Supporting information for

A Facile and Metal-Free Domino Reaction of TsDAM and 2-alkenylarylaldehyde: An easy access to 8-hydroxy-2,8-dihydroindeno [2,1-*c*]pyrazoles

Gopathi Ramu,[a,b,§] Bheeshma Geetanjali Kodiripaka,[a,§] Kalakonda Raga Chaitanya,[a,b] and Bathini Nagendra Babu*[a,b]

[a]Department of Fluoro-Agrochemicals, CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, India
[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201 002, India

* Corresponding author:

Bathini Nagendra Babu, Fax: +91-40-27160512; E-mail: bathini@iict.res.in

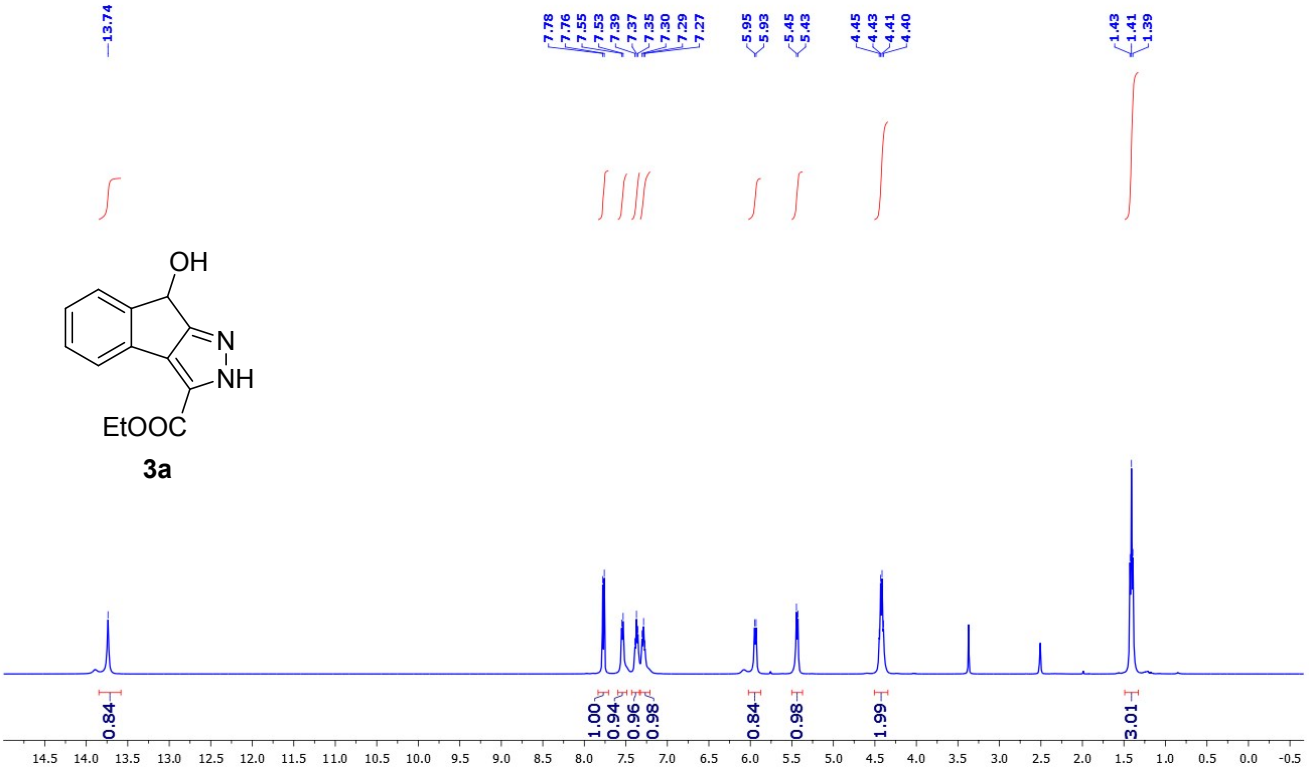
Table of Contents:

General information and Instrumentation:

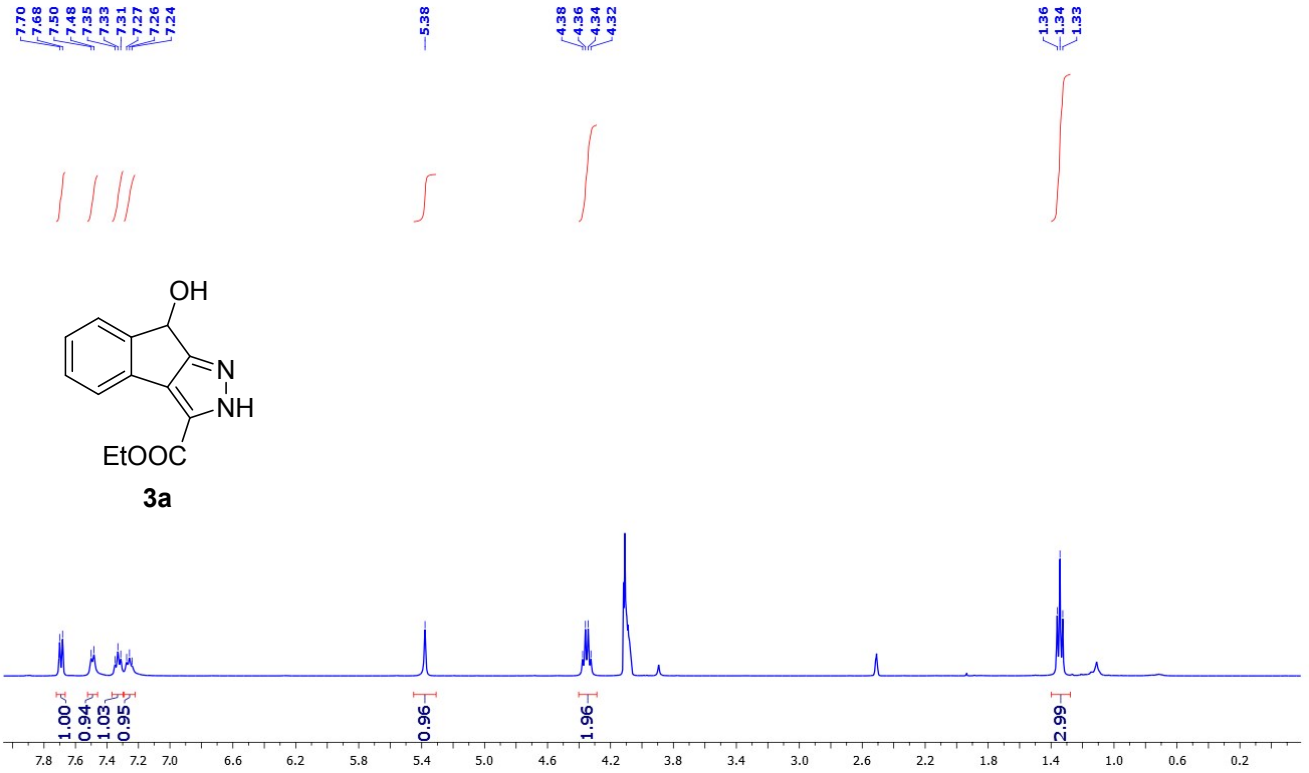
Unless otherwise noted, all reagents were used as received from commercial sources. All air and moisture sensitive reactions were conducted under a nitrogen or argon atmosphere using flame-dried or oven-dried glassware with magnetic stirring. Reactions were monitored by thin-layer chromatography carried out on silica plates (silica gel 60 F254, Merck) using UV-light, iodine and p-anisaldehyde for visualization. Column chromatography was carried out using silica gel (60-120 mesh or 100- 200 mesh) packed in glass columns. Technical grade EtOAc and petroleum ether used for column chromatography and were distilled prior to use. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Room temperature (r.t.) is 23-25°C. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO as solvent on Bruker AVANCE 400, INOVA instruments with 400 and 500 MHz frequencies spectrometers. The coupling constant *J* is given in Hz. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal ($CDCl_3$ δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR), DMSO (^{1}H NMR: δ = 2.54 and ^{13}C NMR: δ = 39.52 ppm). Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard, or TMS (δ = 0.0) as internal standard and signal patterns are indicated as follows: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were recorded on a Waters-TOF spectrometer.

^{1}H, ^{13}C and ^{19}F Spectra of the compounds (3a-3t), 7, 9, 4a-4e, 12-13:

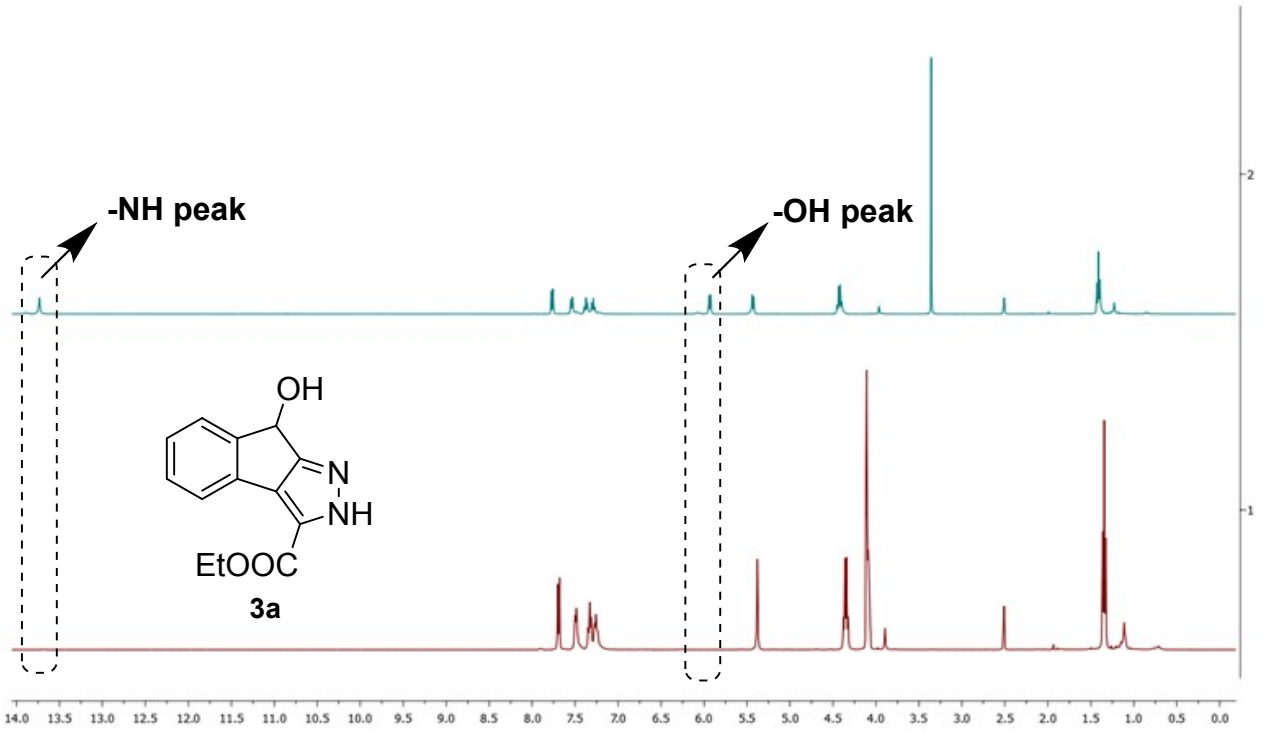
^{1}H NMR spectra of **3a** (400 MHz, DMSO-d_6):



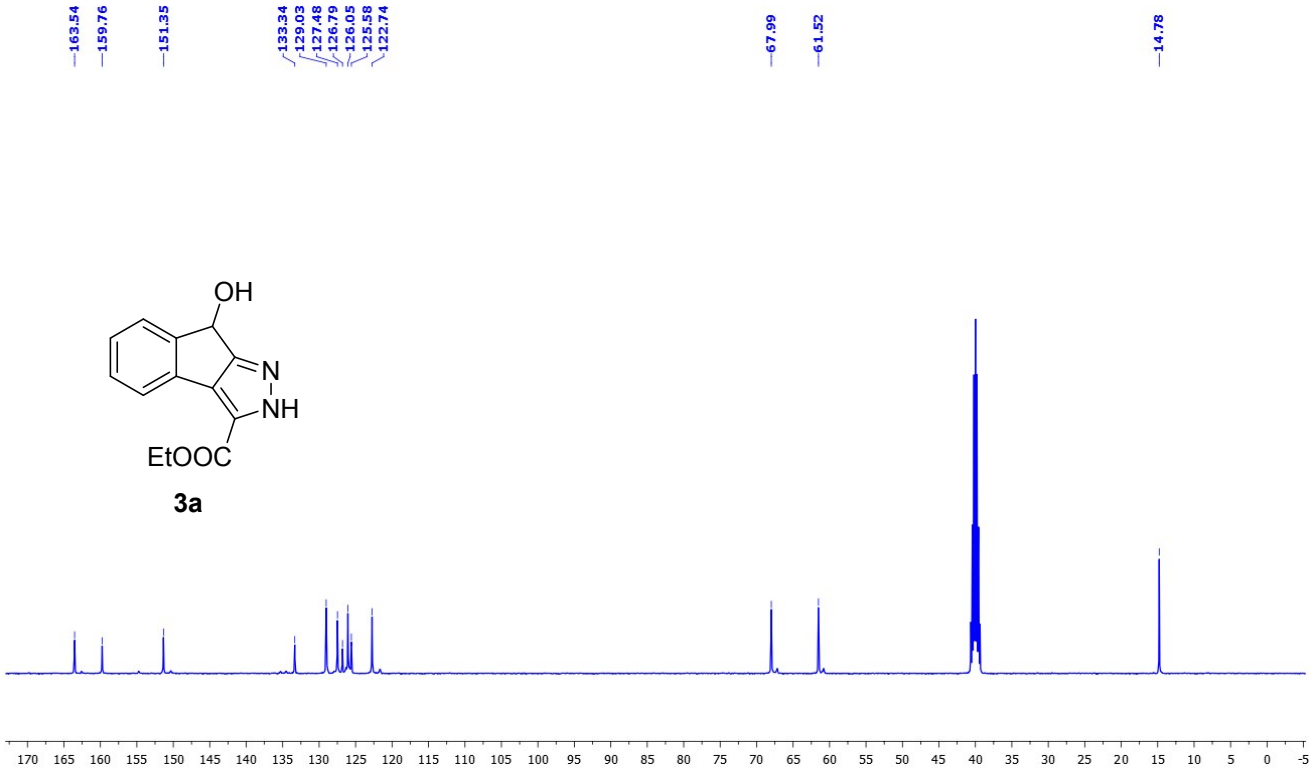
^{1}H NMR spectra of **3a** (400 MHz, DMSO-d_6+ D_2O):



