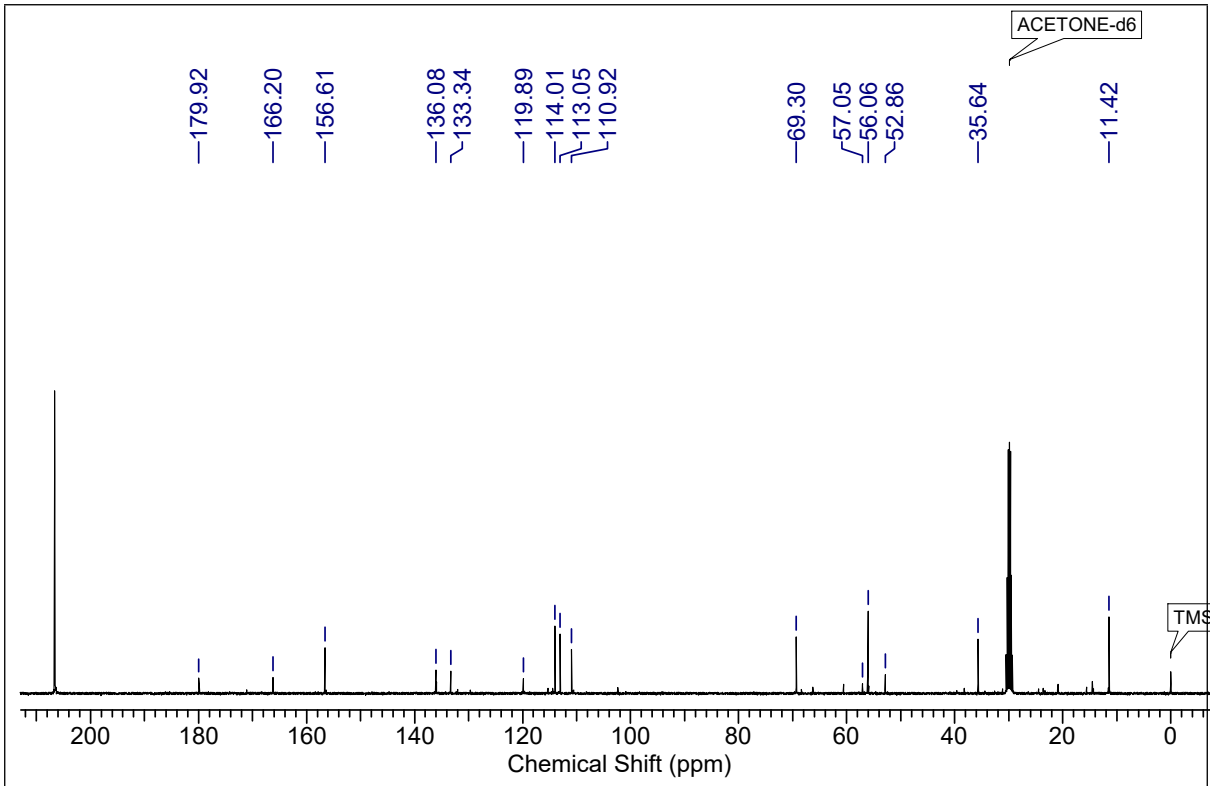


^{1}H NMR spectrum of compound 4Ab (400 MHz, Acetone-d_6)

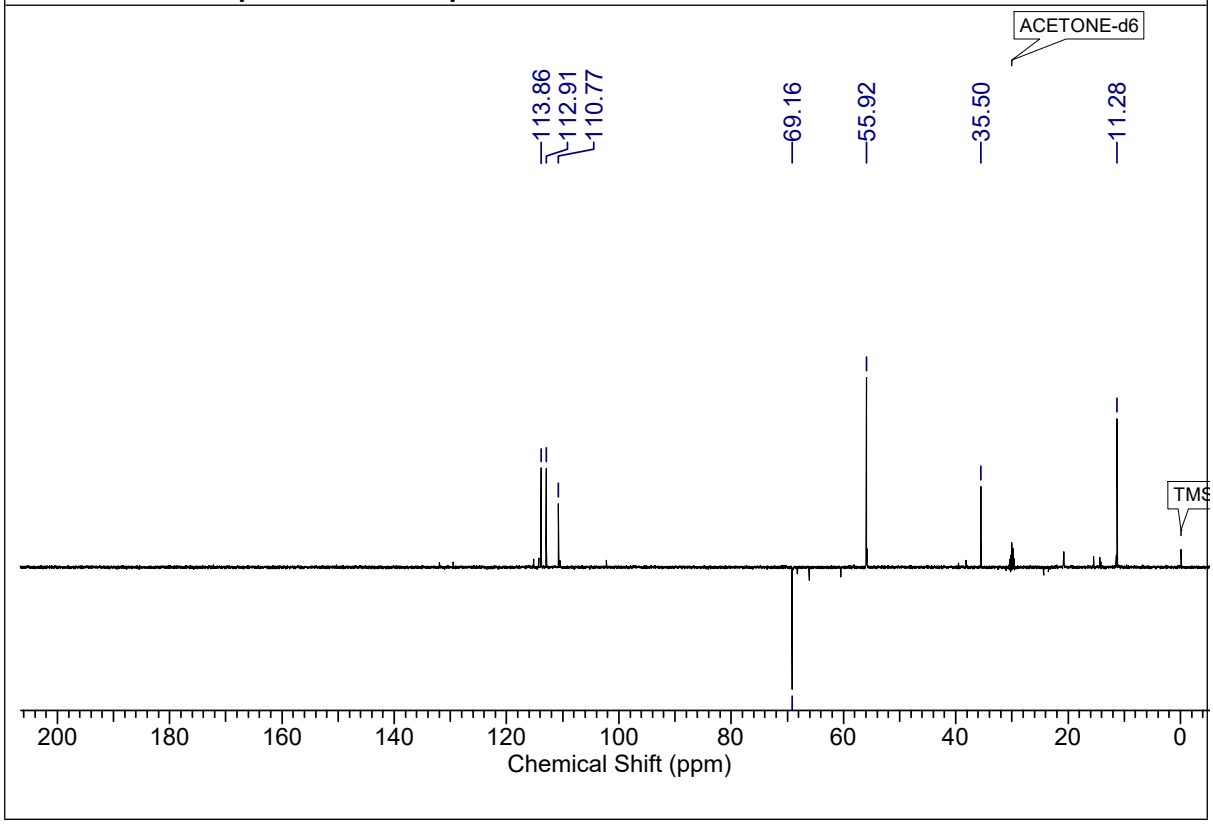


^{13}C NMR spectrum of compound 4Ab (101 MHz, Acetone-d_6)

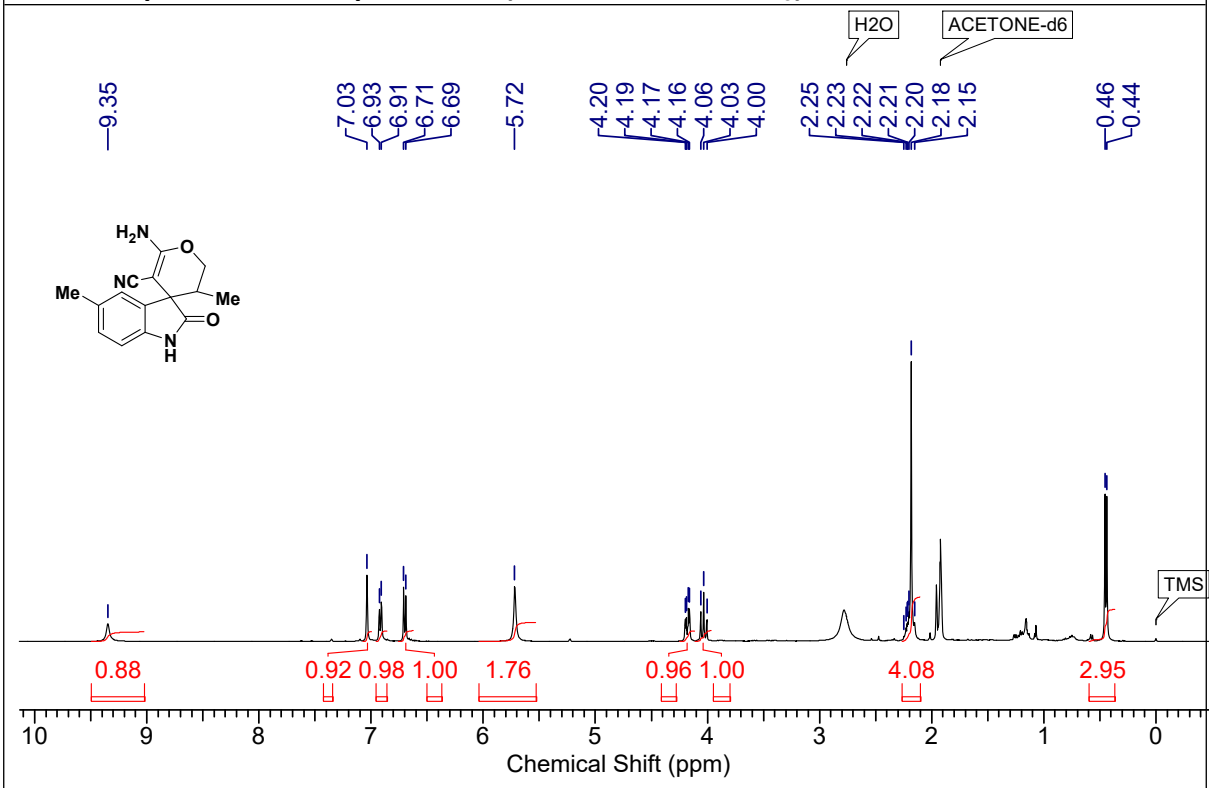




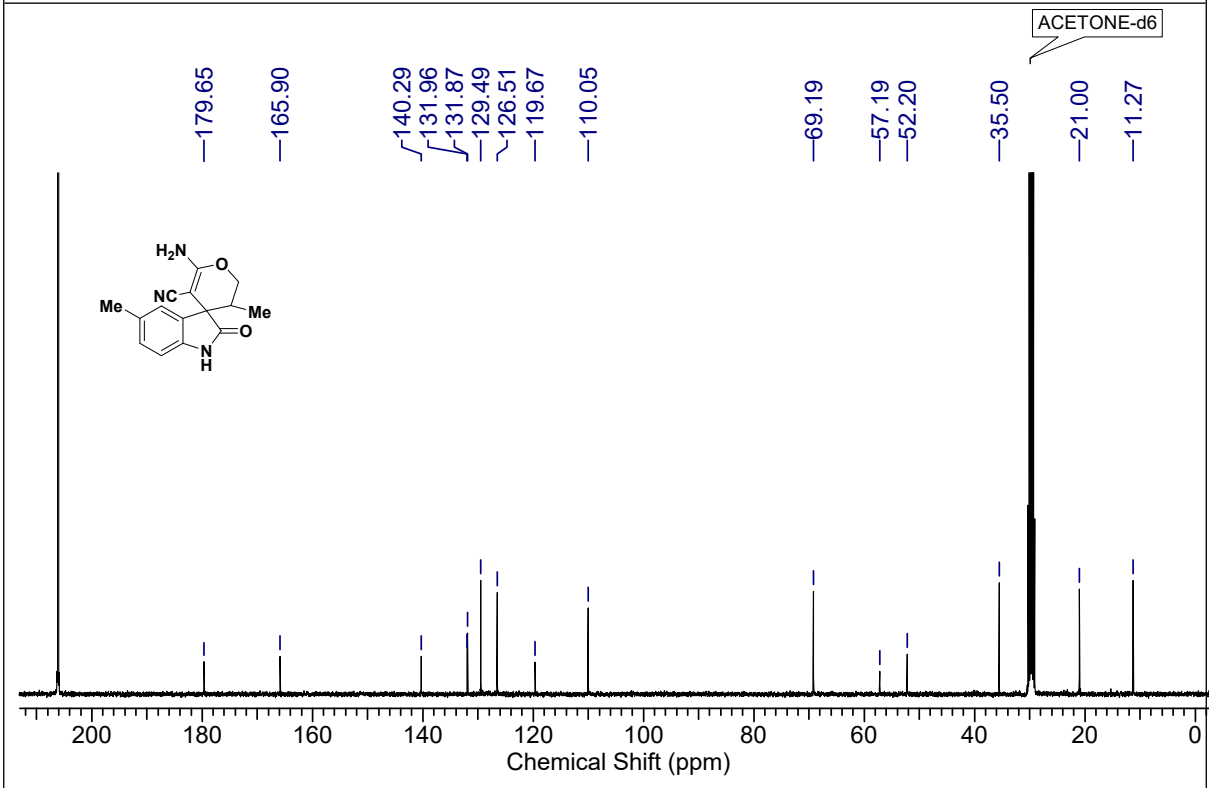
135 DEPT NMR spectrum of compound 4Ab



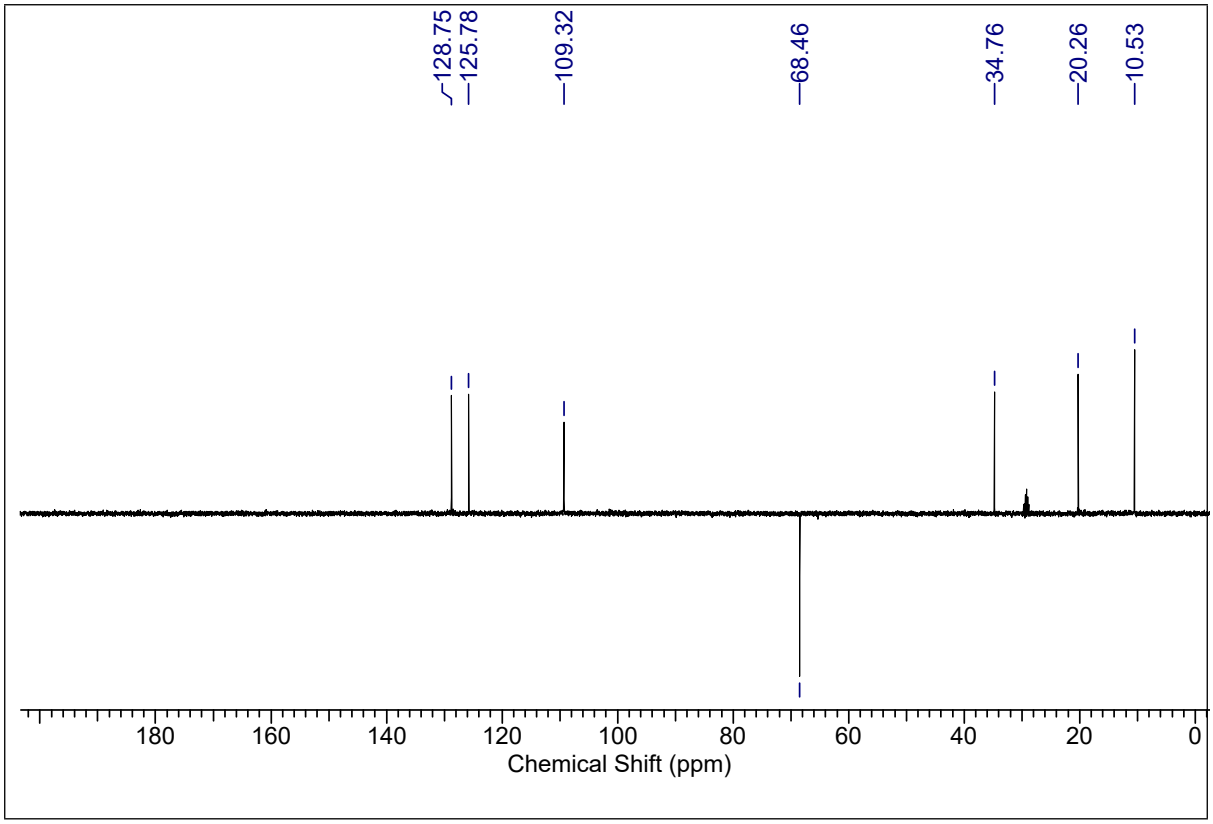
^{1}H NMR spectrum of compound 4Ac (400 MHz, Acetone-d_6)



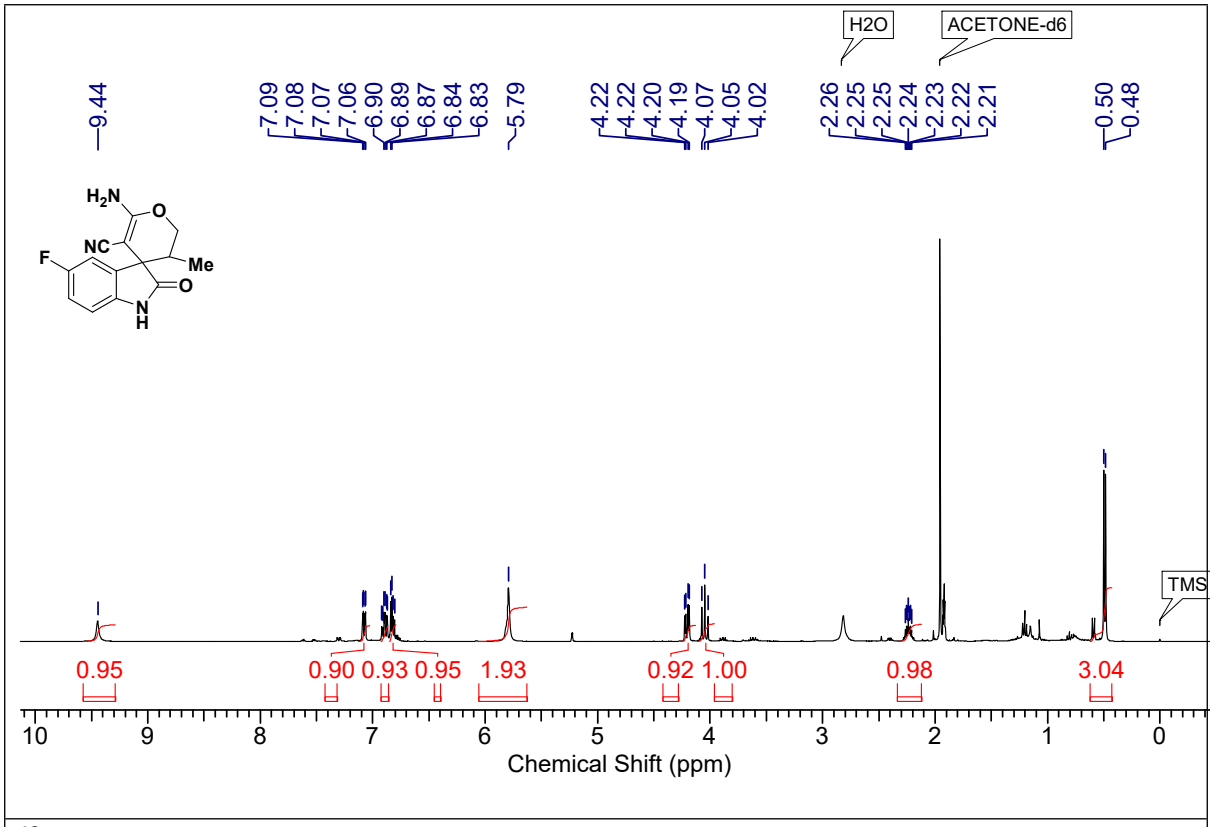
^{13}C NMR spectrum of compound 4Ac (101 MHz, Acetone-d_6)



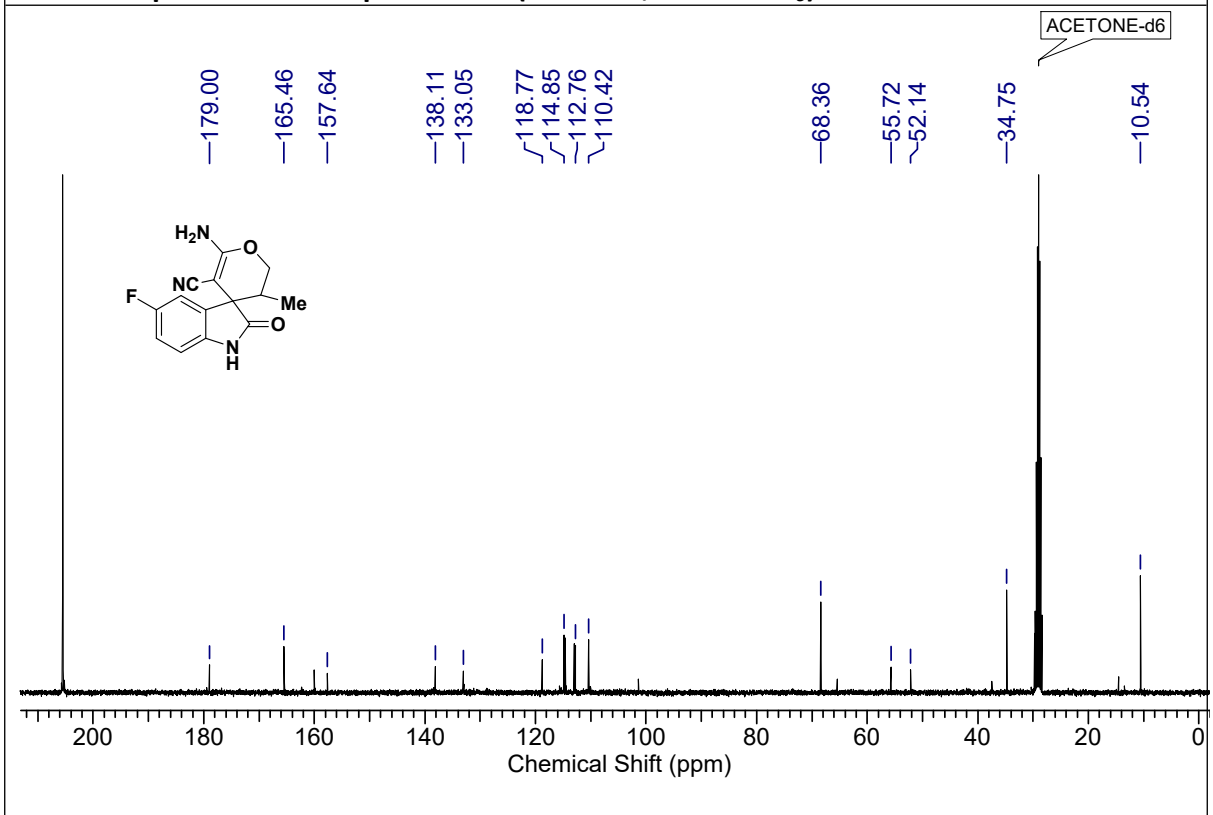
135 DEPT NMR spectrum of compound 4Ac



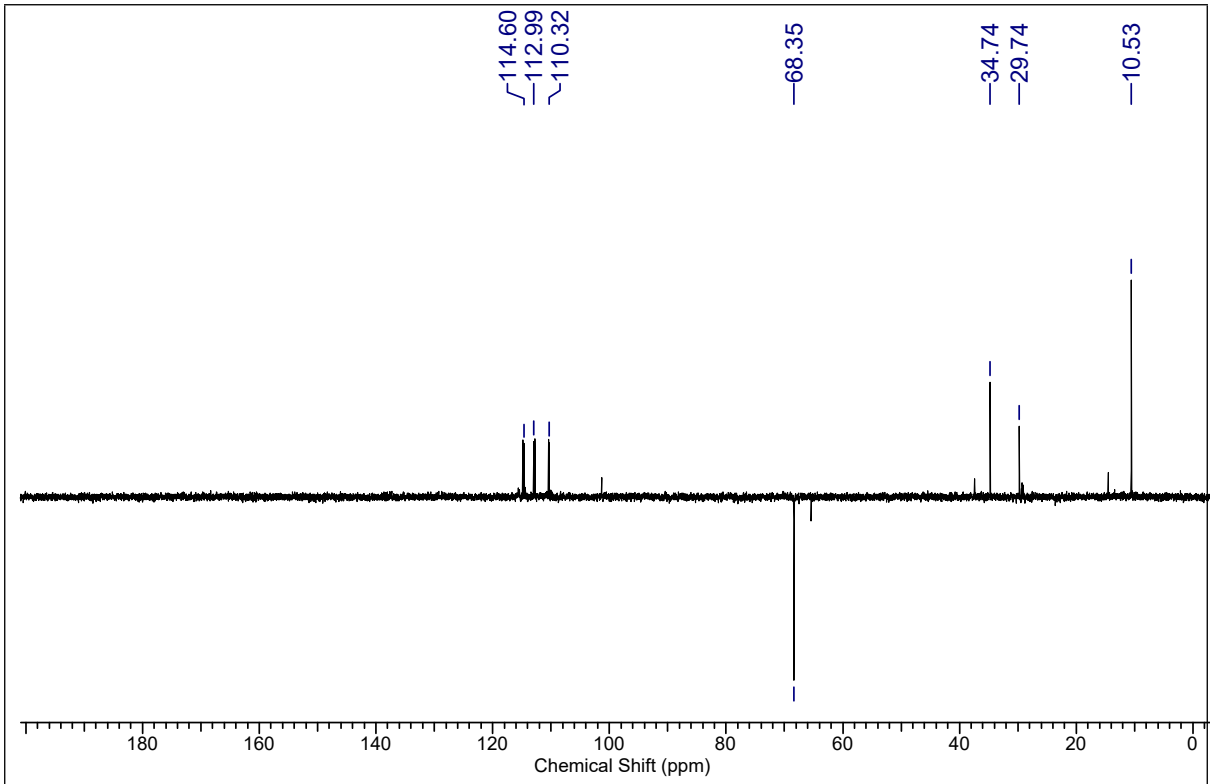
^{1}H NMR spectrum of compound 4Ad (400 MHz, Acetone-d_6)



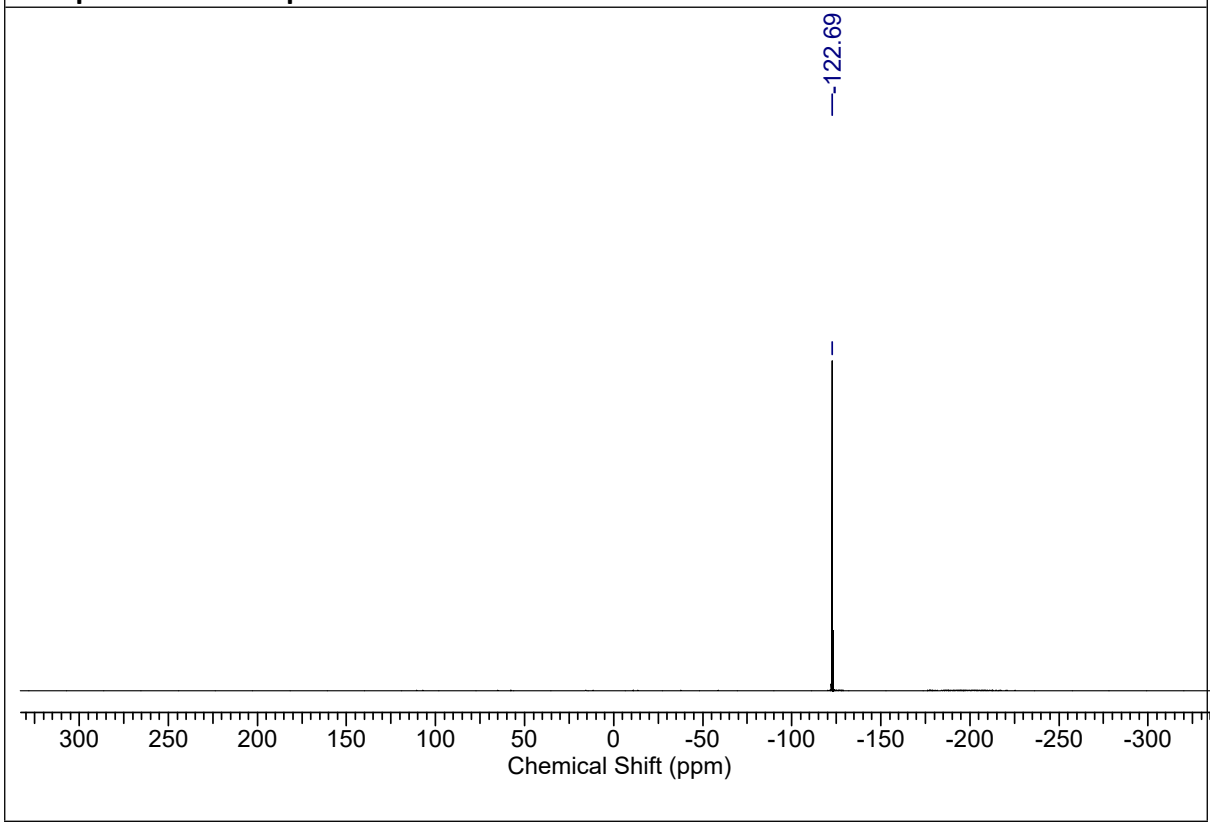
^{13}C NMR spectrum of compound 4Ad (101 MHz, Acetone-d_6)



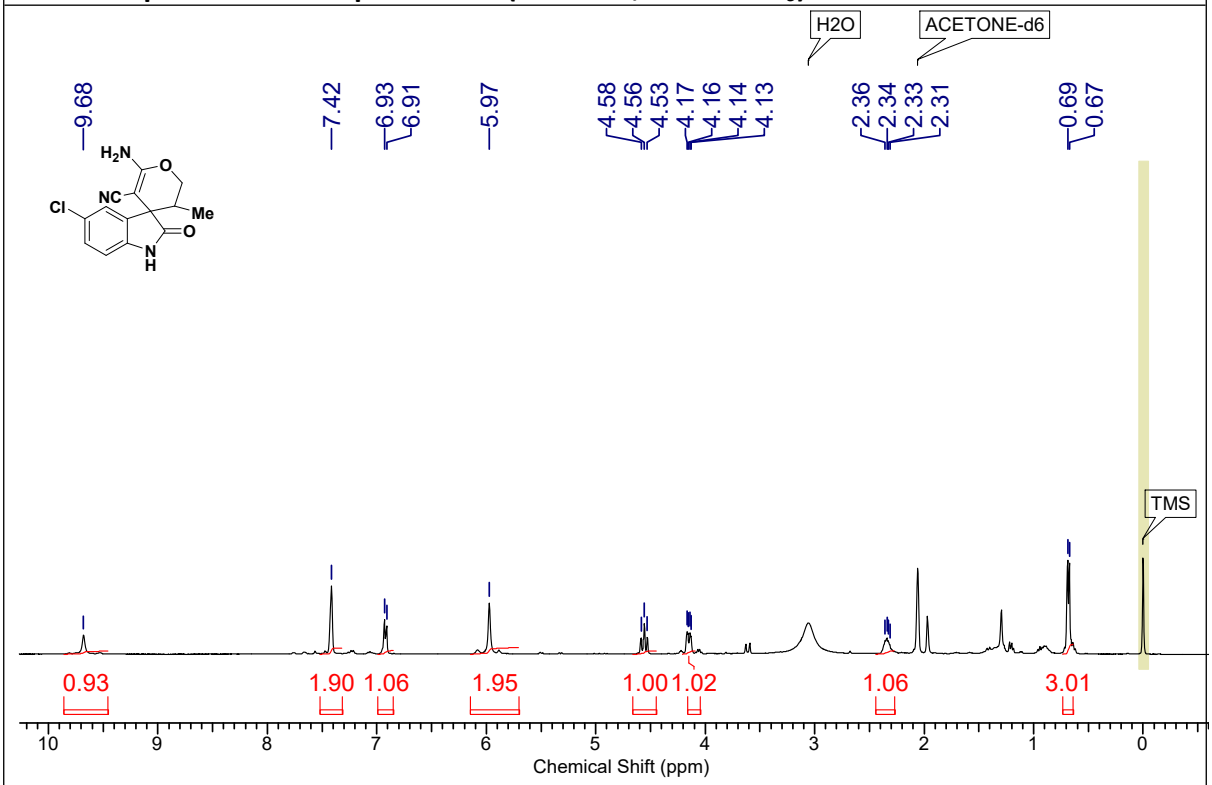
135 DEPT NMR spectrum of compound 4Ad



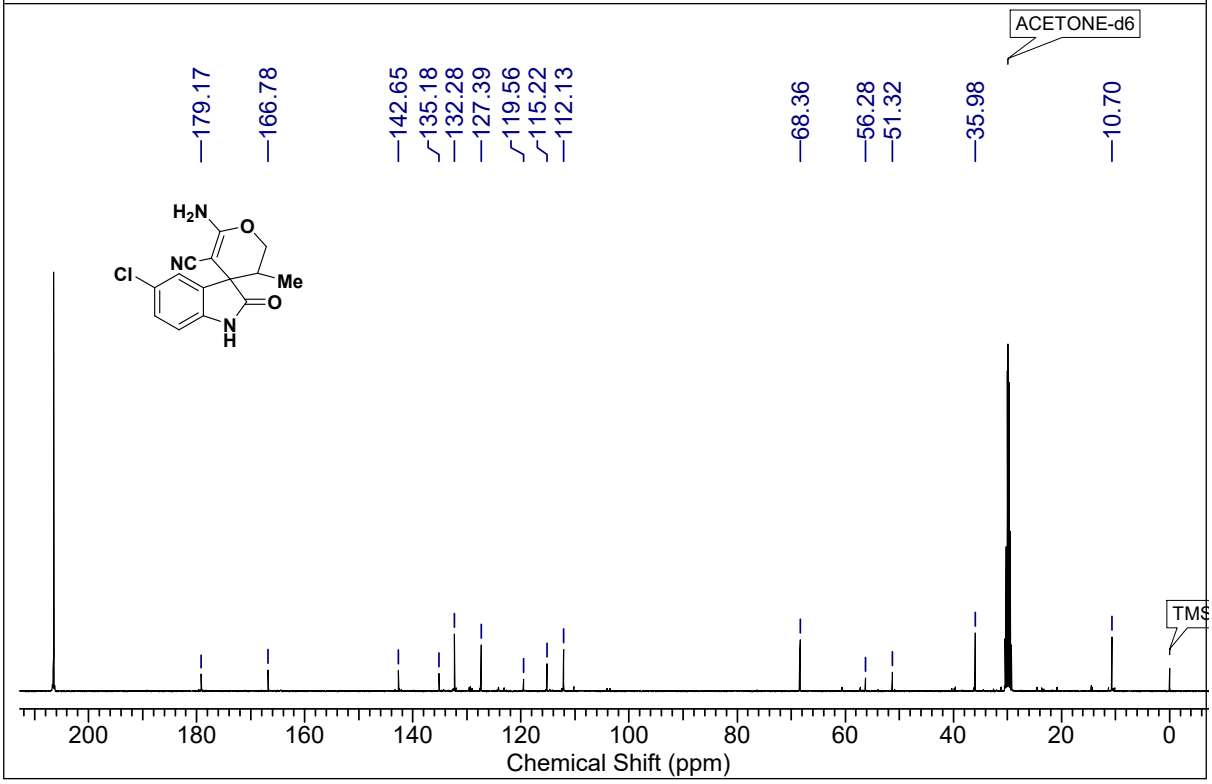
^{19}F spectrum of compound 4Ad



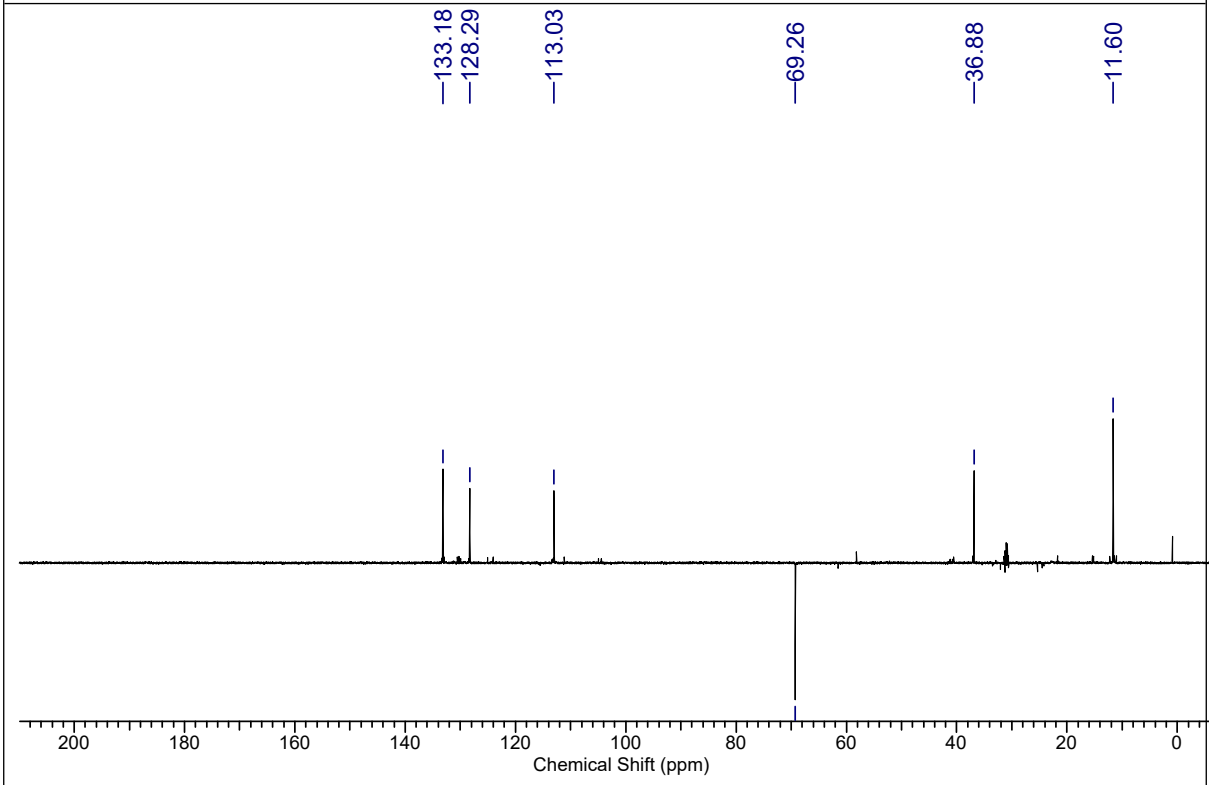
^{1}H NMR spectrum of compound 4Ae (400 MHz, Acetone-d_6)



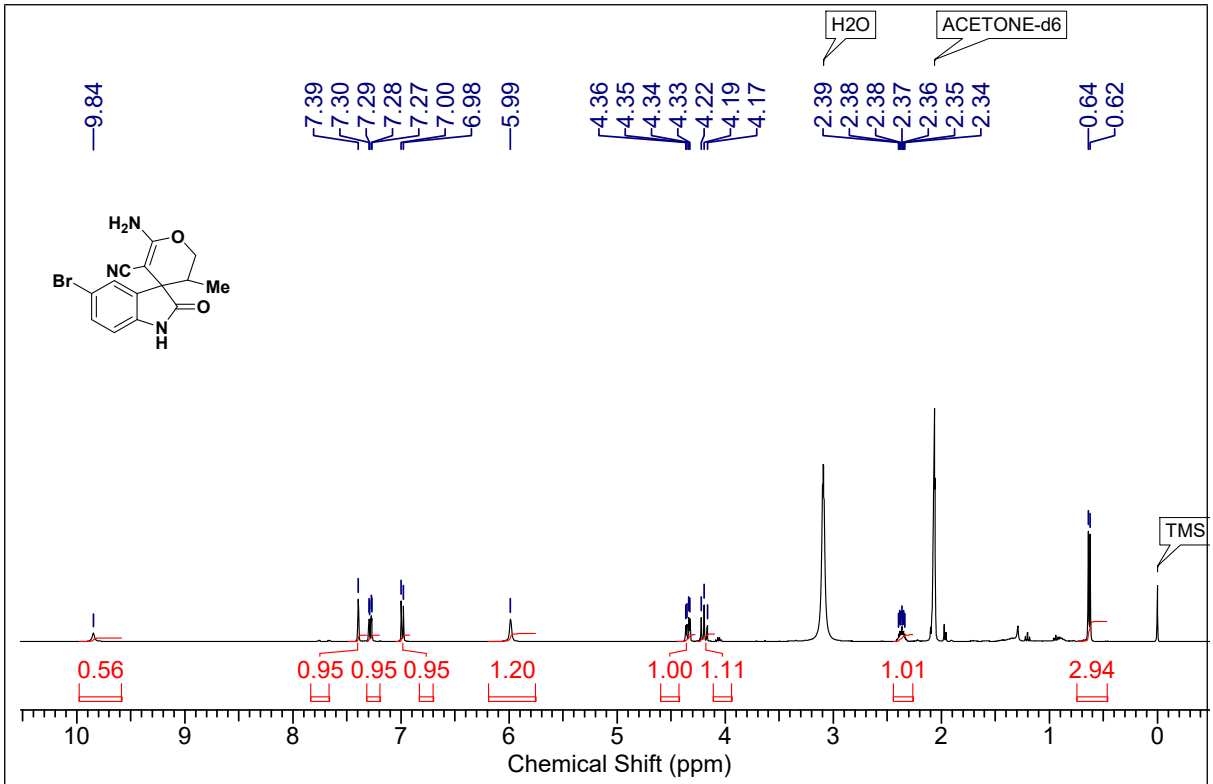
^{13}C NMR spectrum of compound 4Ae (101 MHz, Acetone-d_6)