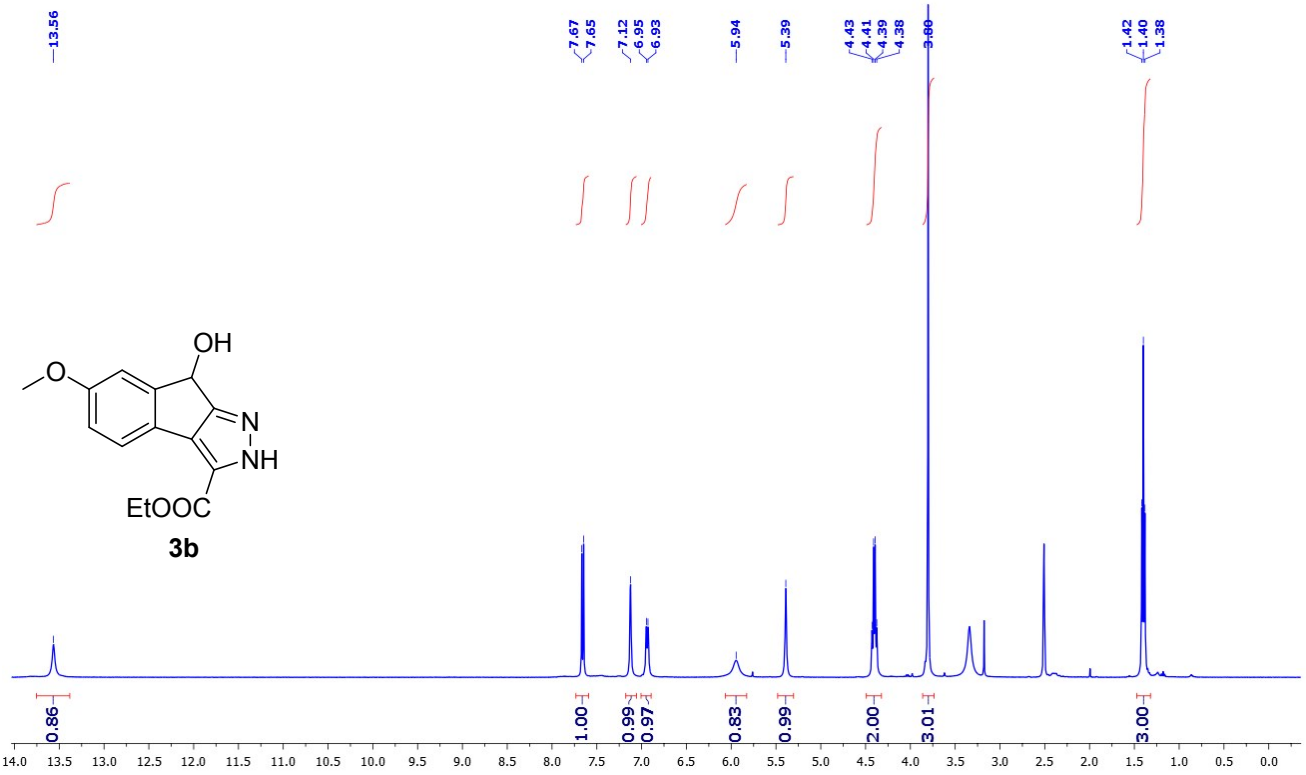
Stacked diagram of compound **3a** (^{1}H NMR/D_2O NMR)



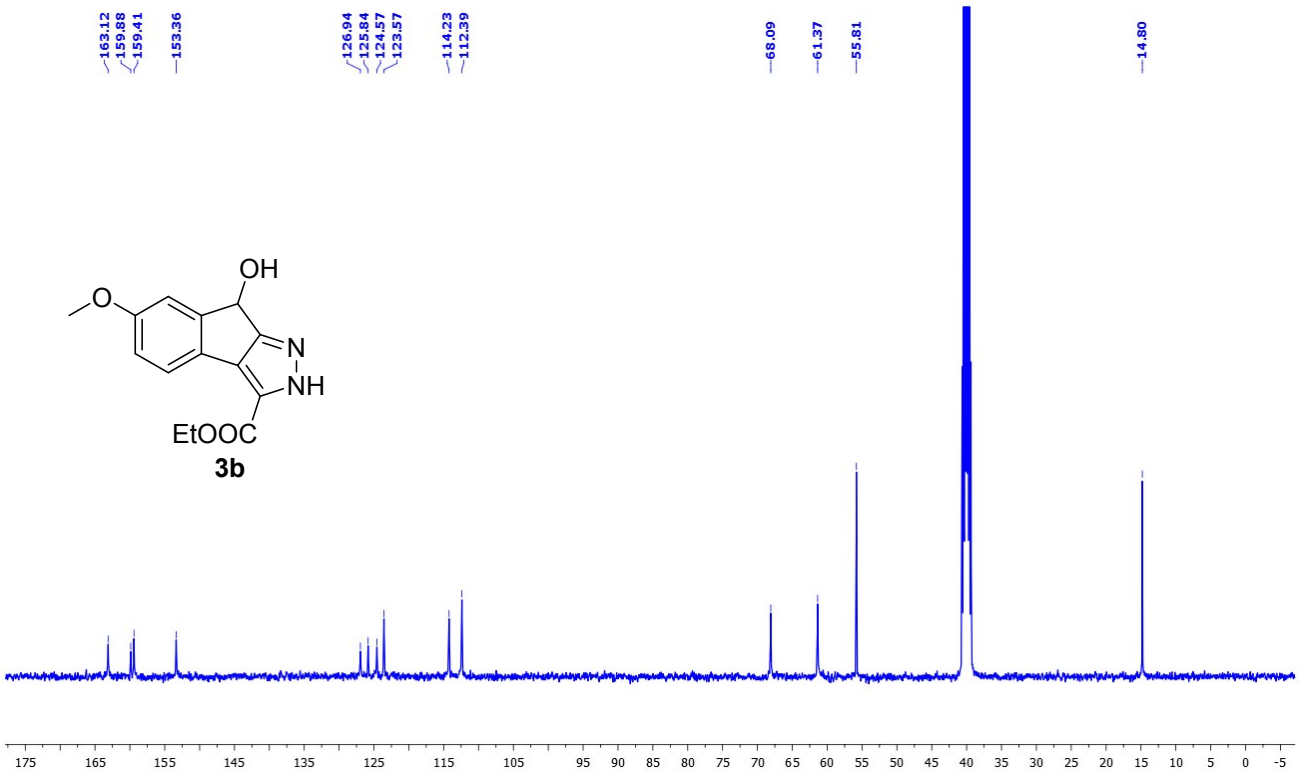
^{13}C NMR spectra of **3a** (101 MHz, DMSO-d_6):



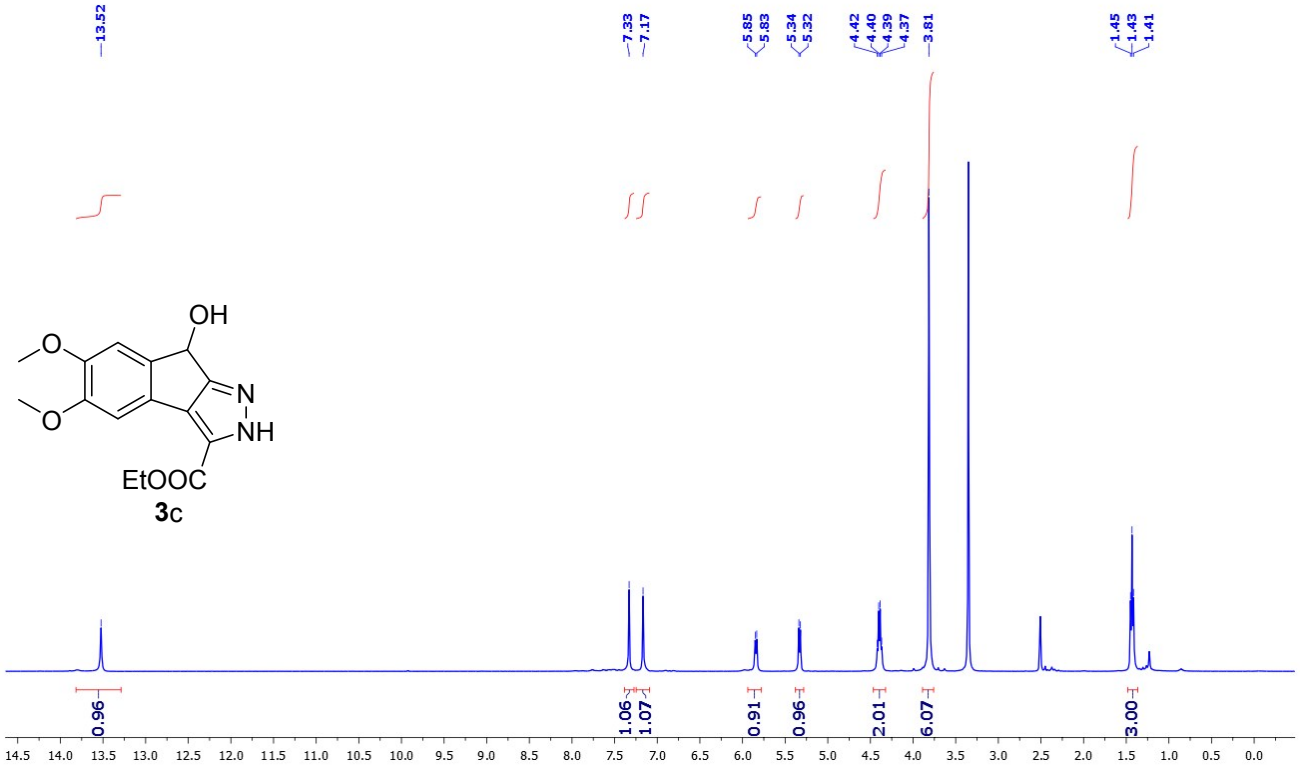
^{1}H NMR spectra of **3b** (400 MHz, DMSO-d_6):



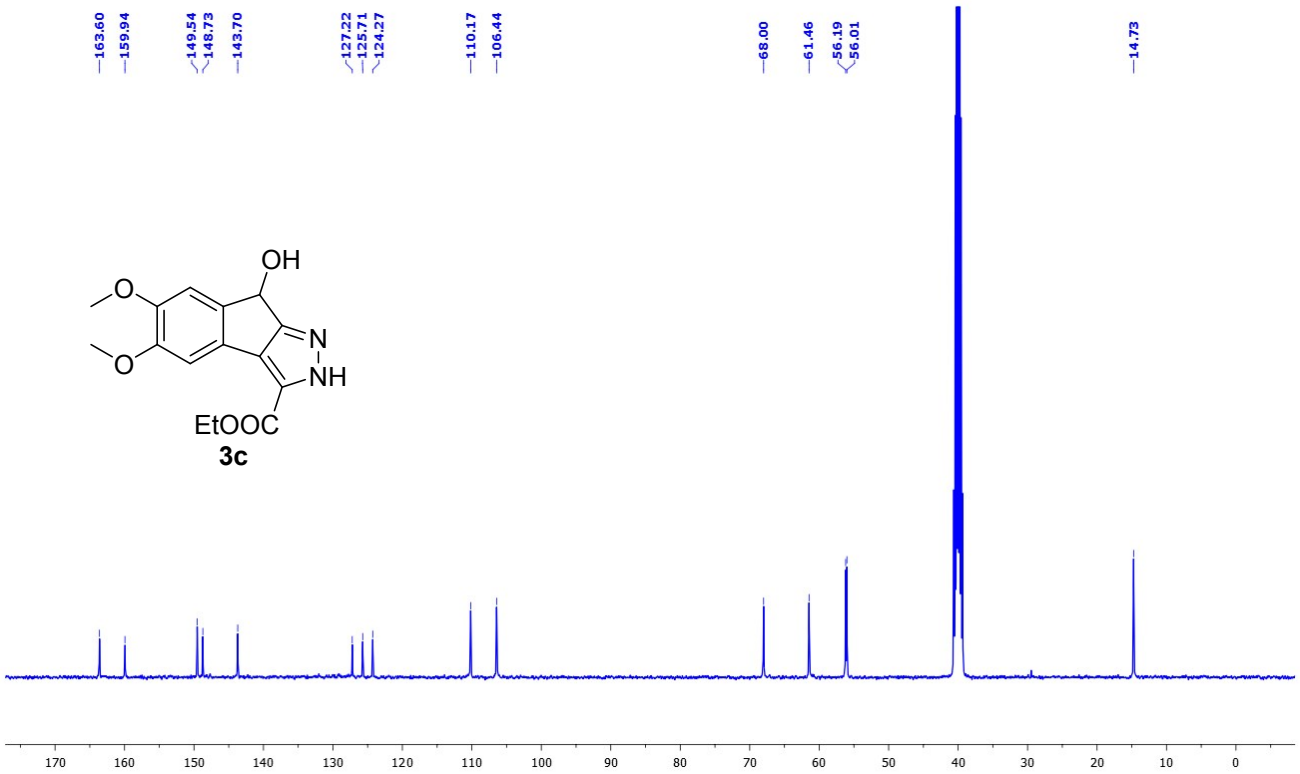
^{13}C NMR spectra of **3b** (101 MHz, DMSO-d_6):