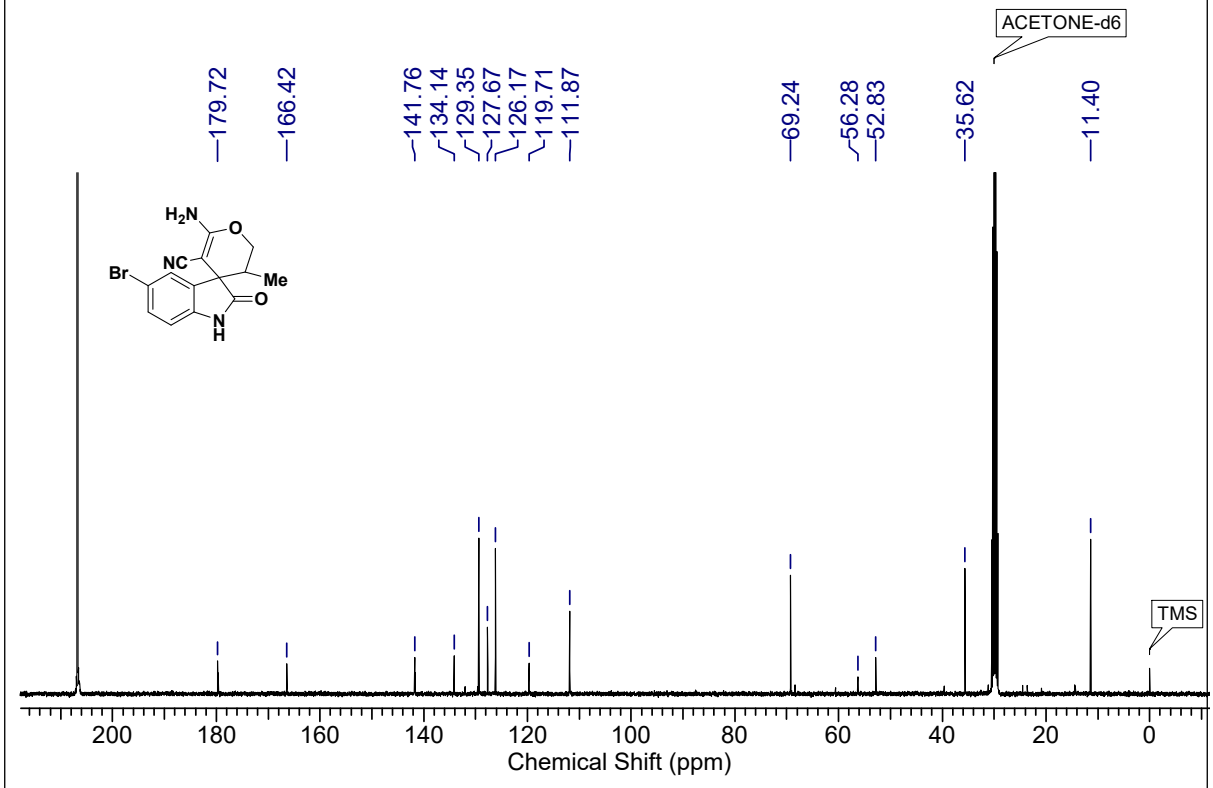
135 DEPT NMR spectrum of compound 4Ae



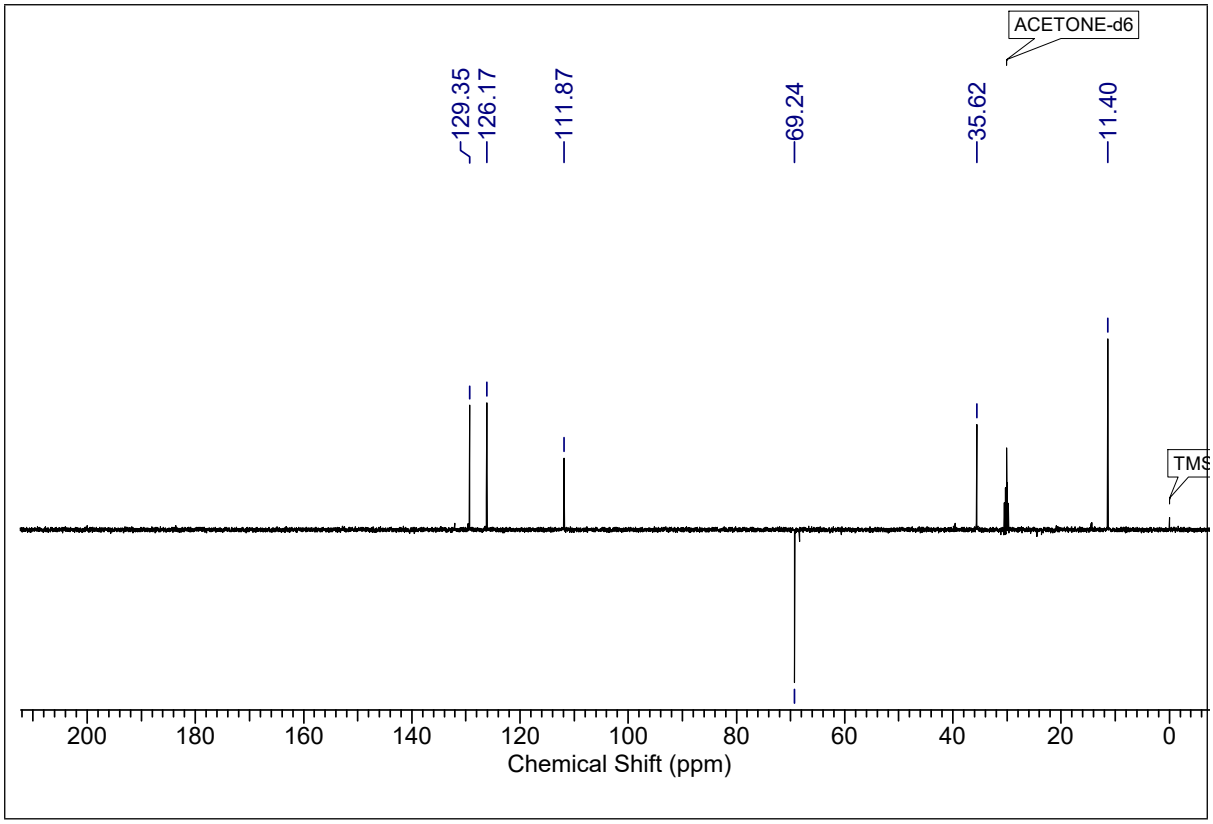
^{1}H NMR spectrum of compound 4Af (400 MHz, Acetone-d_6)



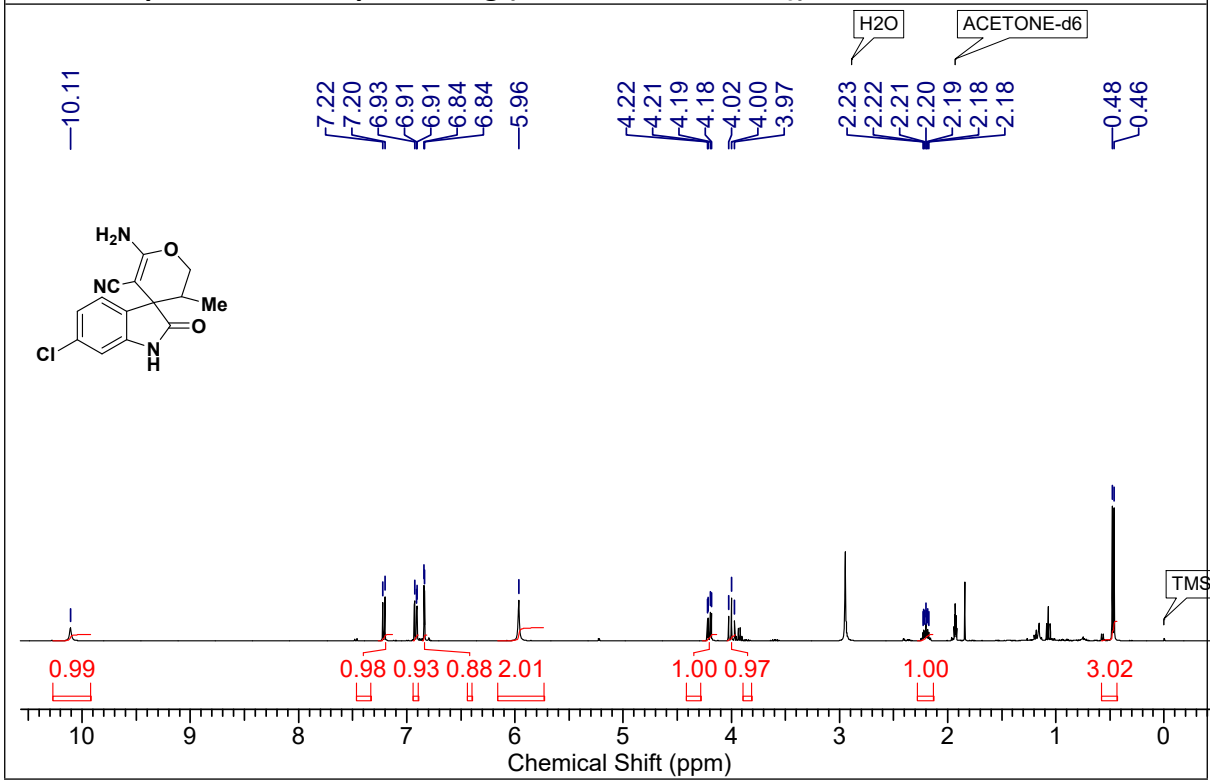
^{13}C NMR spectrum of compound 4Af (101 MHz, Acetone-d_6)



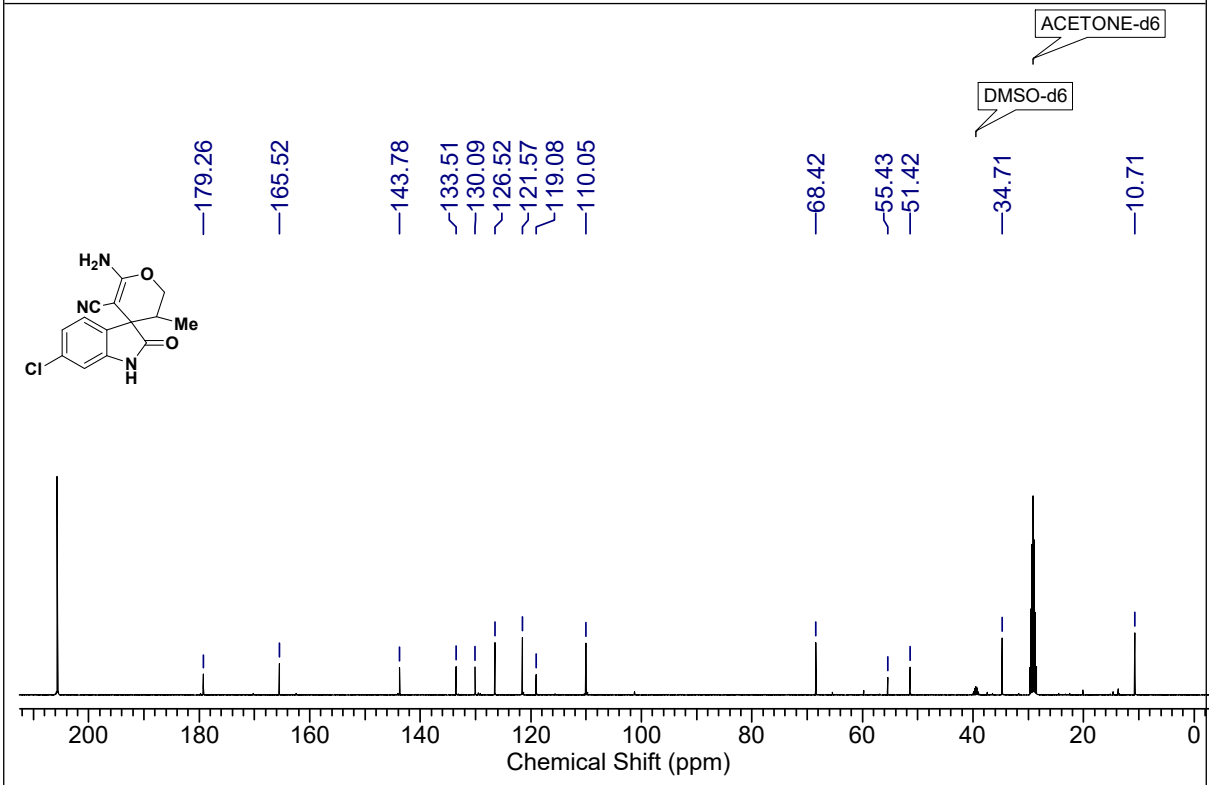
135 DEPT NMR spectrum of compound 4Af



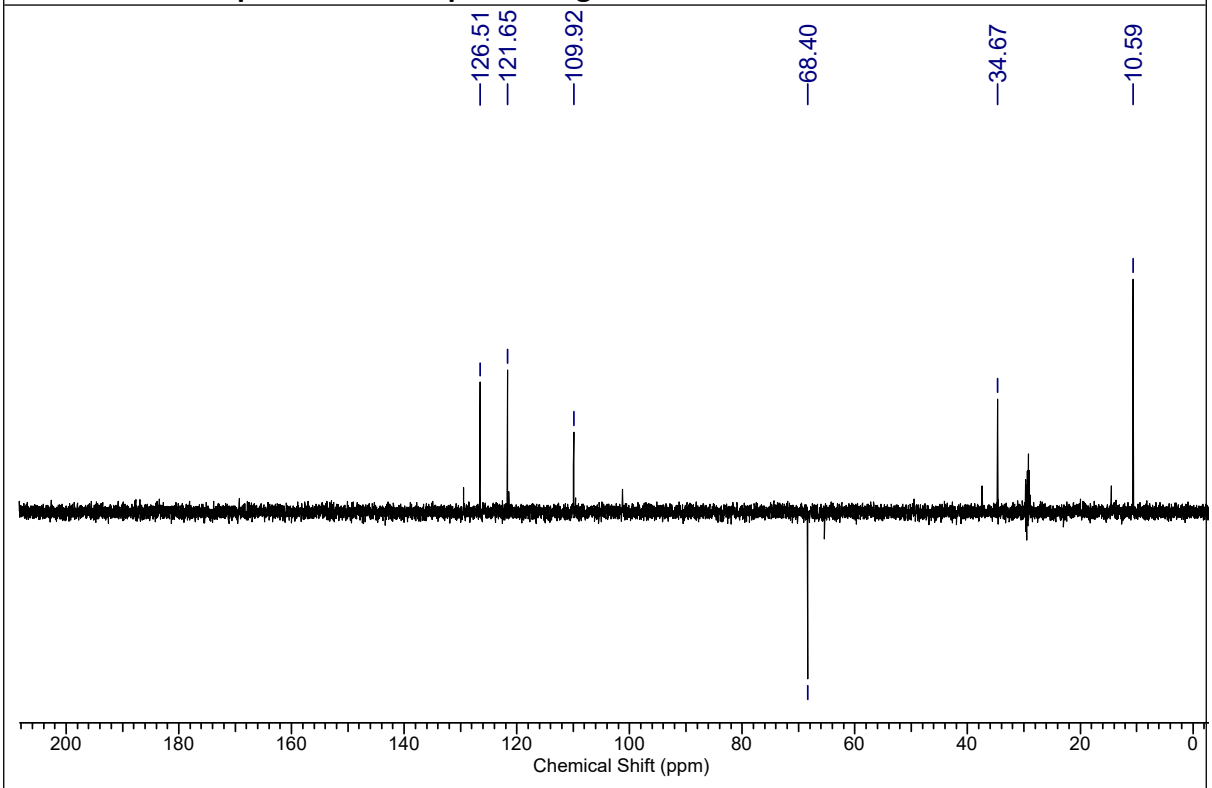
^{1}H NMR spectrum of compound 4Ag (400 MHz, Acetone-d_6)



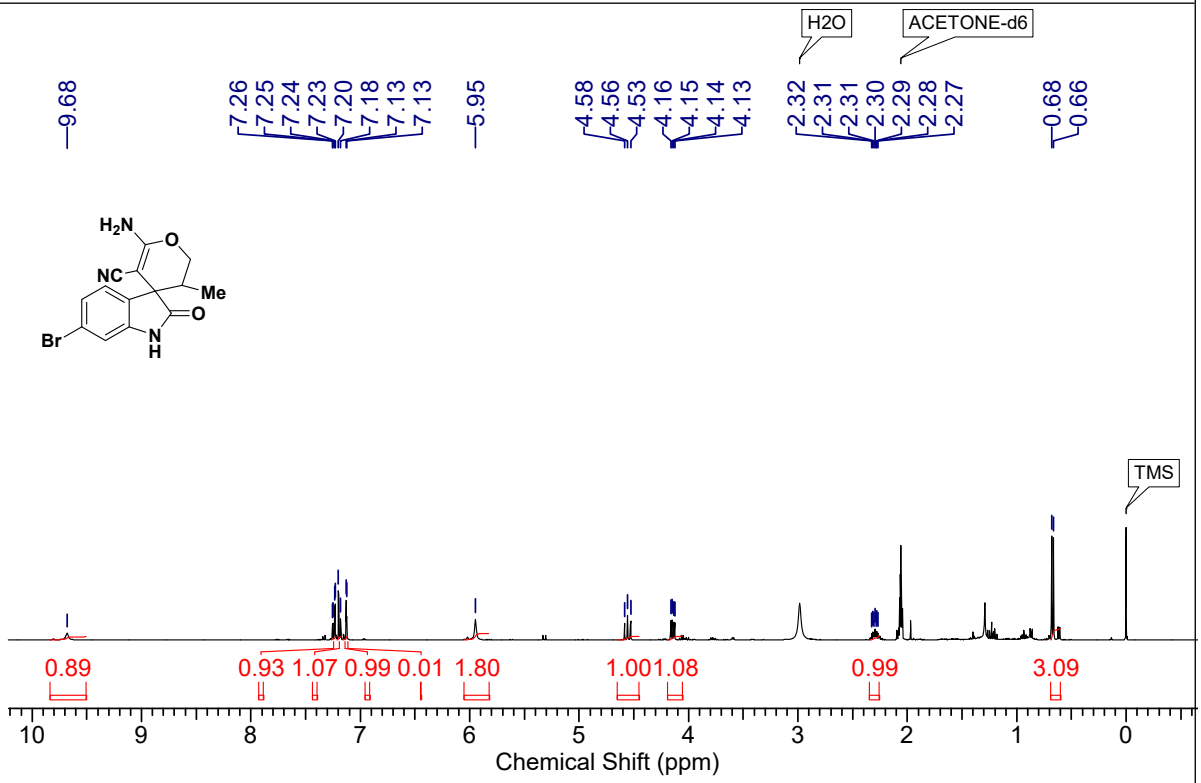
^{13}C NMR spectrum of compound 4Ag (101 MHz, Acetone-d_6)



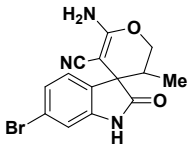
135 DEPT NMR spectrum of compound 4Ag

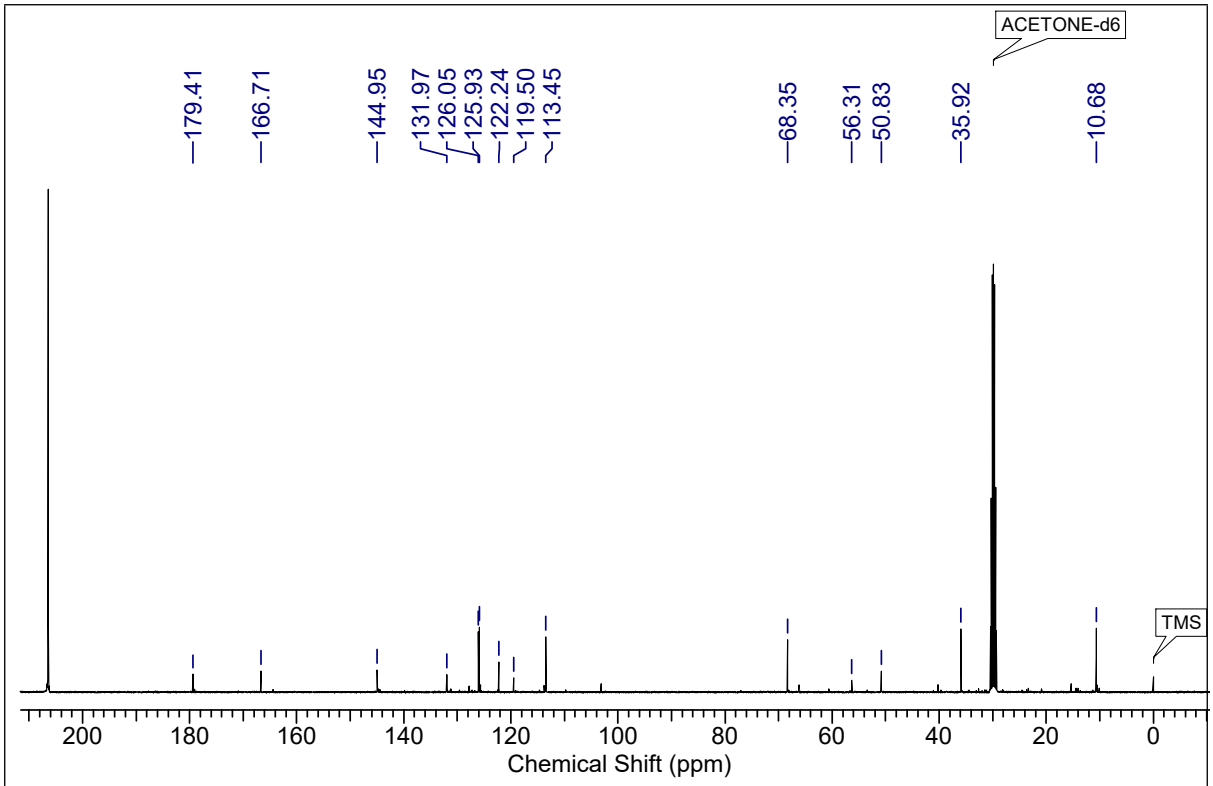


^{1}H NMR spectrum of compound 4Ah (400 MHz, Acetone-d_6)

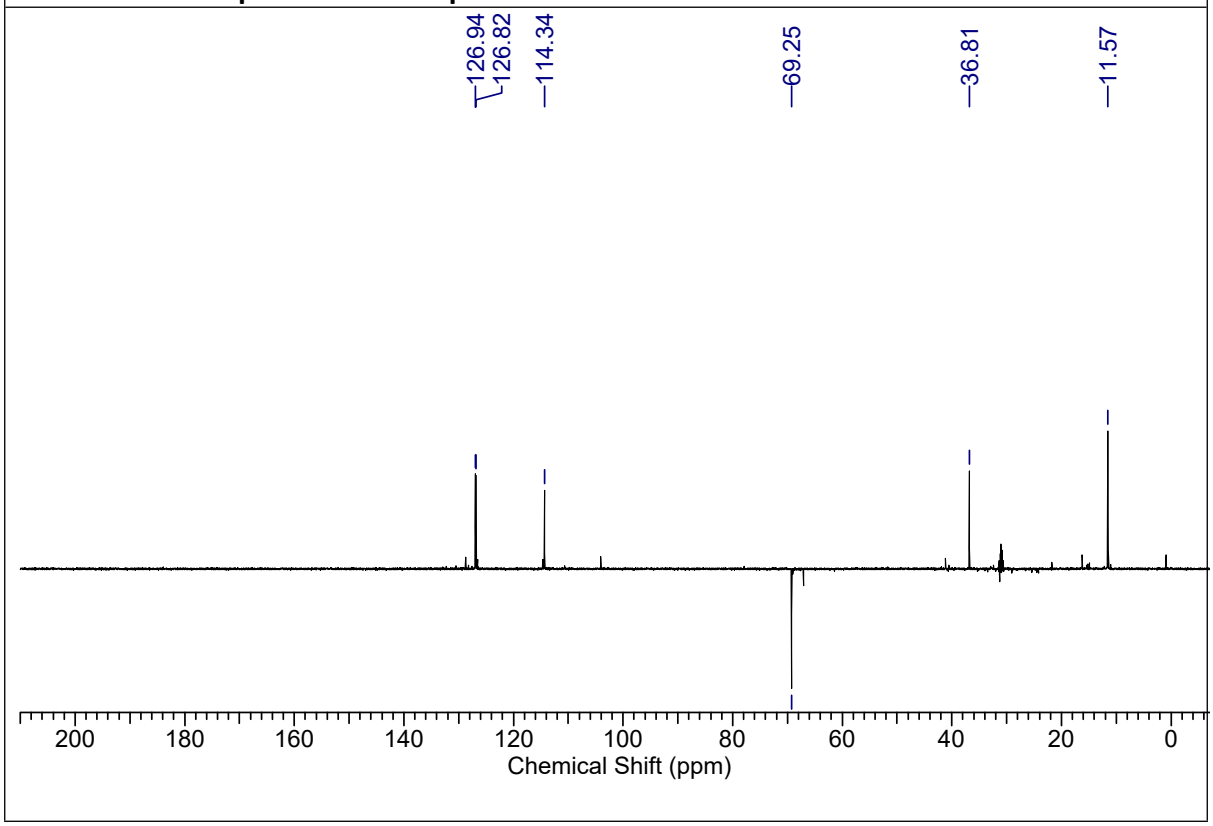


^{13}C NMR spectrum of compound 4Ah (101 MHz, Acetone-d_6)

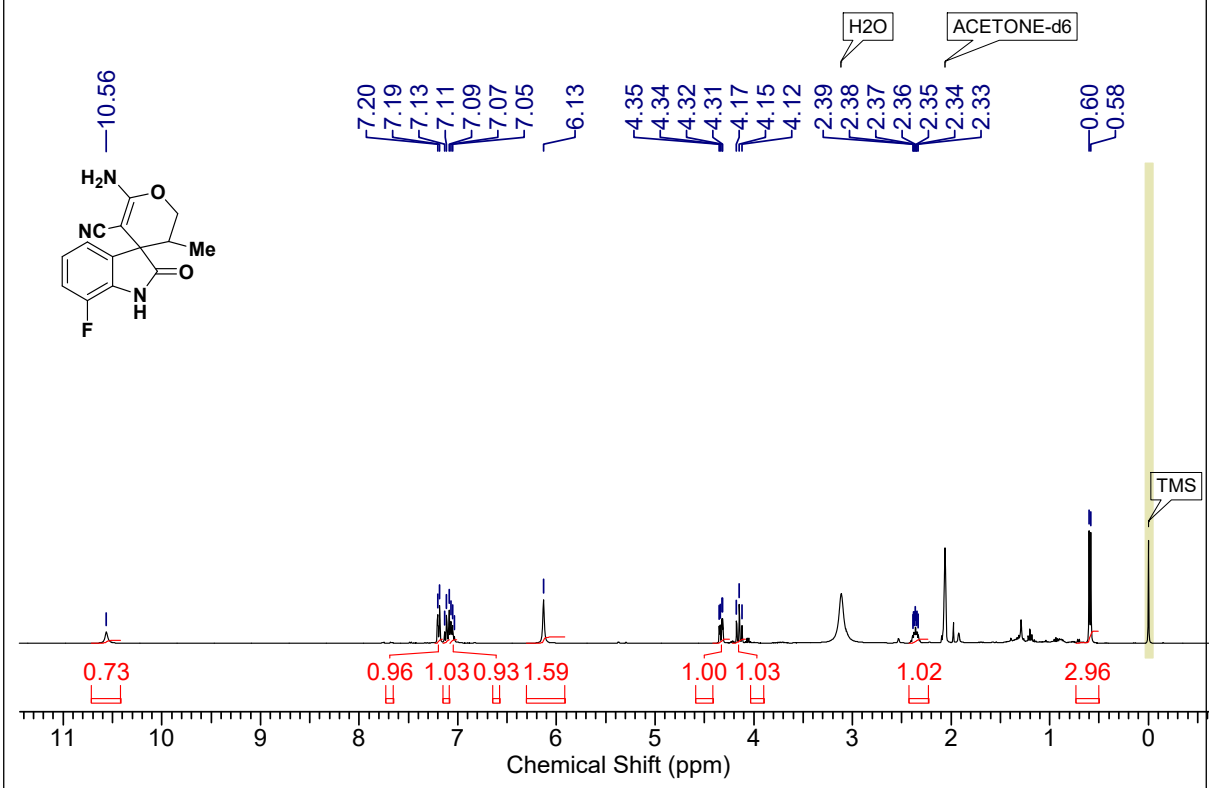




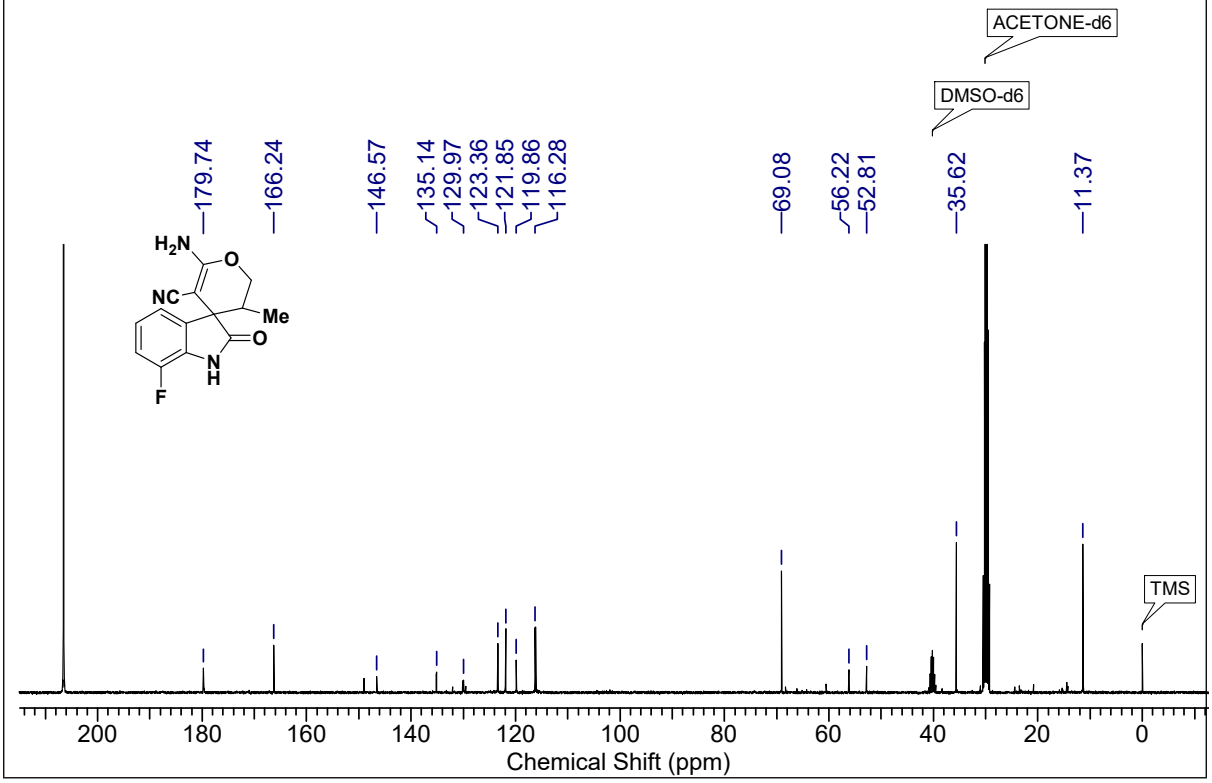
135 DEPT NMR spectrum of compound 4Ah



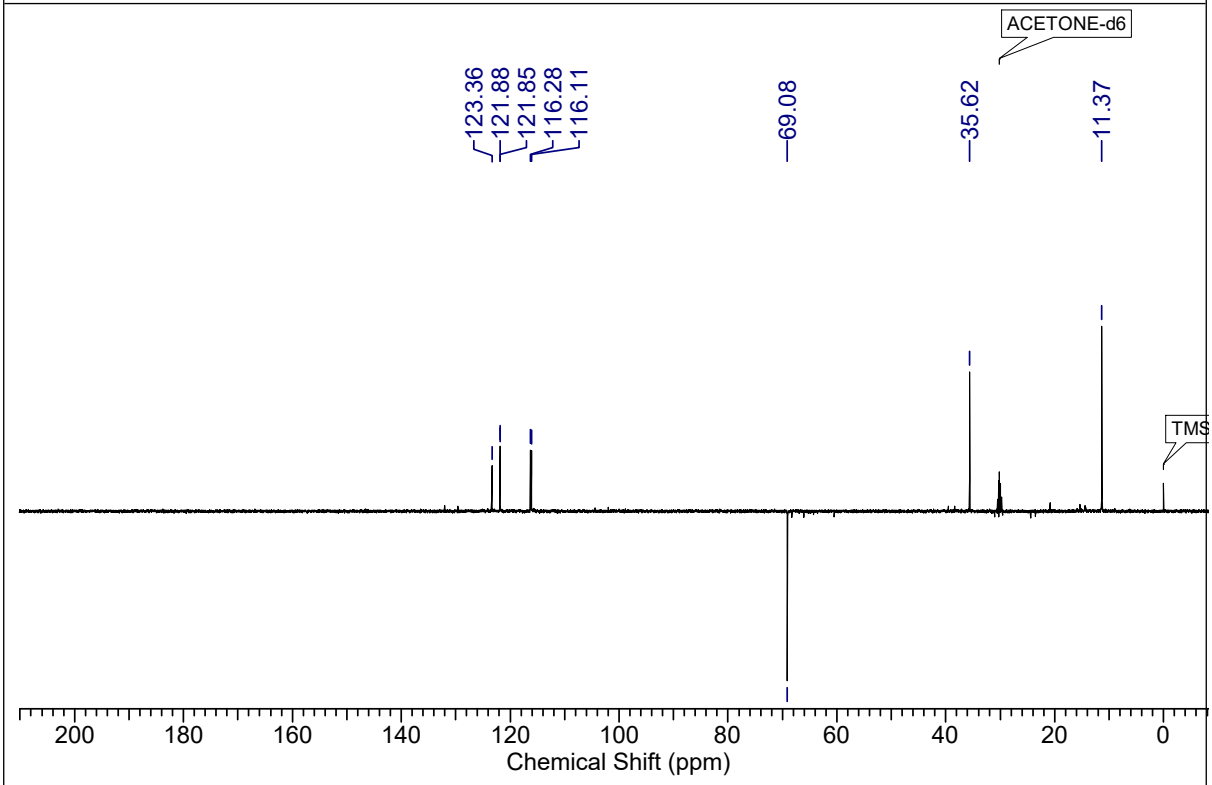
^{1}H NMR spectrum of compound 4Ai (400 MHz, Acetone-d_6)



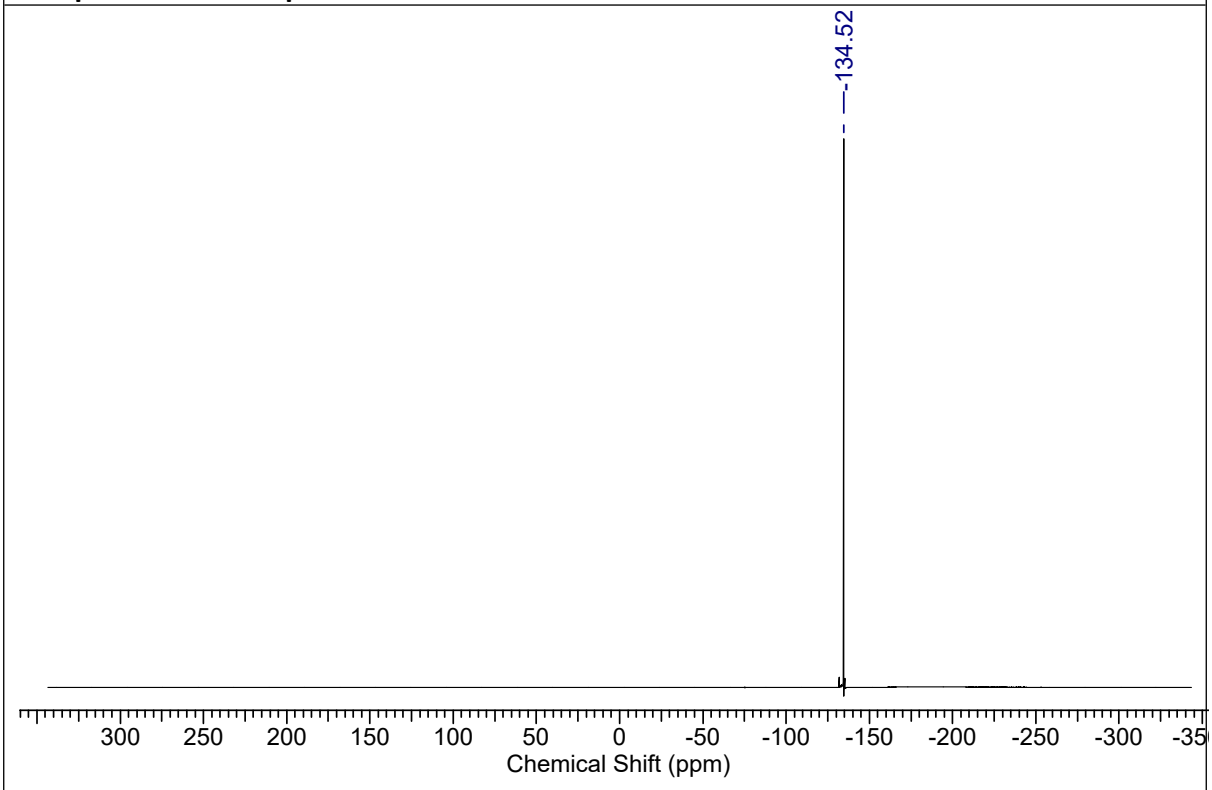
^{13}C NMR spectrum of compound 4Ai (101 MHz, Acetone-d_6)



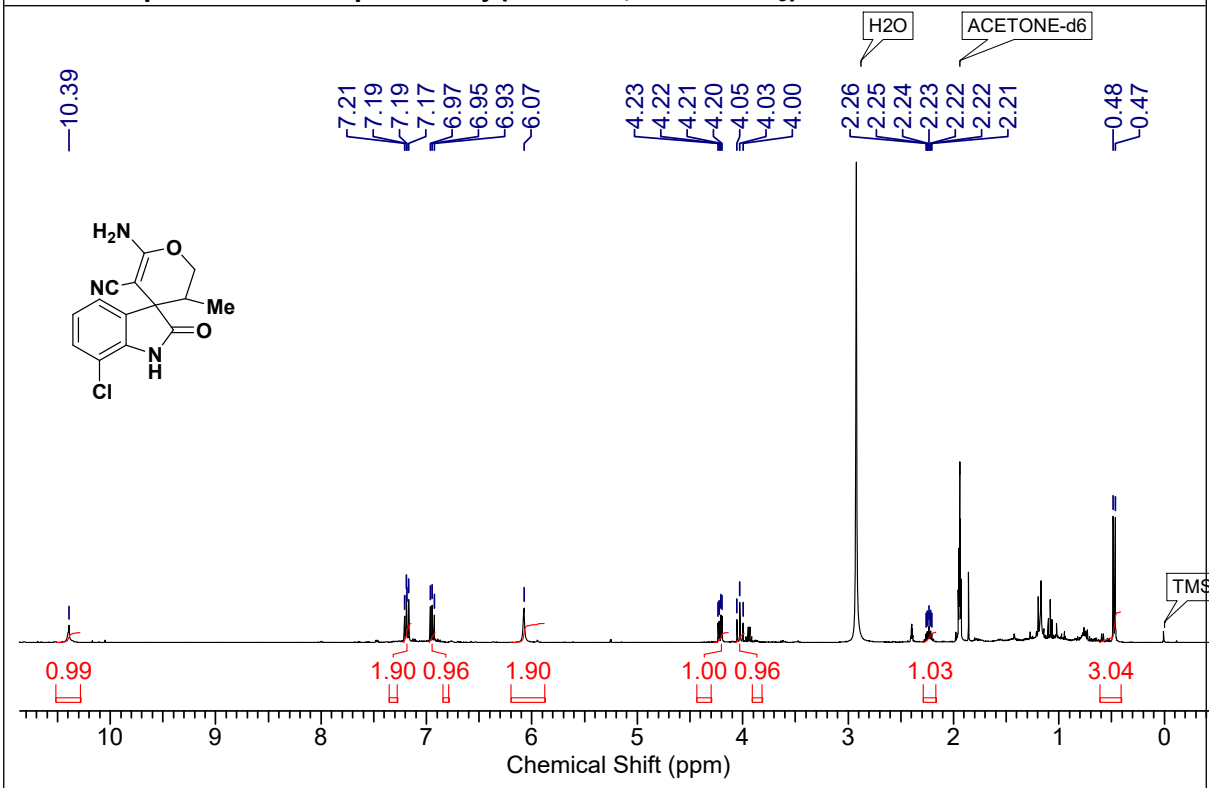
135 DEPT NMR spectrum of compound 4Ai



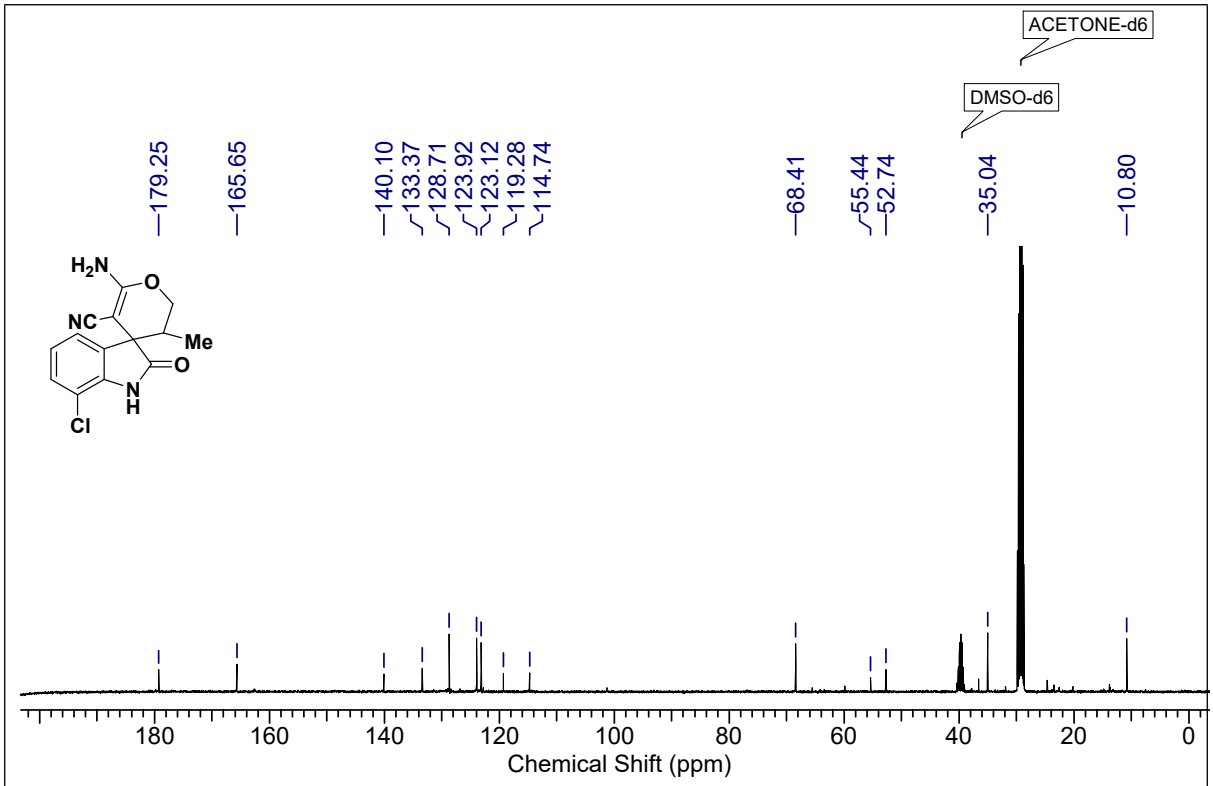
^{19}F spectrum of compound 4Ai



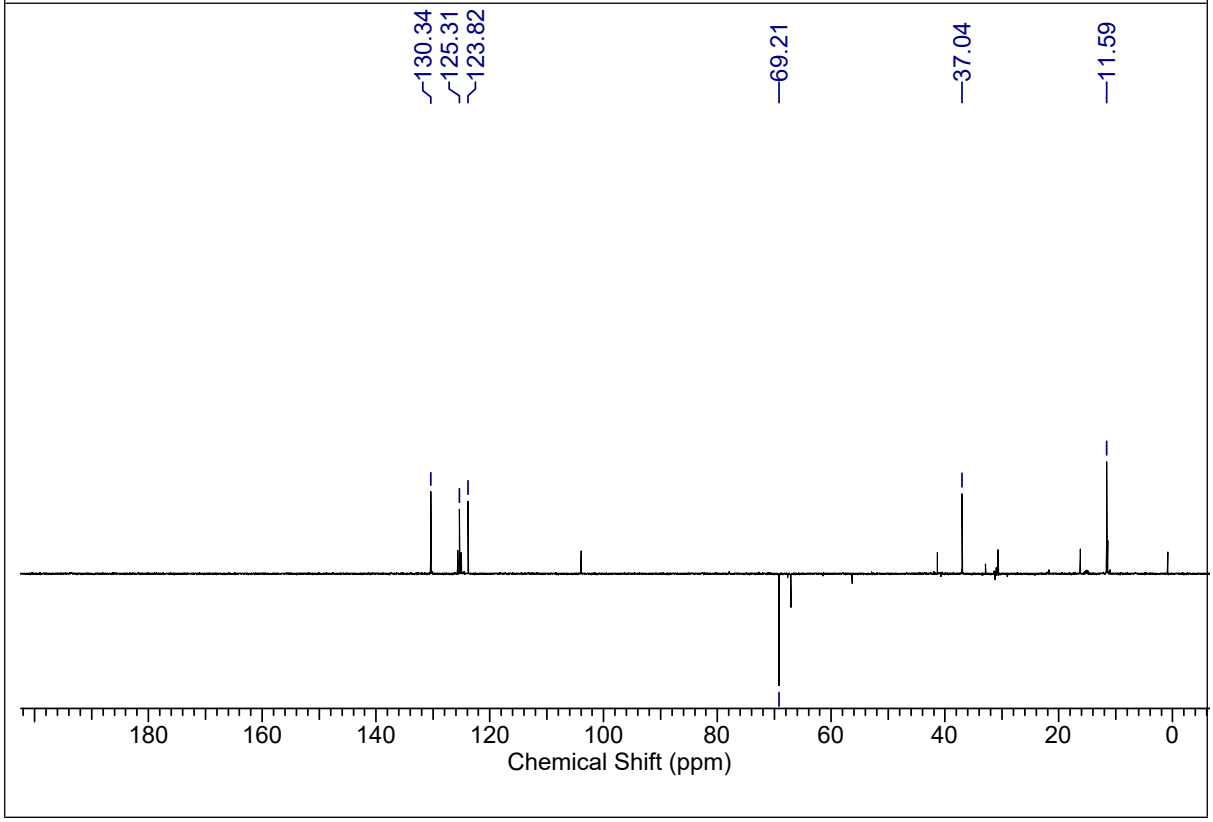
^{1}H NMR spectrum of compound 4Aj (400 MHz, Acetone-d_6)



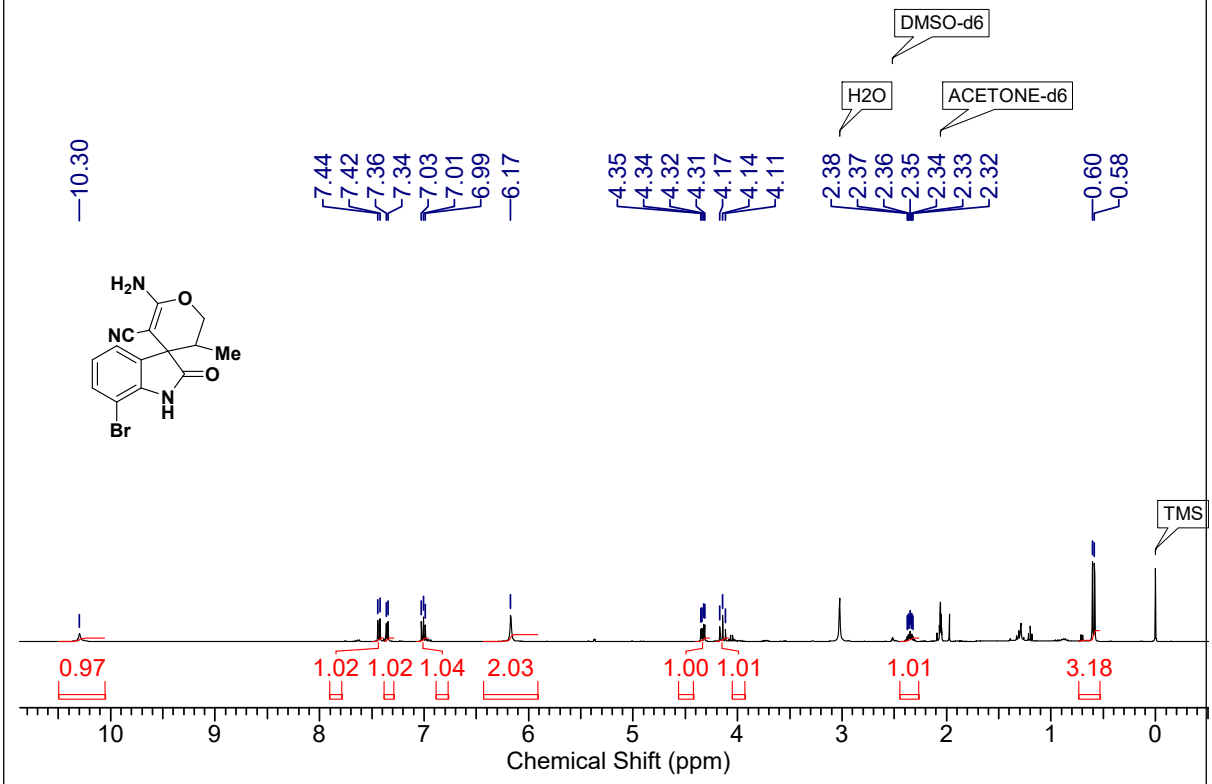
^{13}C NMR spectrum of compound 4Aj (101 MHz, Acetone-d_6)



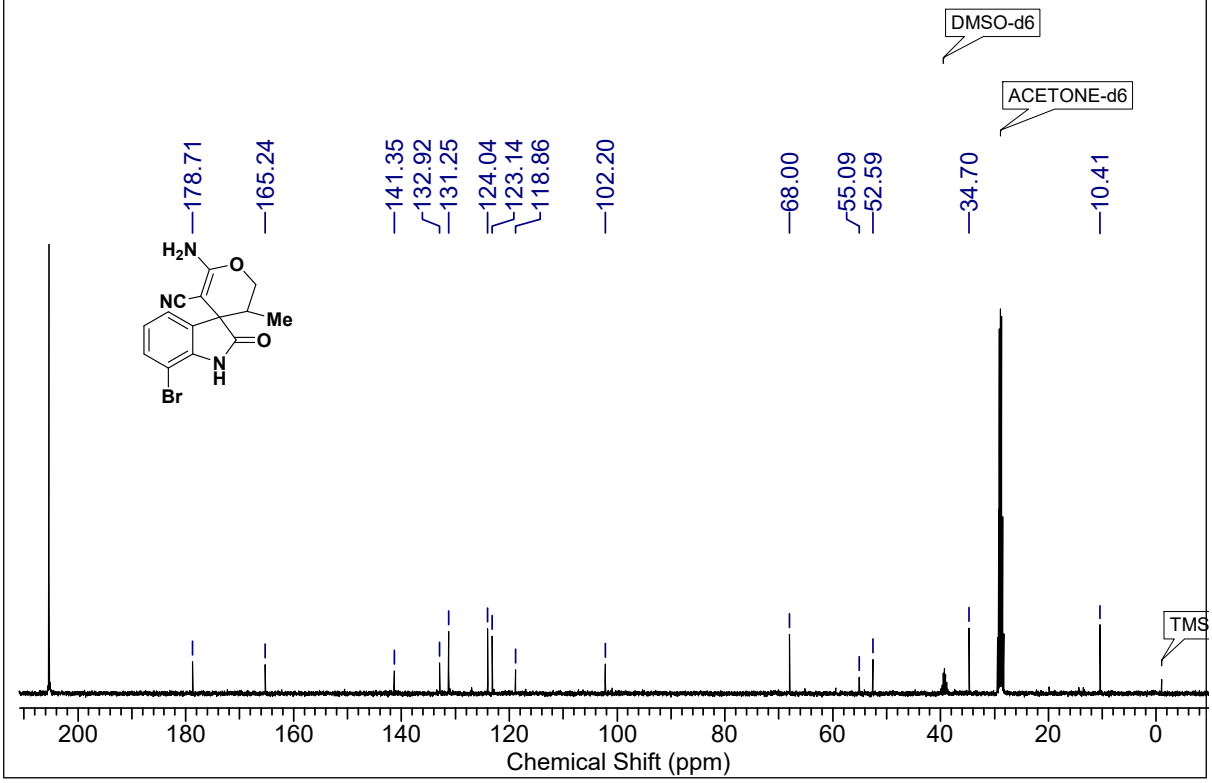
135 DEPT NMR spectrum of compound 4Aj



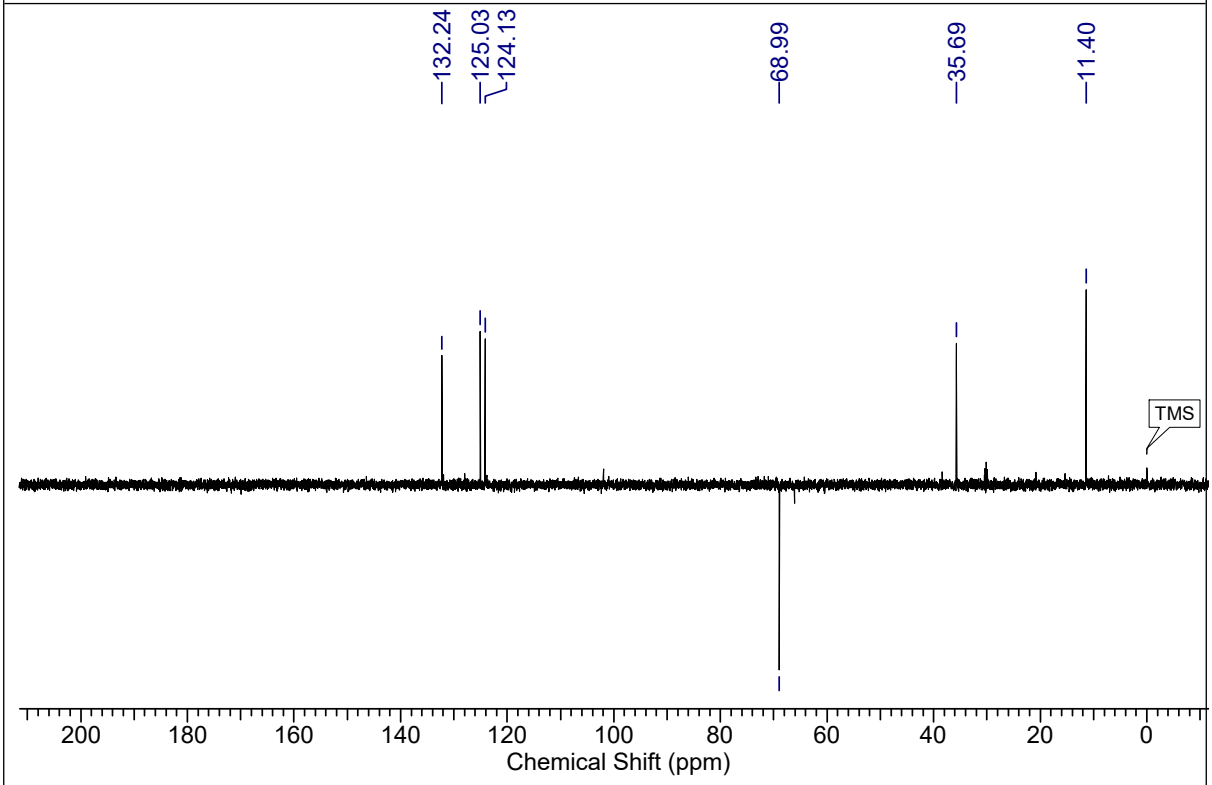
^{1}H NMR spectrum of compound 4Ak (400 MHz, Acetone-d_6)



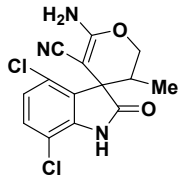
^{13}C NMR spectrum of compound 4Ak (101 MHz, Acetone-d_6)

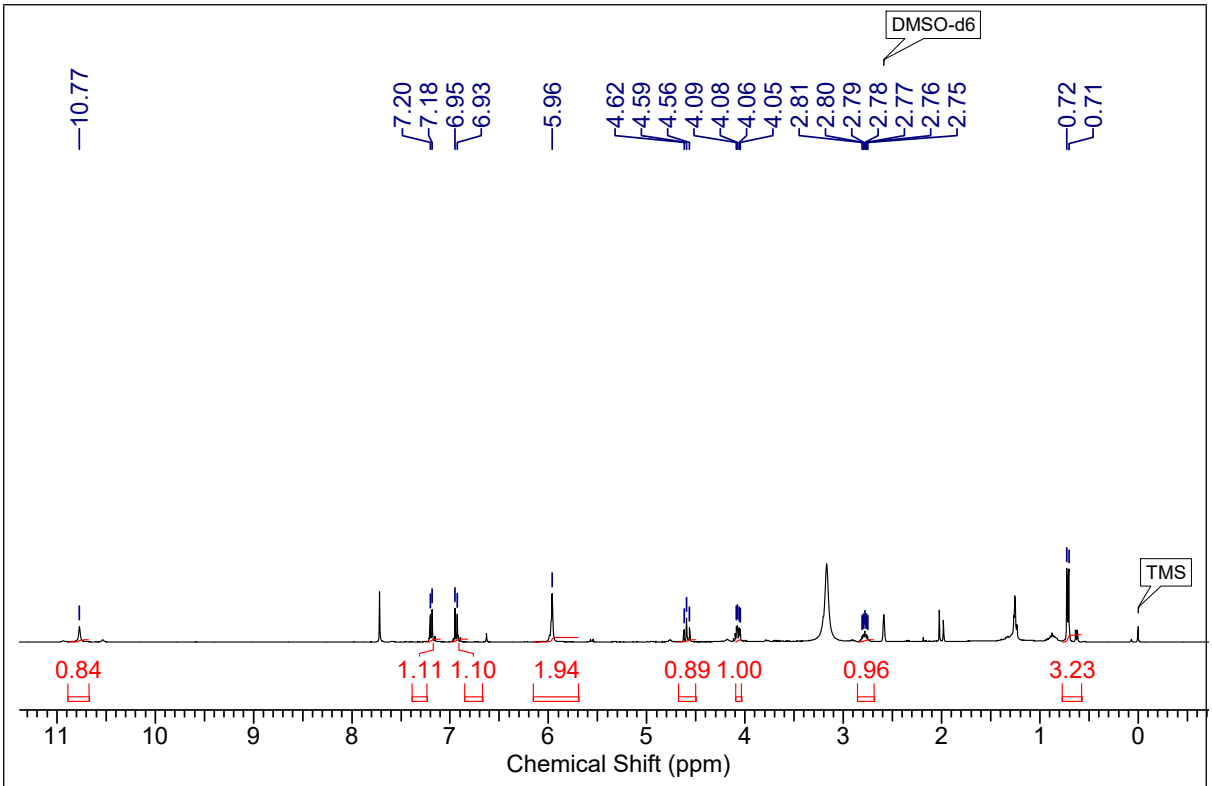


135 DEPT NMR spectrum of compound 4Ak

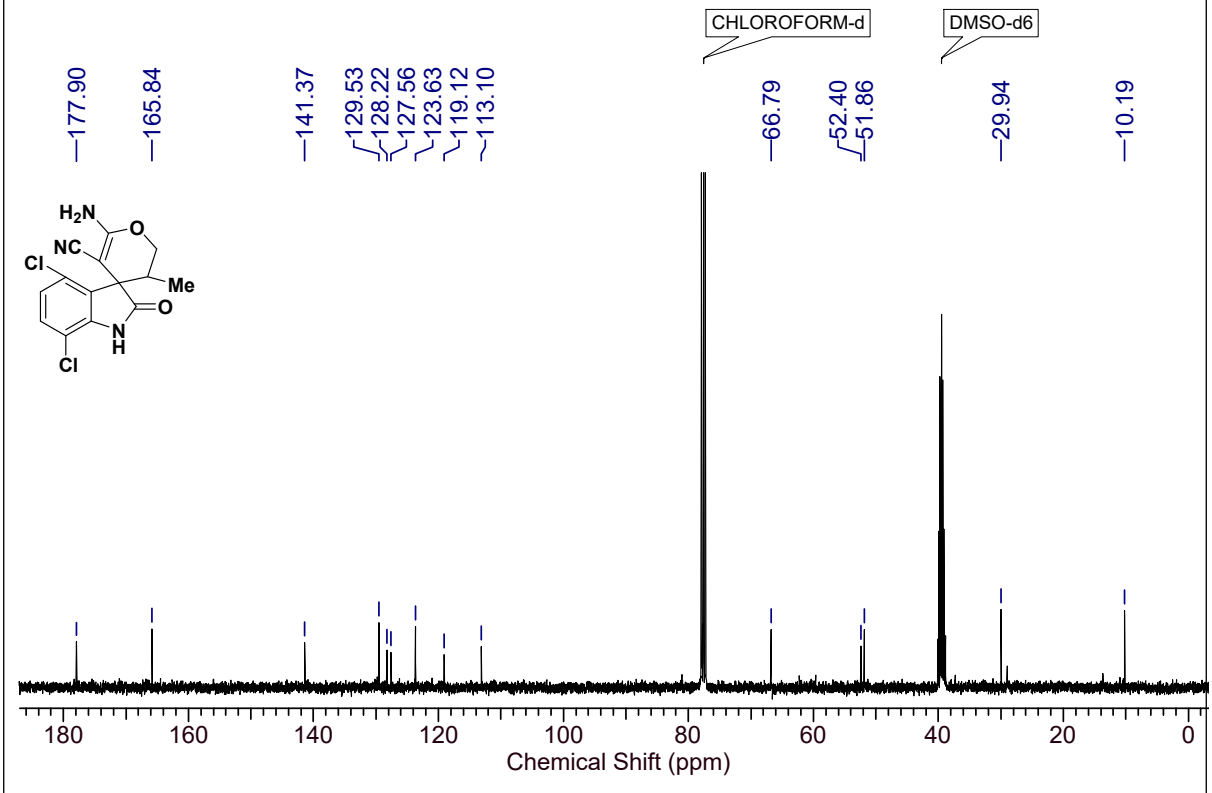


^{1}H NMR spectrum of compound 4Al (400 MHz, Acetone-d_6)

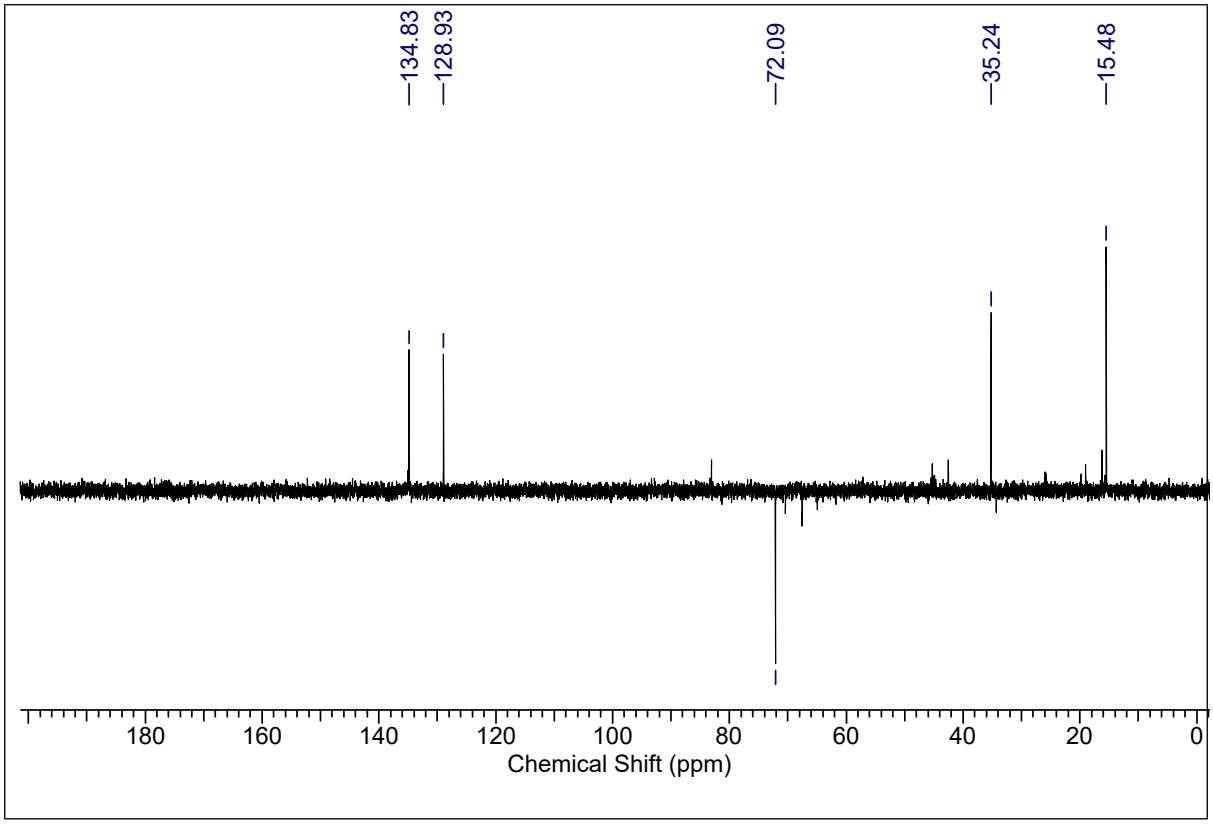




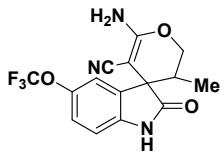
^{13}C NMR spectrum of compound 4Al (101 MHz, Acetone-d_6)

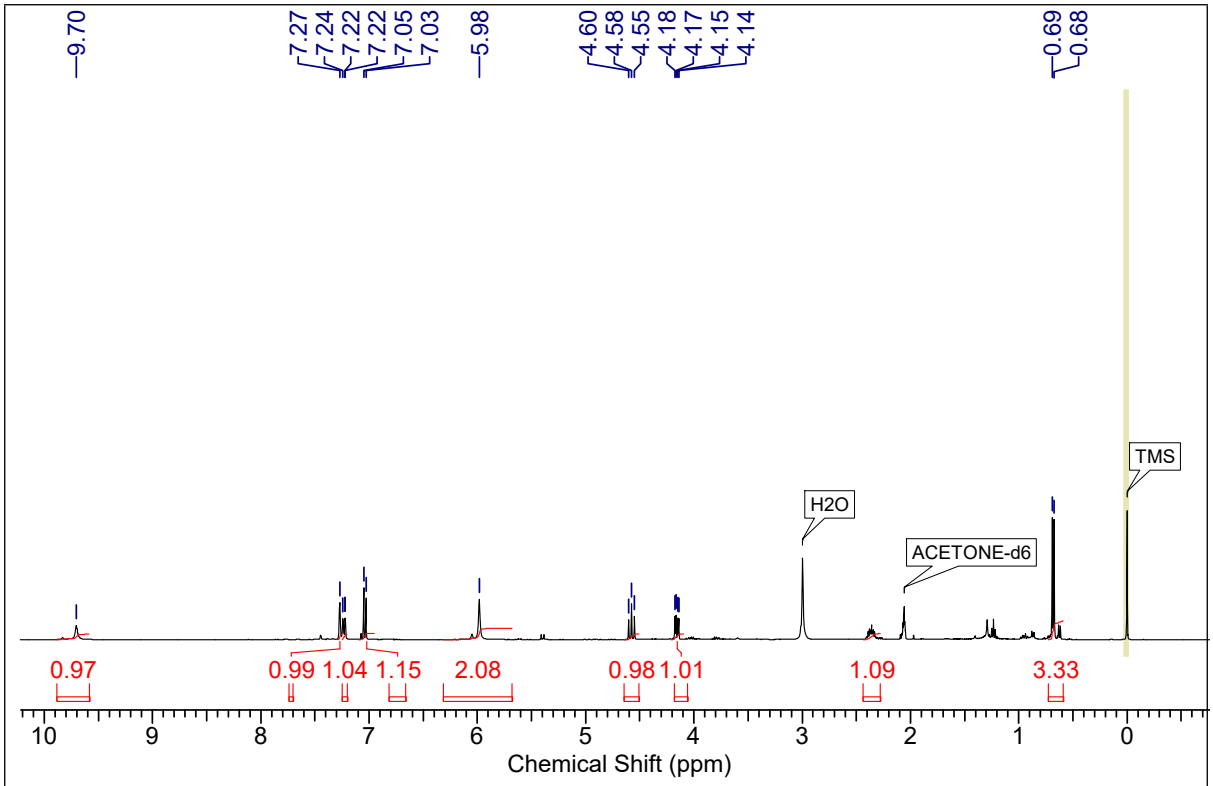


135 DEPT NMR spectrum of compound 4Al

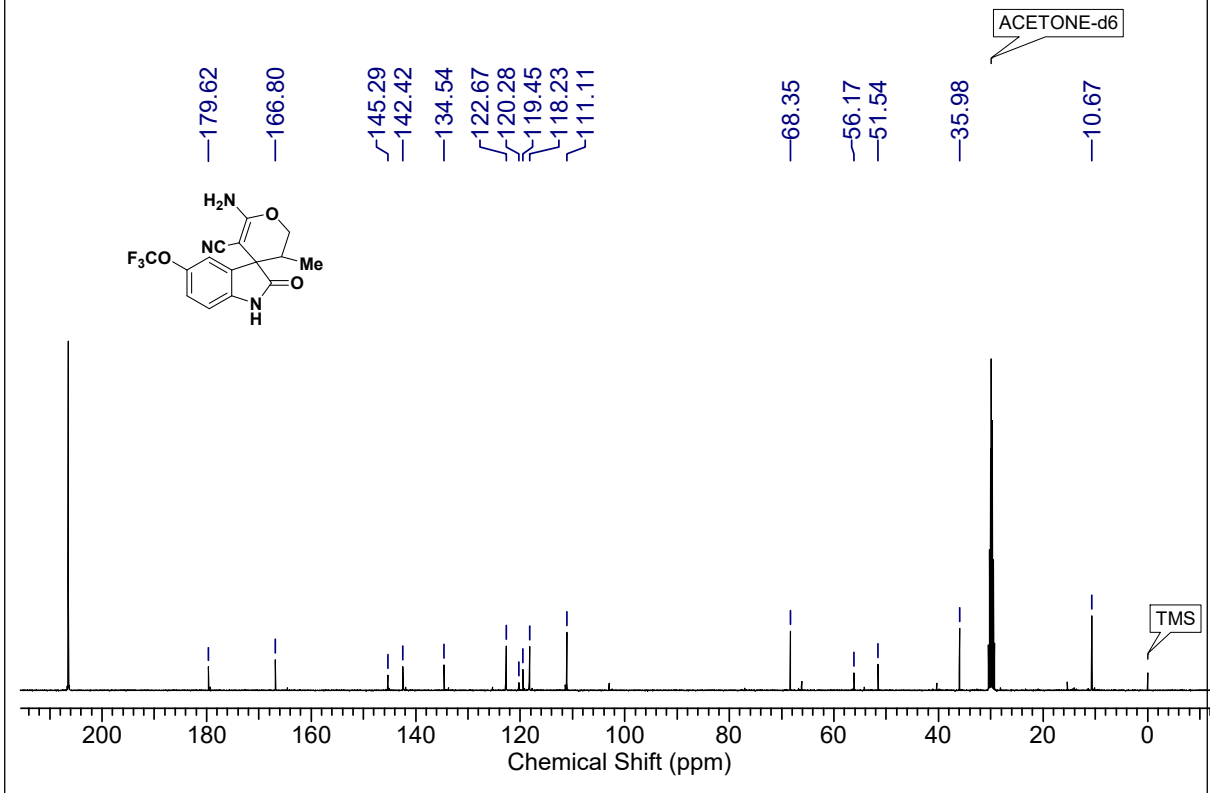


^{1}H NMR spectrum of compound 4Am (400 MHz, Acetone-d_6)

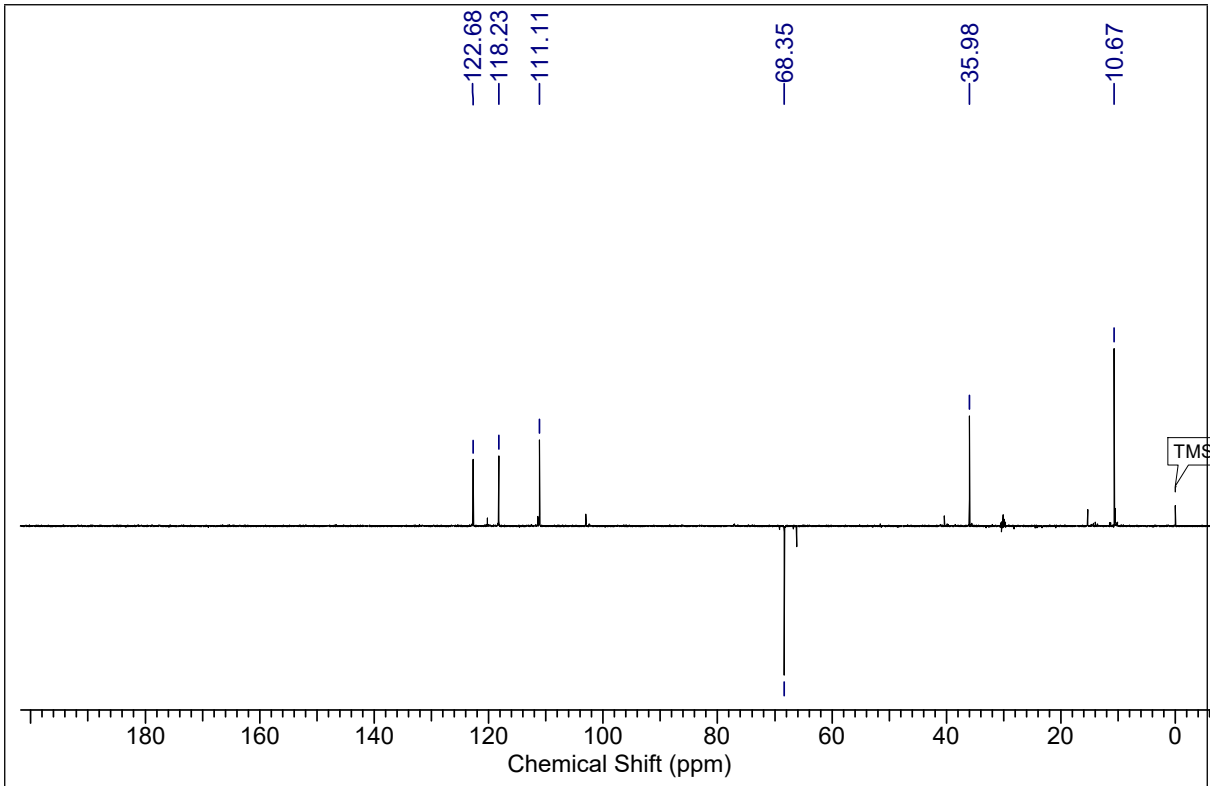




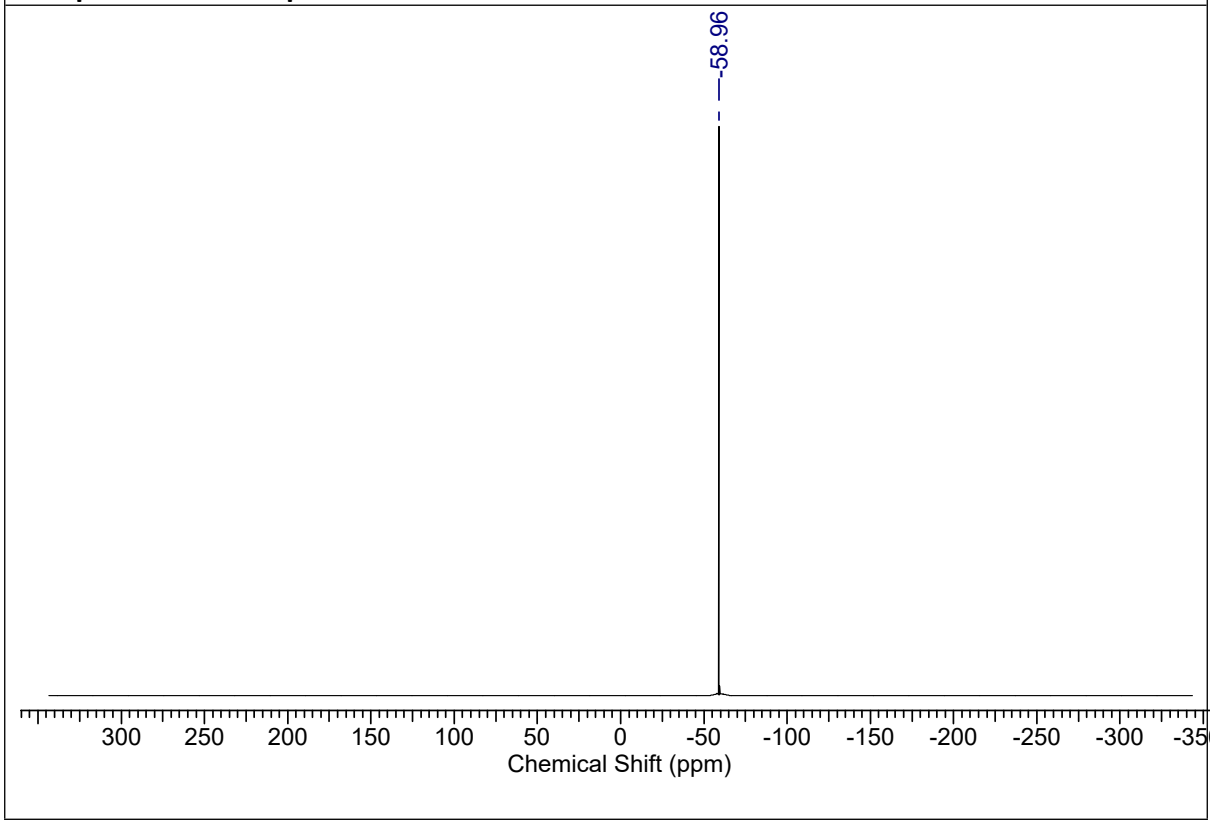
^{13}C NMR spectrum of compound 4Am (101 MHz, Acetone-d_6)