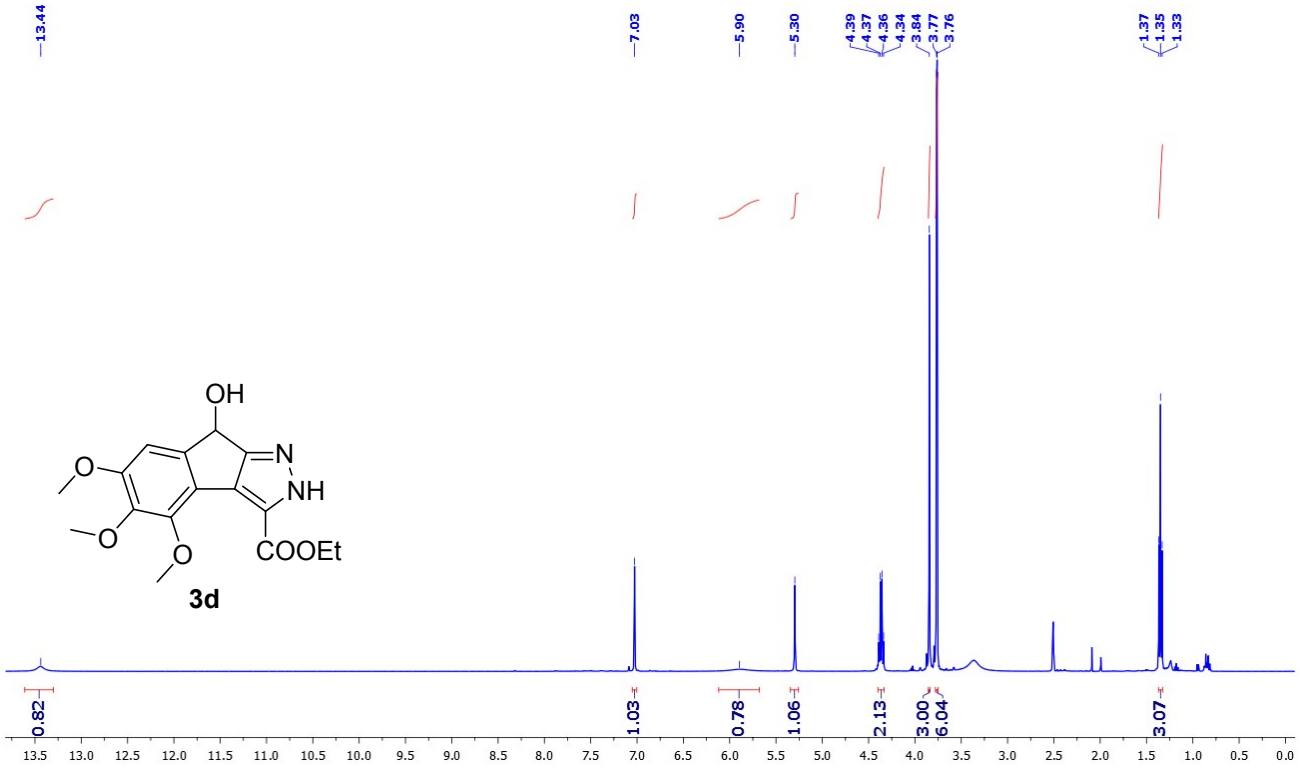
^{1}H NMR spectra of **3c** (400 MHz, DMSO-d_6):



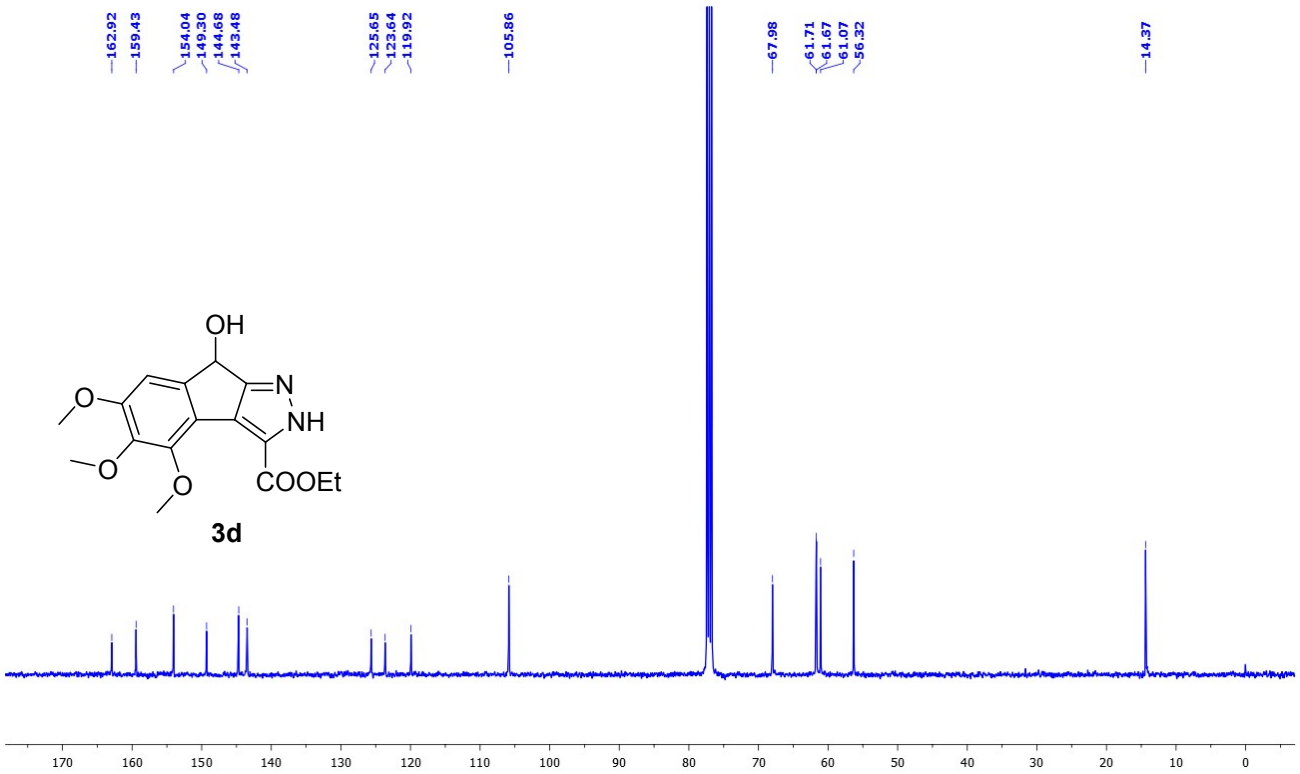
^{13}C NMR spectra of **3c** (101 MHz, DMSO-d_6):



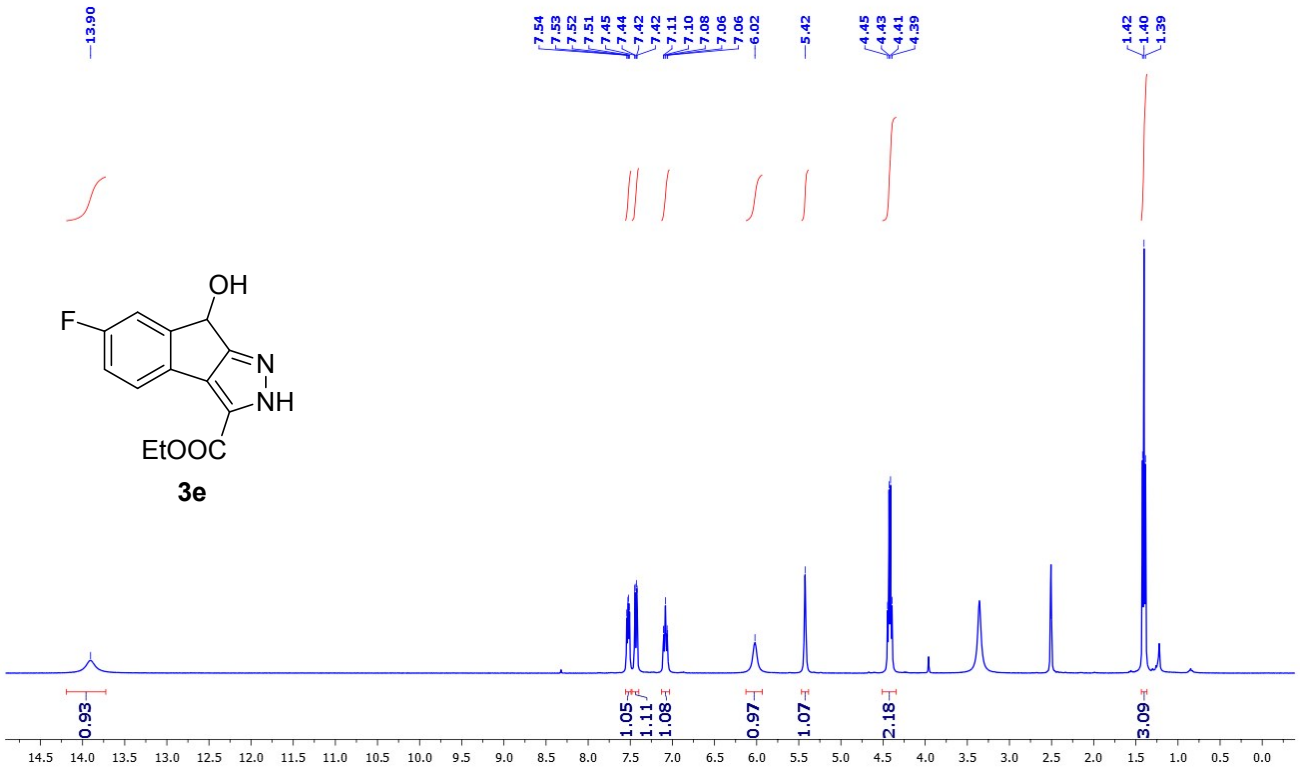
^{1}H NMR spectra of **3d** (400 MHz, DMSO-d_6):



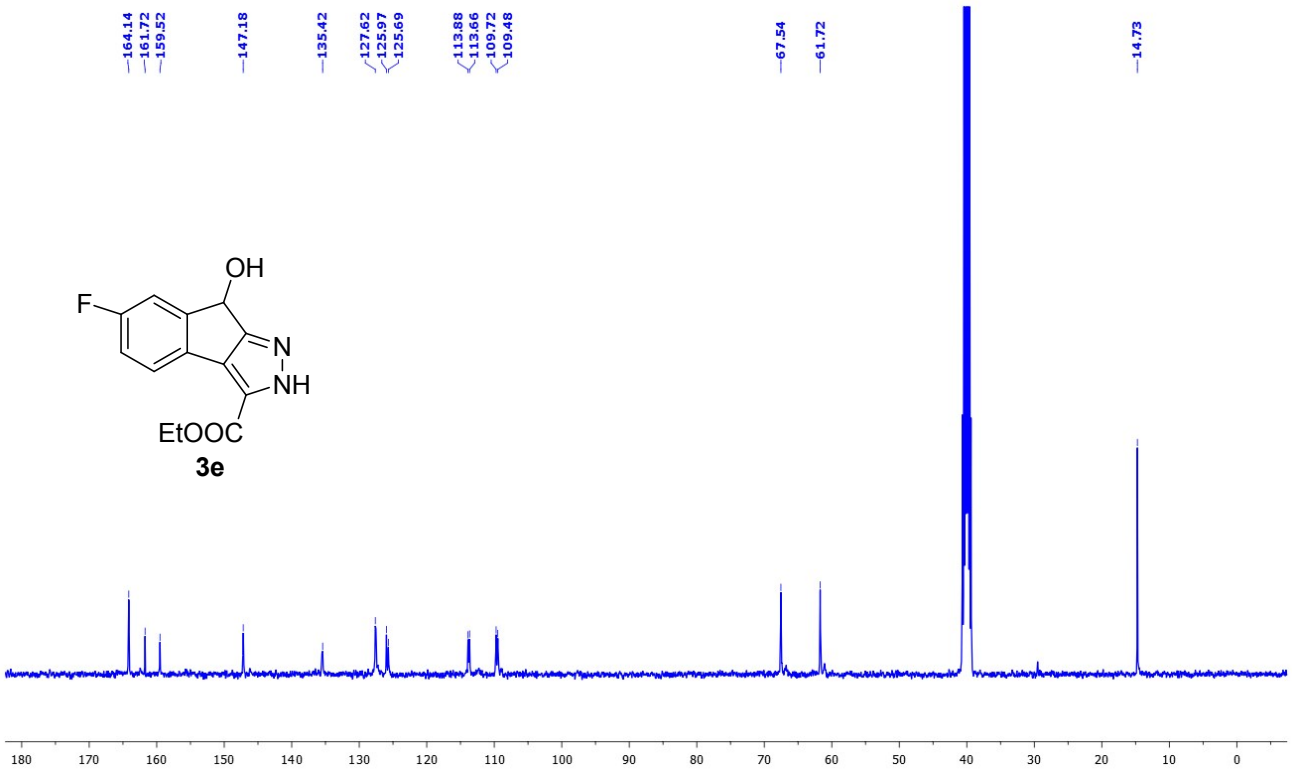
^{13}C NMR spectra of **3d** (101 MHz, $CDCl_3$):



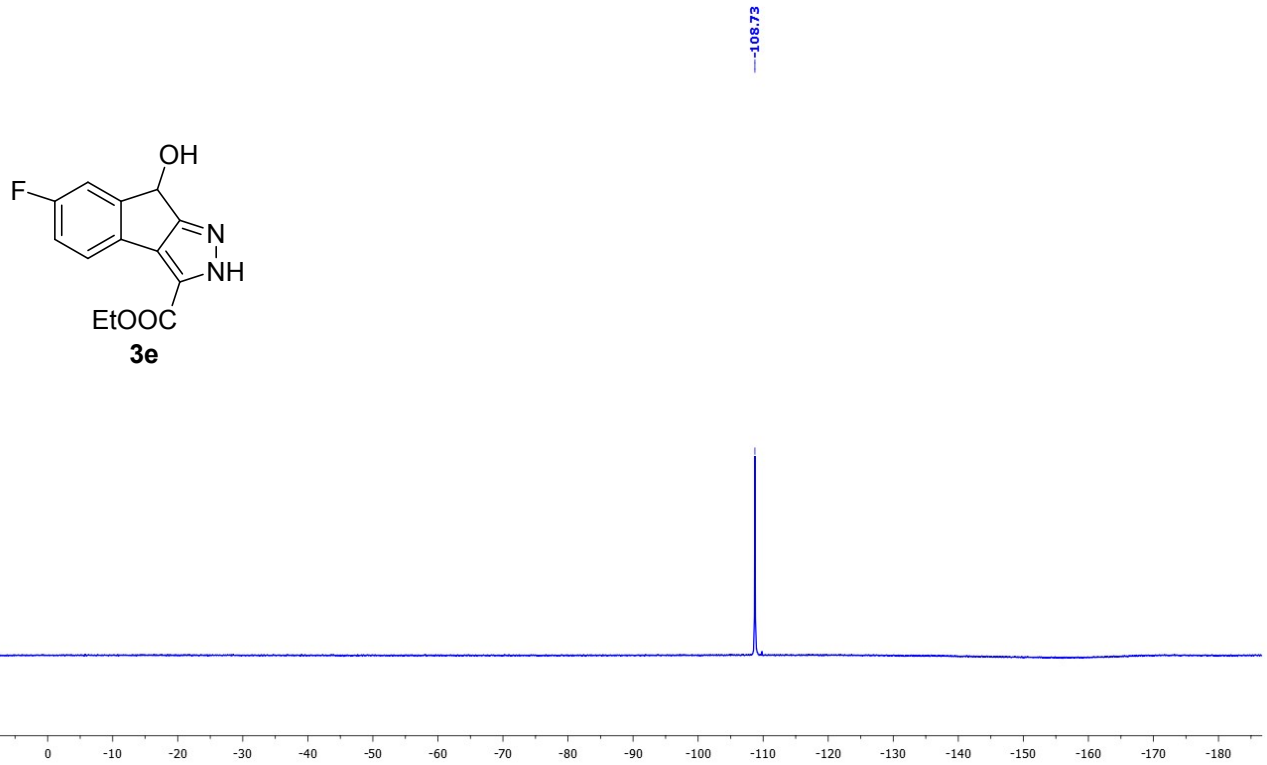
^{1}H NMR spectra of **3e** (400 MHz, DMSO-d_6):