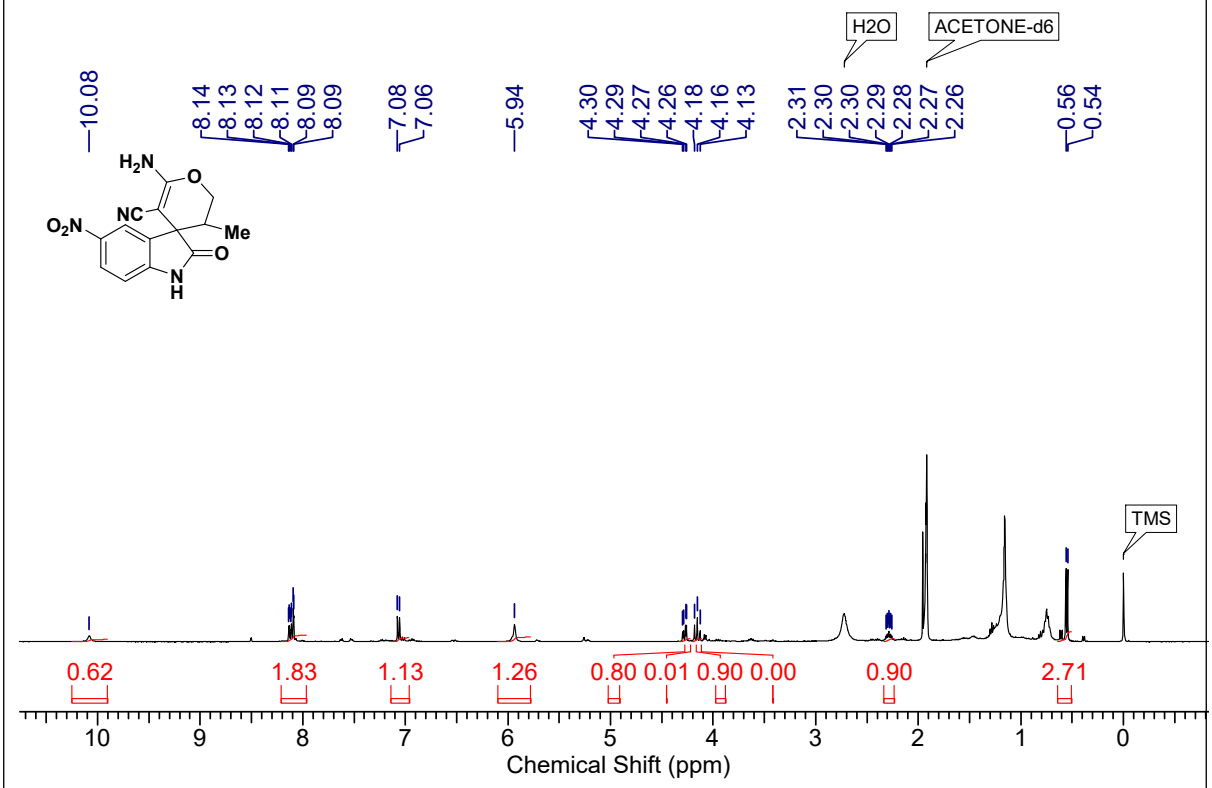
135 DEPT NMR spectrum of compound 4Am



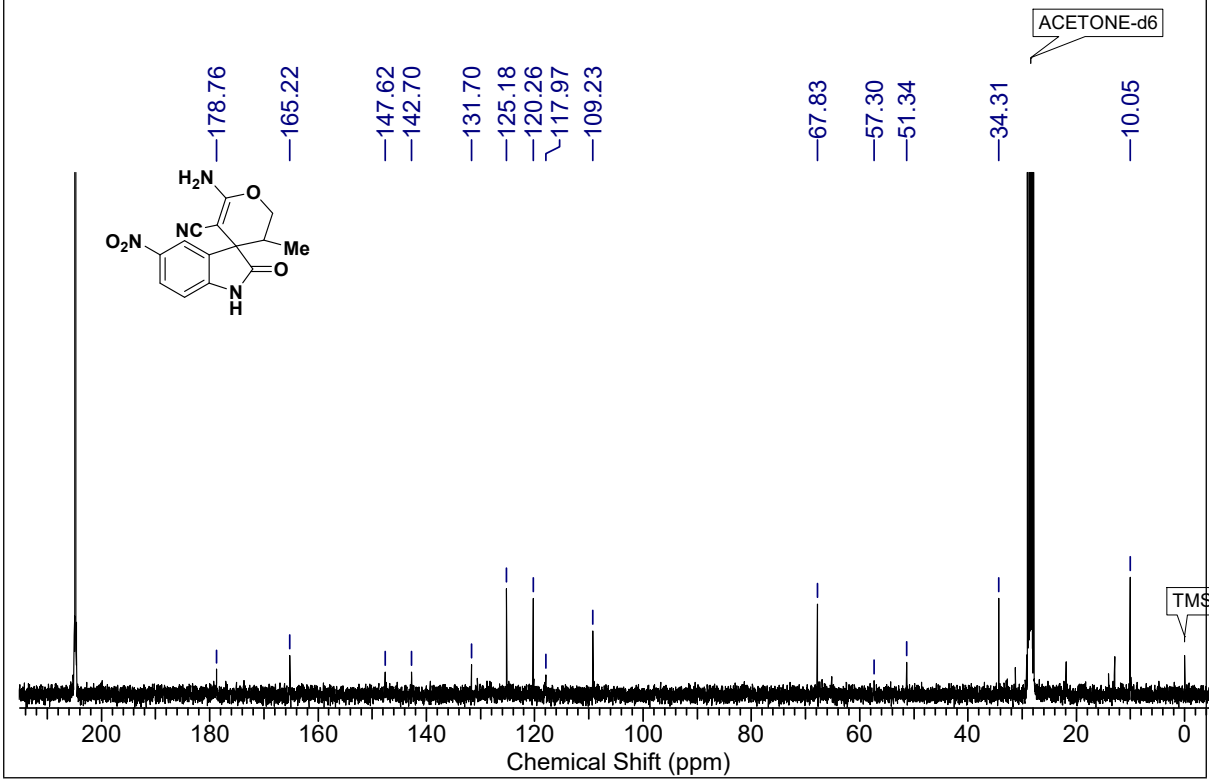
^{19}F spectrum of compound 4Am



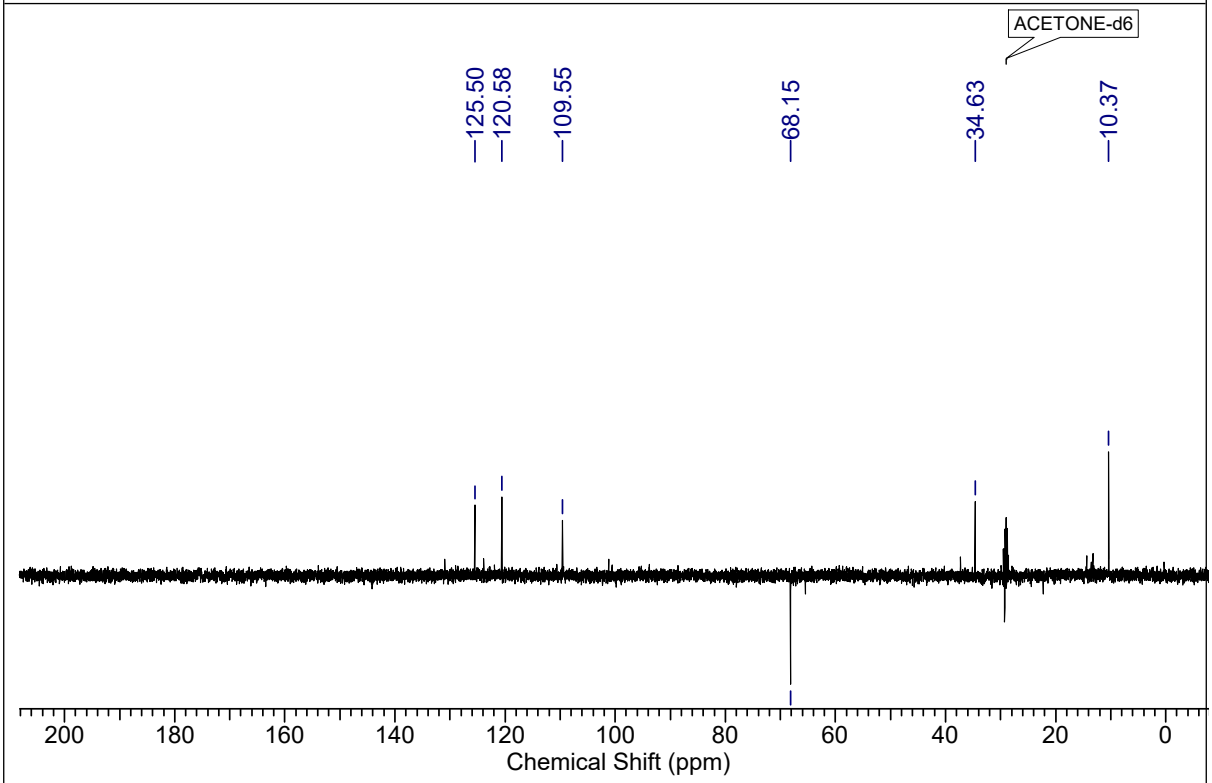
^{1}H NMR spectrum of compound 4An (400 MHz, Acetone-d_6)



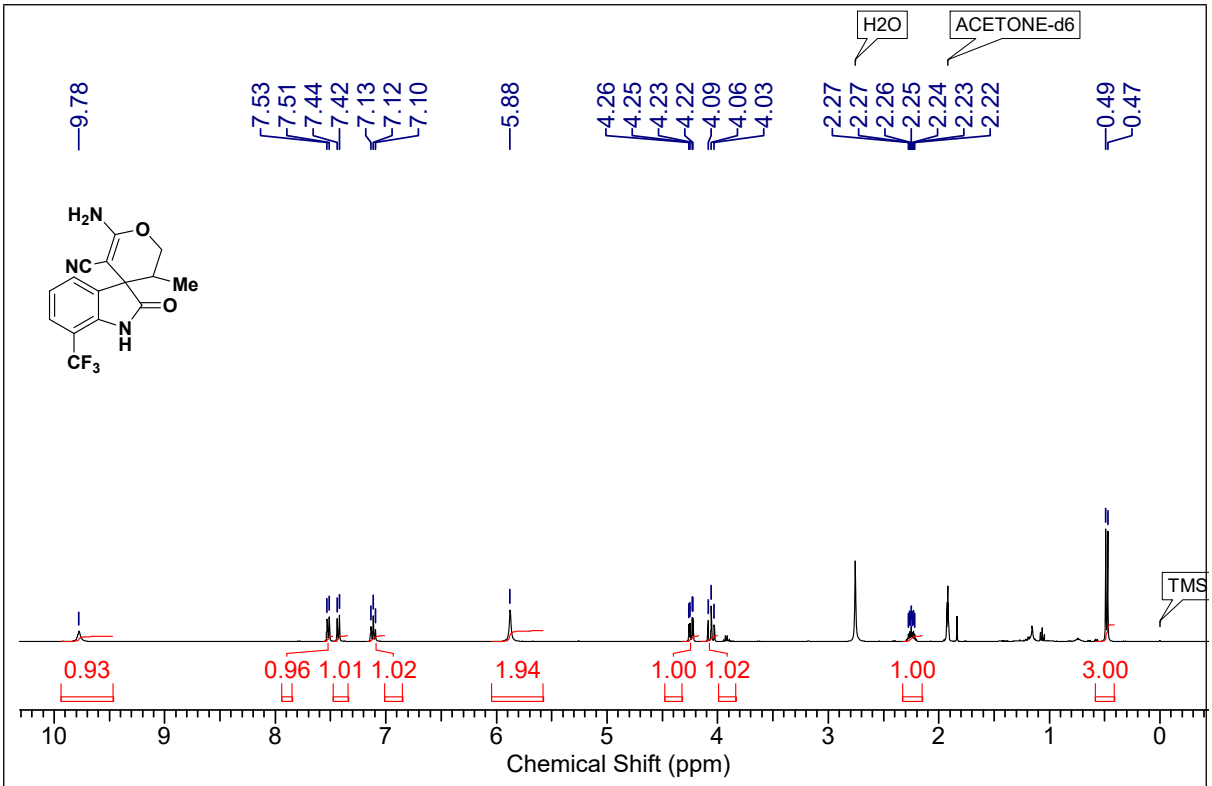
^{13}C NMR spectrum of compound 4An (101 MHz, Acetone-d_6)



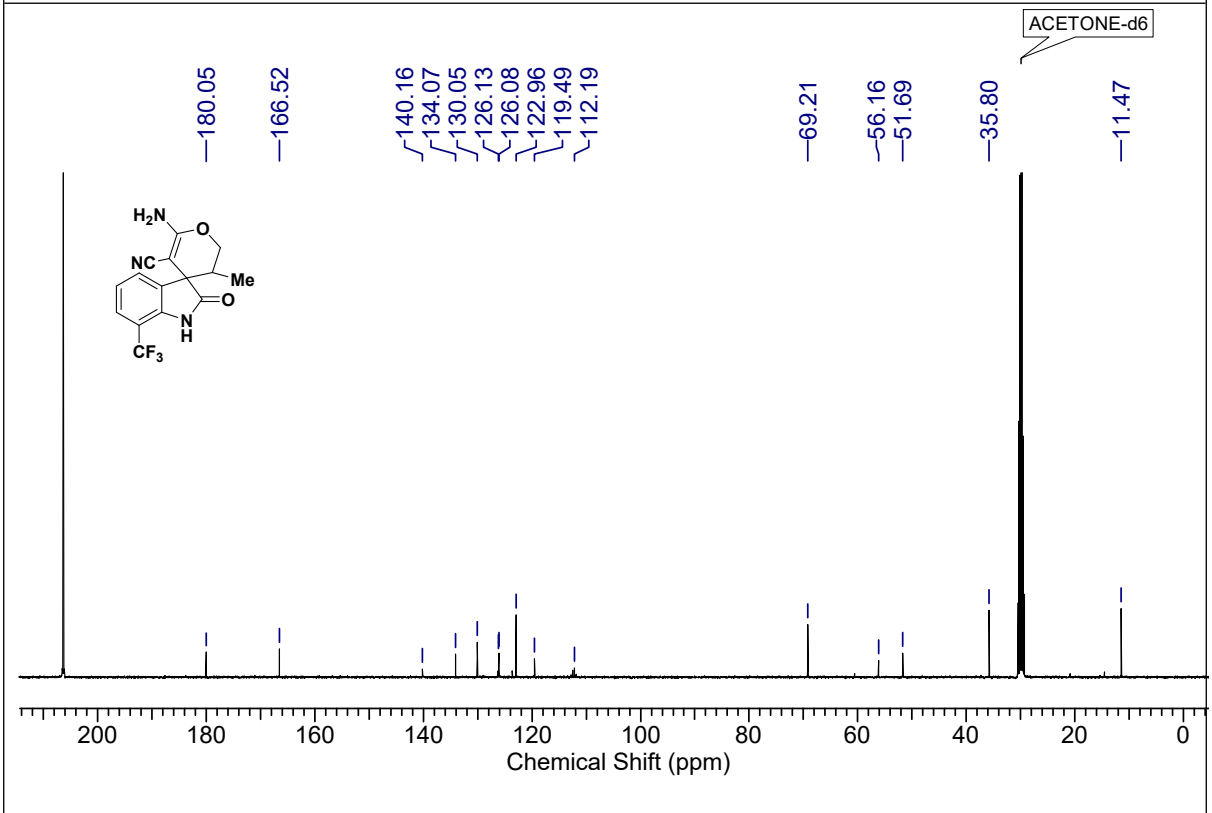
135 DEPT NMR spectrum of compound 4An



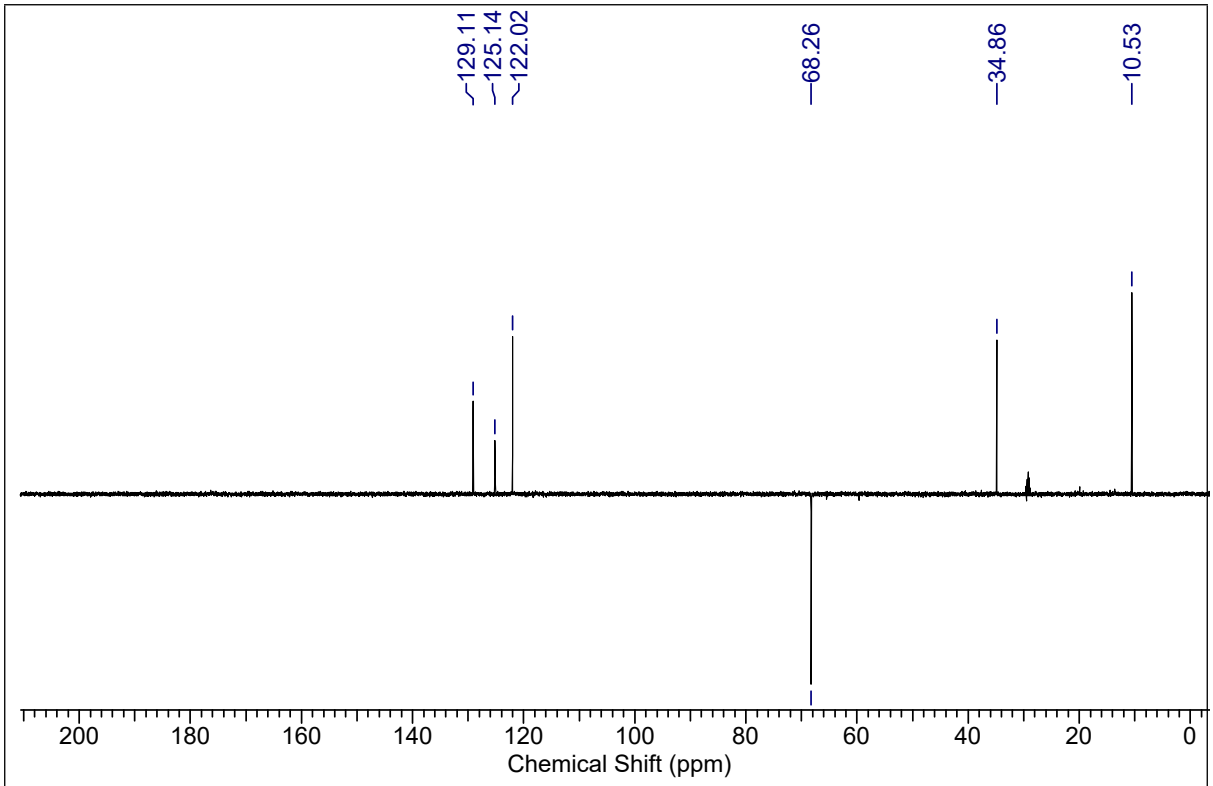
^{1}H NMR spectrum of compound 4Ao (400 MHz, Acetone-d_6)



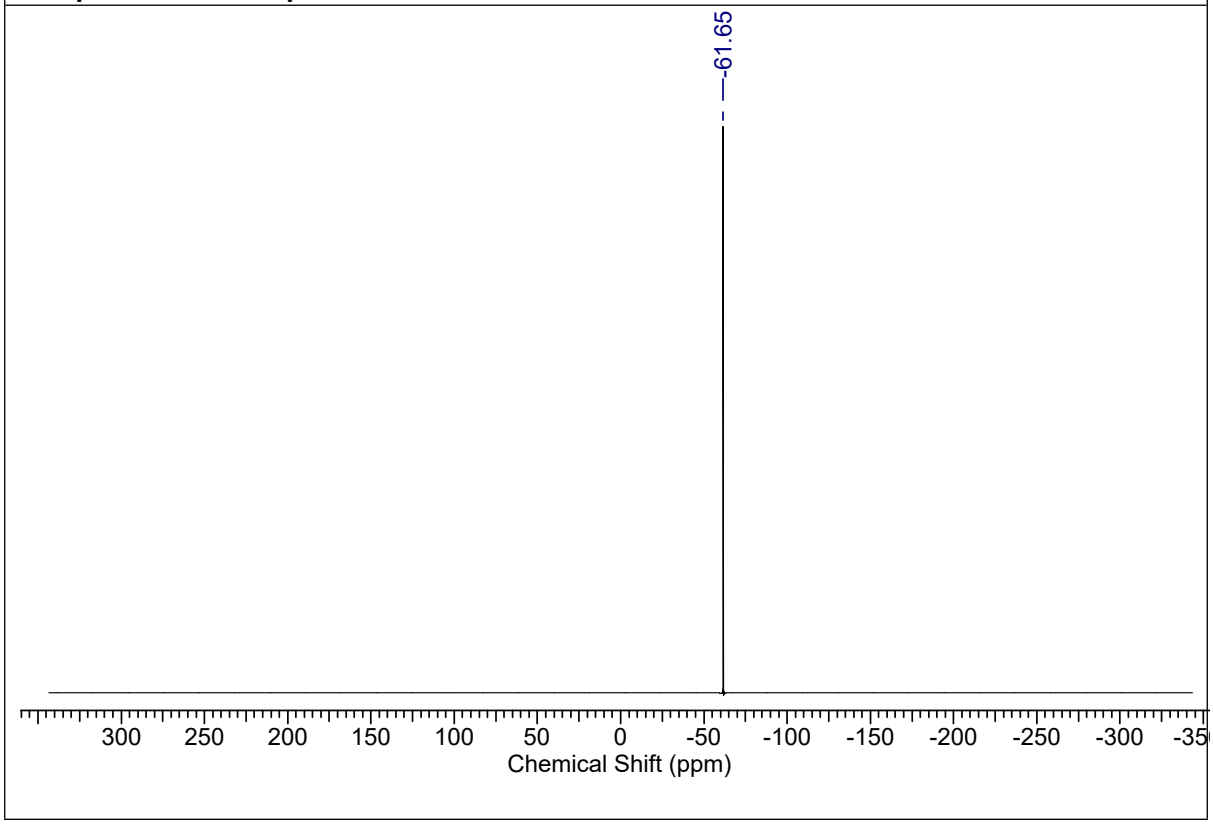
^{13}C NMR spectrum of compound 4Ao (101 MHz, Acetone-d_6)



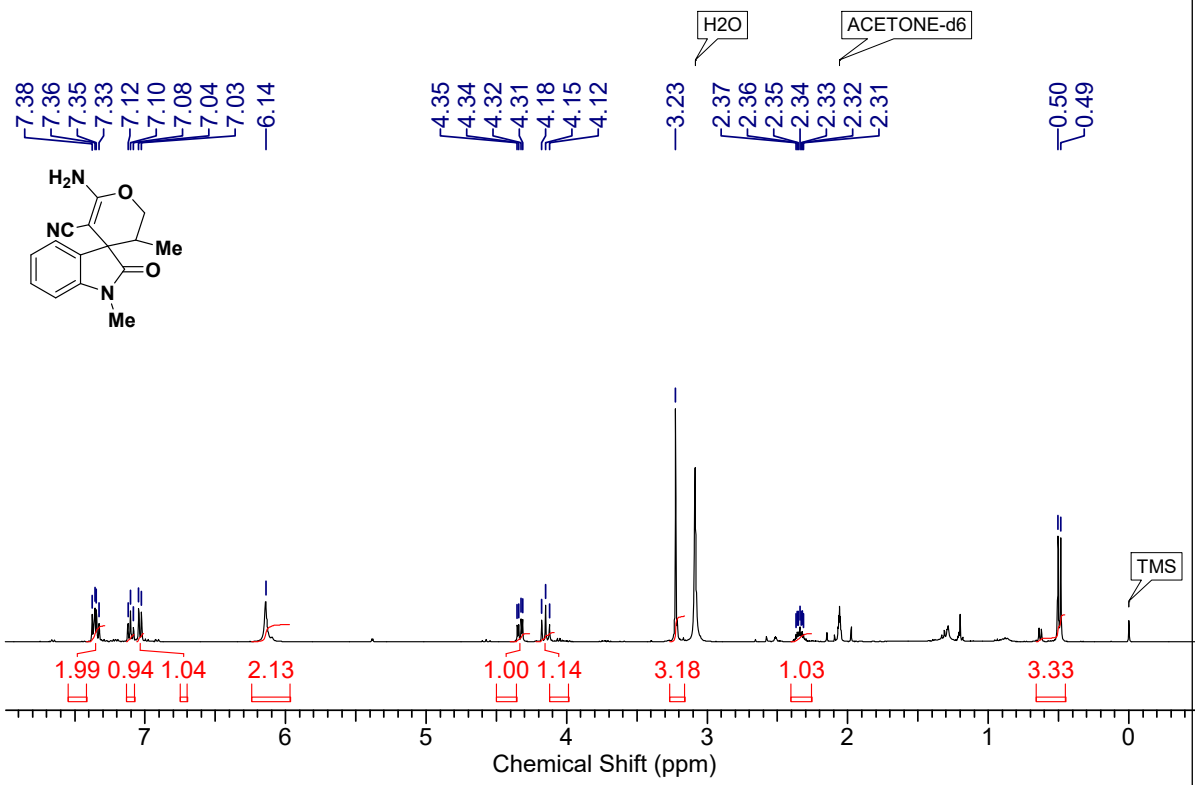
135 DEPT NMR spectrum of compound 4Ao



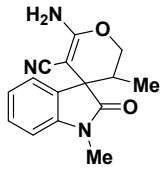
^{19}F spectrum of compound 4Ao

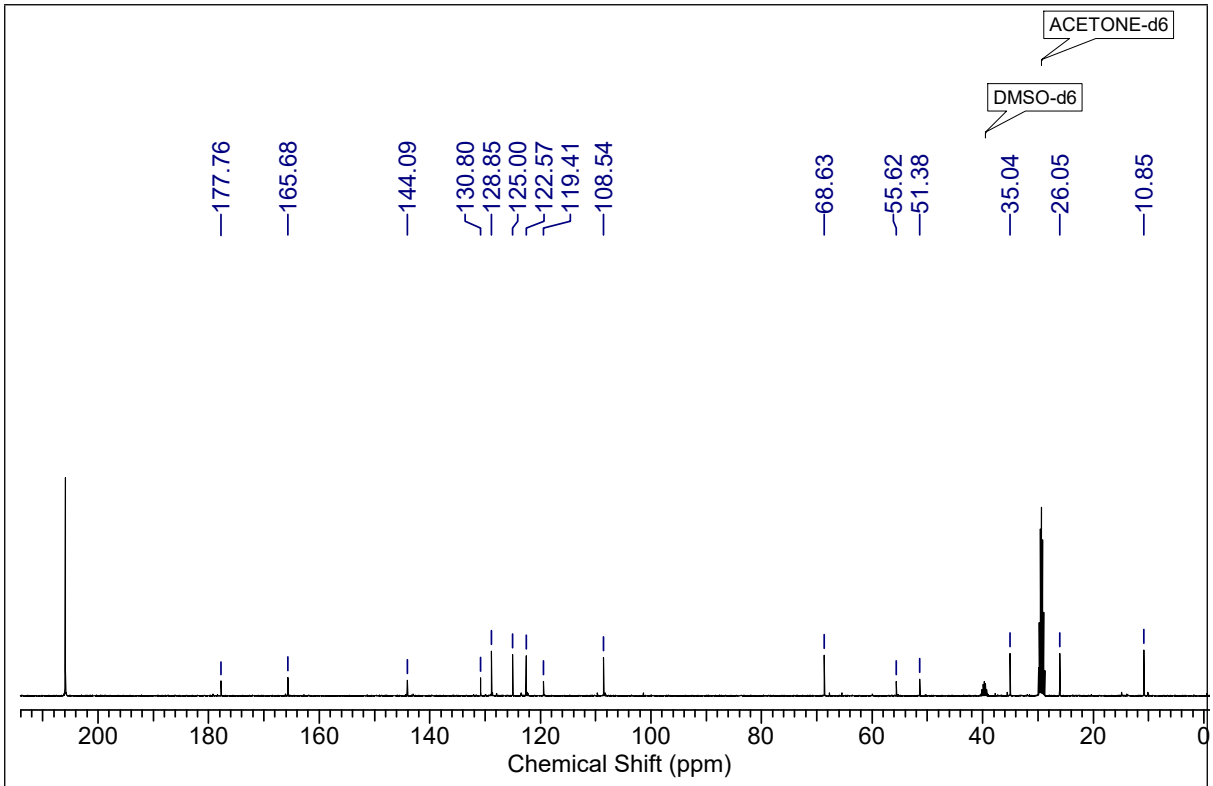


^{1}H NMR spectrum of compound 4Ba (400 MHz, Acetone-d_6)

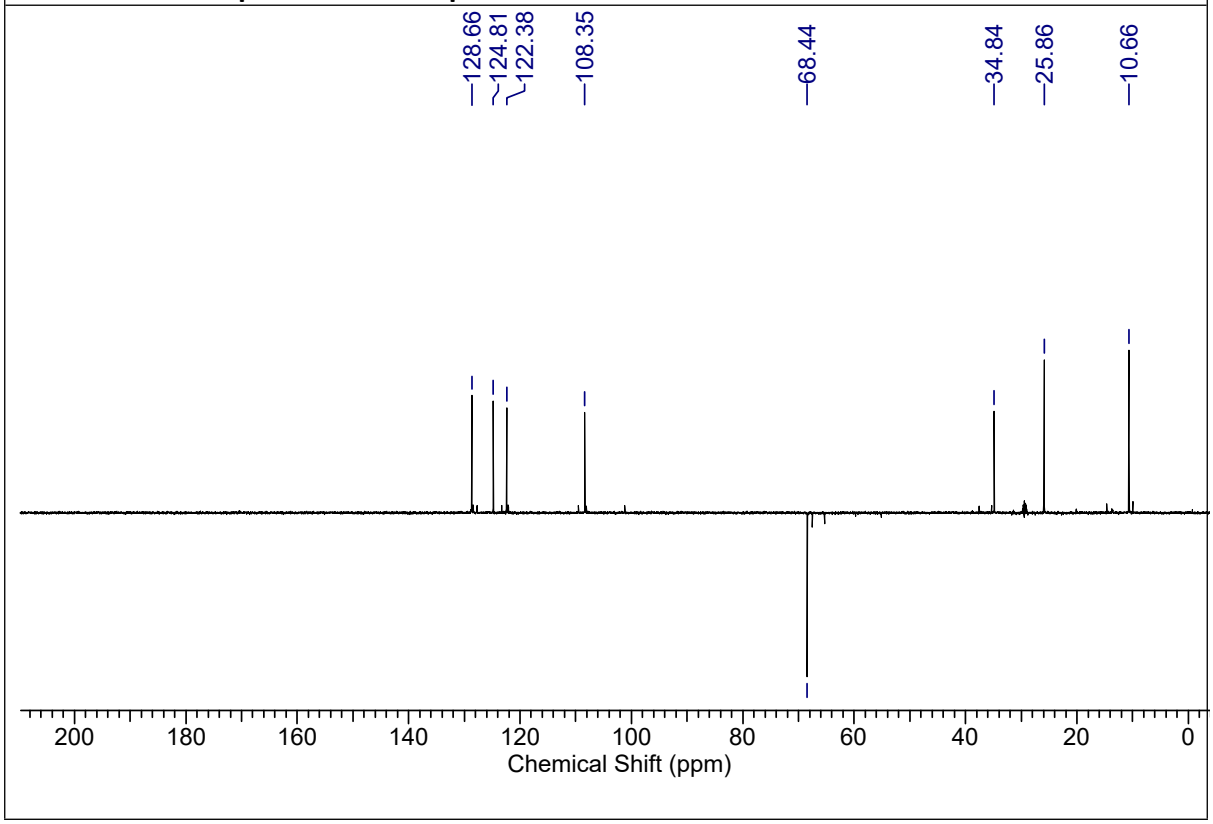


^{13}C NMR spectrum of compound 4Ba (101 MHz, Acetone-d_6)

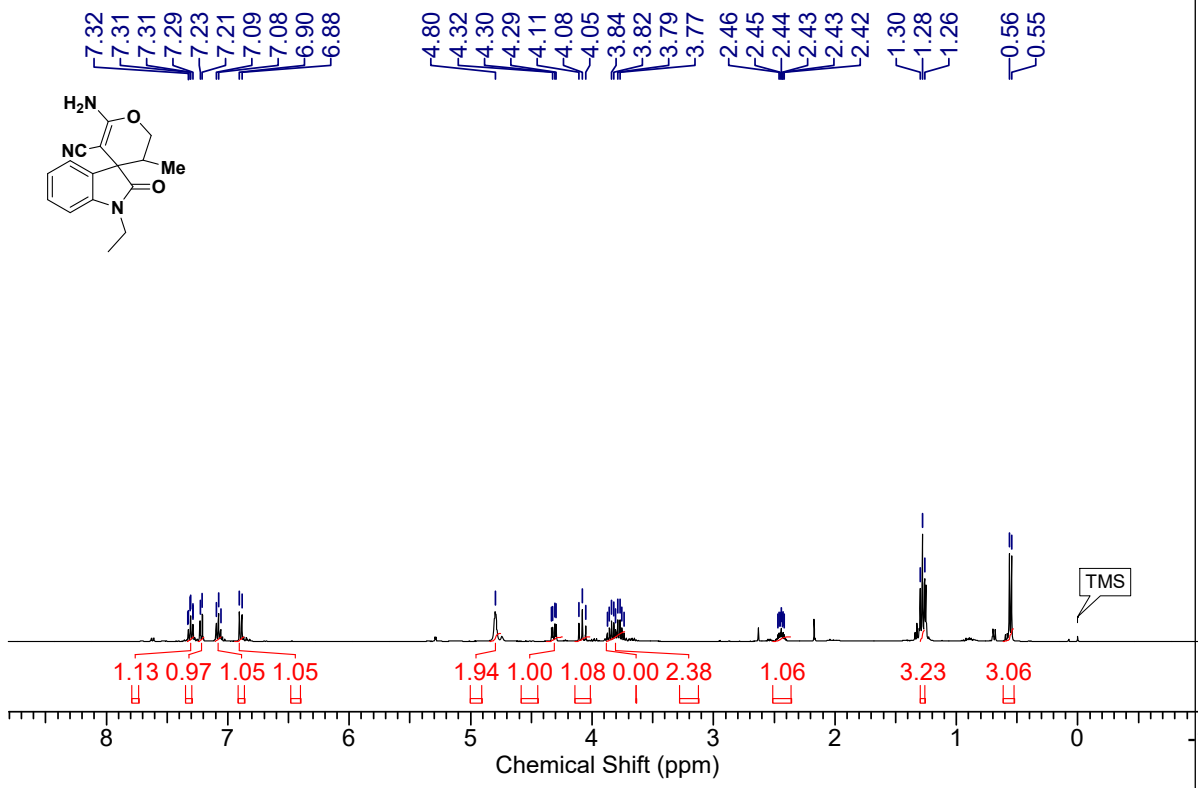




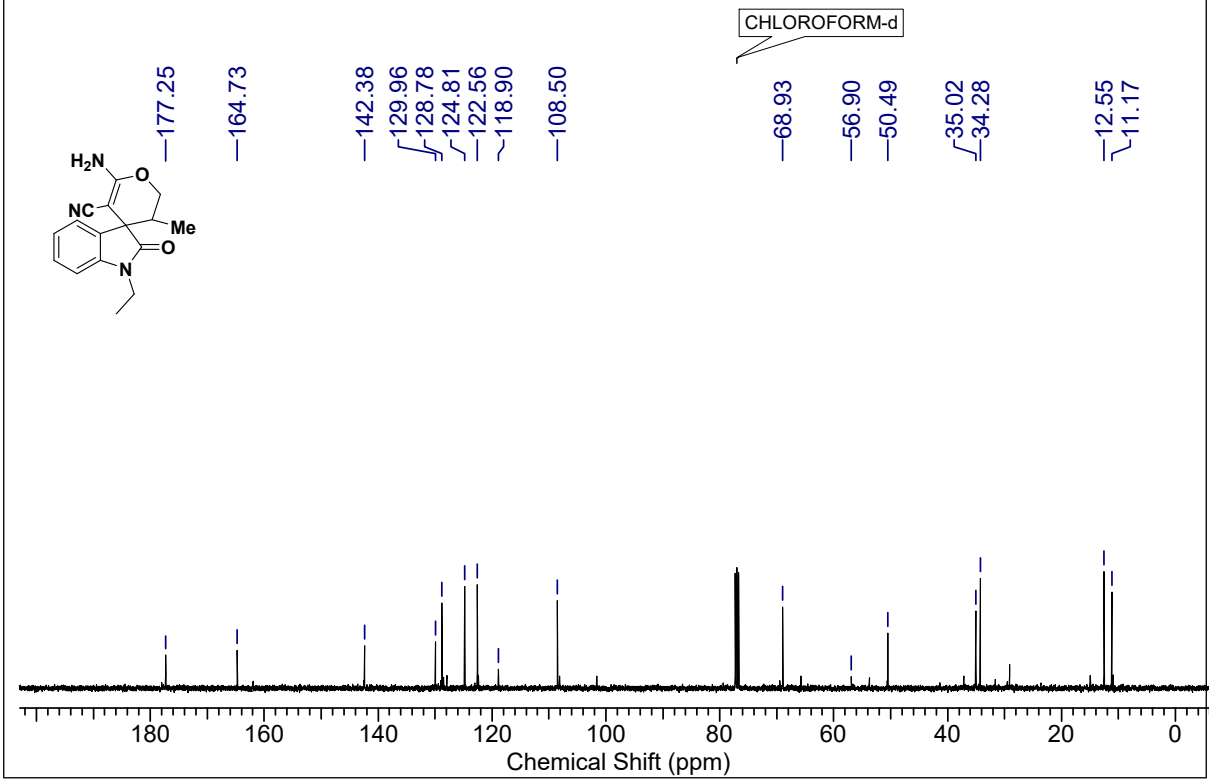
135 DEPT NMR spectrum of compound 4Ba



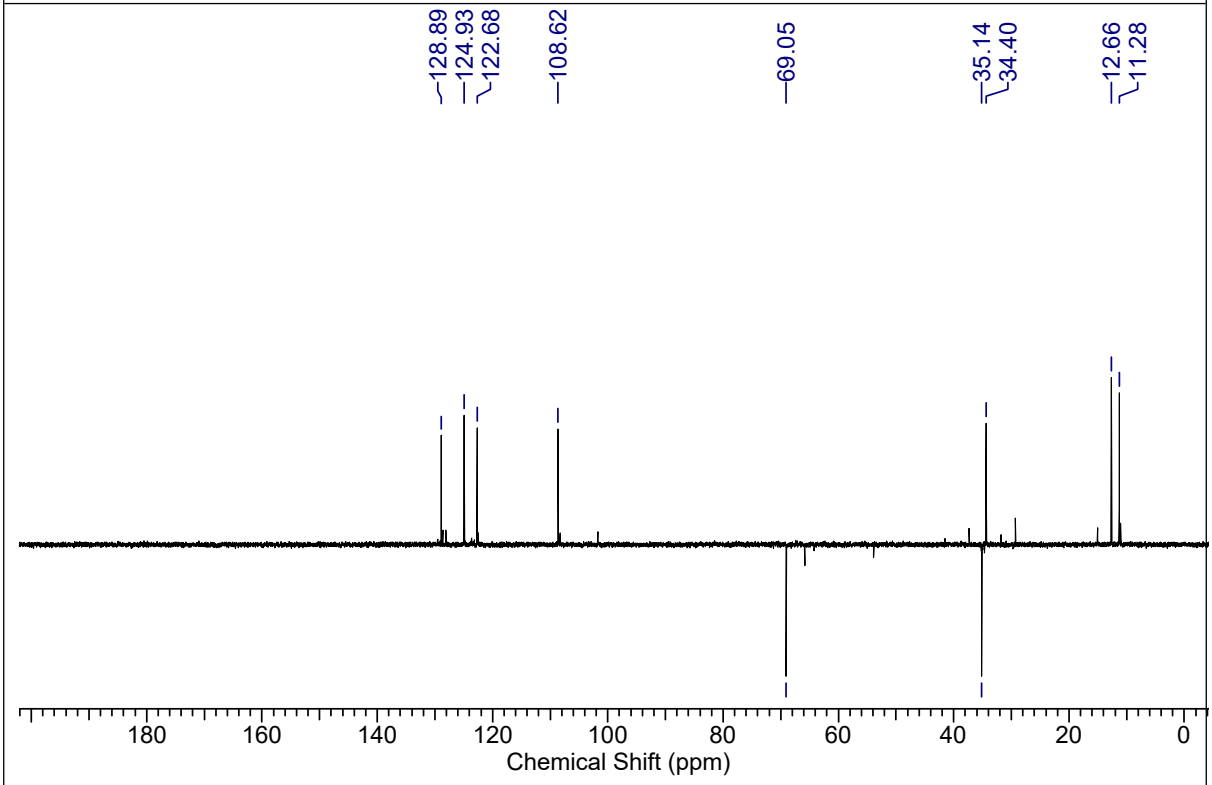
^{1}H NMR spectrum of compound 4Bb (400 MHz, $CDCl_3$)



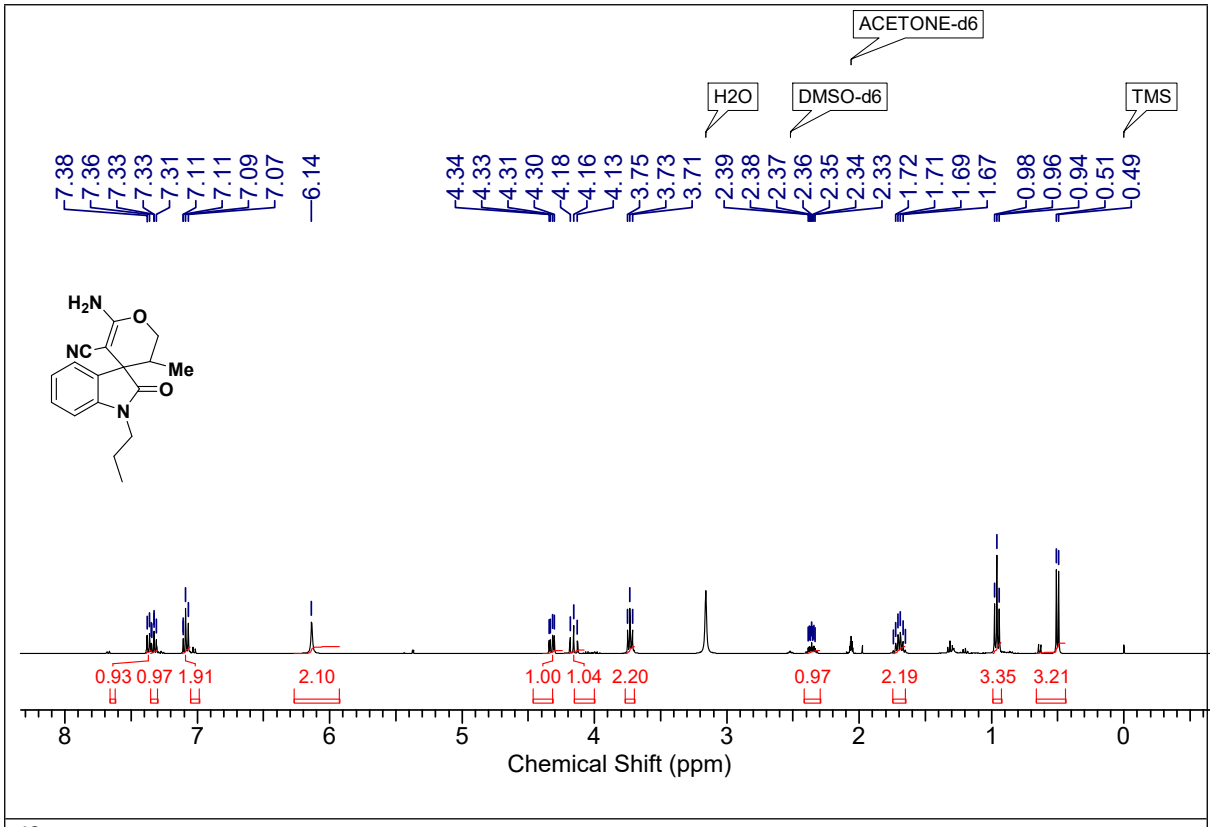
^{13}C NMR spectrum of compound 4Bb (101 MHz, $CDCl_3$)