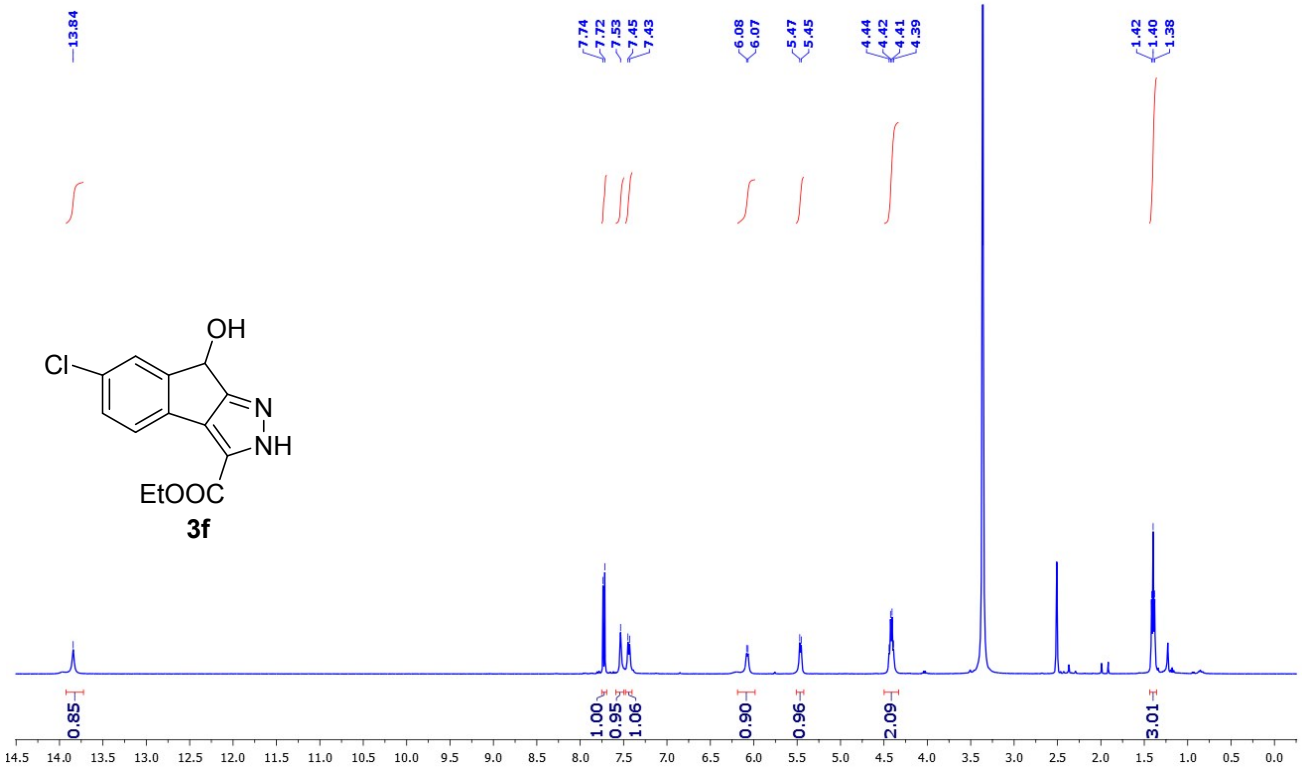
^{13}C NMR spectra of **3e** (101 MHz, DMSO-d_6):



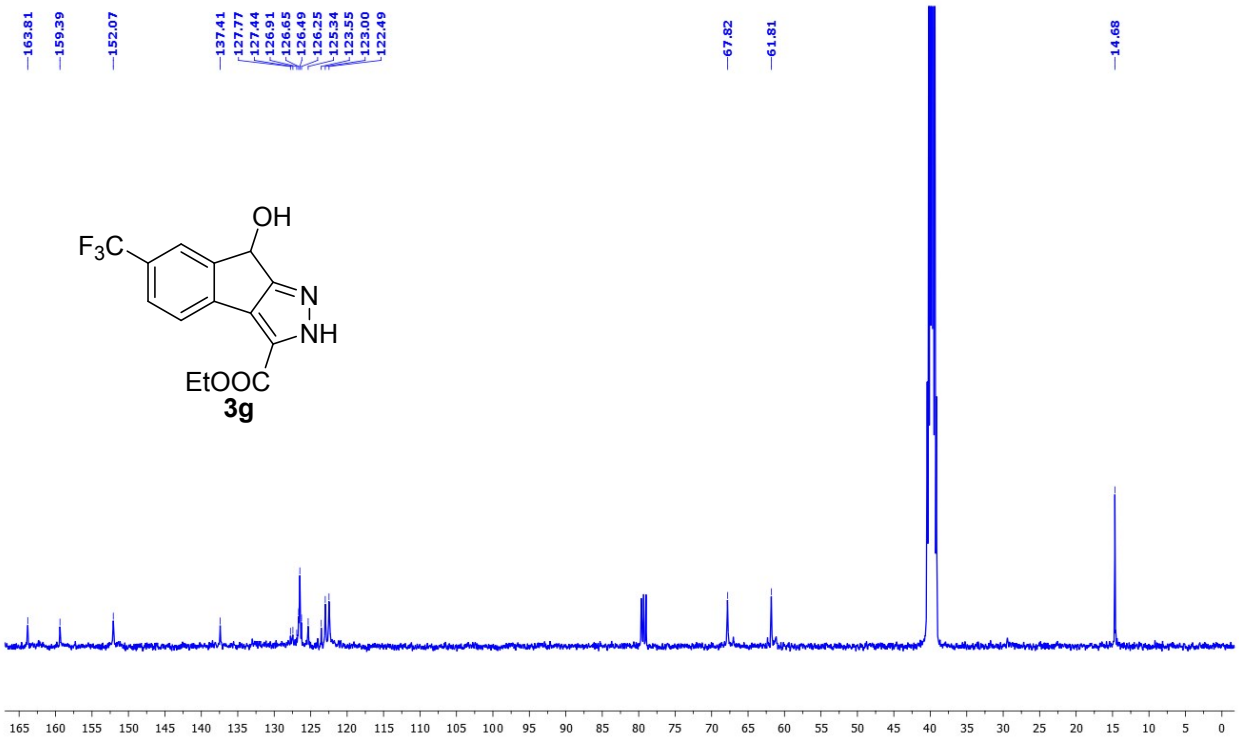
^{19}F NMR spectra of **3e** (376 MHz, DMSO-d_6):



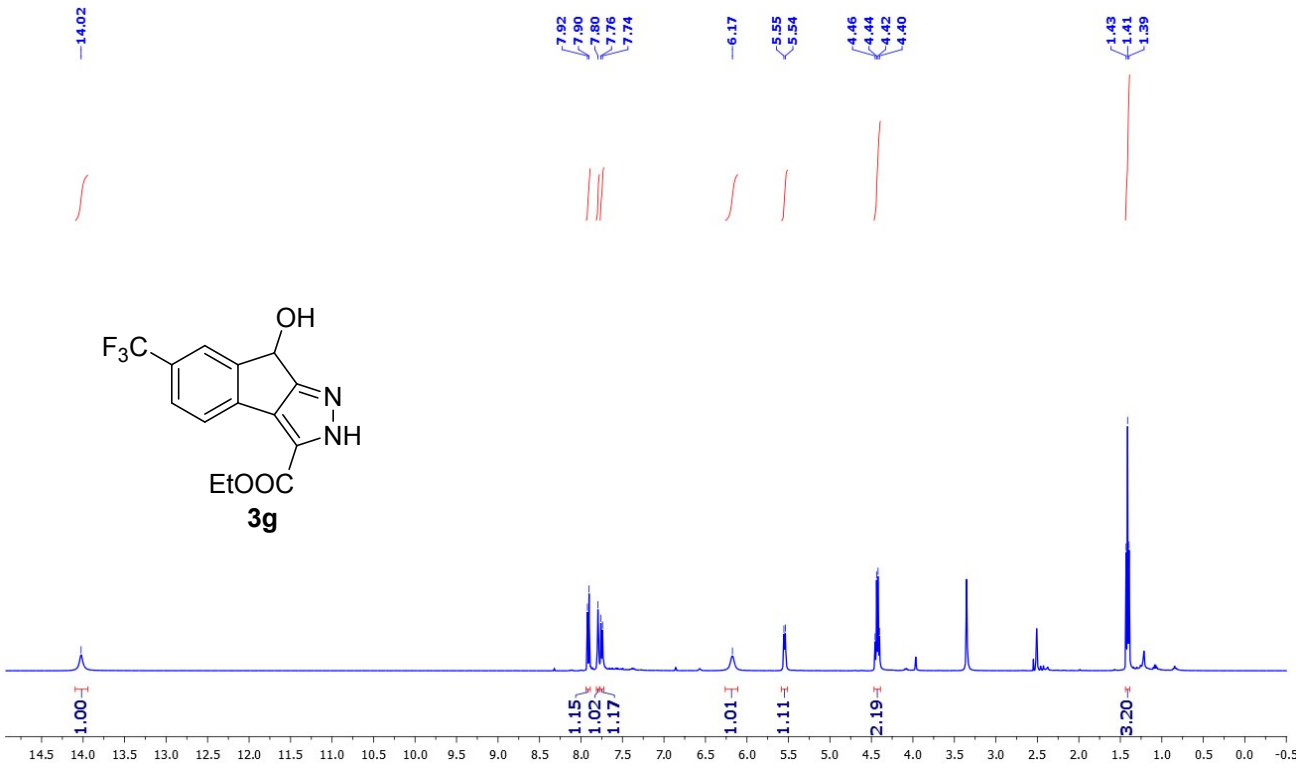
^{1}H NMR spectra of **3f** (400 MHz, DMSO-d_6):



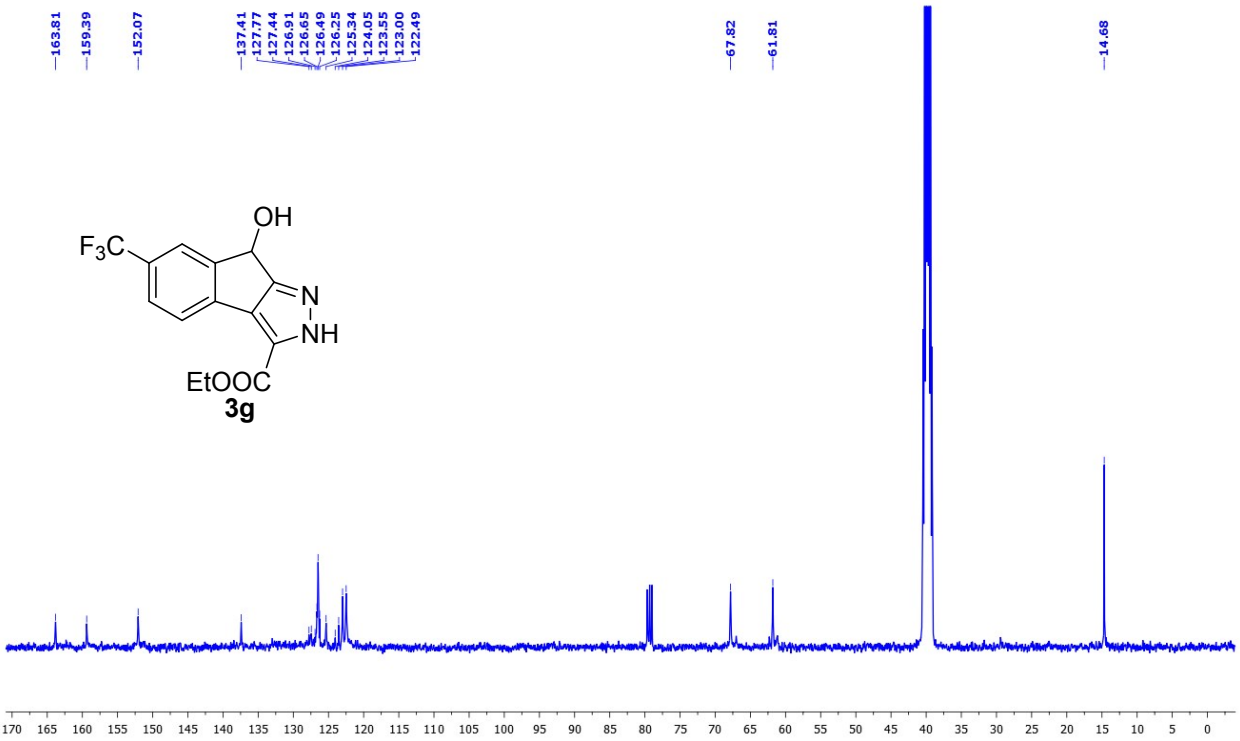
^{13}C NMR spectra of **3g** (101 MHz, $CDCl_3$ + DMSO-d_6):



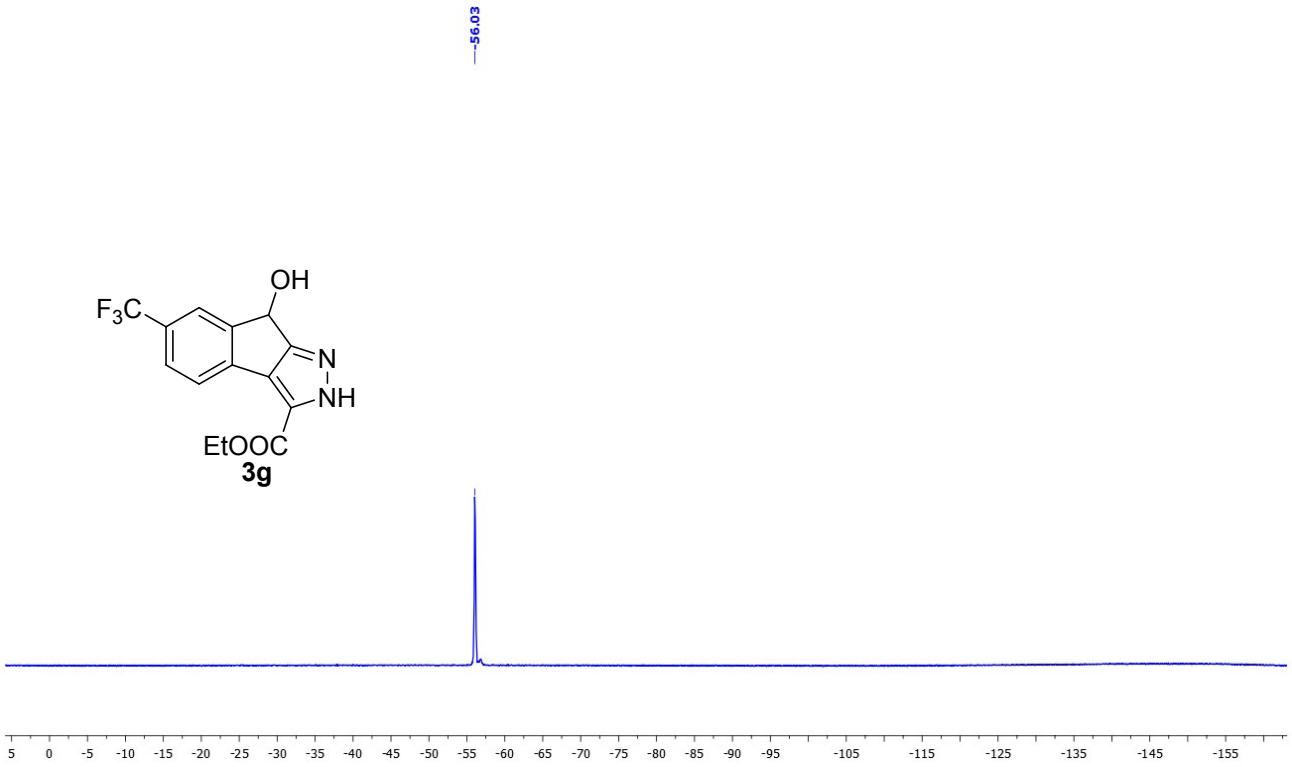
^{19}F NMR spectra of **3g** (376 MHz, DMSO-d_6):



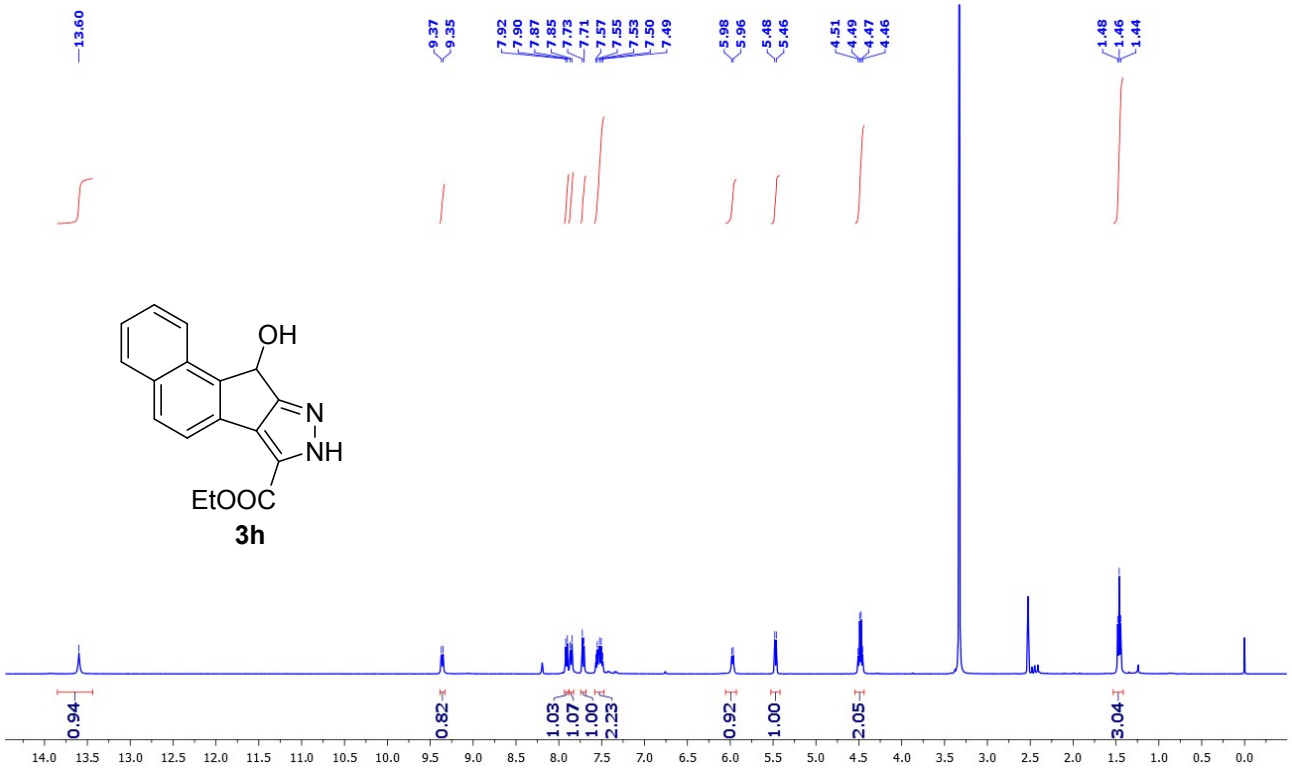
^{13}C NMR spectra of **3g** (101 MHz, $CDCl_3$ + DMSO-d_6):



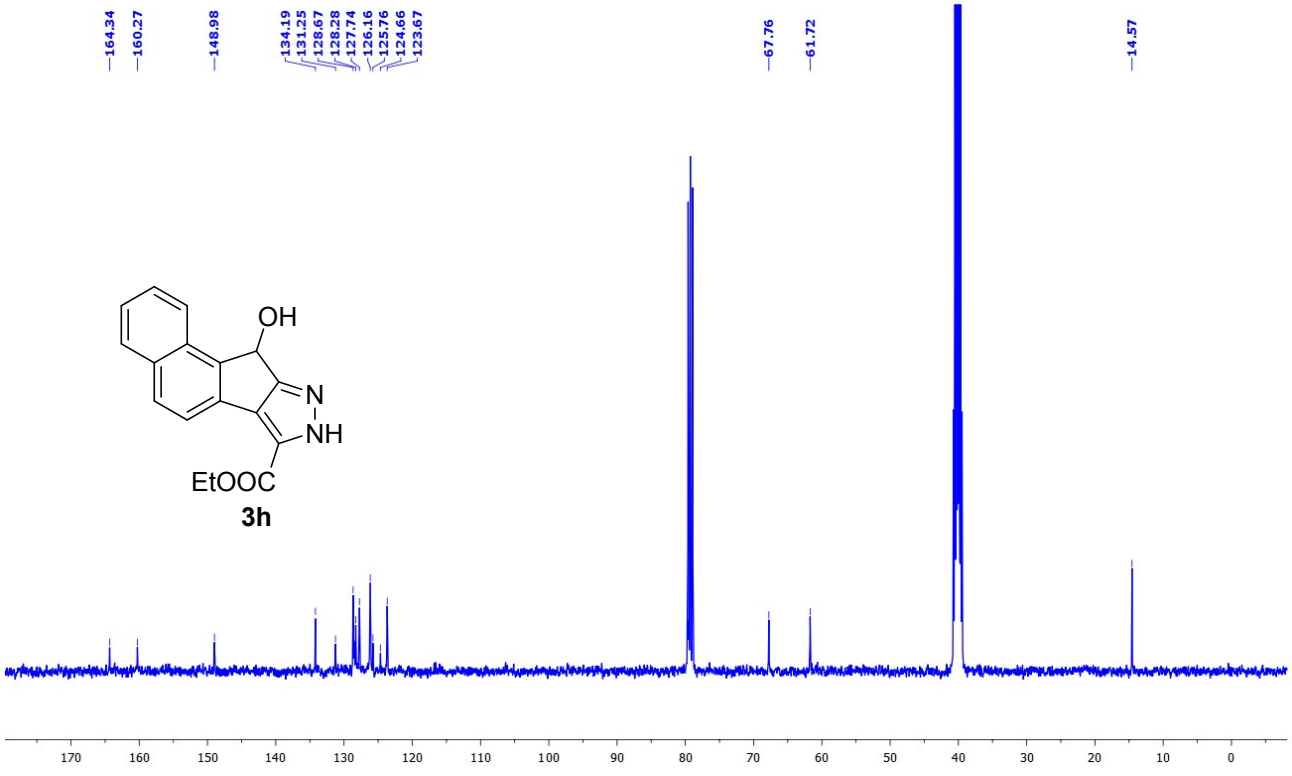
^{19}F NMR spectra of **3g** (376 MHz, DMSO-d_6):



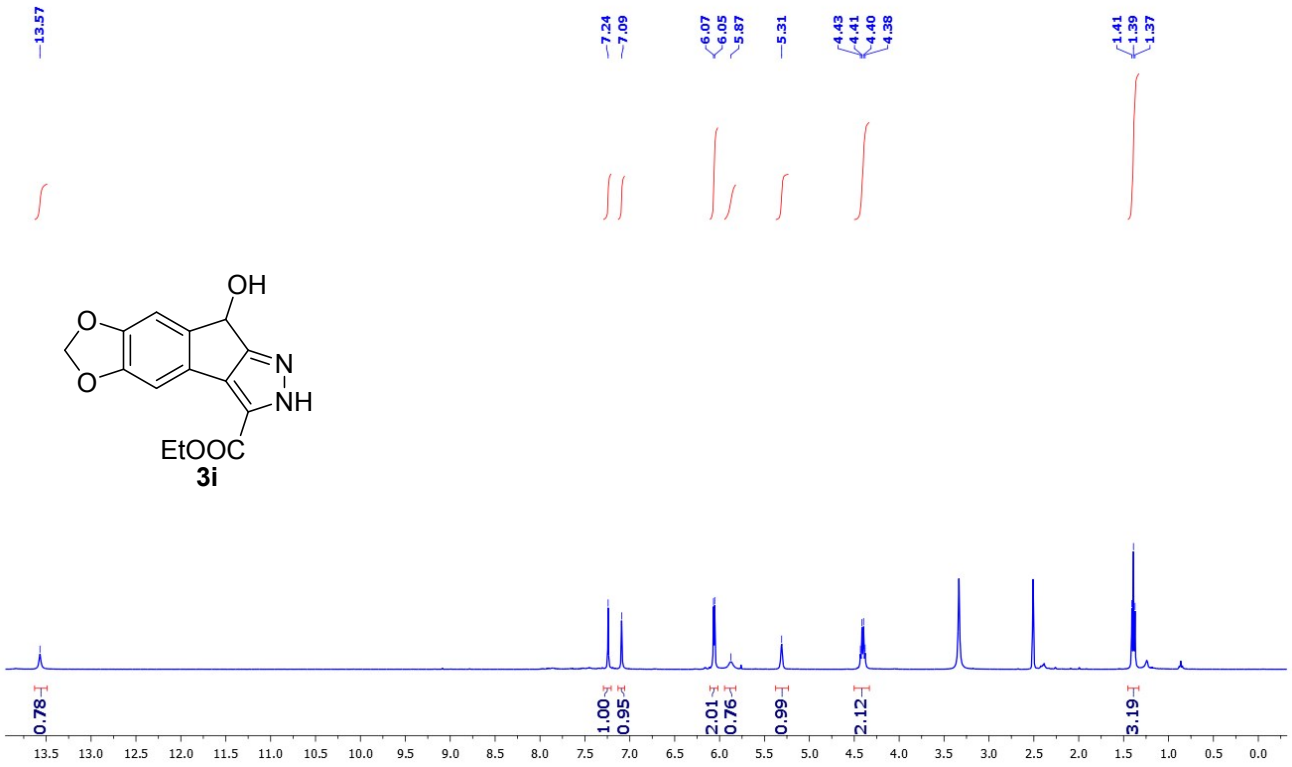
^{1}H NMR spectra of **3h** (400 MHz, $CDCl_3$ + DMSO-d_6):



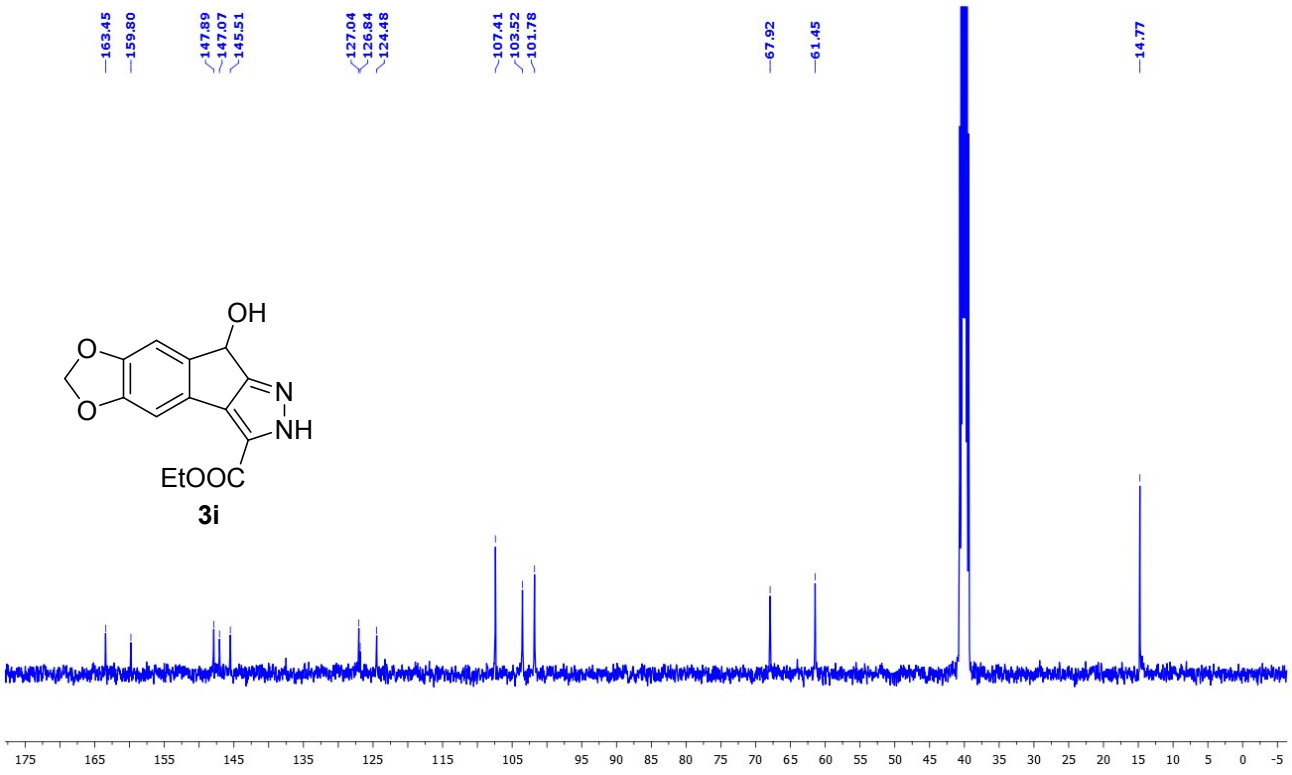
^{13}C NMR spectra of **3h** (101 MHz, $CDCl_3$ + DMSO-d_6):