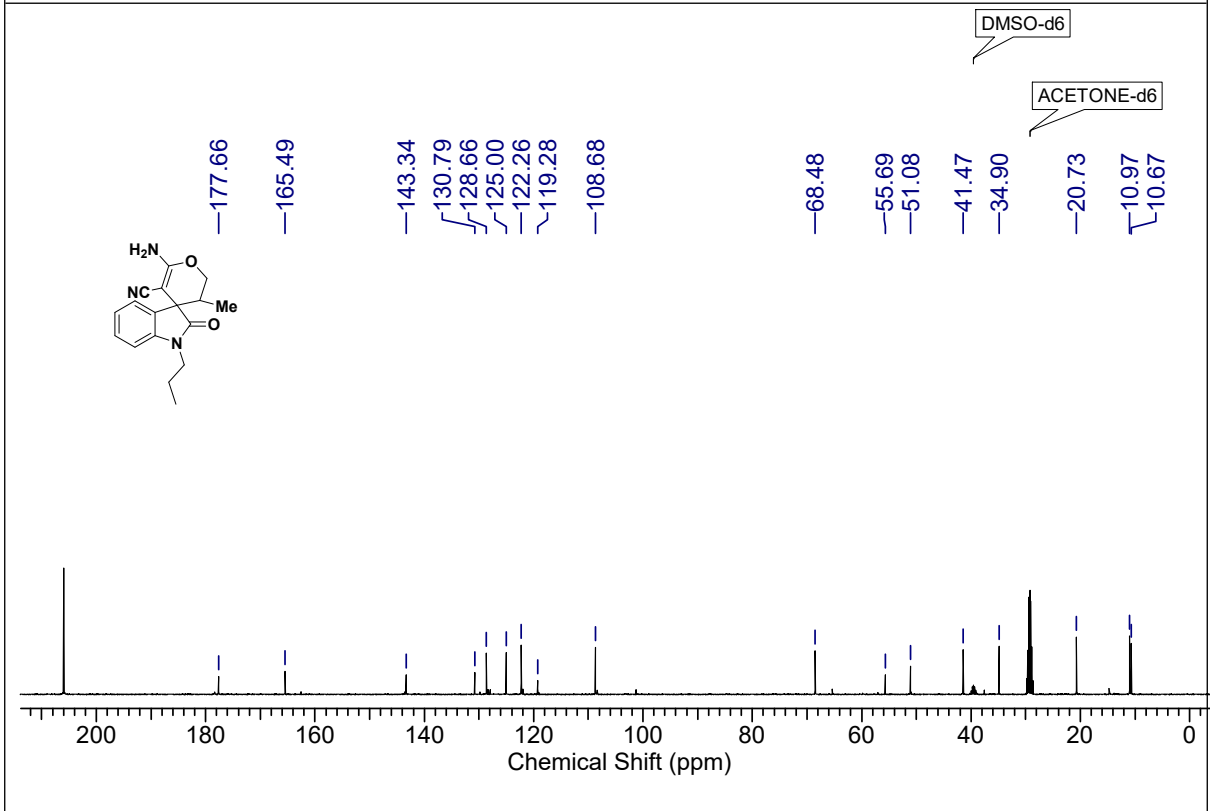
135 DEPT NMR spectrum of compound 4Bb



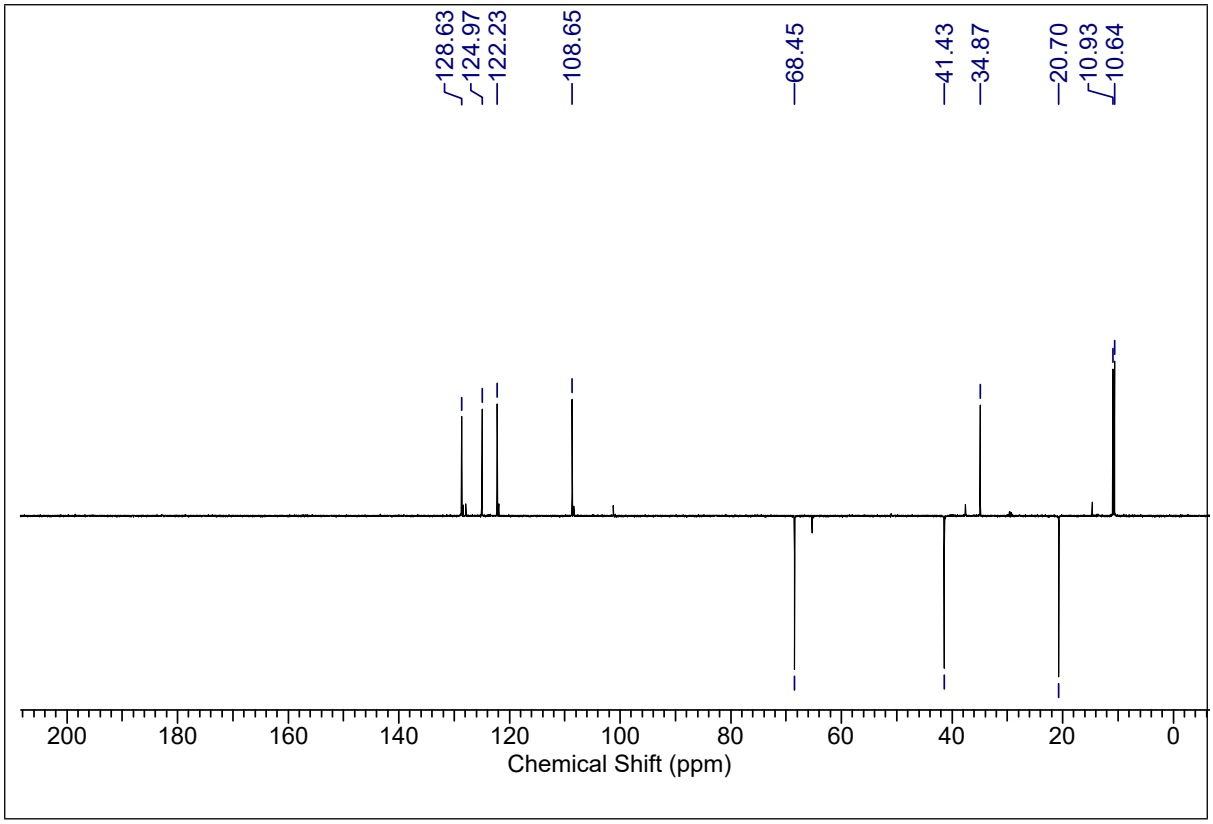
^{1}H NMR spectrum of compound 4Bc (400 MHz, Acetone-d_6)



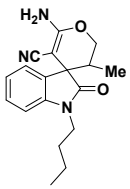
^{13}C NMR spectrum of compound 4Bc (101 MHz, Acetone-d_6)

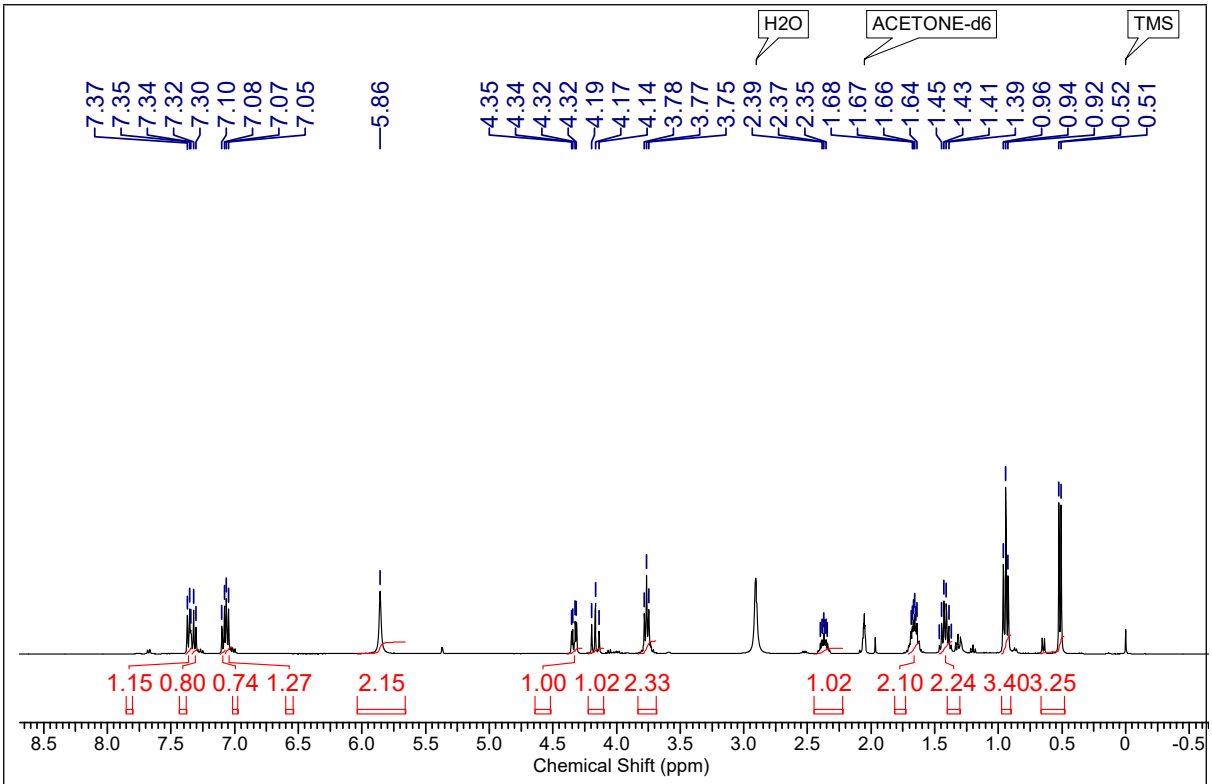


135 DEPT NMR spectrum of compound 4Bc

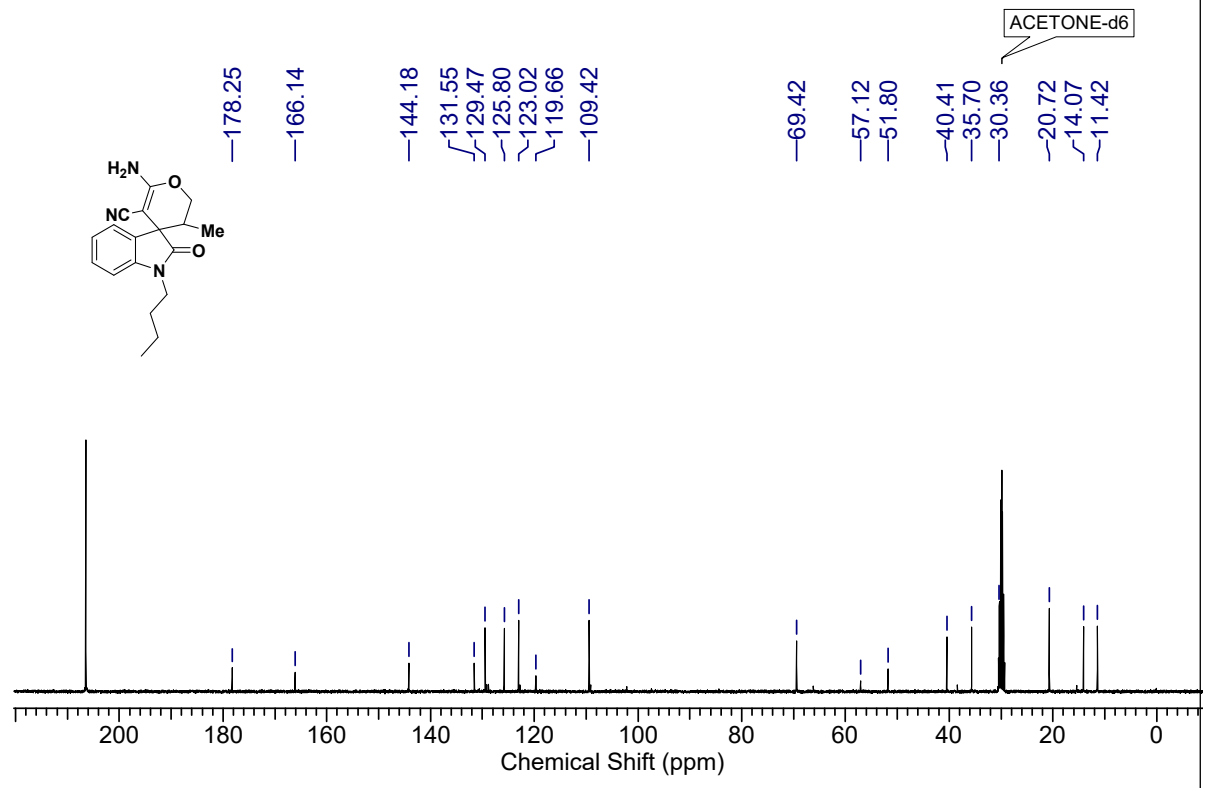


^{1}H NMR spectrum of compound 4Bd (400 MHz, Acetone-d_6)

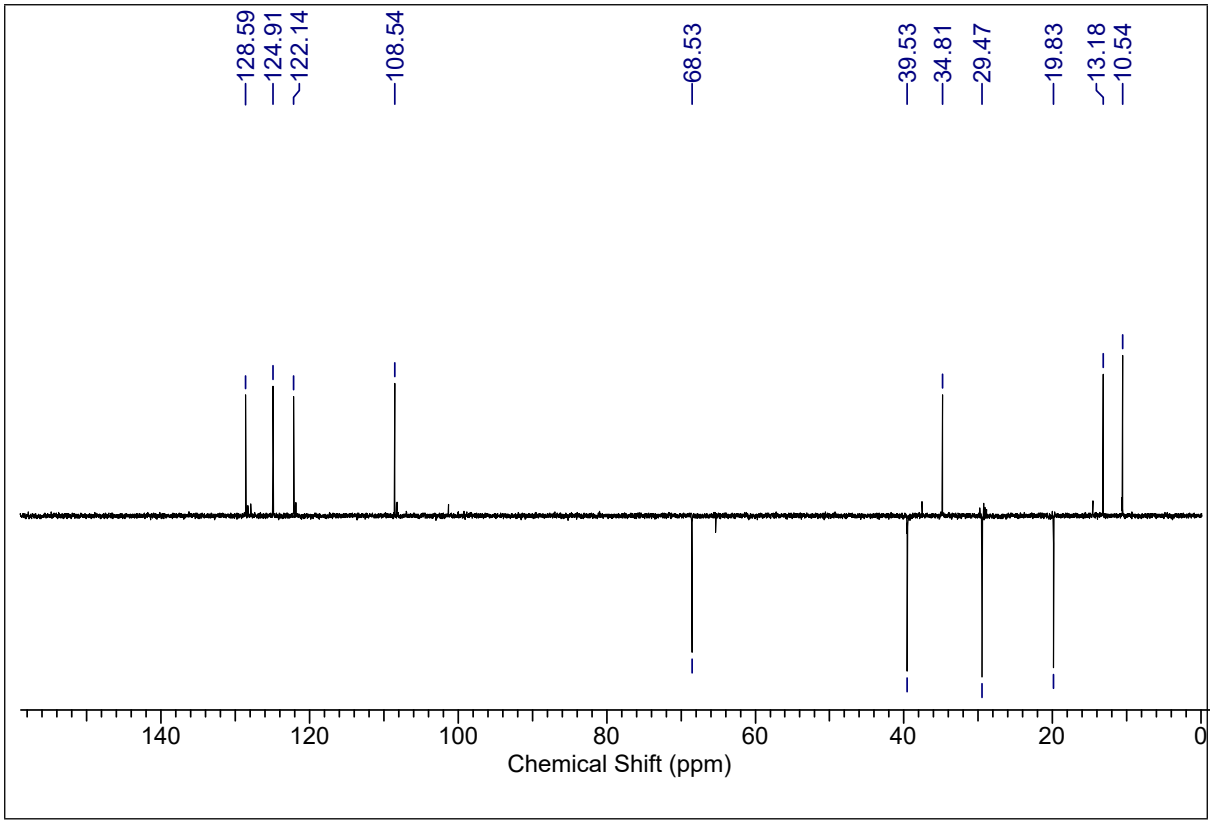




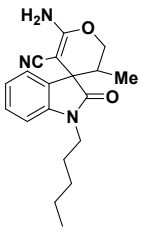
^{13}C NMR spectrum of compound 4Bd (101 MHz, Acetone-d_6)

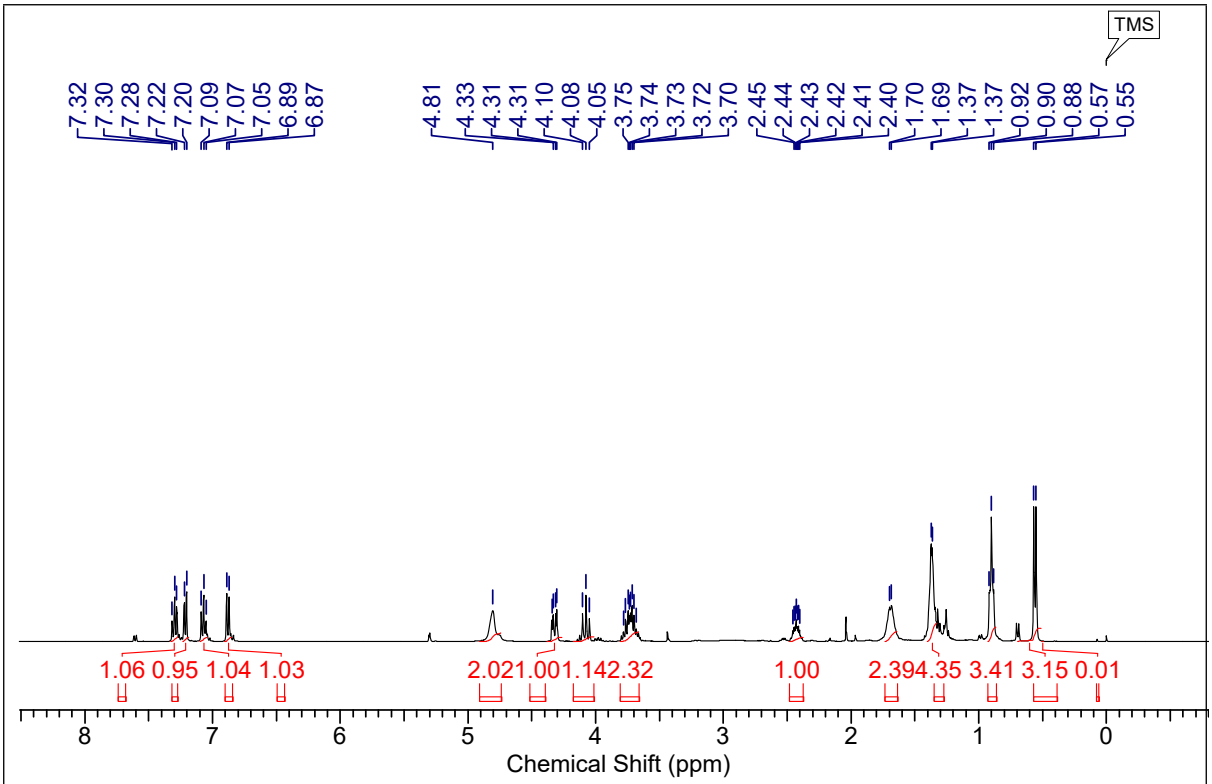


135 DEPT NMR spectrum of compound 4Bd

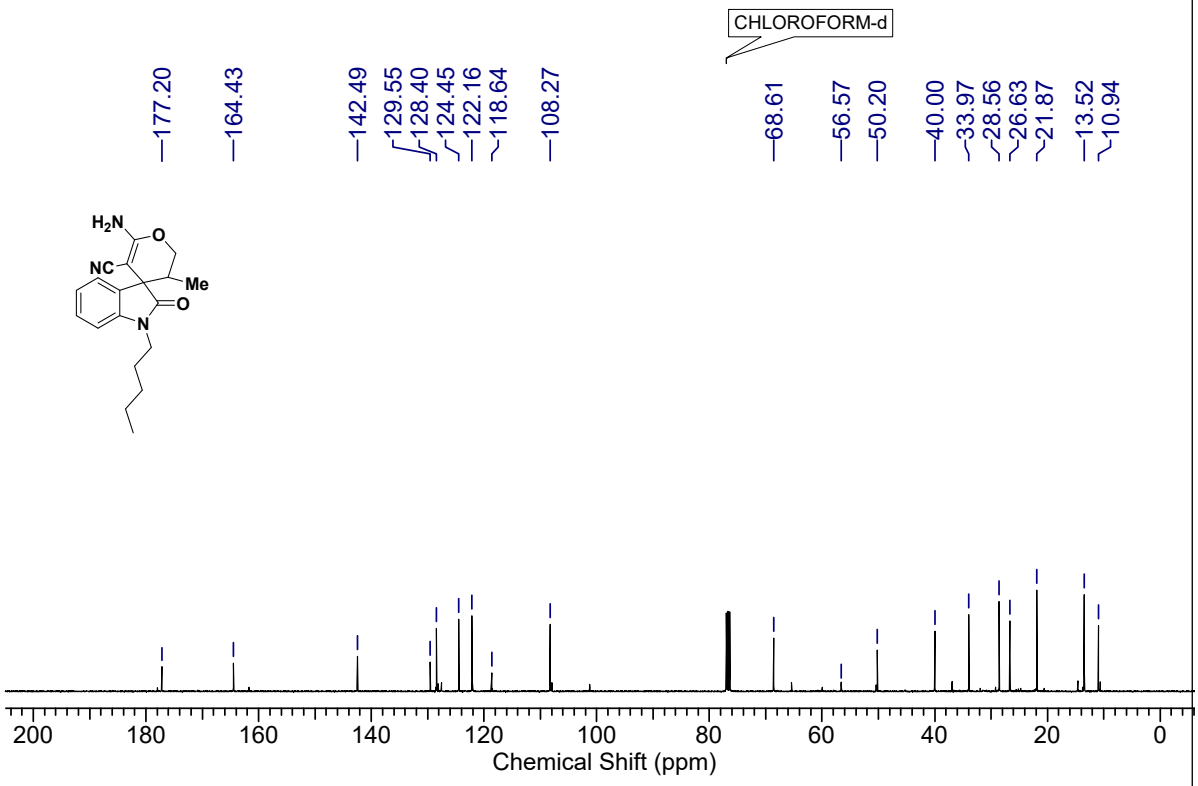


^{1}H NMR spectrum of compound 4Be (400 MHz, $CDCl_3$)

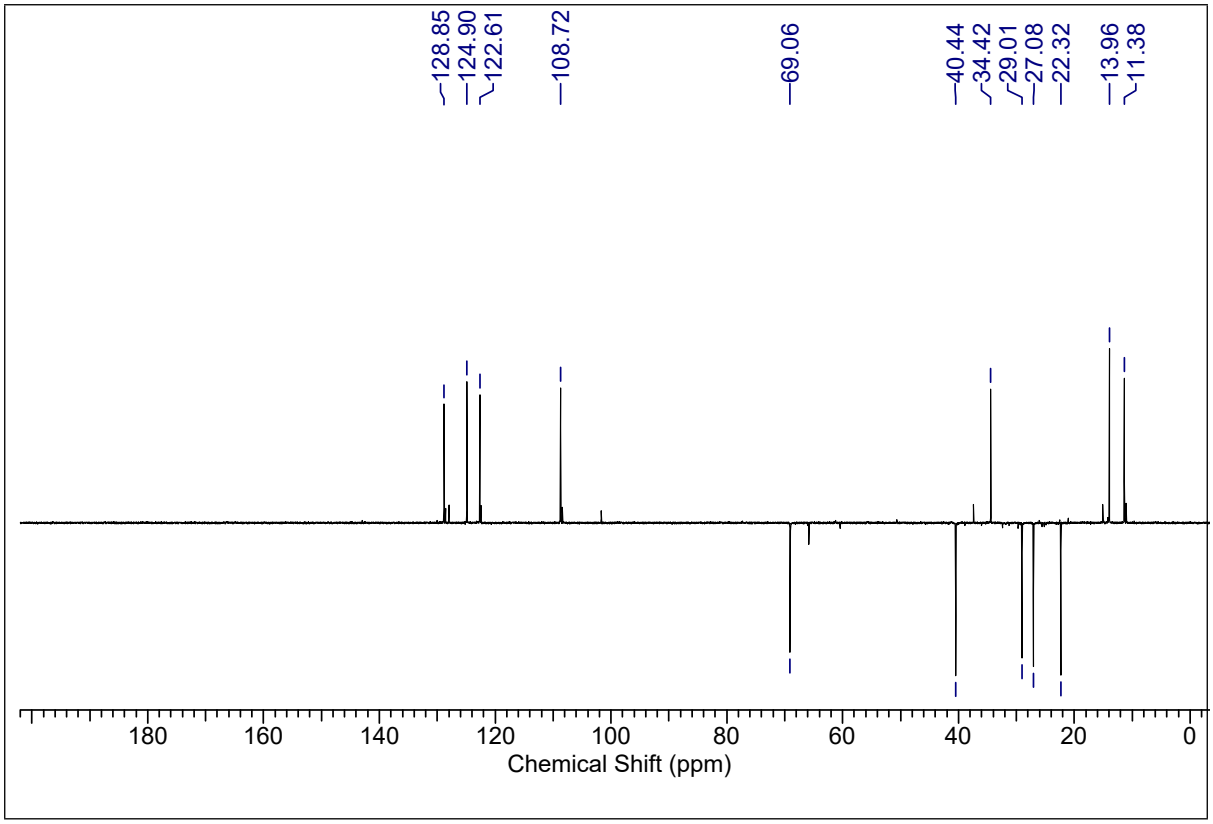




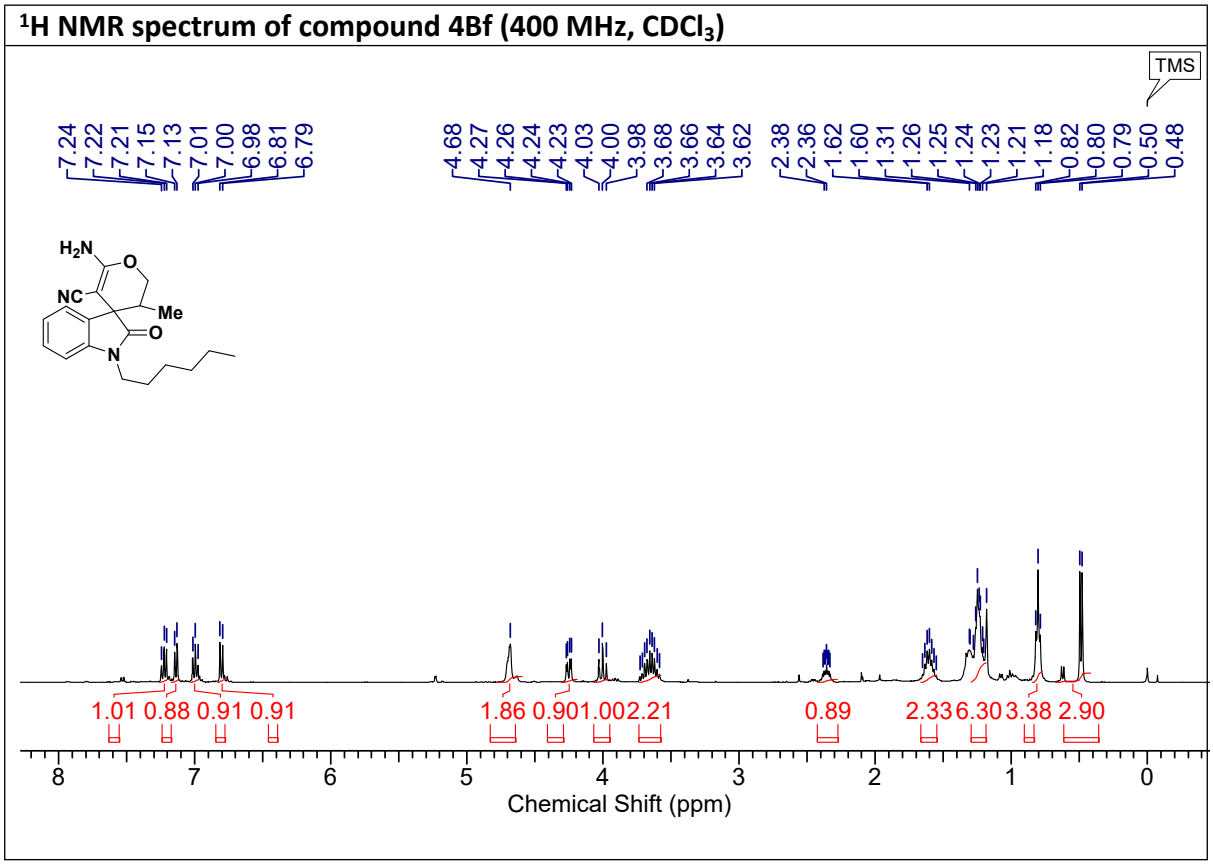
^{13}C NMR spectrum of compound 4Be (101 MHz, $CDCl_3$)



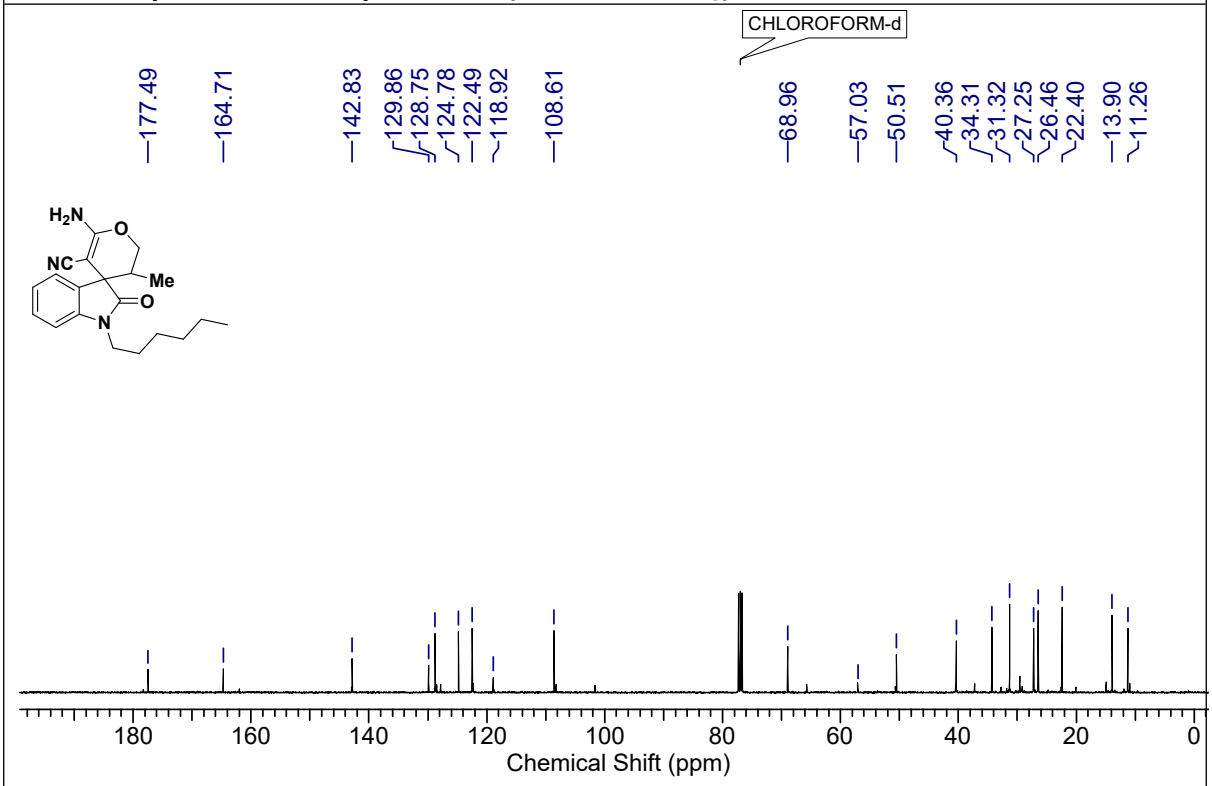
135 DEPT NMR spectrum of compound 4Be



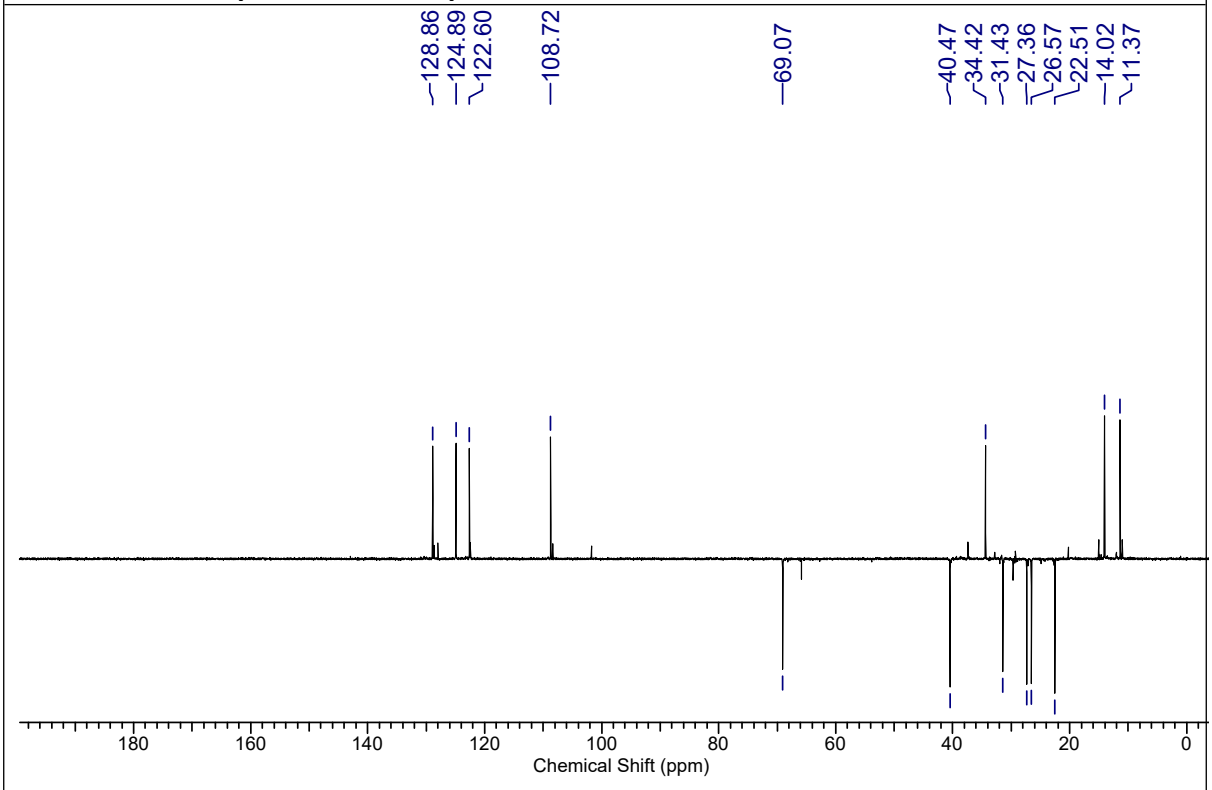
^{1}H NMR spectrum of compound 4Bf (400 MHz, $CDCl_3$)



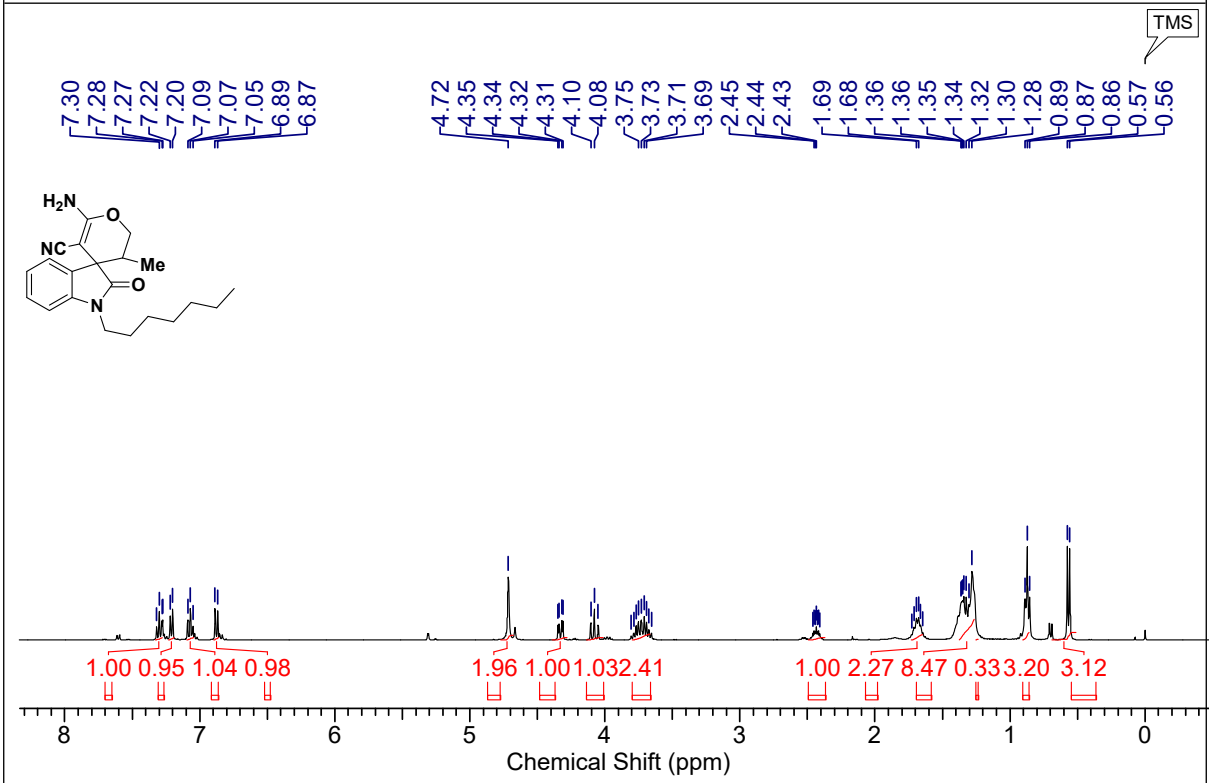
^{13}C NMR spectrum of compound 4Bf (101 MHz, $CDCl_3$)



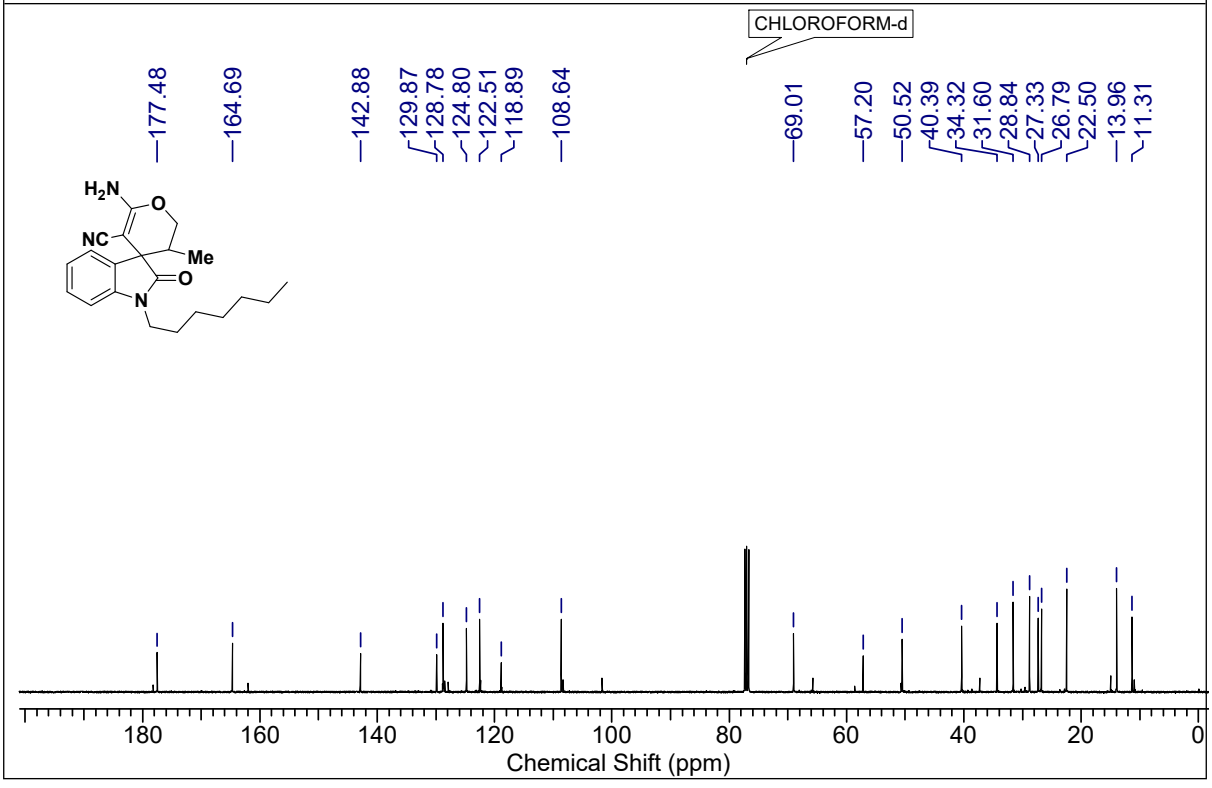
135 DEPT NMR spectrum of compound 4Bf



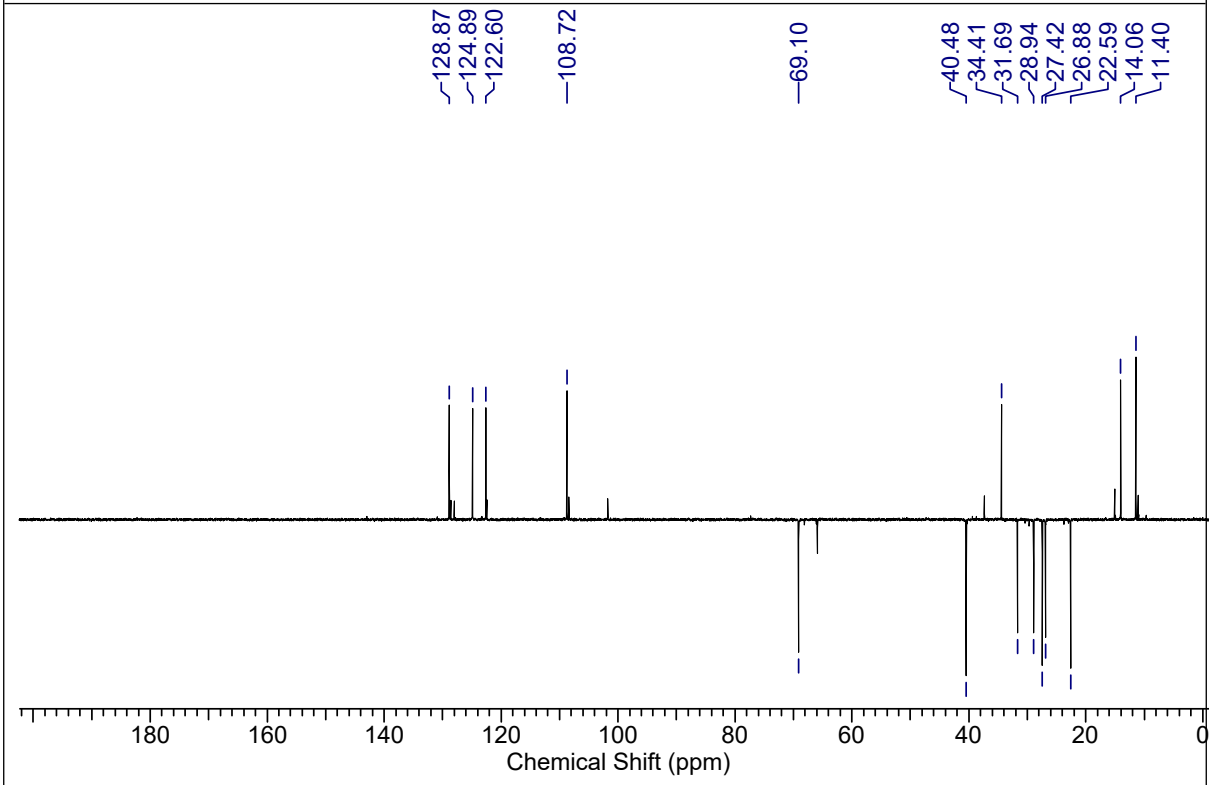
^{1}H NMR spectrum of compound 4Bg (400 MHz, $CDCl_3$)