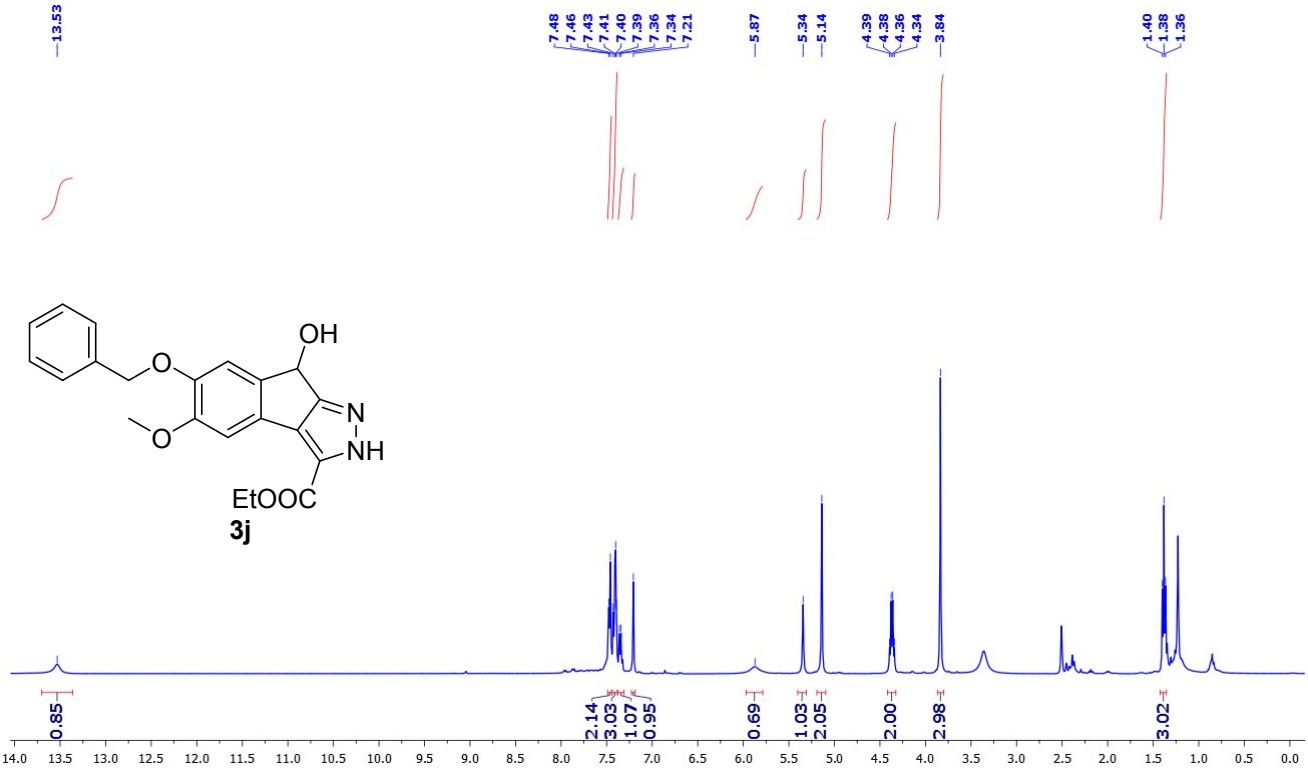
^{1}H NMR spectra of **3i** (400 MHz, DMSO-d_6):



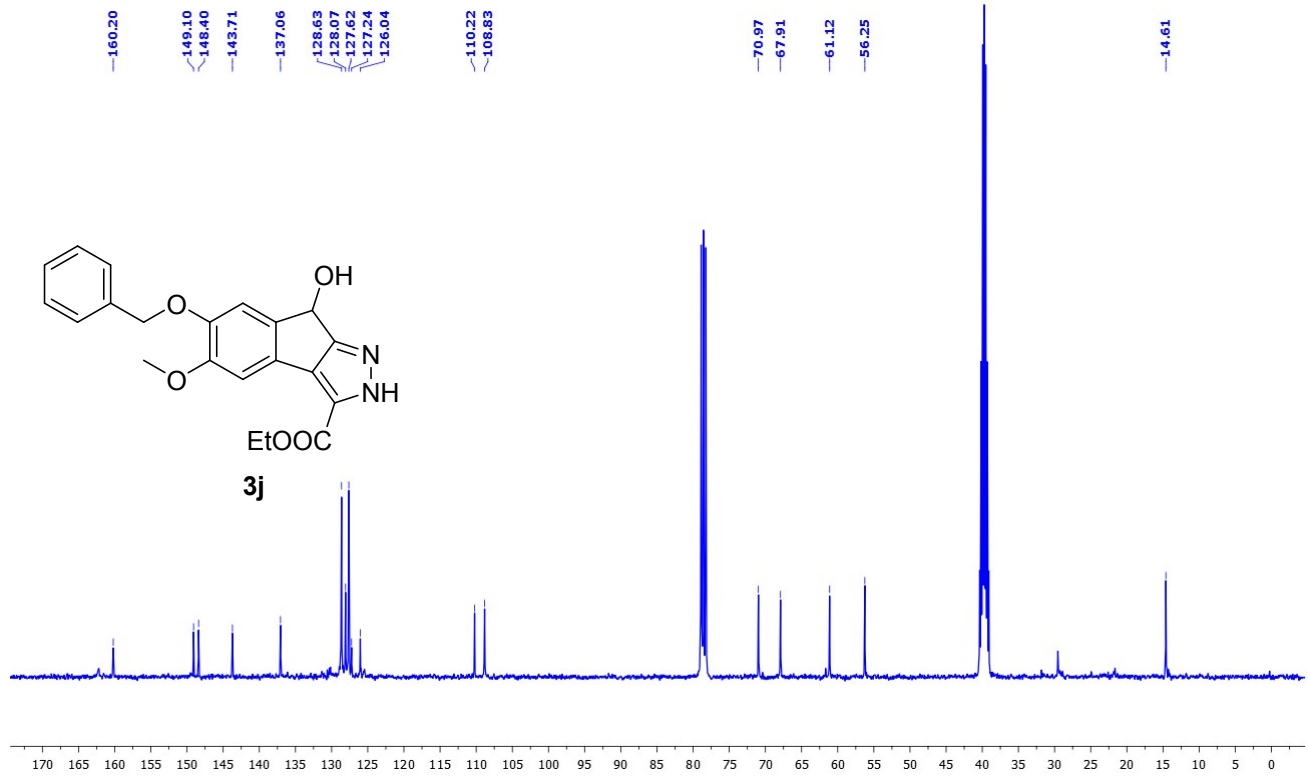
^{13}C NMR spectra of **3i** (101 MHz, DMSO-d_6):



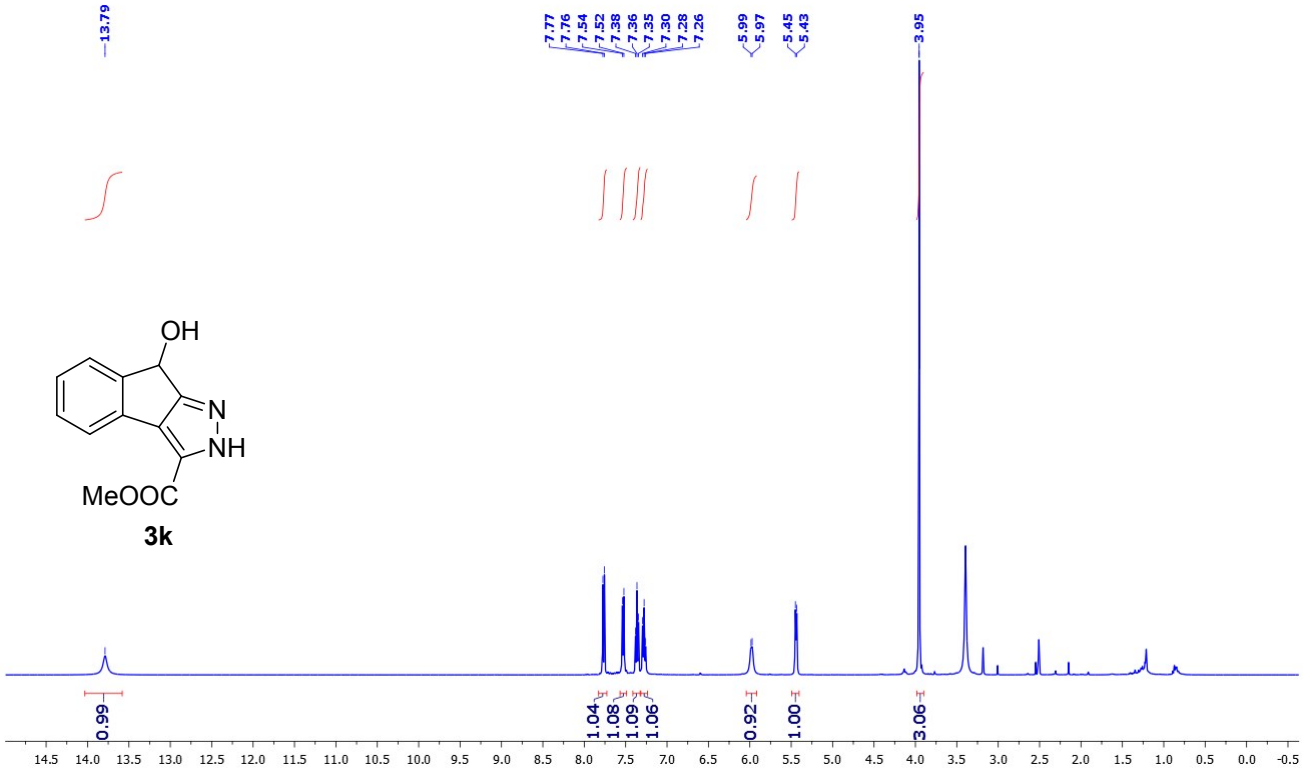
^{1}H NMR spectra of **3j** (400 MHz, DMSO-d_6):



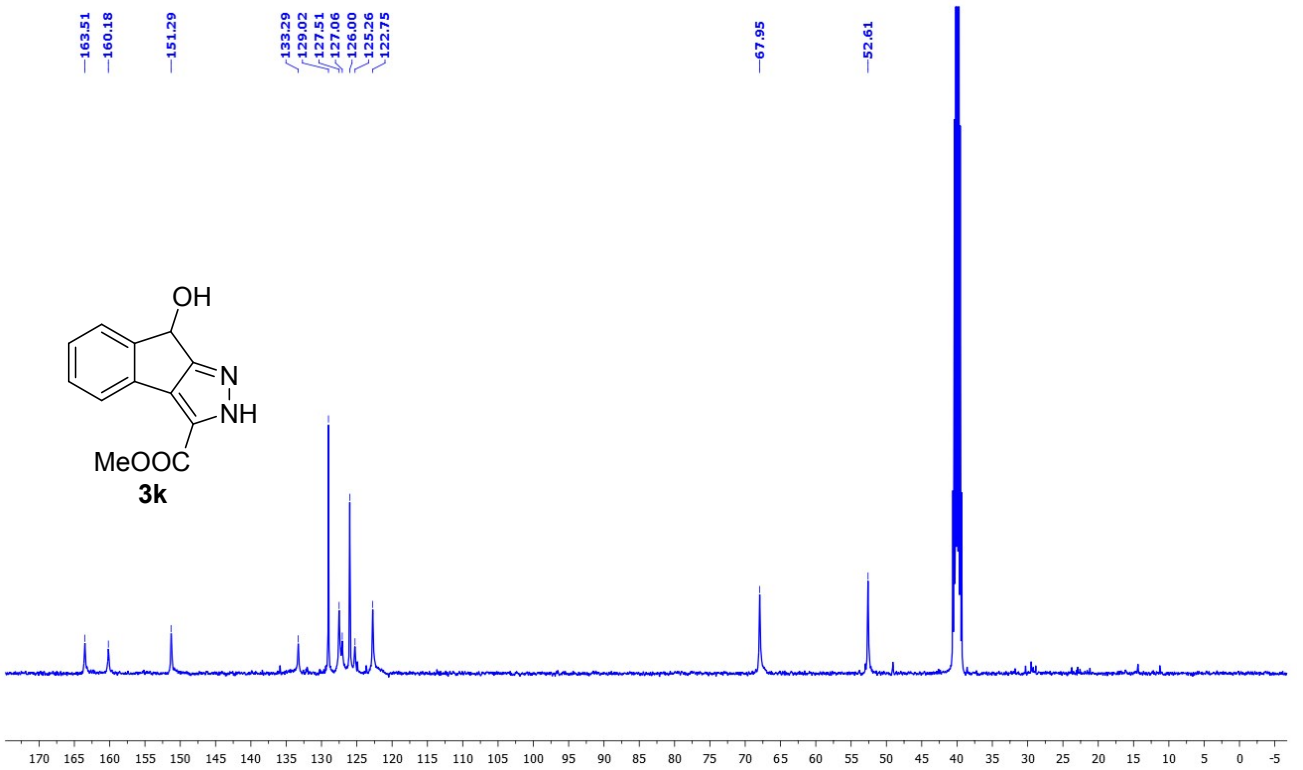
^{13}C NMR spectra of **3j** (101 MHz, $CDCl_3$ + DMSO-d_6):