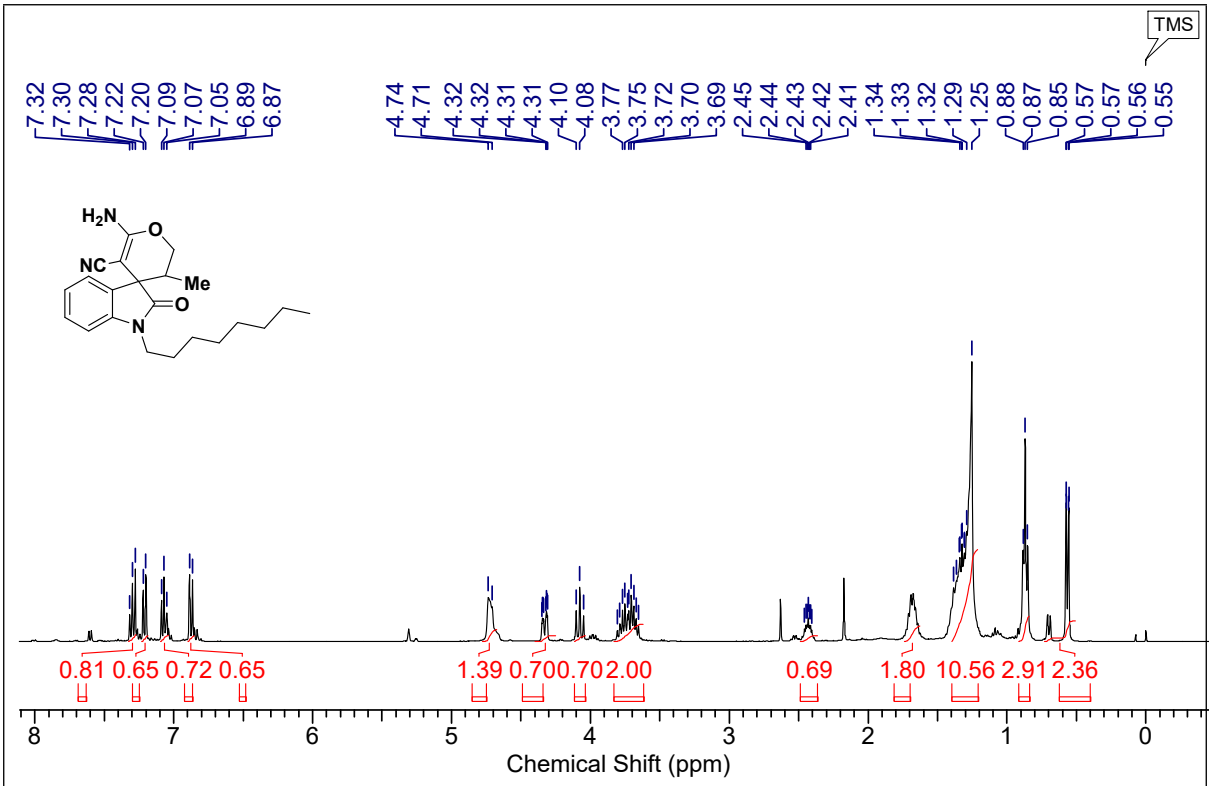
^{13}C NMR spectrum of compound 4Bg (101 MHz, $CDCl_3$)



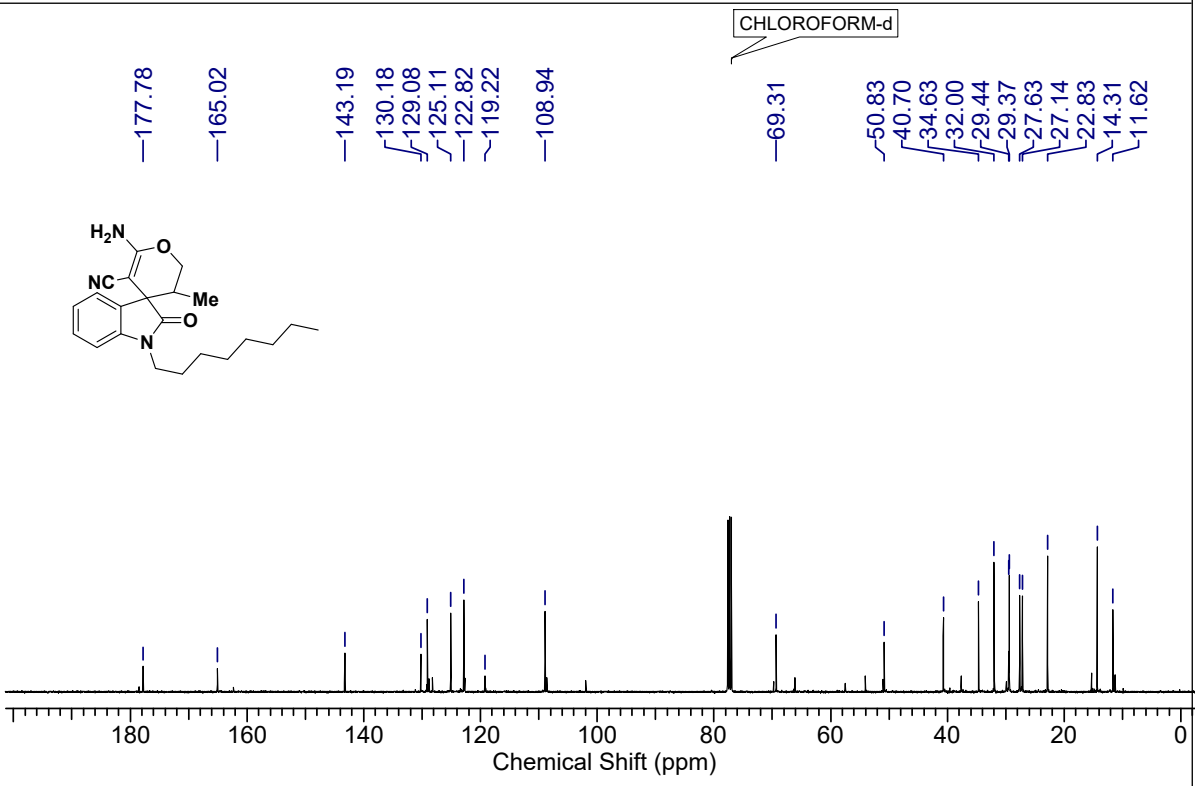
135 DEPT NMR spectrum of compound 4Bg



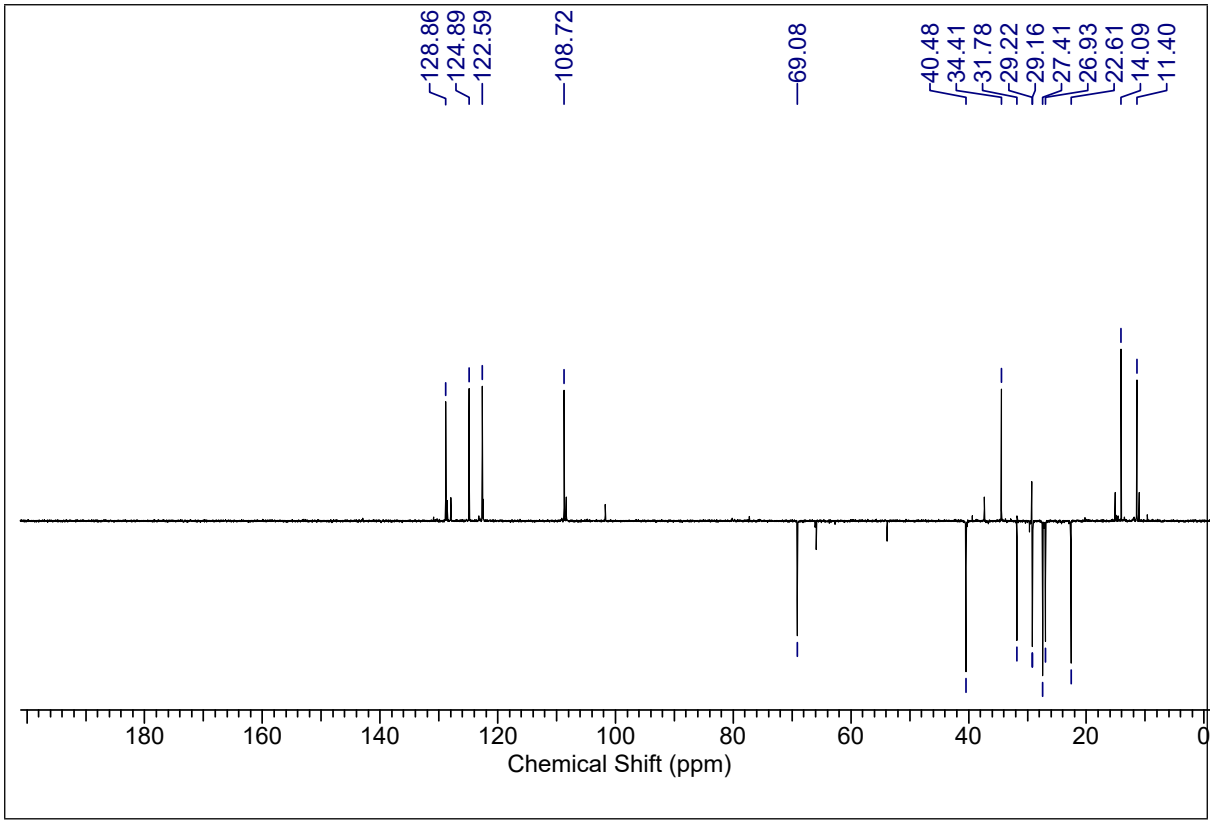
^{1}H NMR spectrum of compound 4Bh (400 MHz, $CDCl_3$)



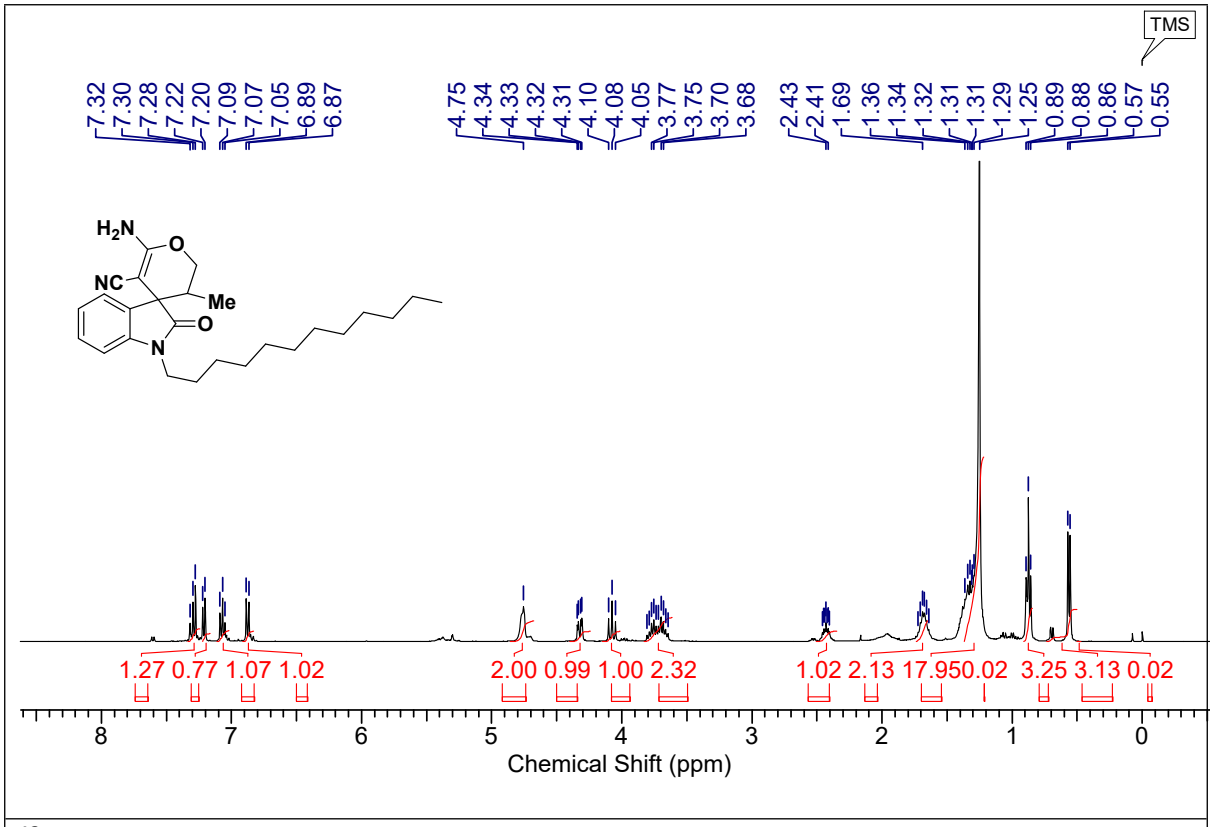
^{13}C NMR spectrum of compound 4Bh (101 MHz, $CDCl_3$)



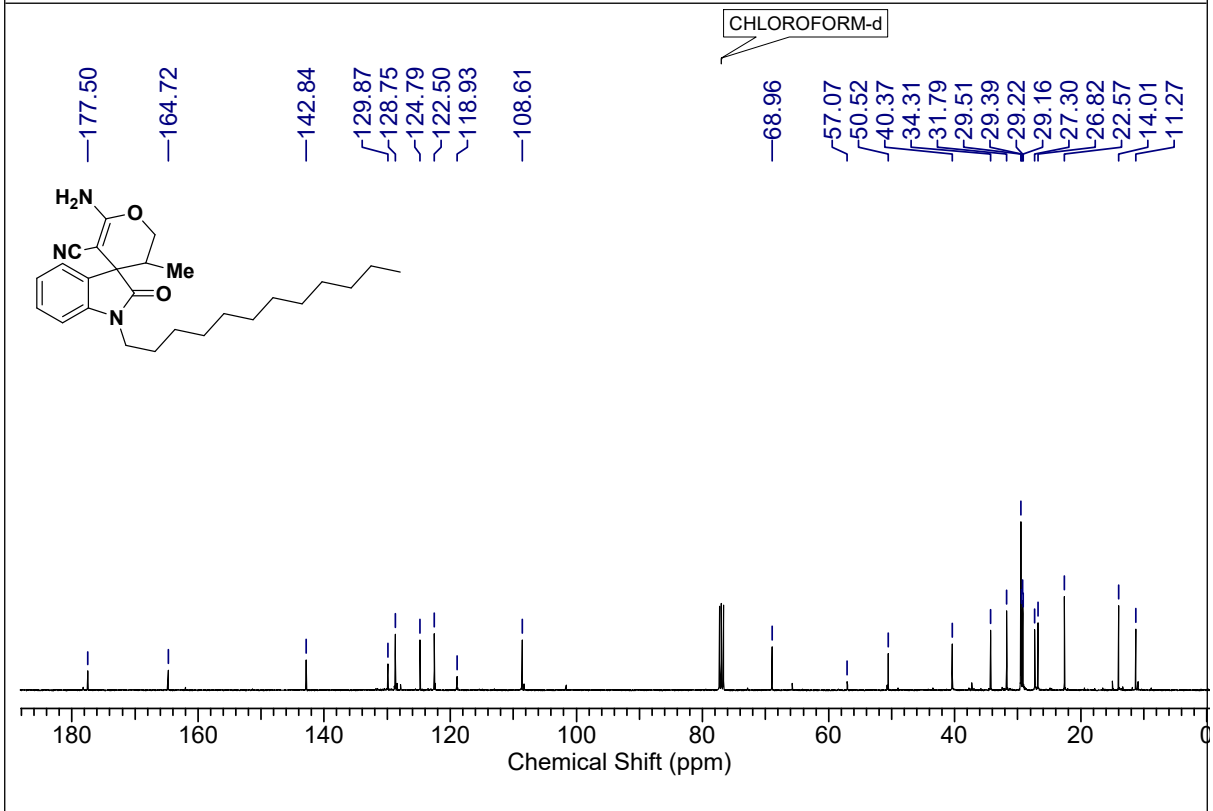
135 DEPT NMR spectrum of compound 4Bh



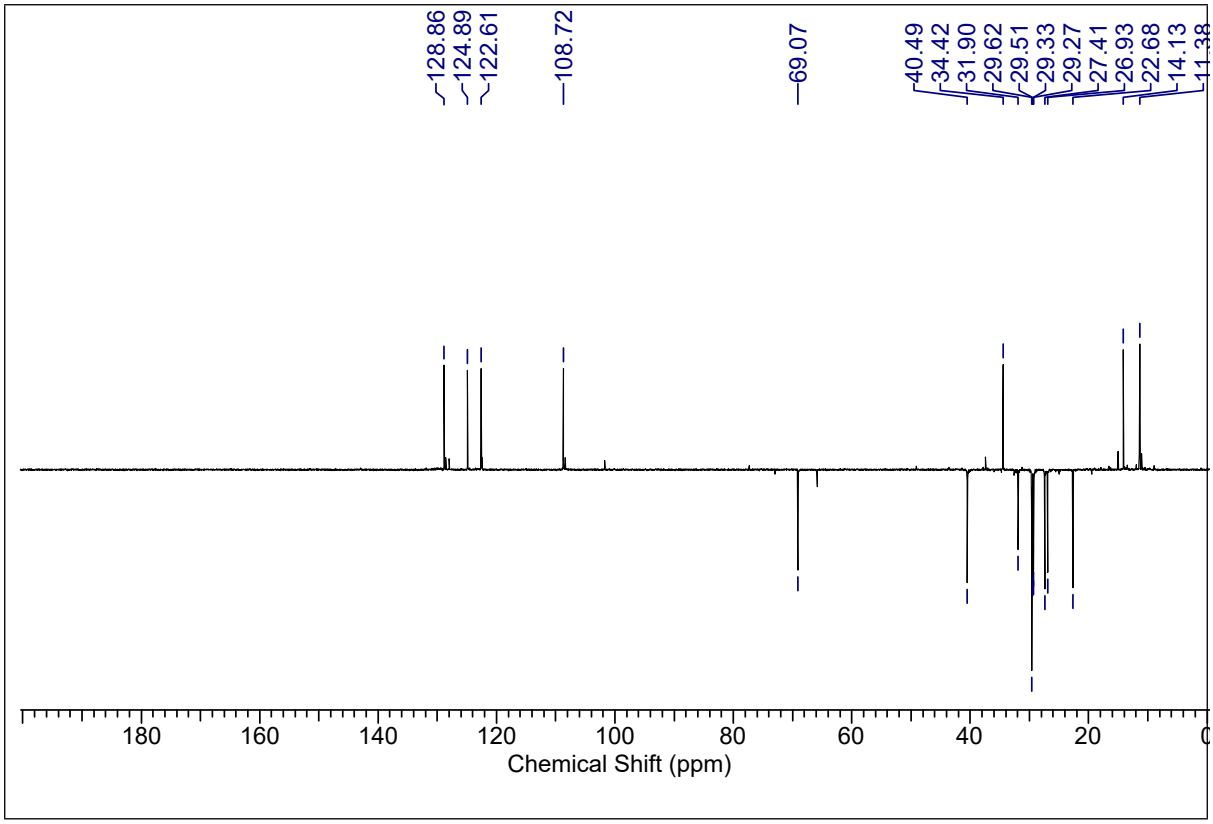
^{1}H NMR spectrum of compound 4Bi (400 MHz, $CDCl_3$)



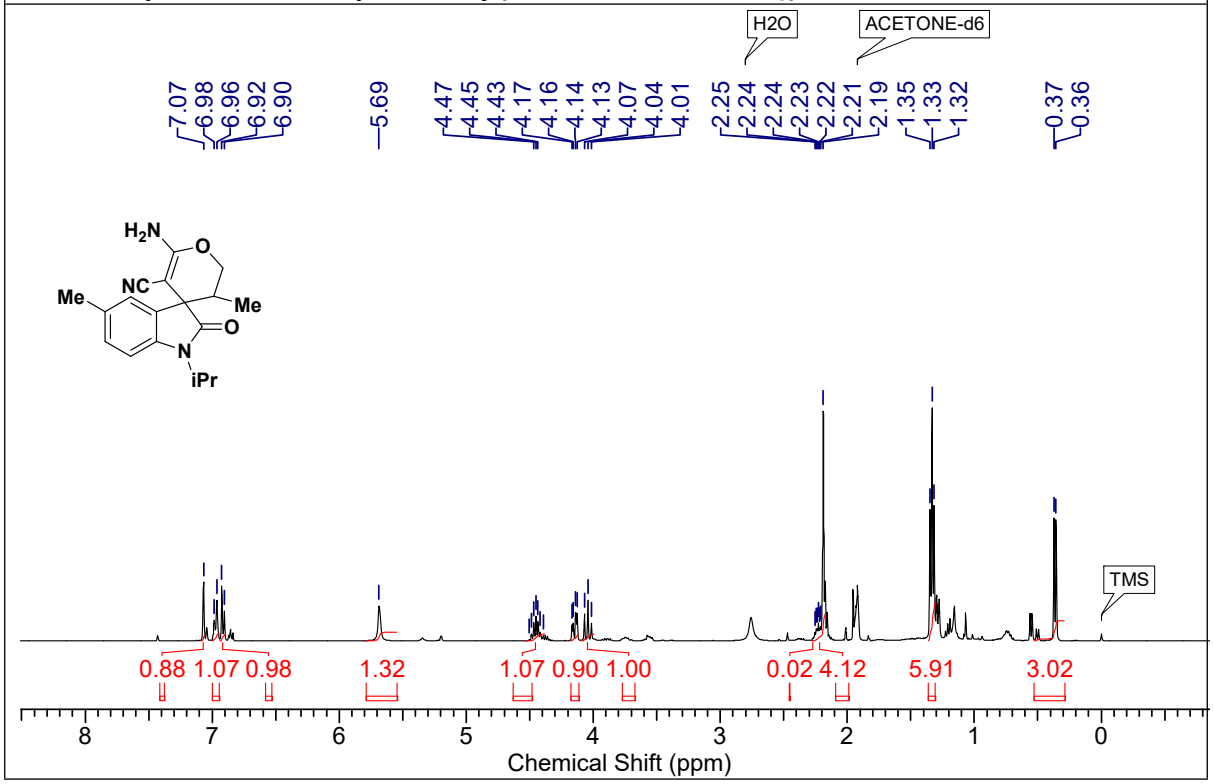
^{13}C NMR spectrum of compound 4Bi (101 MHz, $CDCl_3$)



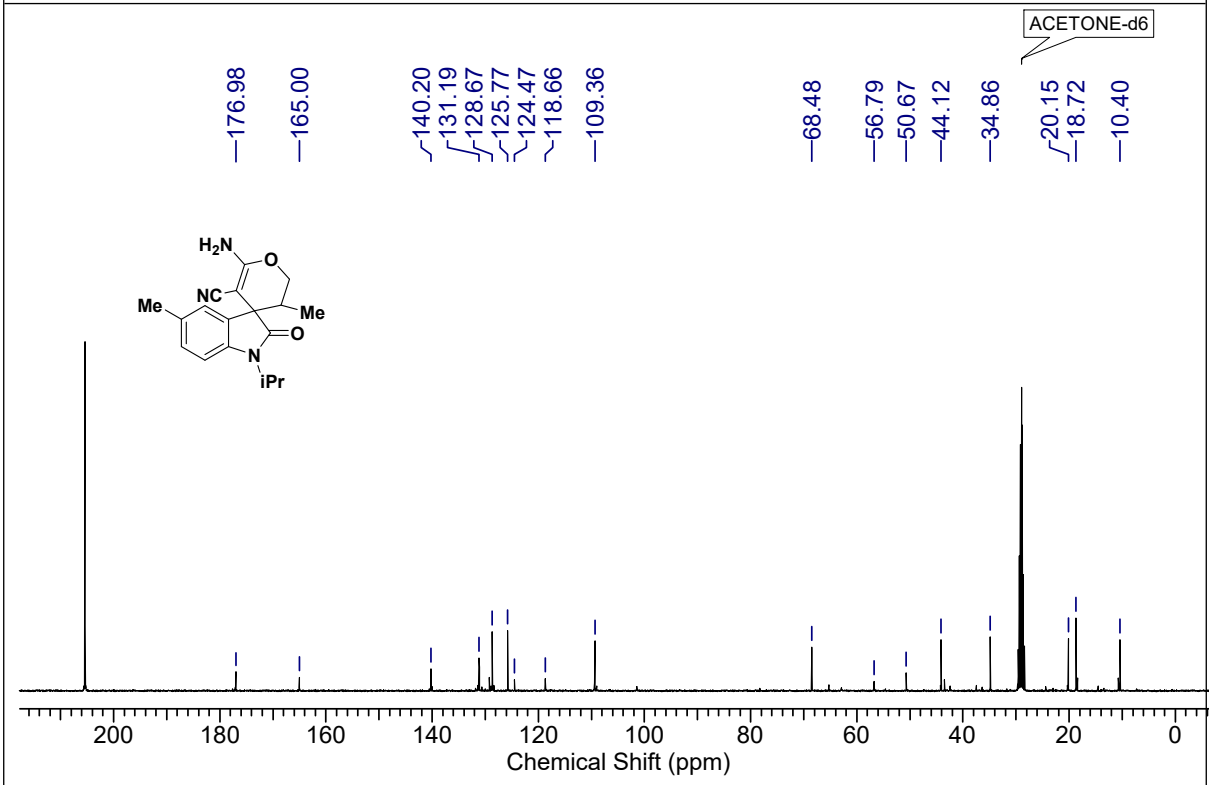
135 DEPT NMR spectrum of compound 4Bi



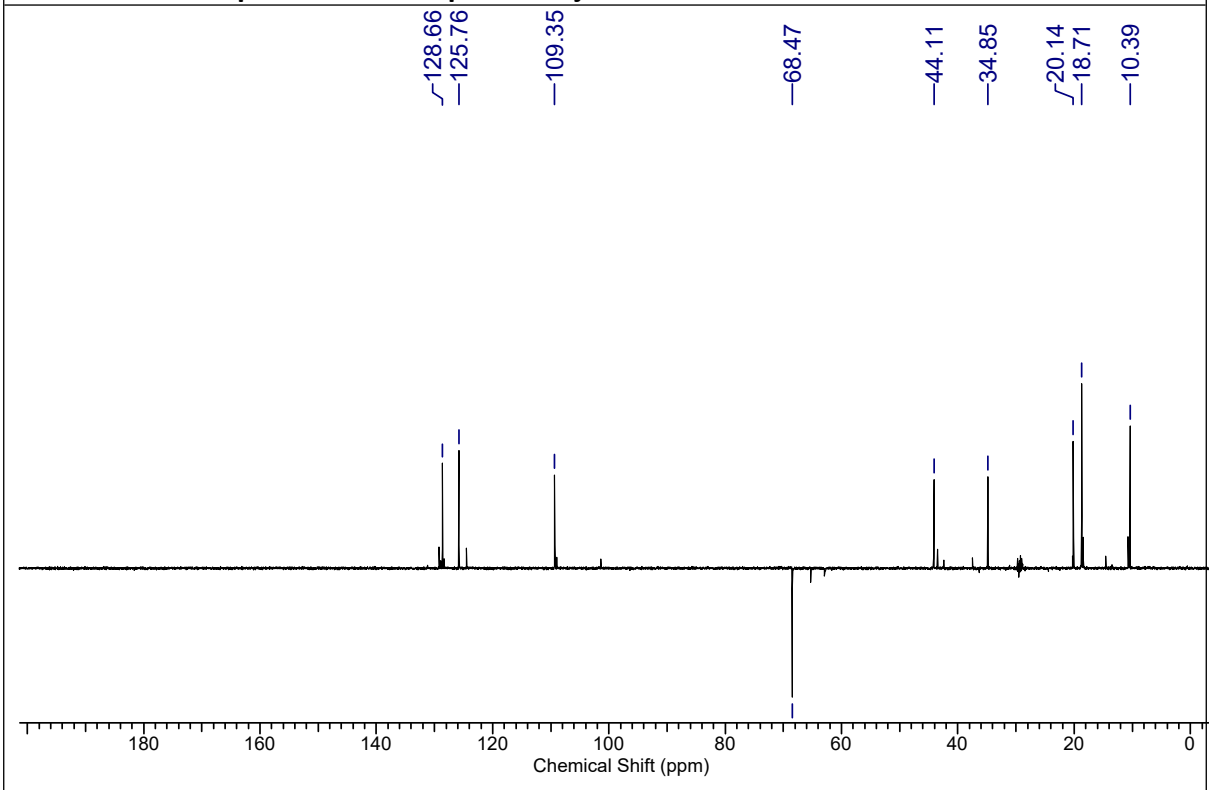
^{1}H NMR spectrum of compound 4Bj (400 MHz, Acetone-d_6)



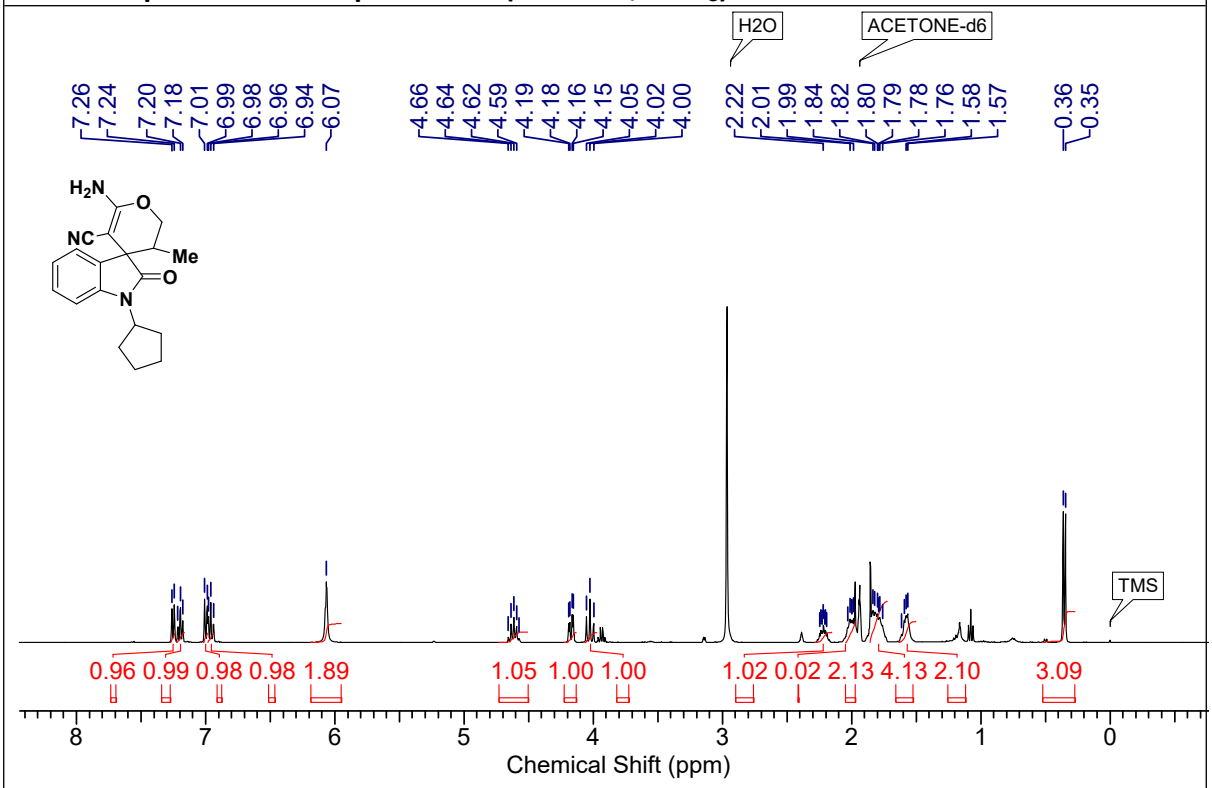
^{13}C NMR spectrum of compound 4Bj (101 MHz, Acetone-d_6)



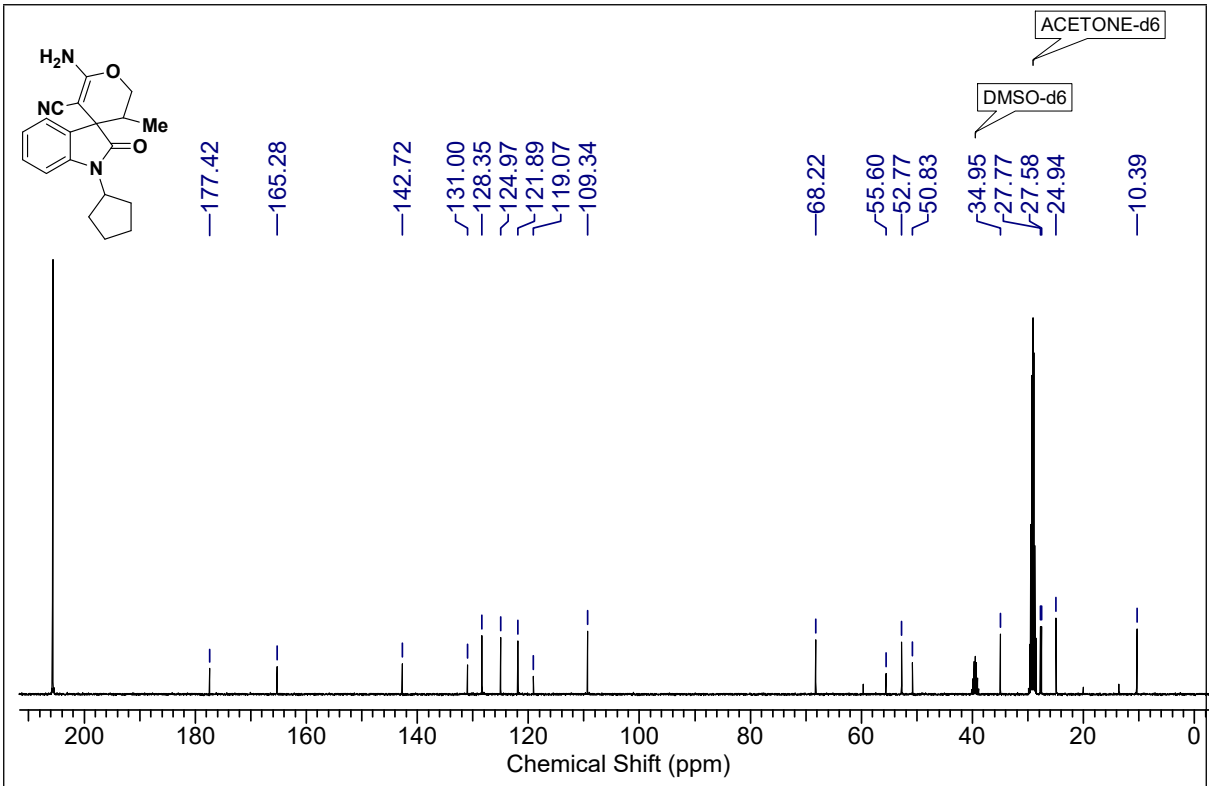
135 DEPT NMR spectrum of compound 4Bj



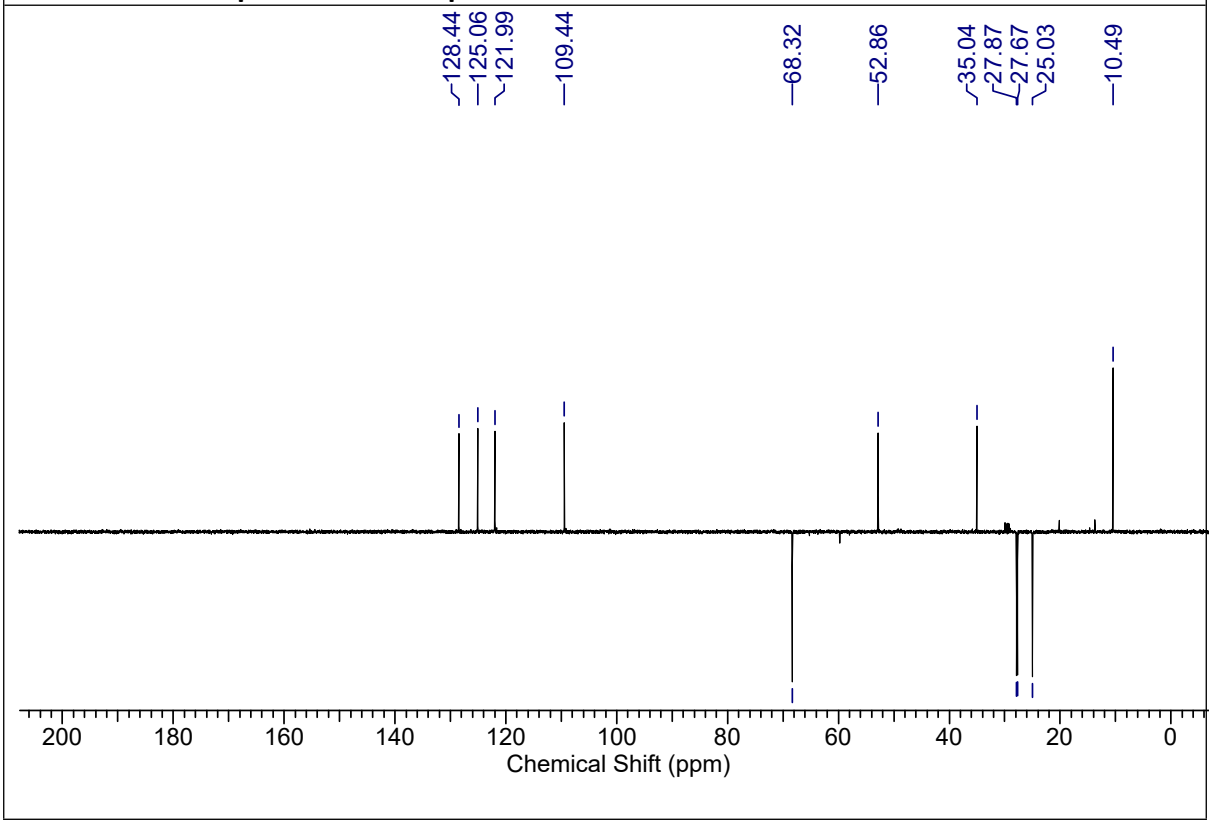
^{1}H NMR spectrum of compound 4Bk (400 MHz, $CDCl_3$)