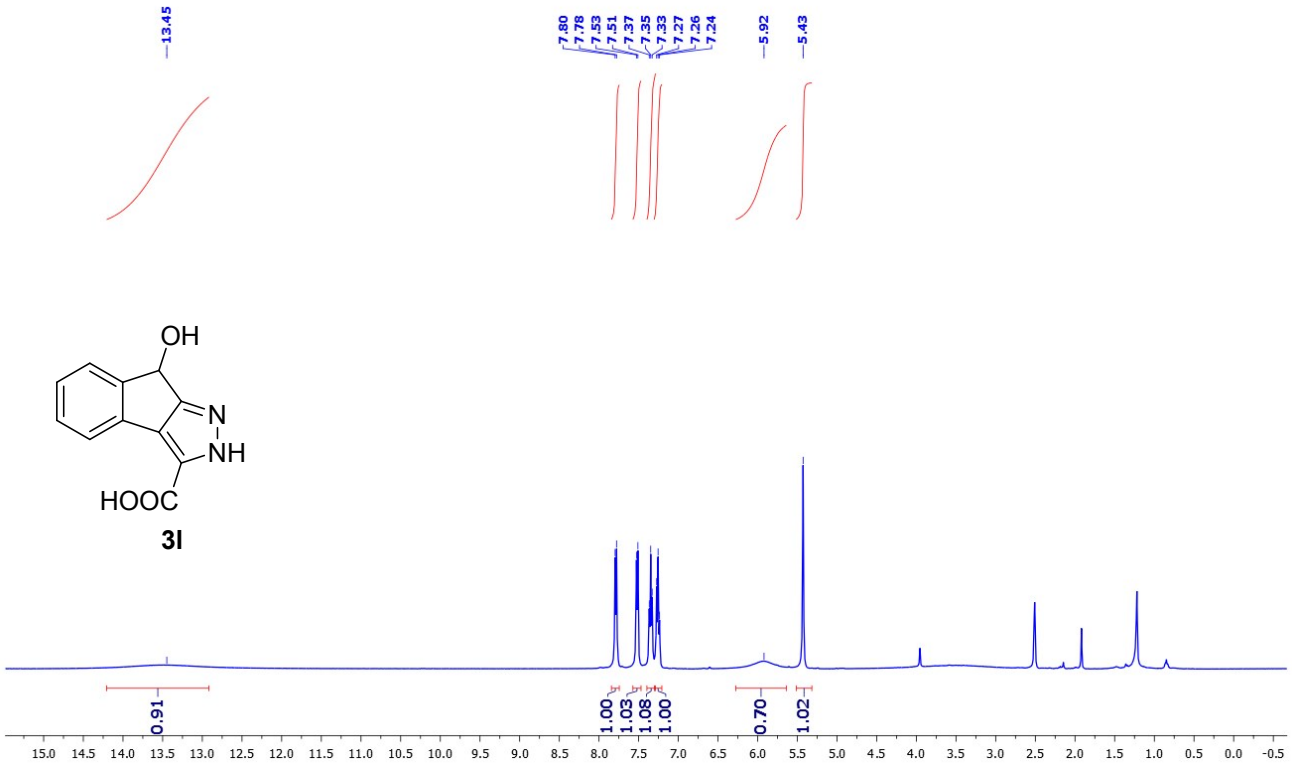
^{1}H NMR spectra of **3k** (400 MHz, DMSO-d_6):



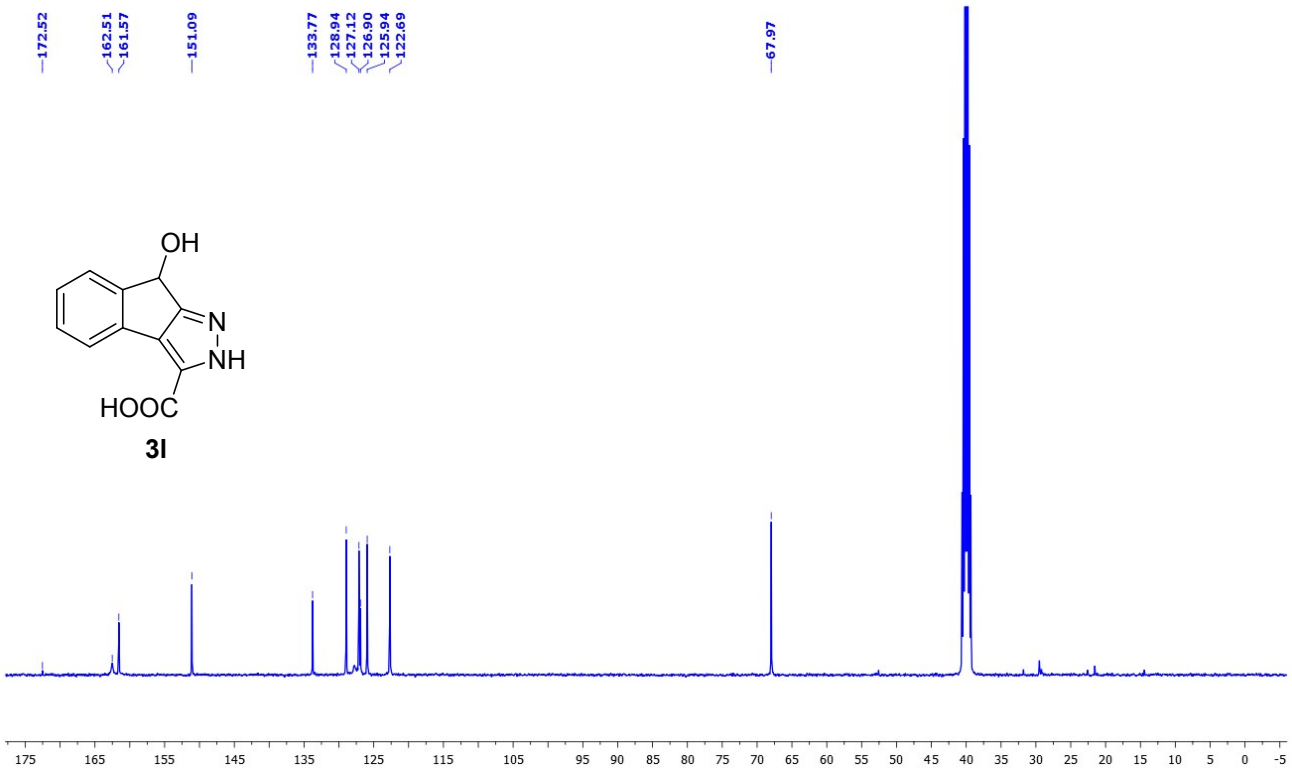
^{13}C NMR spectra of **3k** (101 MHz, DMSO-d_6):



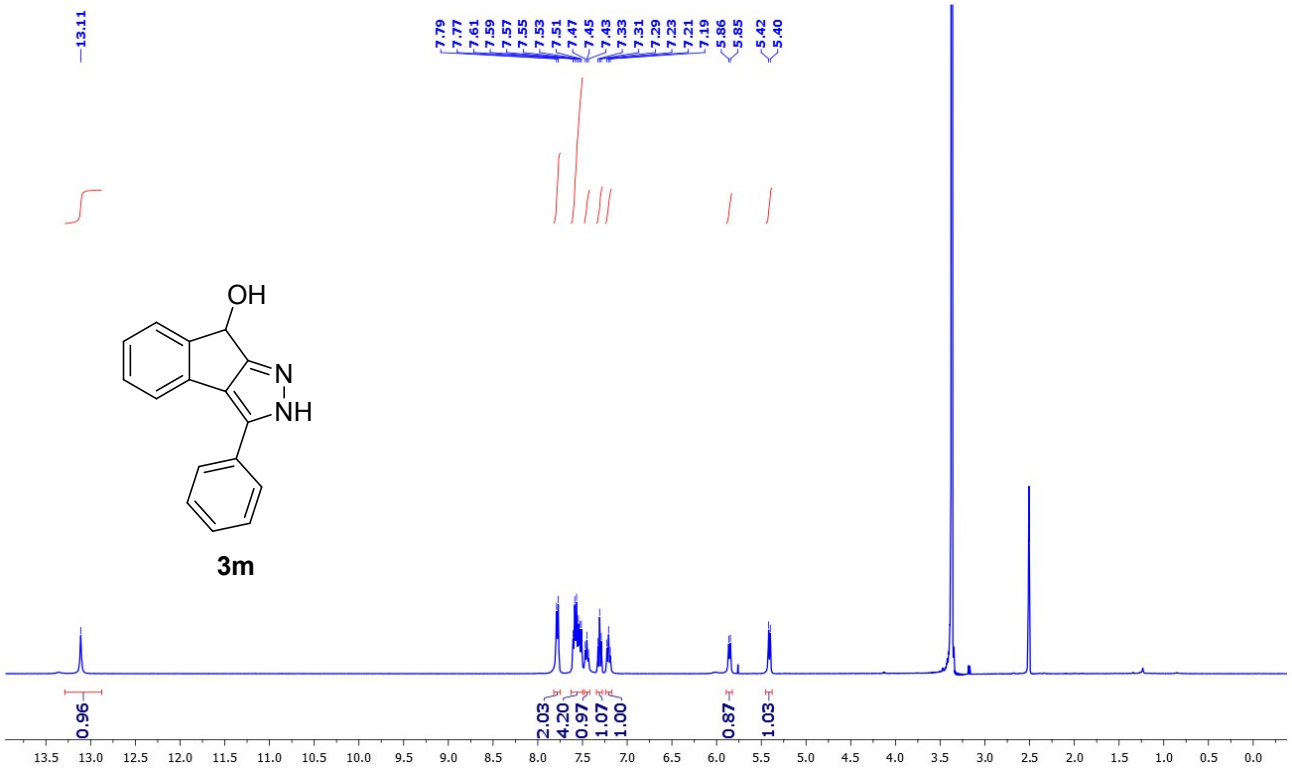
^{1}H NMR spectra of **3l** (400 MHz, DMSO-d_6):



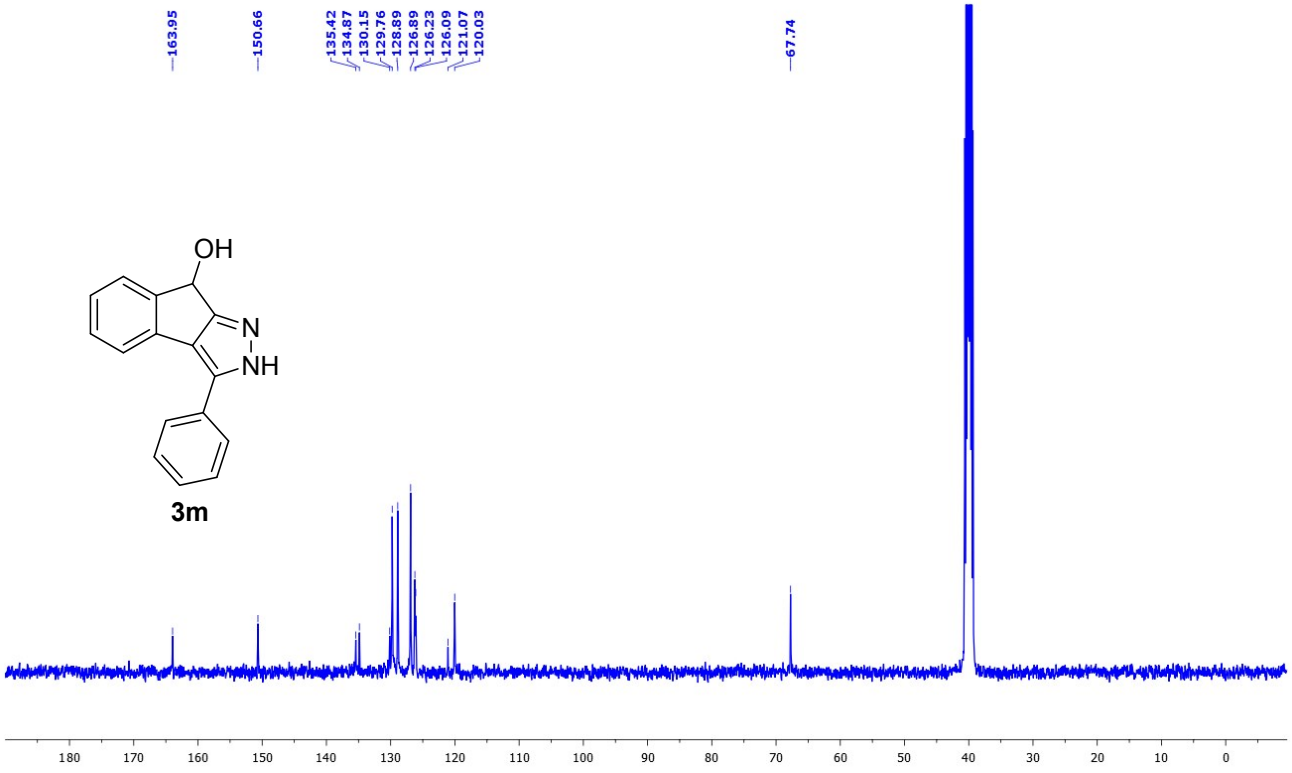
^{13}C NMR spectra of **3l** (101 MHz, DMSO-d_6):



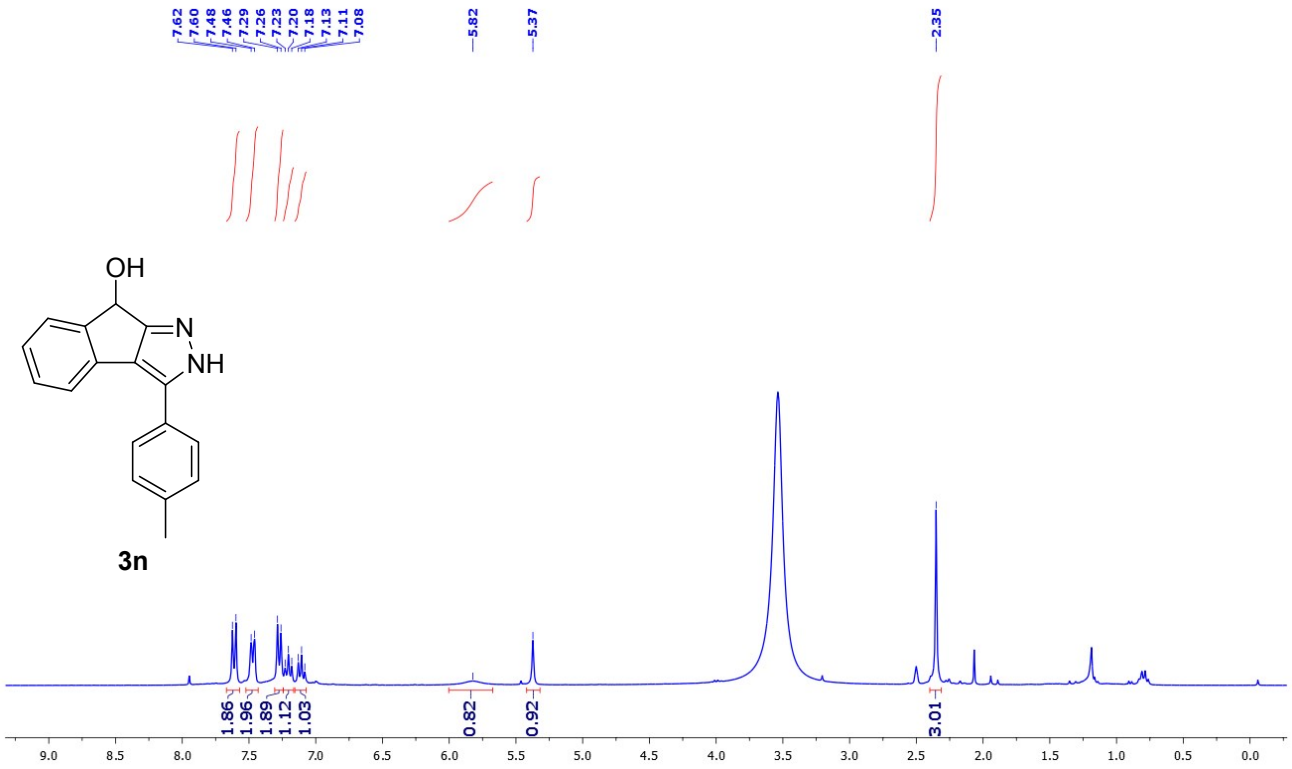
^{1}H NMR spectra of **3m** (400 MHz, DMSO-d_6):