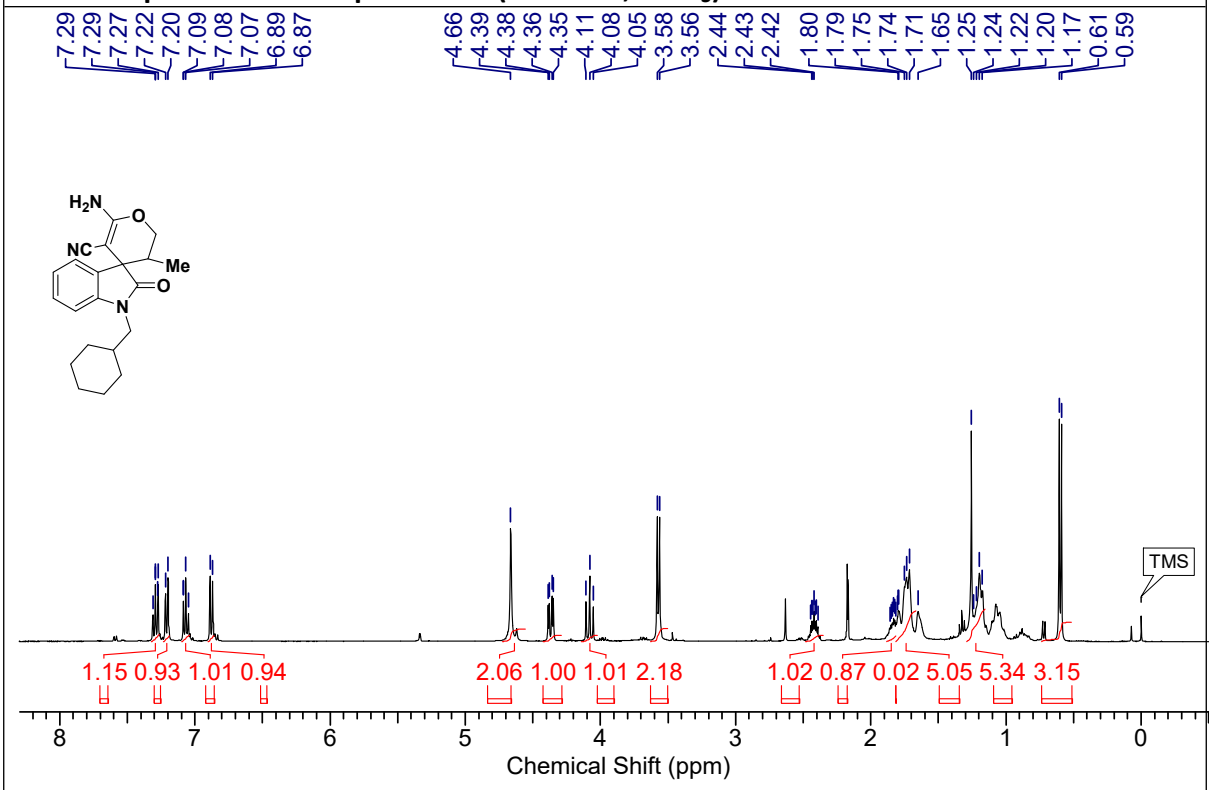
^{13}C NMR spectrum of compound 4Bk (101 MHz, $CDCl_3$)



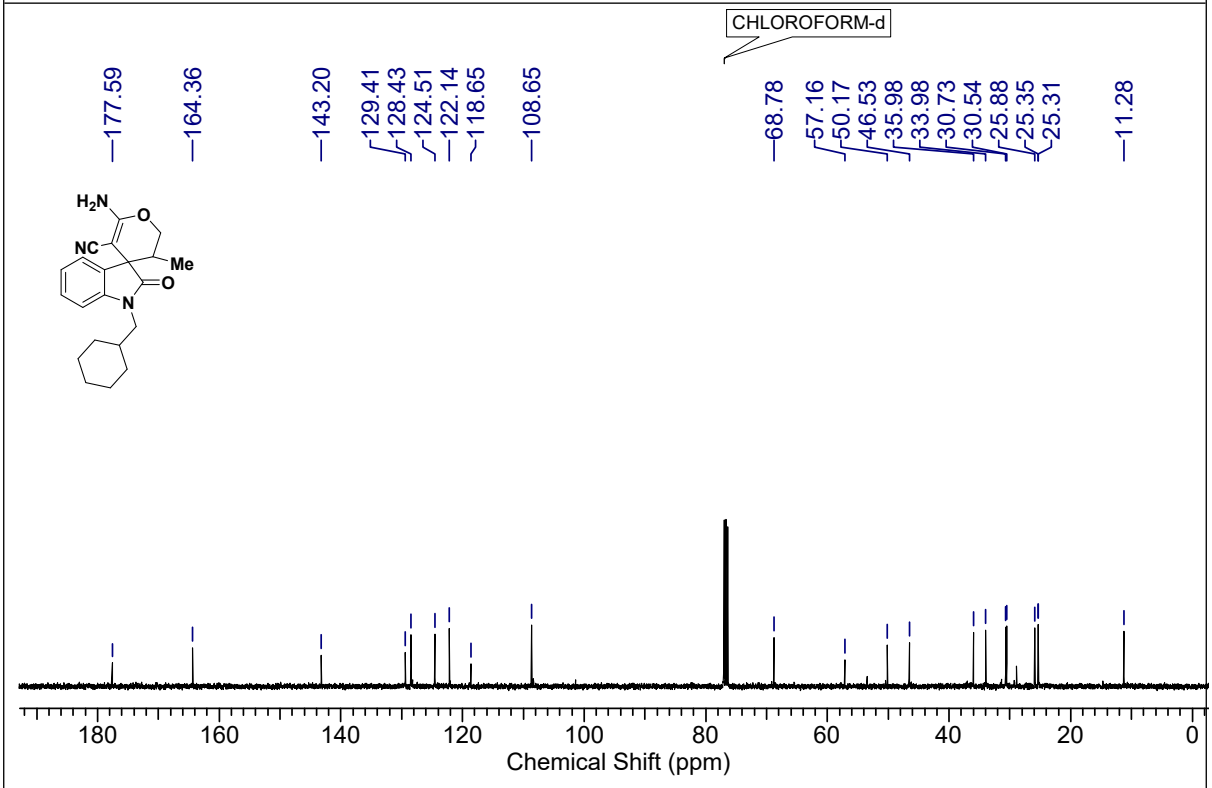
135 DEPT NMR spectrum of compound 4Bk



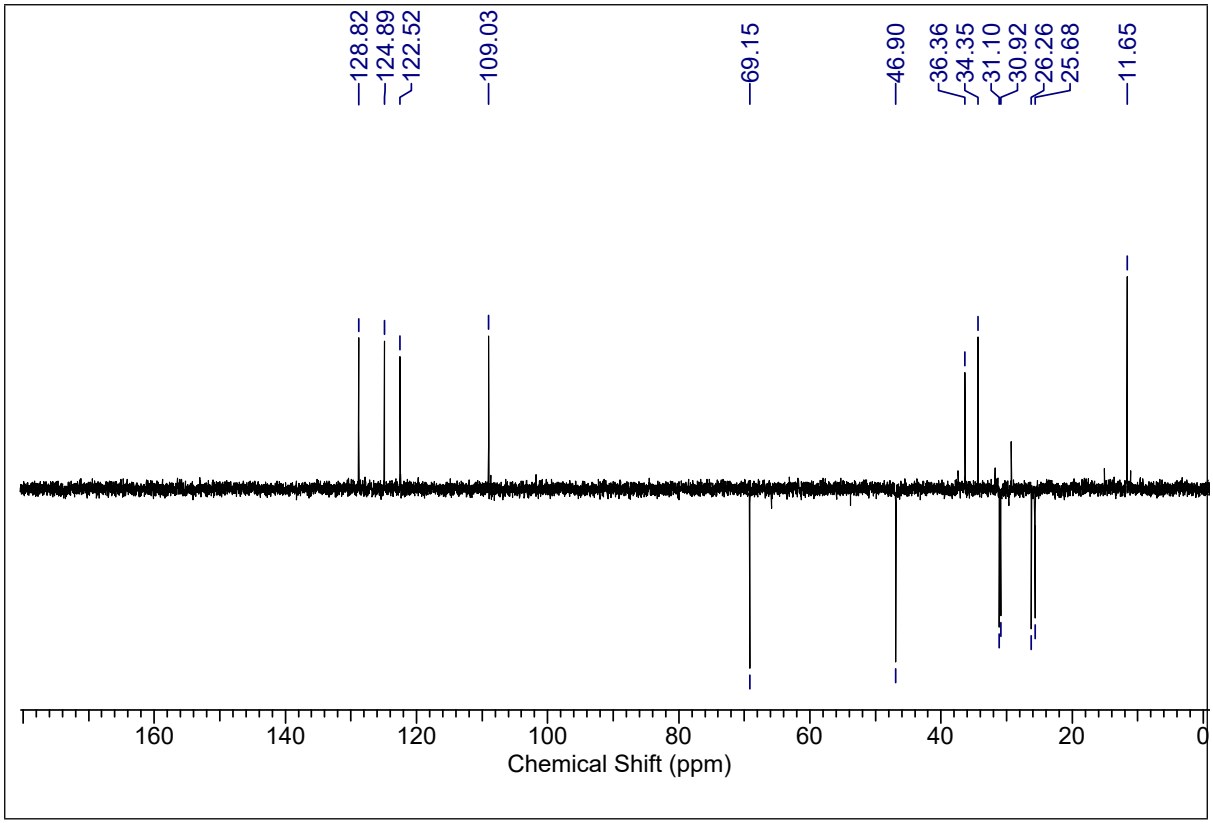
^{1}H NMR spectrum of compound 4Bl (400 MHz, $CDCl_3$)



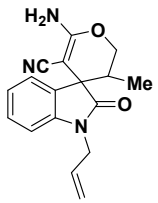
^{13}C NMR spectrum of compound 4Bl (101 MHz, $CDCl_3$)

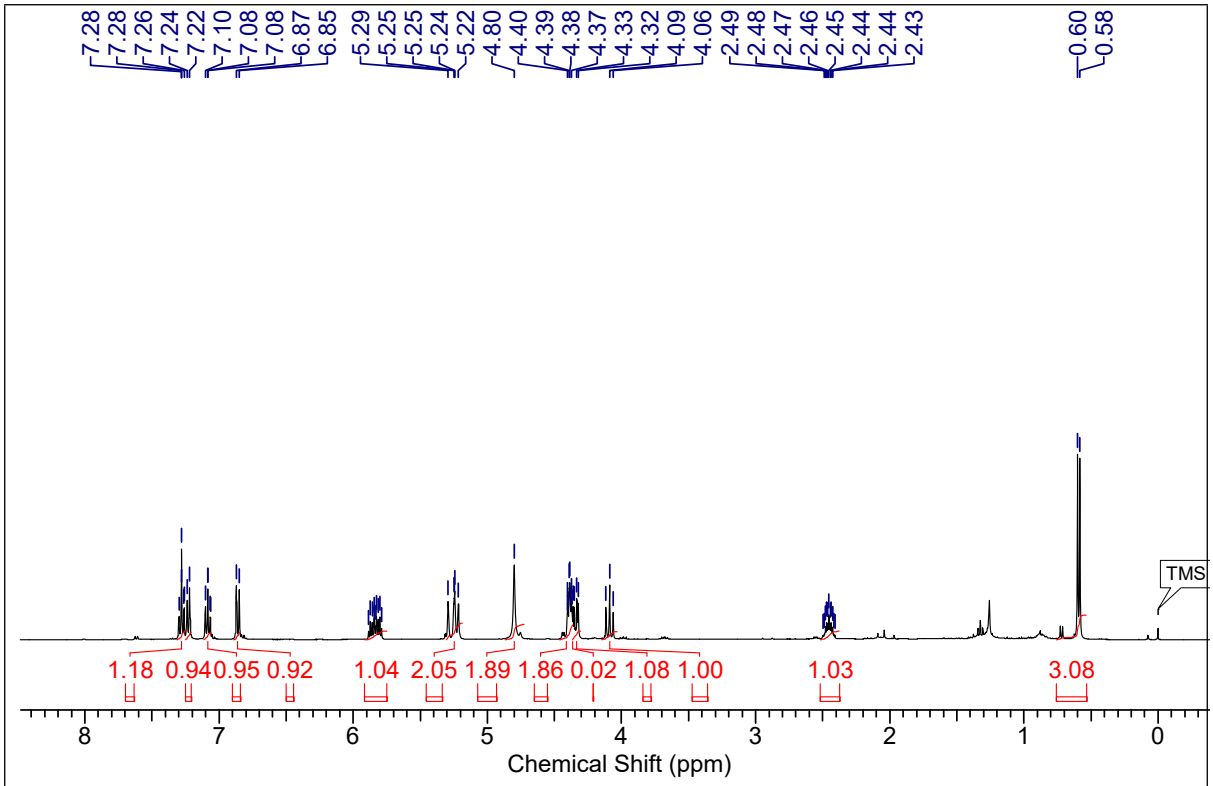


135 DEPT NMR spectrum of compound 4Bl

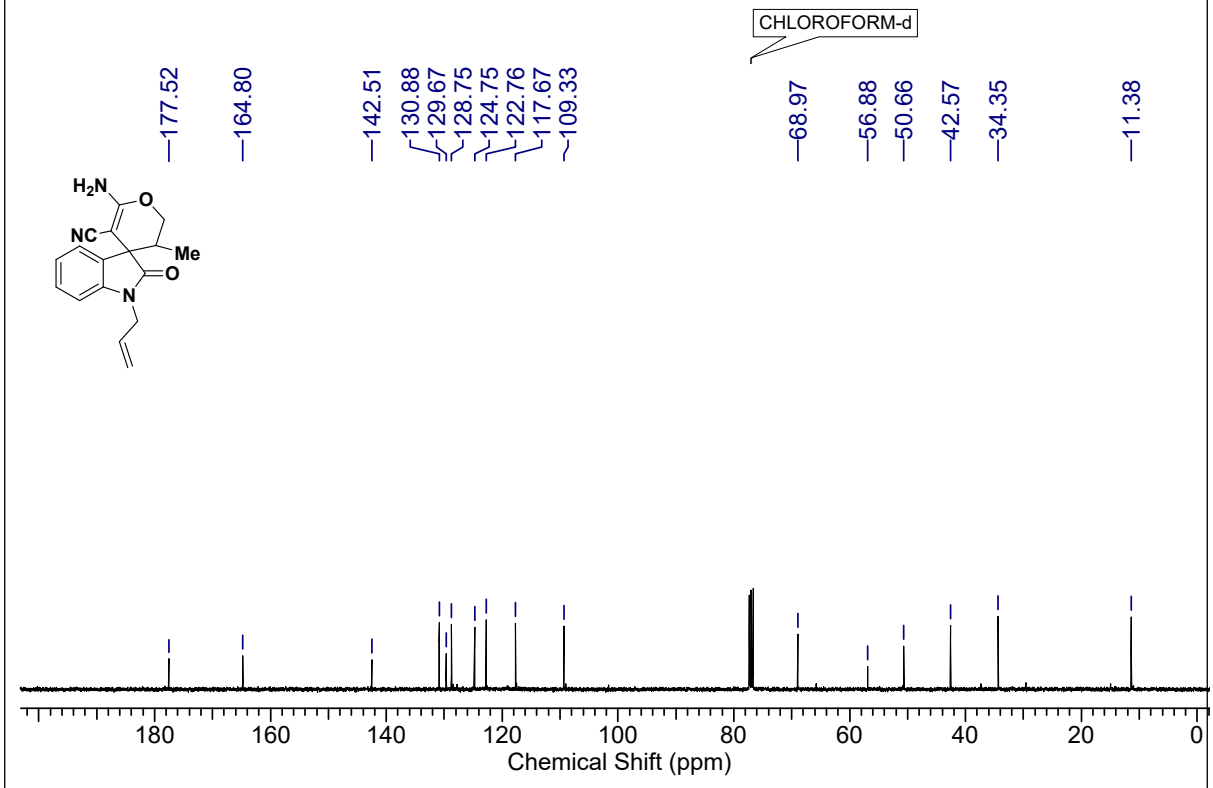


^{1}H NMR spectrum of compound 4Bm (400 MHz, $CDCl_3$)

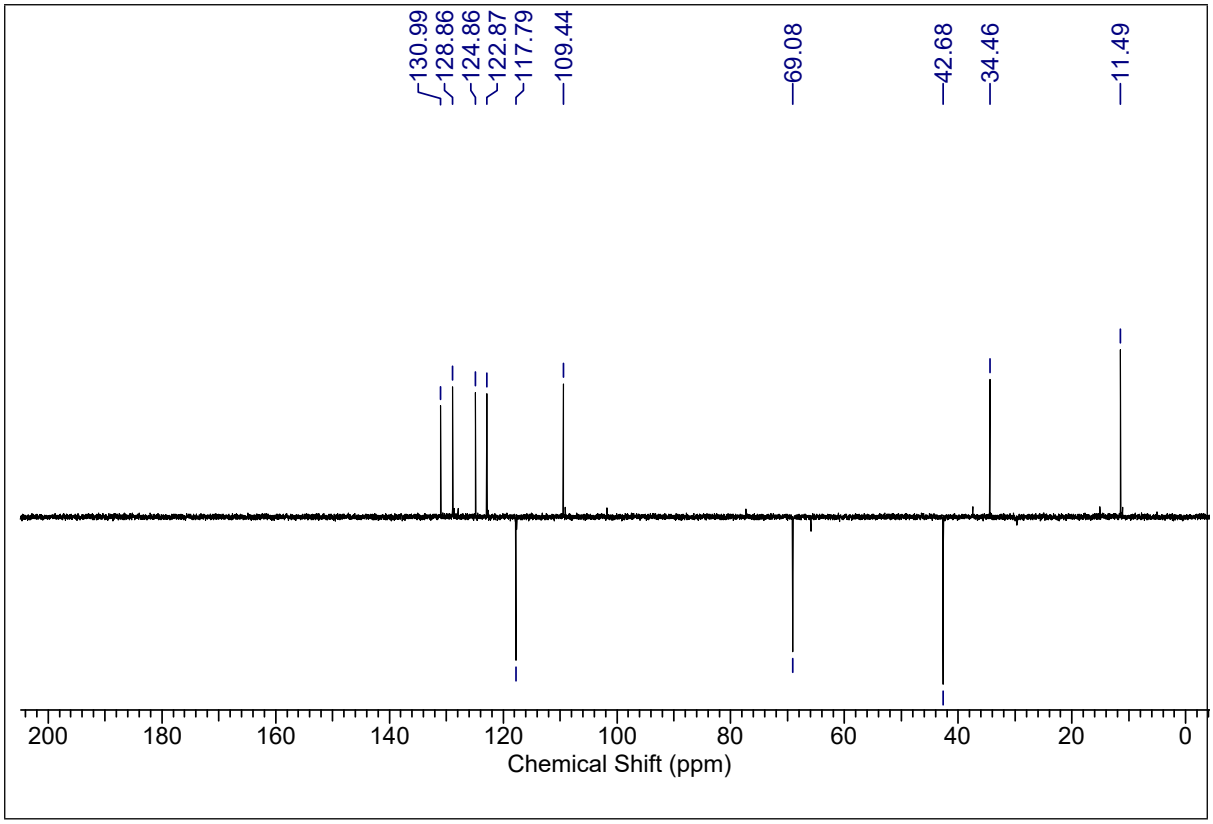




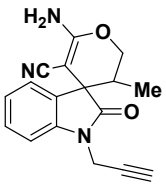
^{13}C NMR spectrum of compound 4Bm (101 MHz, $CDCl_3$)

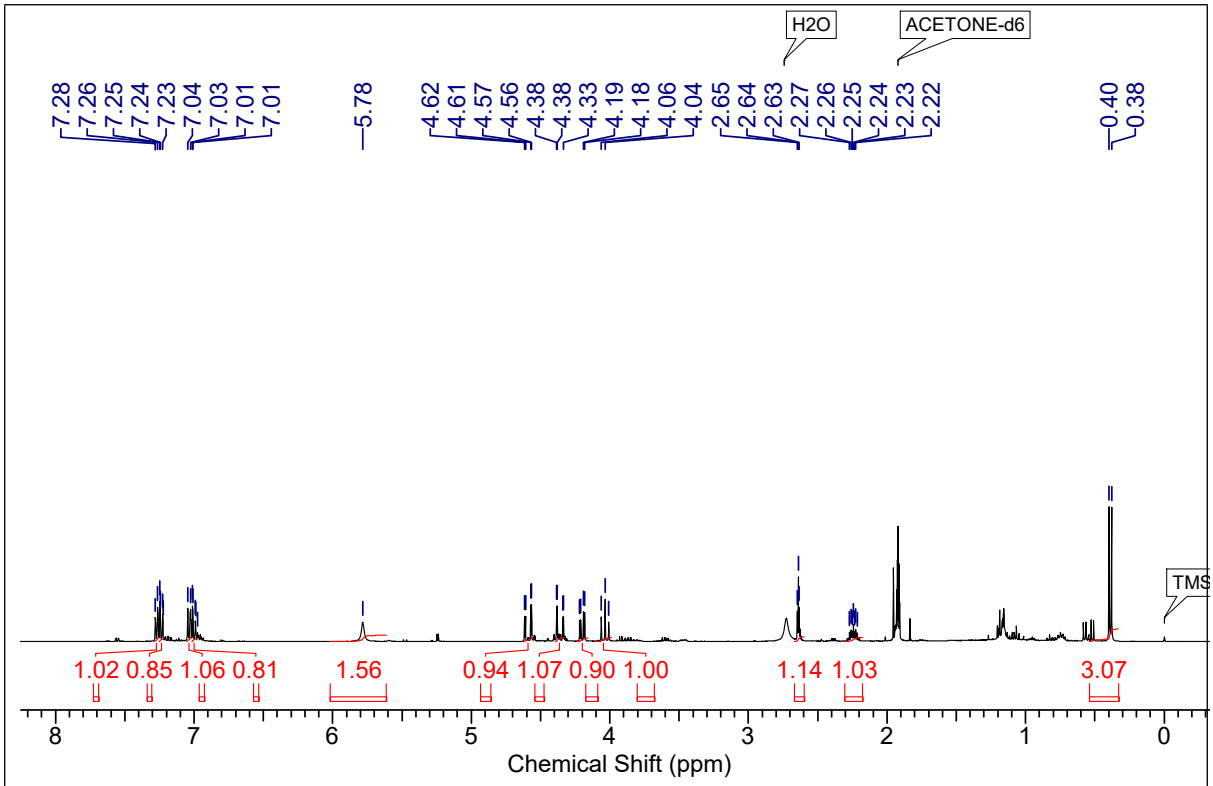


135 DEPT NMR spectrum of compound 4Bm

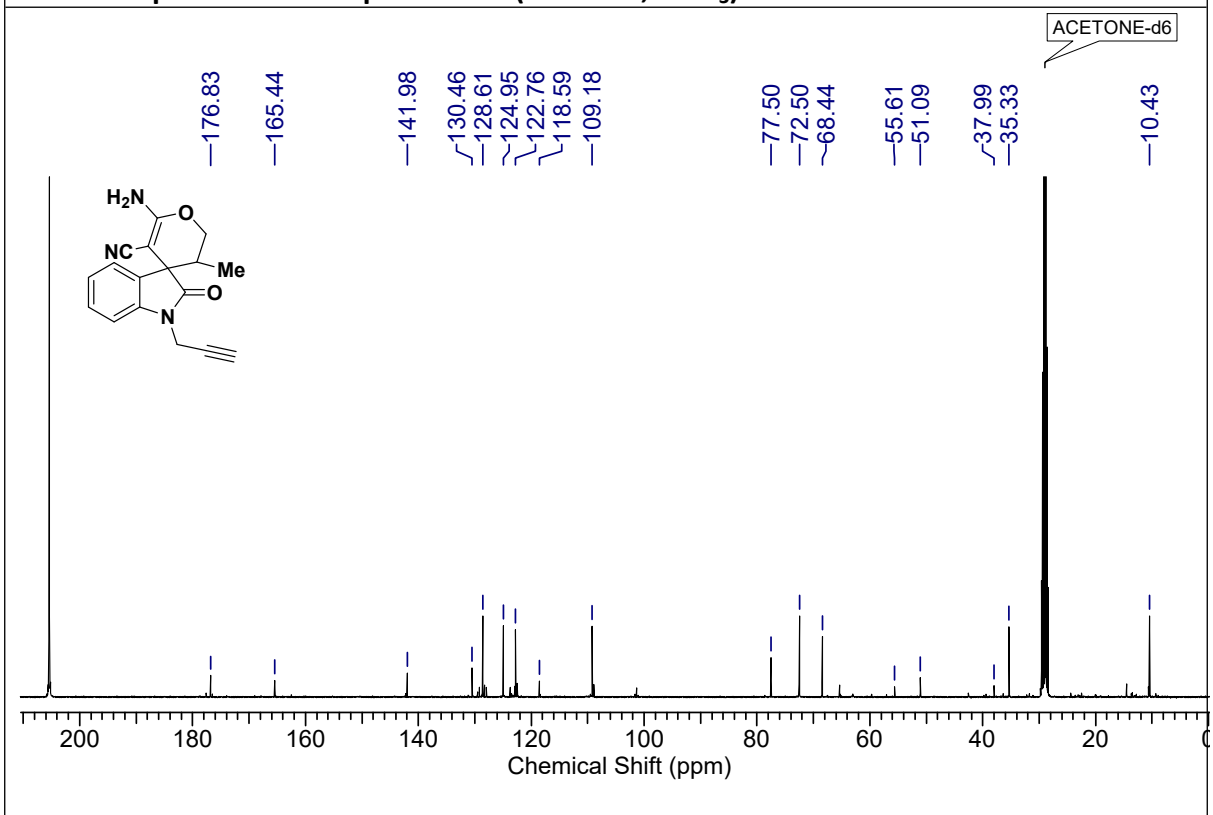


^{1}H NMR spectrum of compound 4Bn (400 MHz, $CDCl_3$)

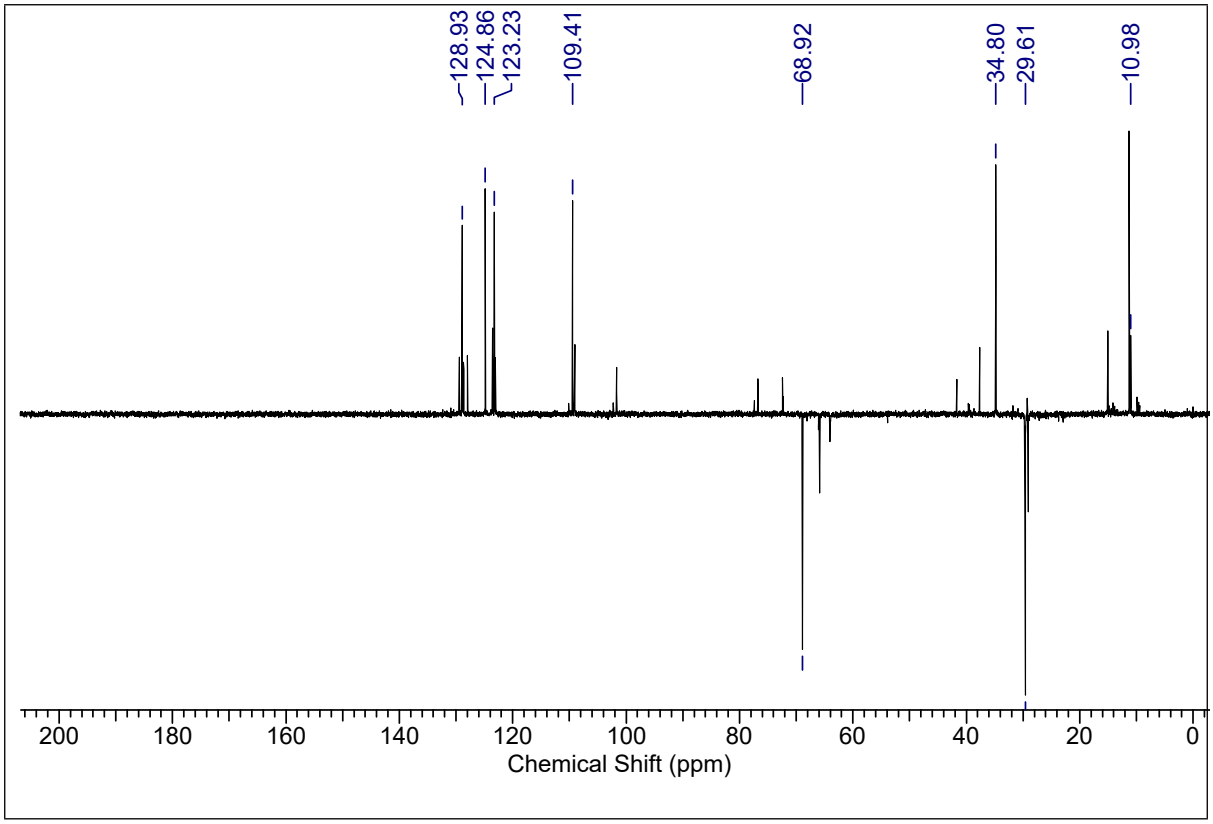


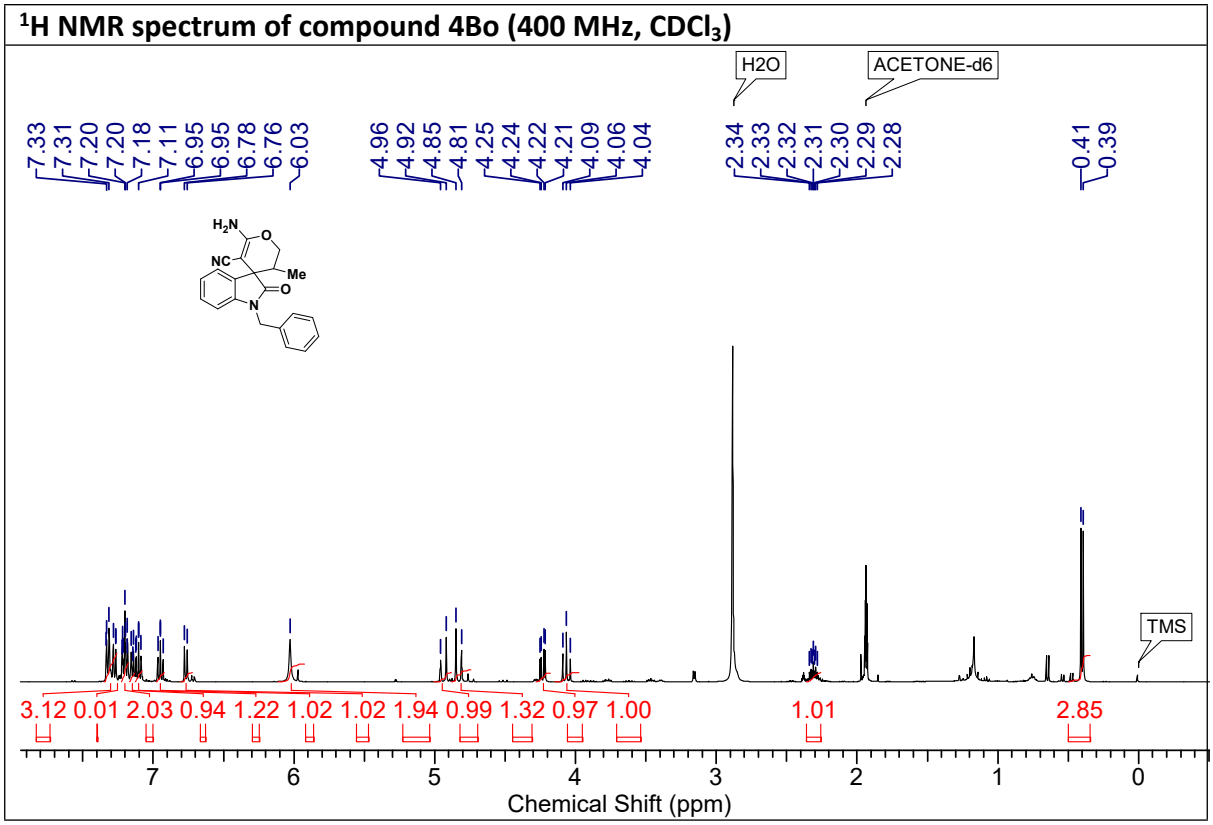


^{13}C NMR spectrum of compound 4Bn (101 MHz, $CDCl_3$)

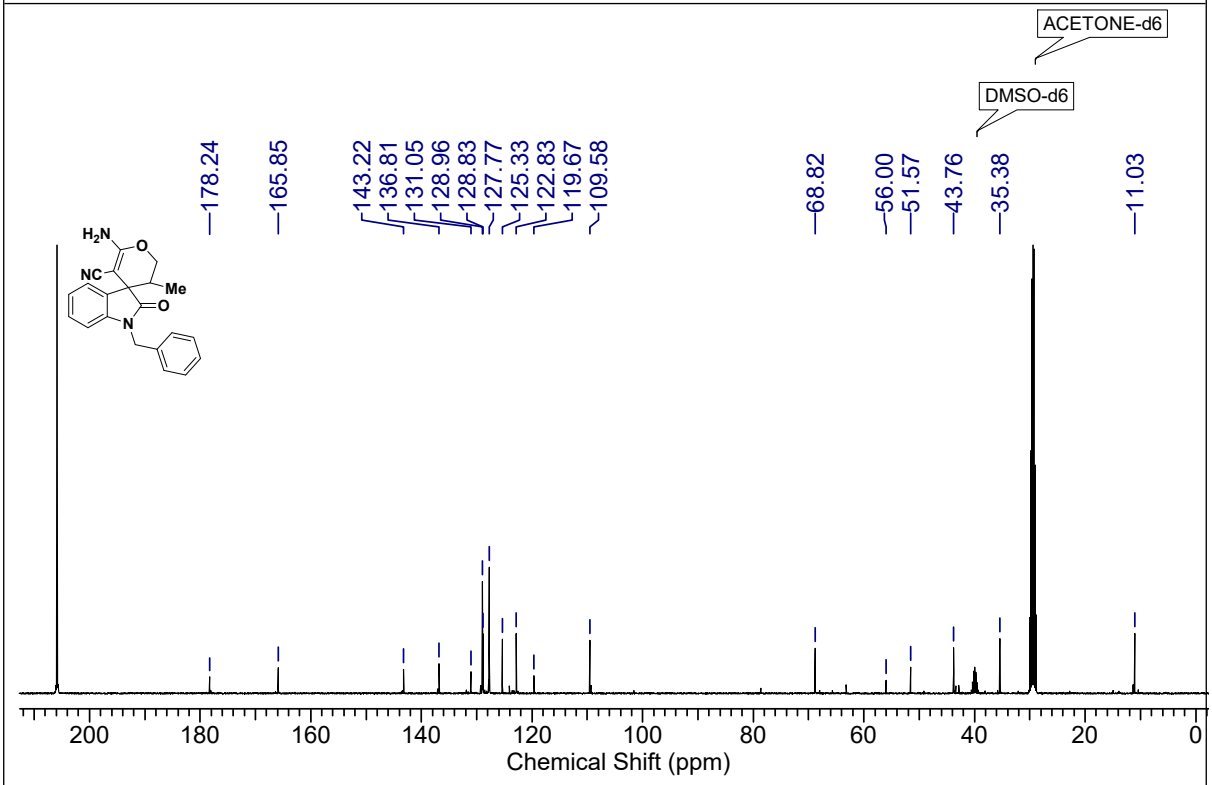


135 DEPT NMR spectrum of compound 4Bn

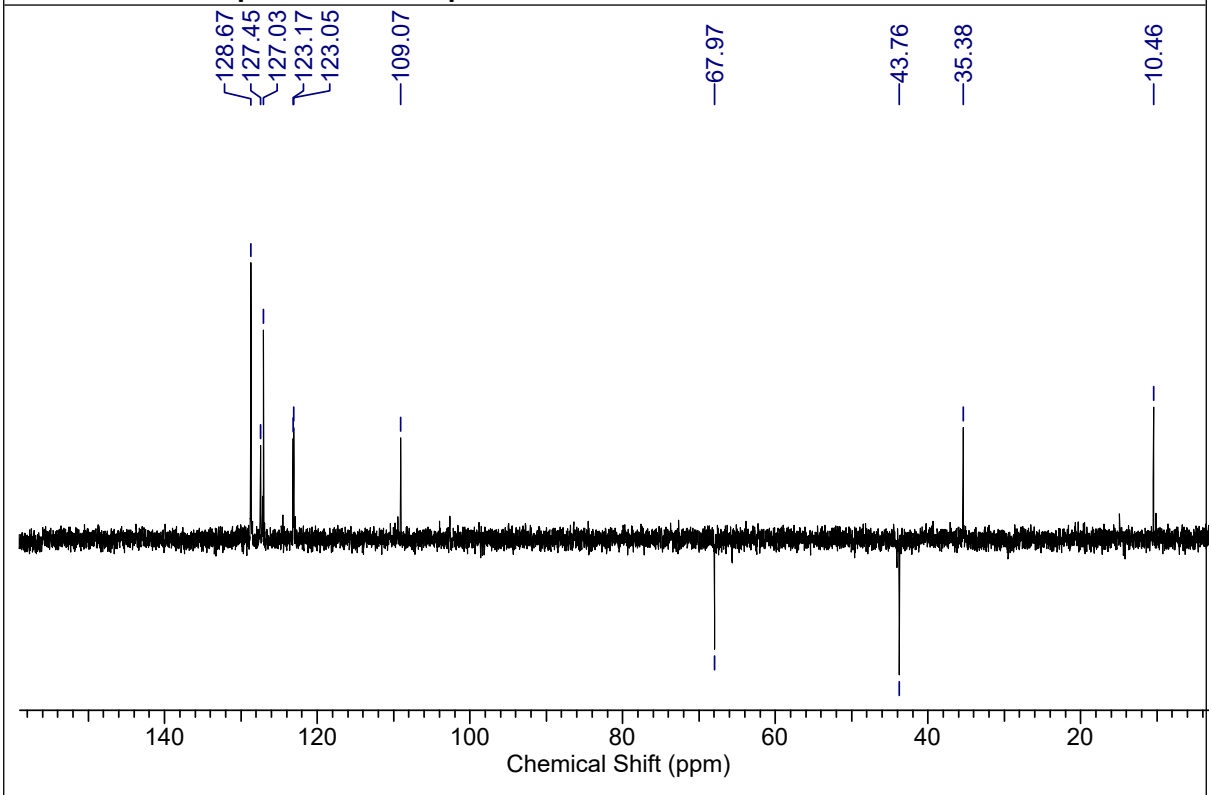

128.93
124.86
123.23
109.41
68.92
34.80
29.61
10.98
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


¹H NMR spectrum of compound 4Bo (400 MHz, CDCl3)
H2O
ACETONE-d6
7.33
7.31
7.20
7.20
7.18
7.11
6.95
6.95
6.78
6.76
6.03
4.96
4.92
4.85
4.81
4.25
4.24
4.22
4.21
4.09
4.06
4.04
2.34
2.33
2.32
2.31
2.30
2.29
2.28
0.41
0.39
H2N
O
NC
Me
O
N
TMS
3.12 0.01 2.03 0.94 1.22 1.02 1.02 1.94 0.99 1.32 0.97 1.00
1.01
2.85
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

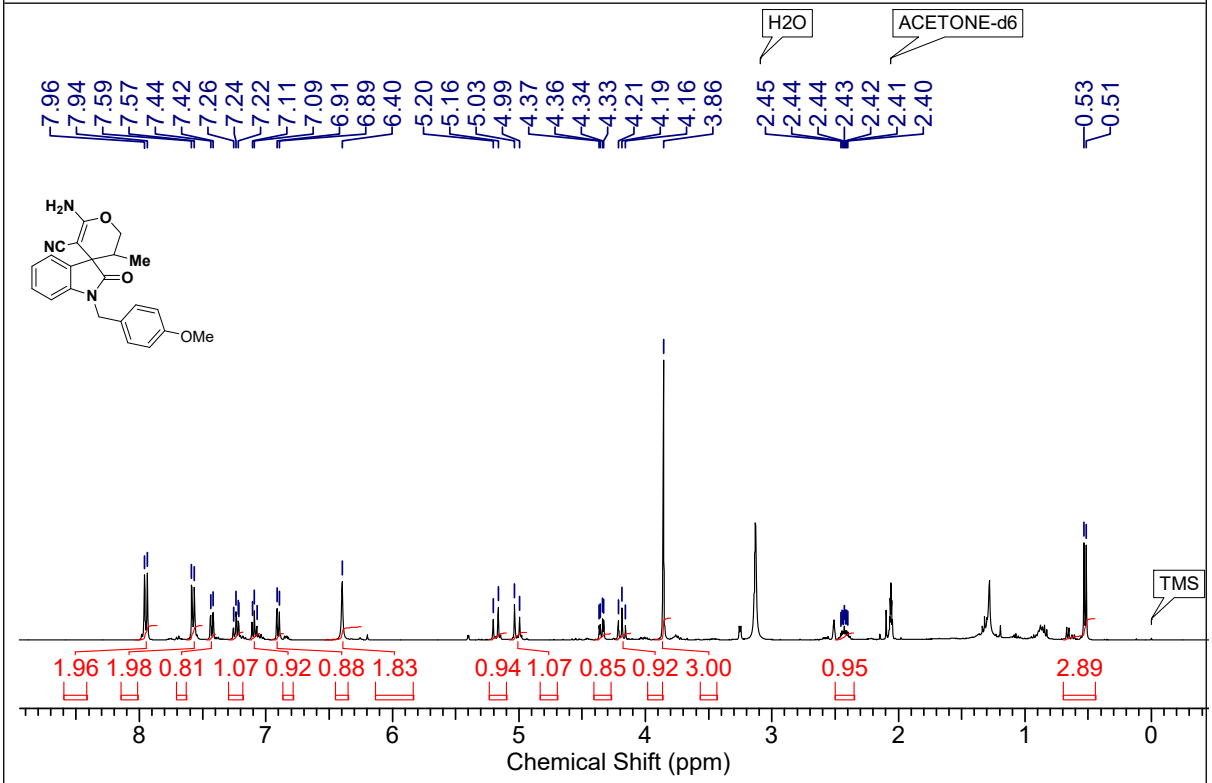
^{13}C NMR spectrum of compound 4Bo (101 MHz, $CDCl_3$)



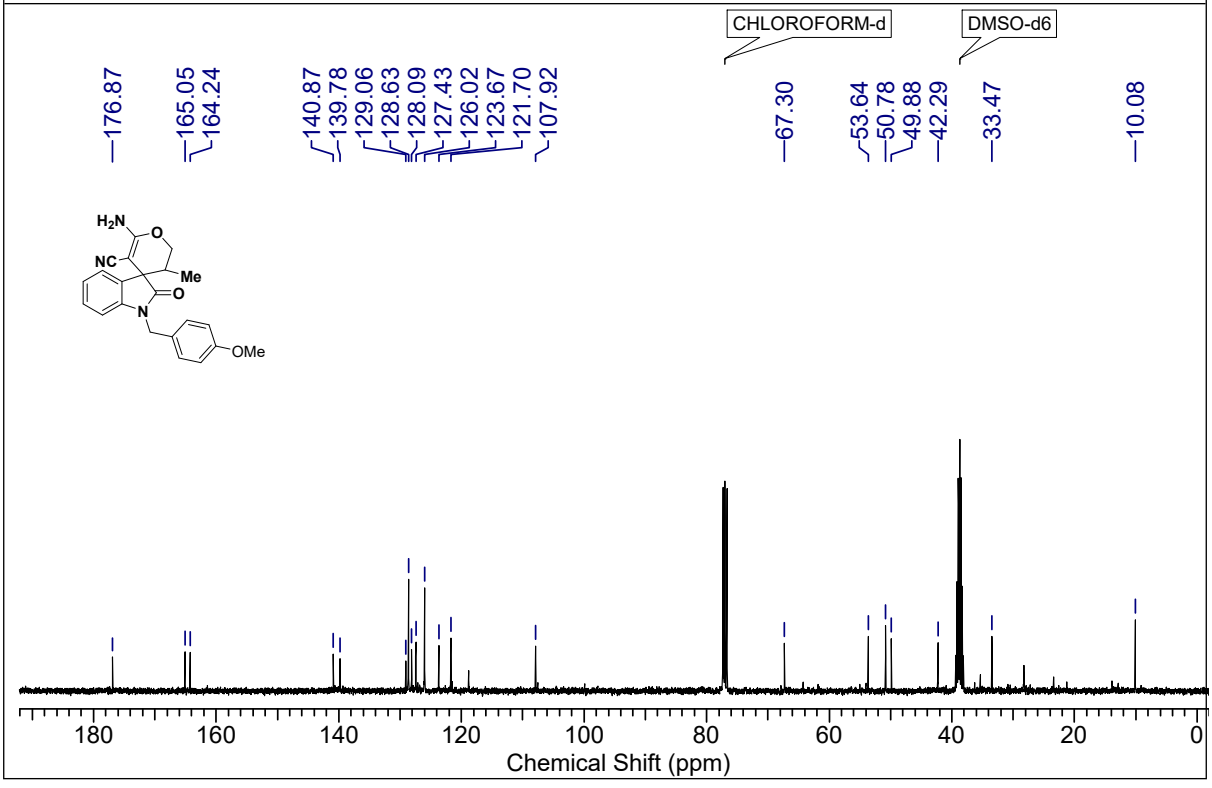
135 DEPT NMR spectrum of compound 4Bo



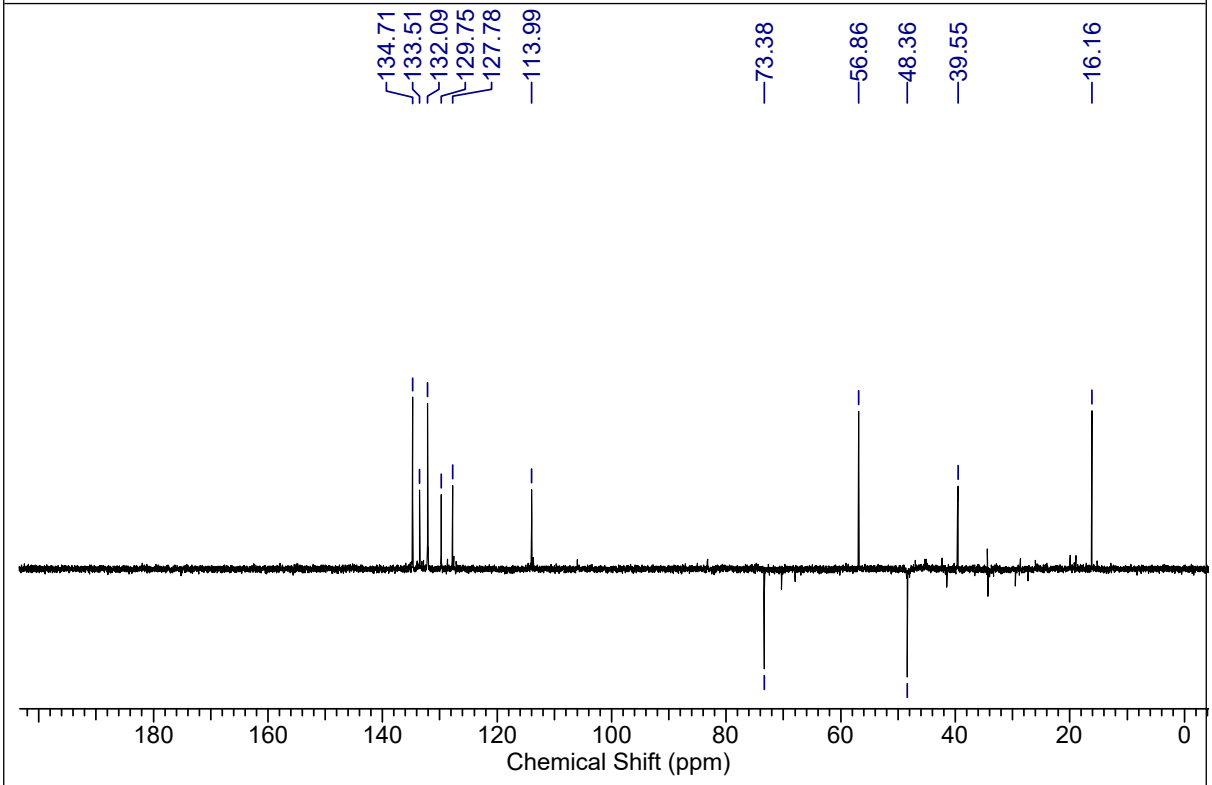
^{1}H NMR spectrum of compound 4Bp (400 MHz, Acetone-d_6)



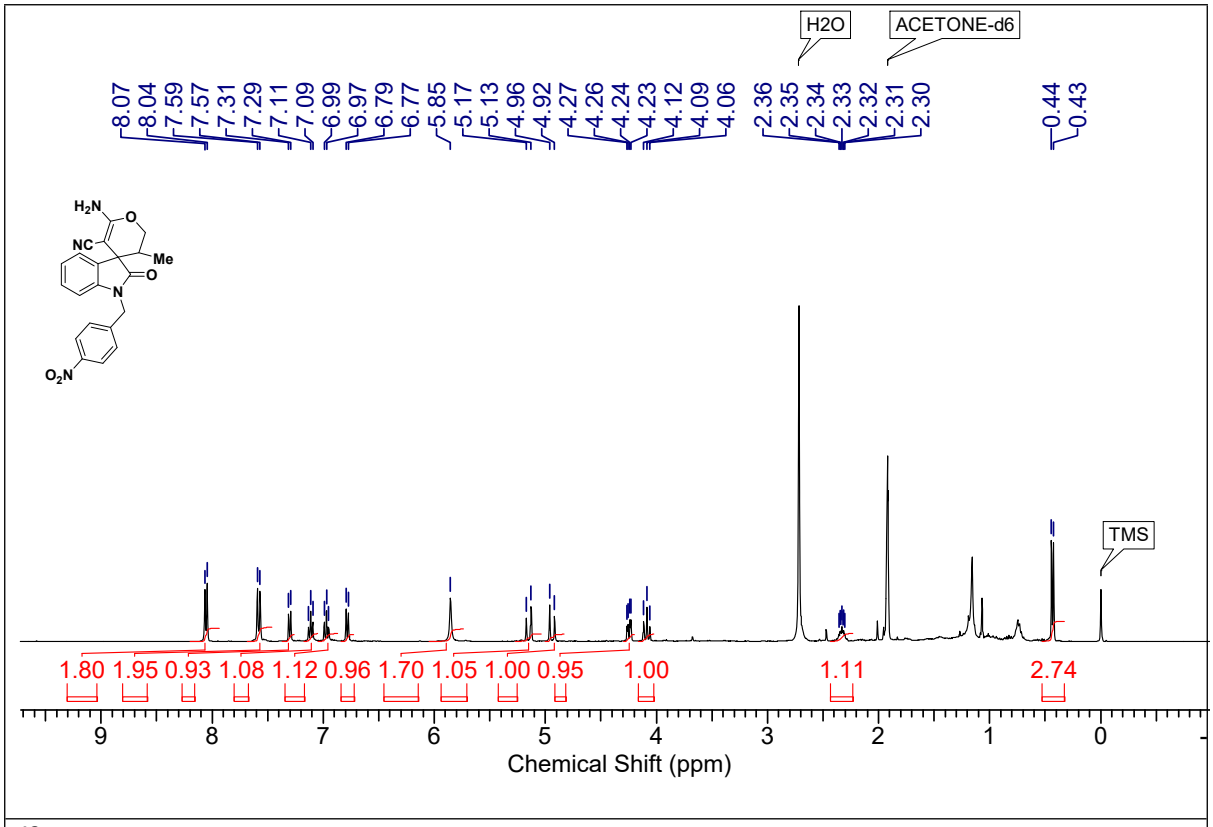
^{13}C NMR spectrum of compound 4Bp (101 MHz, Acetone-d_6)



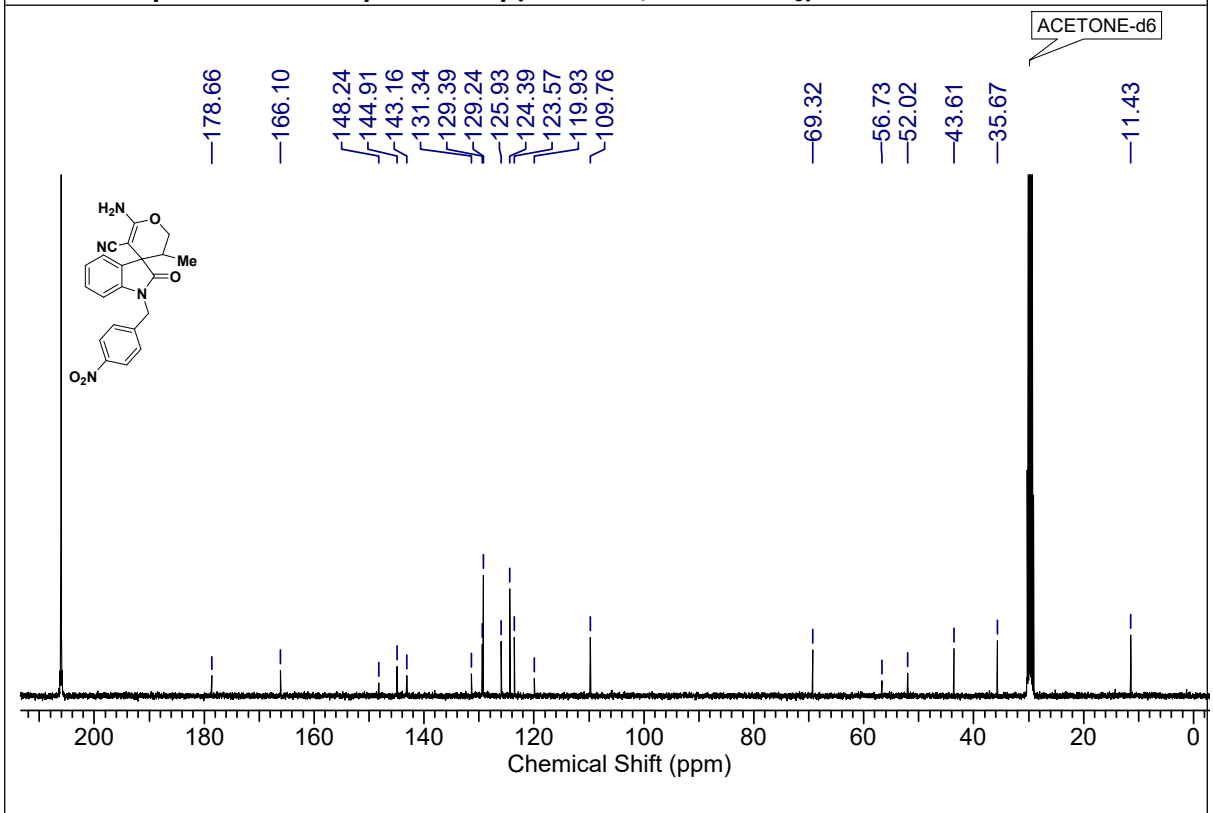
135 DEPT NMR spectrum of compound 4Bp



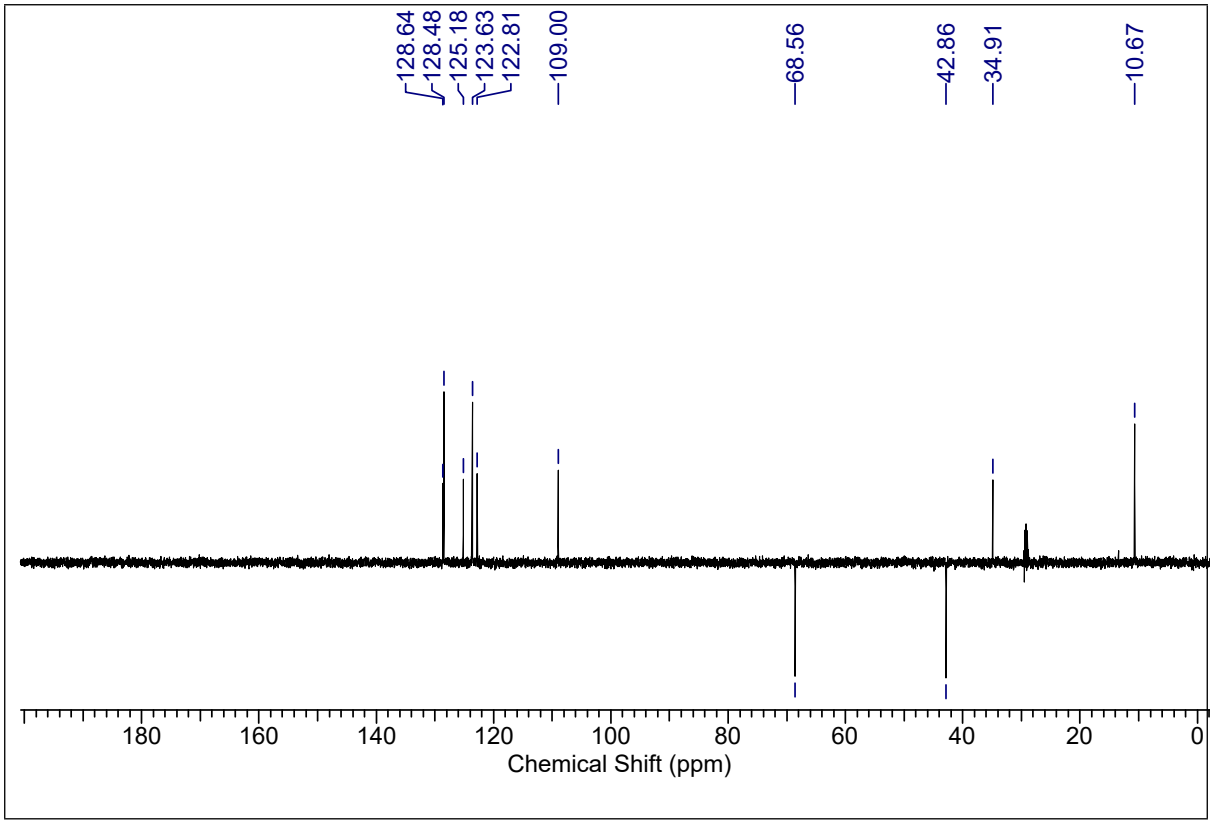
^{1}H NMR spectrum of compound 4Bq (400 MHz, Acetone-d_6)



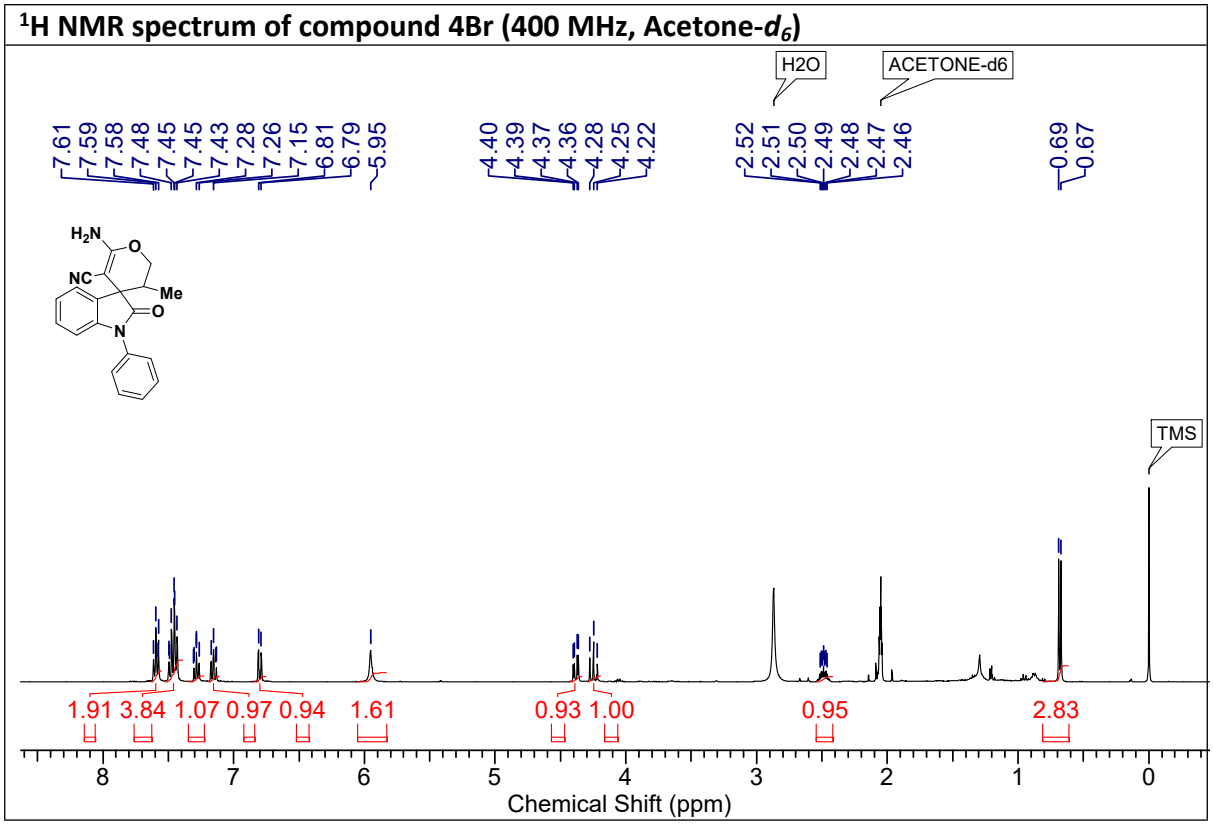
^{13}C NMR spectrum of compound 4Bq (101 MHz, Acetone-d_6)



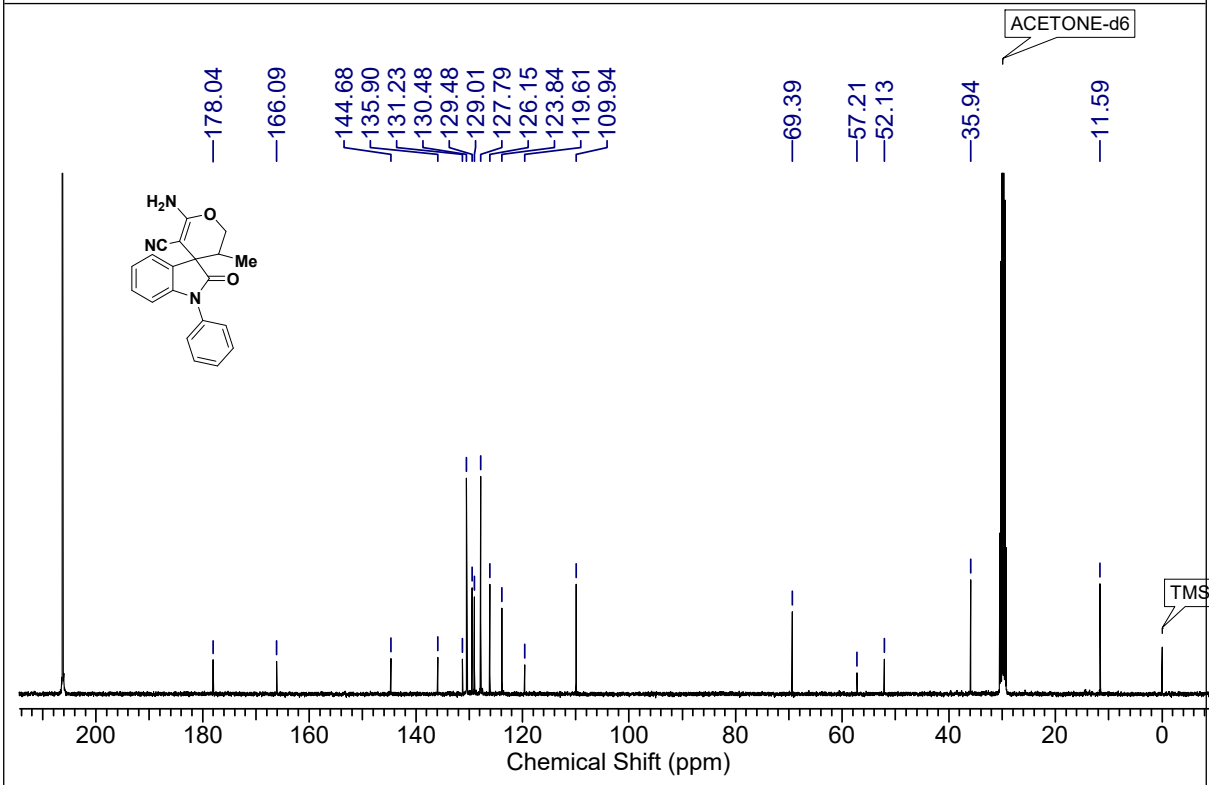
135 DEPT NMR spectrum of compound 4Bq



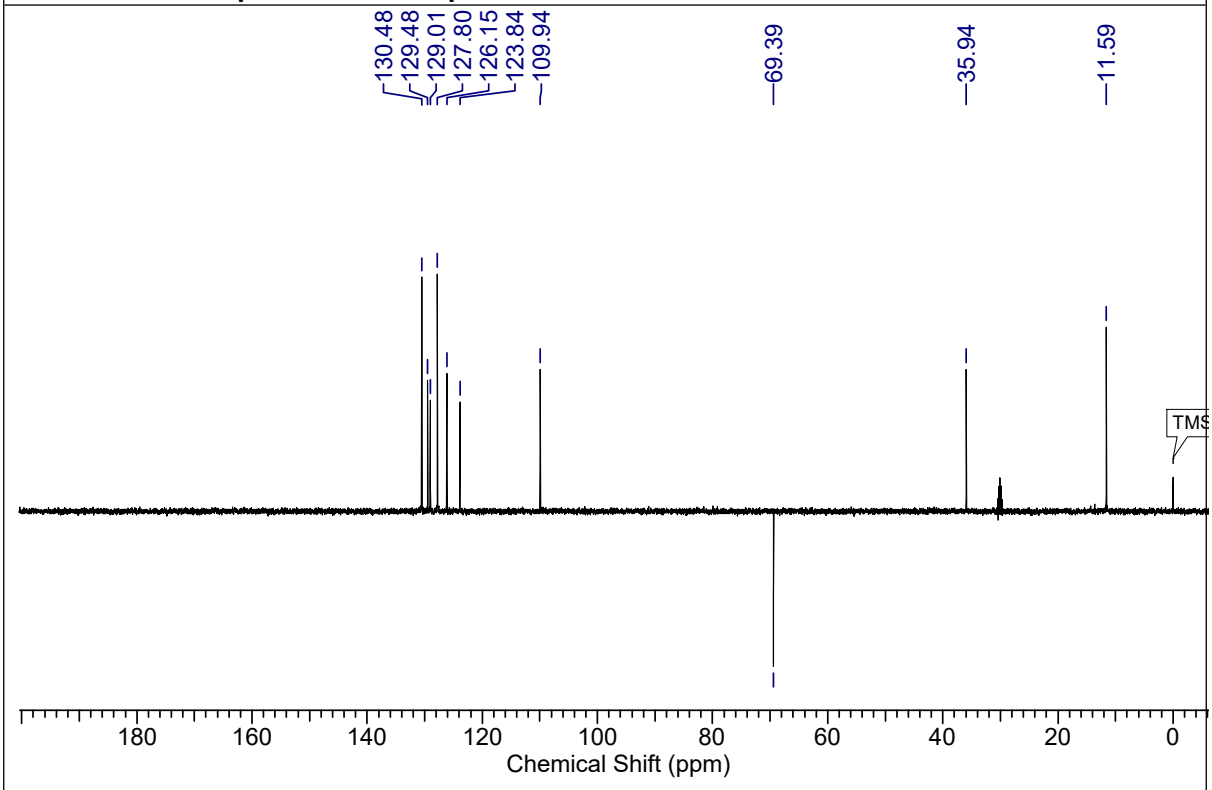
^{1}H NMR spectrum of compound 4Br (400 MHz, Acetone-d_6)



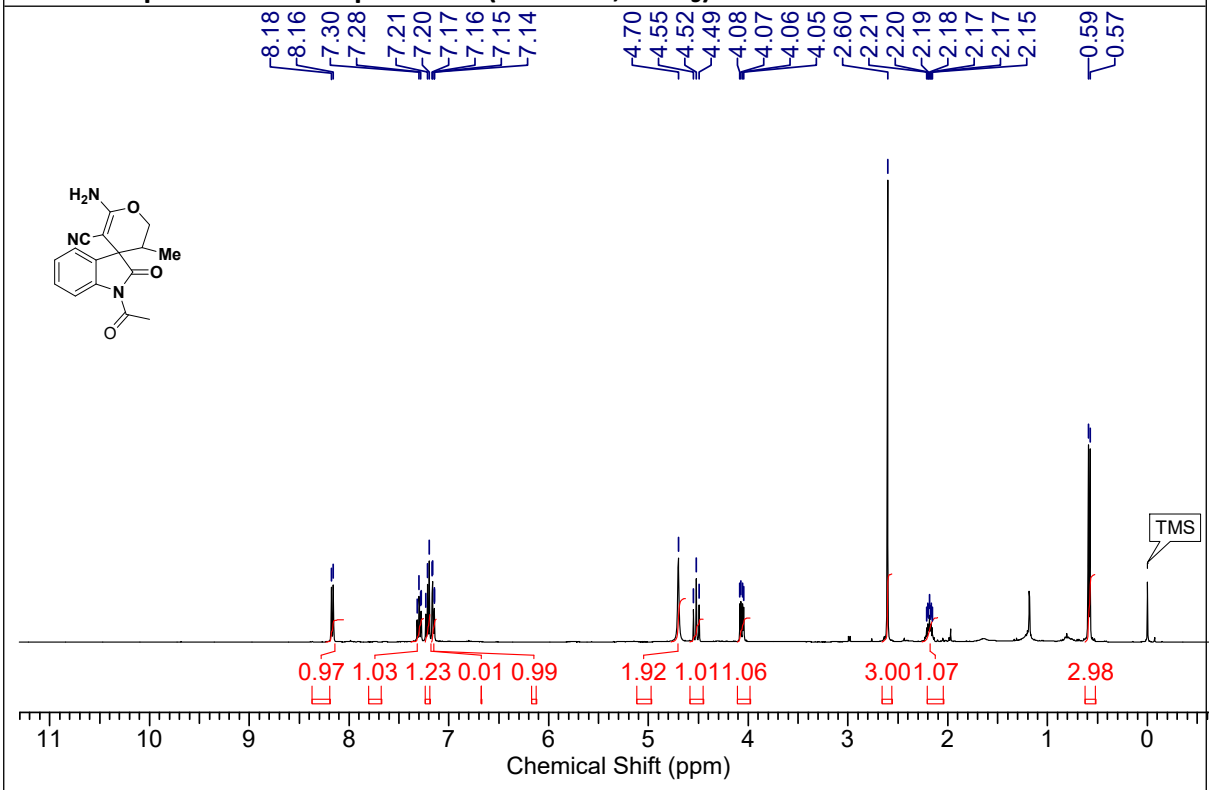
^{13}C NMR spectrum of compound 4Br (101 MHz, Acetone-d_6)



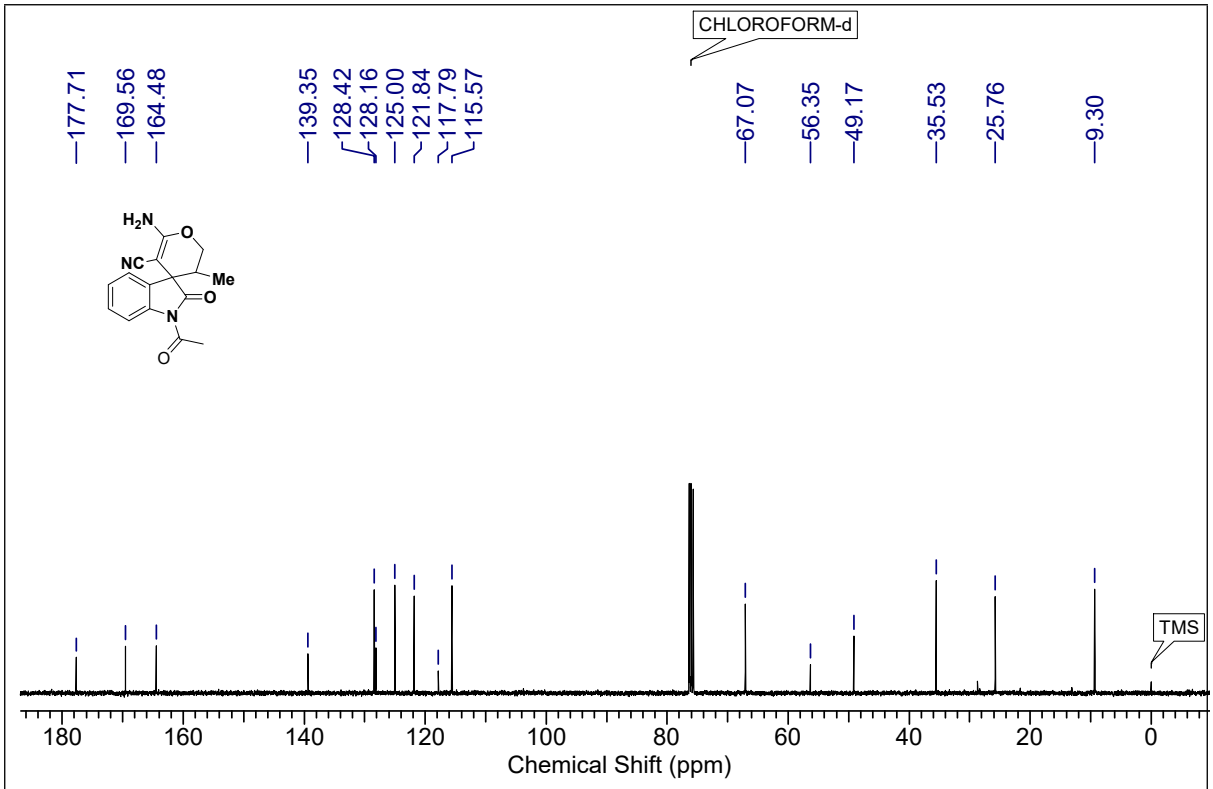
135 DEPT NMR spectrum of compound 4Br



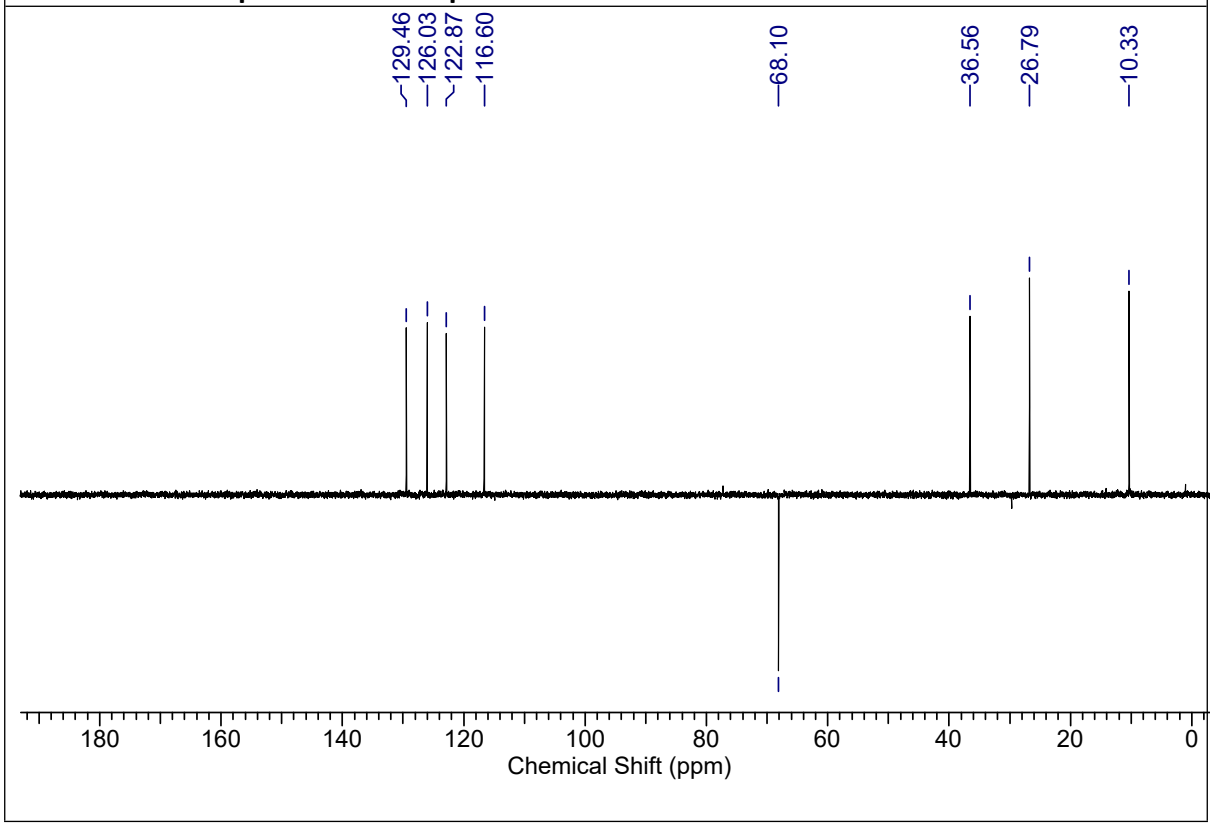
^{1}H NMR spectrum of compound 5a (400 MHz, $CDCl_3$)



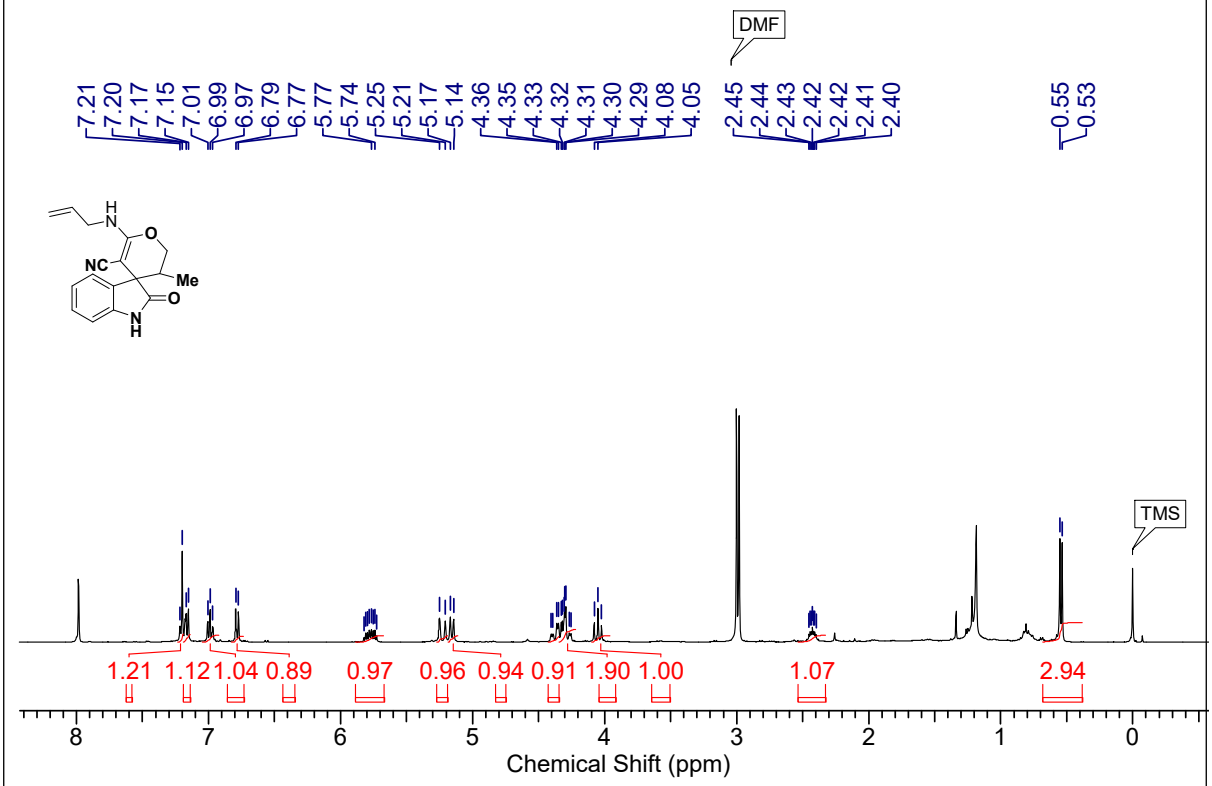
^{13}C NMR spectrum of compound 5a (400 MHz, $CDCl_3$)



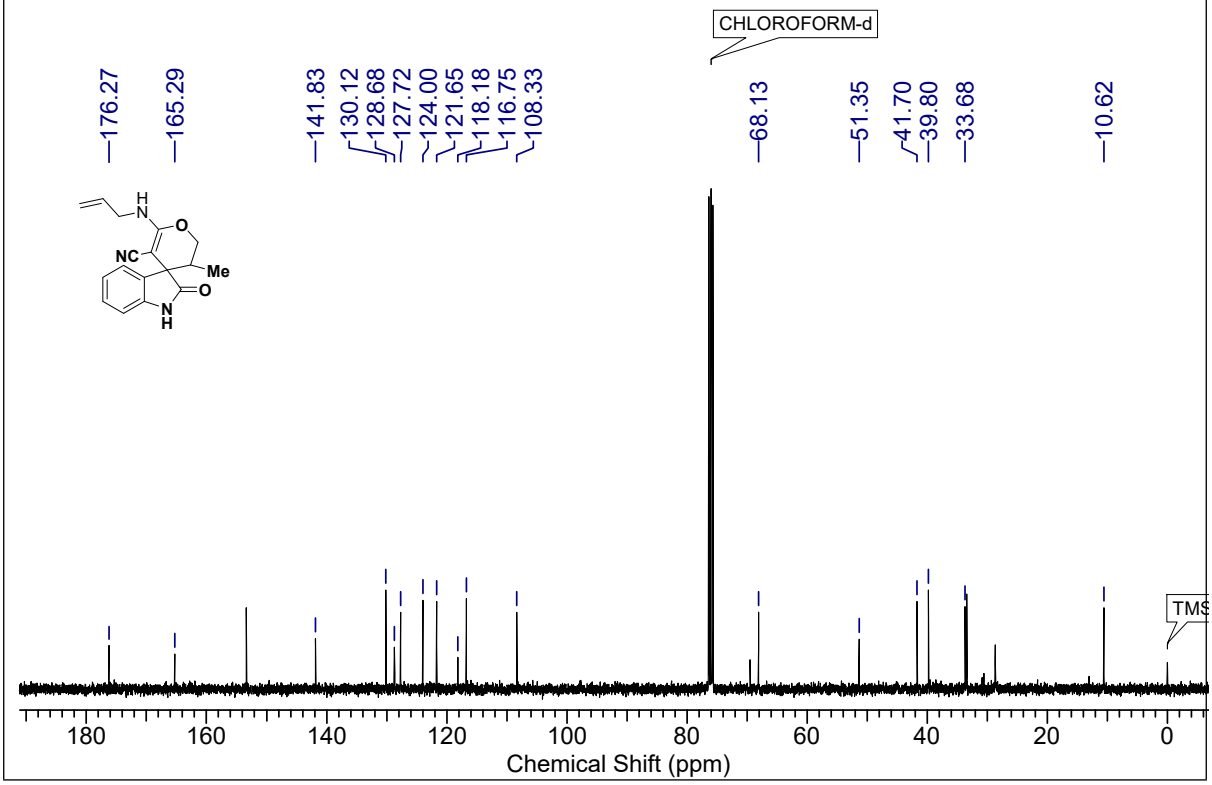
135 DEPT NMR spectrum of compound 5a



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



^{13}C NMR spectrum of compound 6a (400 MHz, $CDCl_3$)



135 DEPT NMR spectrum of compound 6a