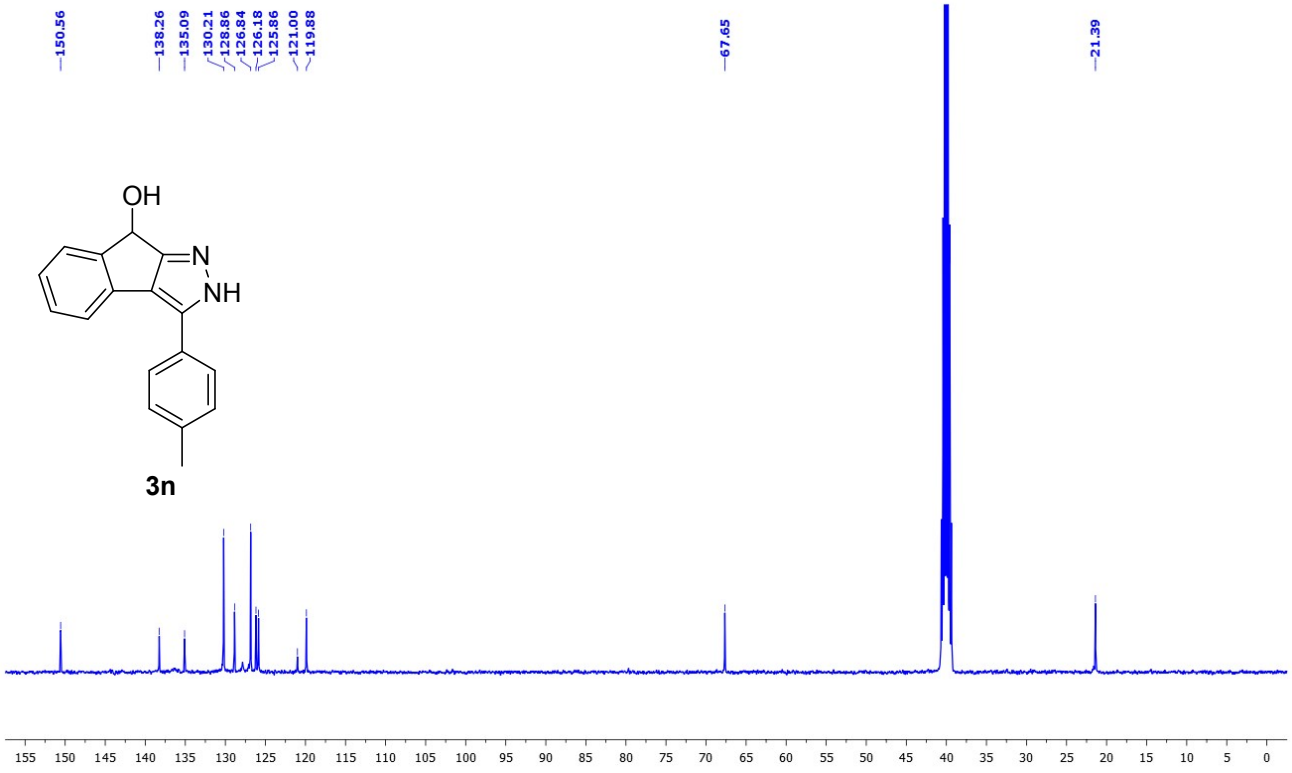
^{13}C NMR spectra of **3m** (101 MHz, DMSO-d_6):



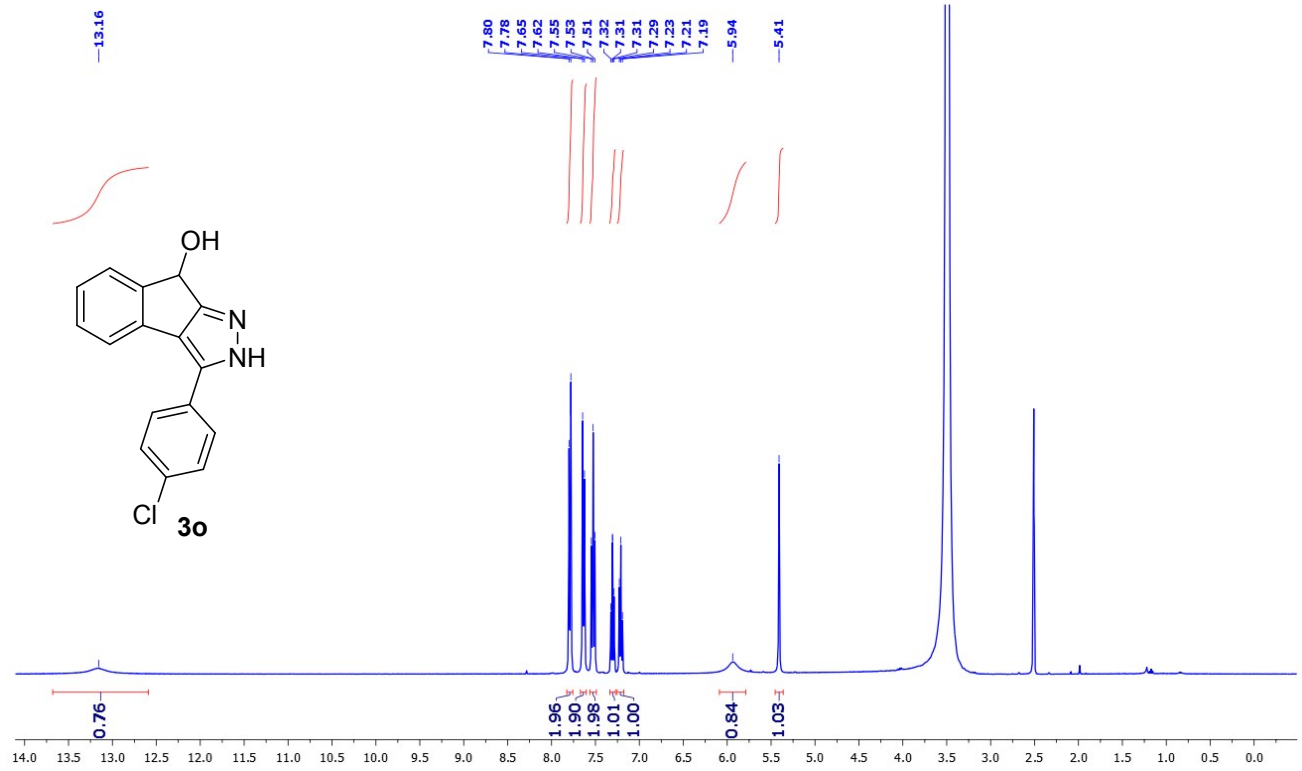
^{1}H NMR spectra of **3n** (300 MHz, DMSO-d_6):



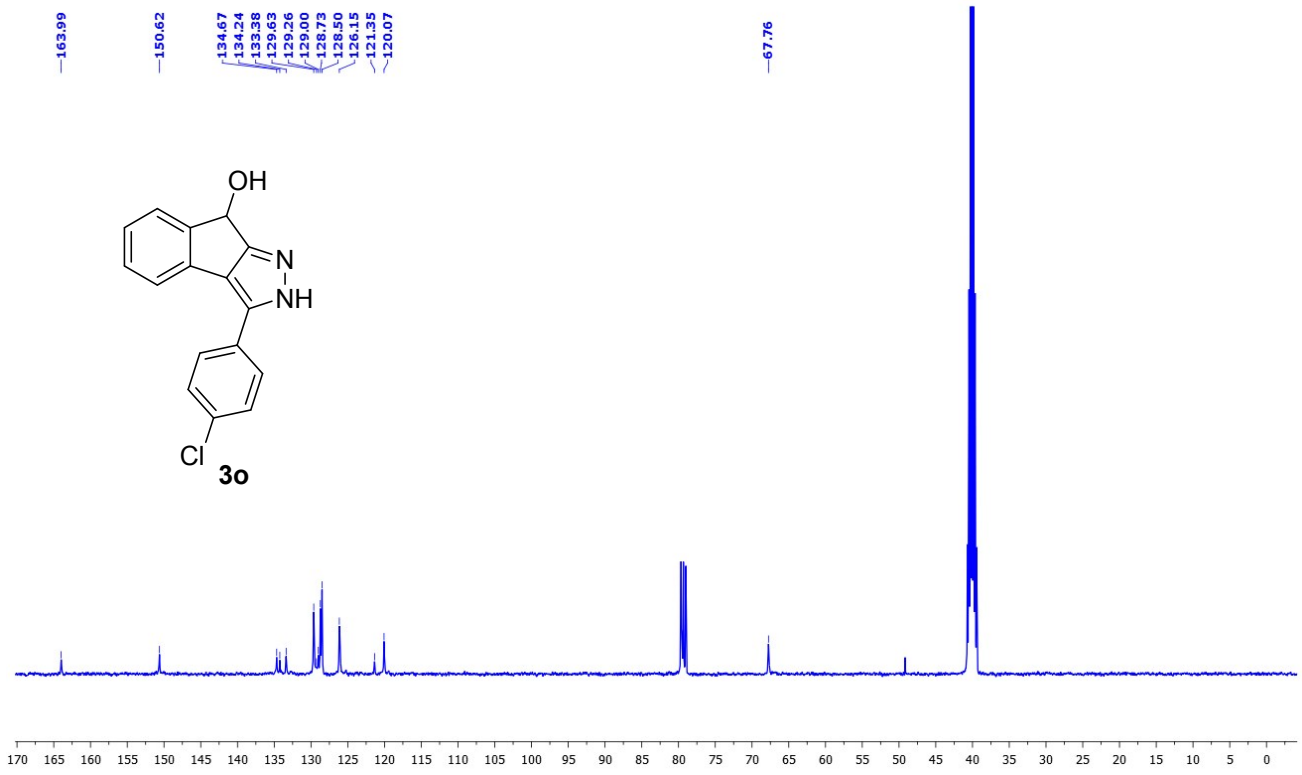
^{13}C NMR spectra of **3n** (101 MHz, DMSO-d_6):



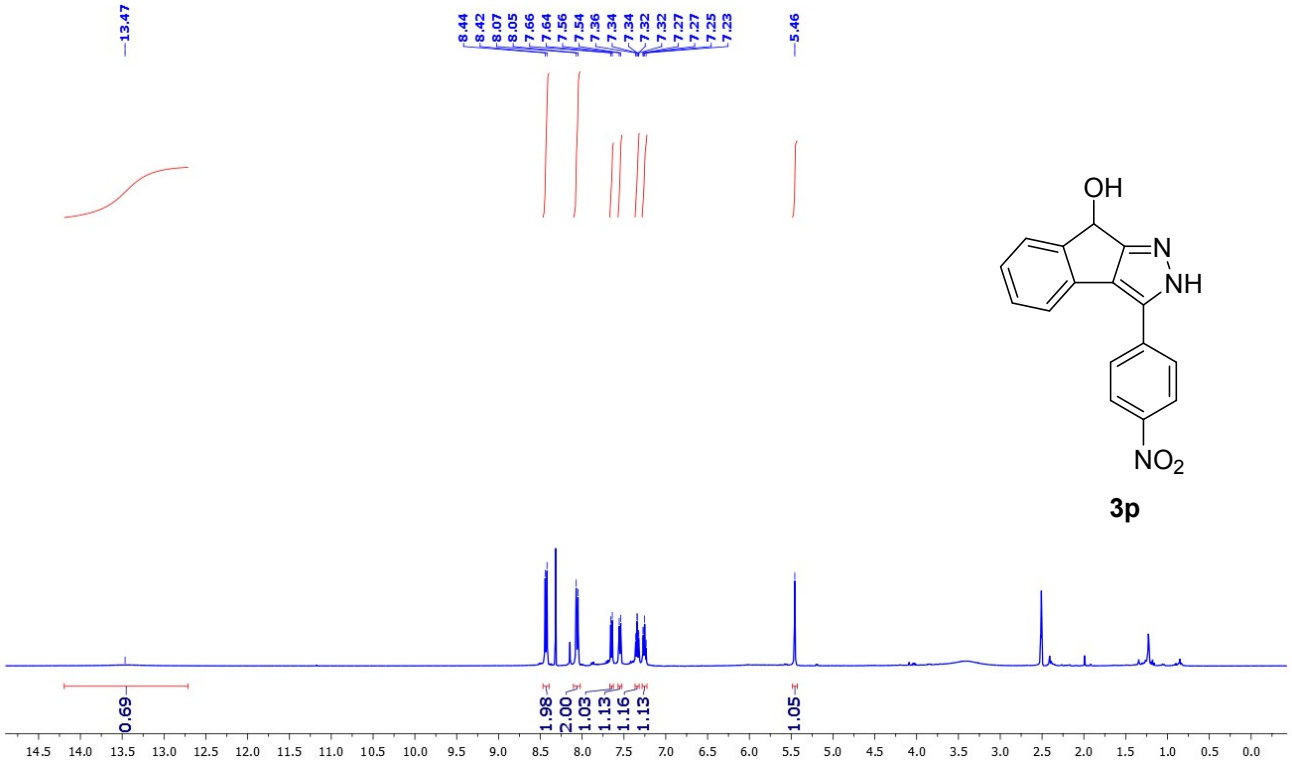
^{1}H NMR spectra of **3o** (400 MHz, DMSO-d_6):



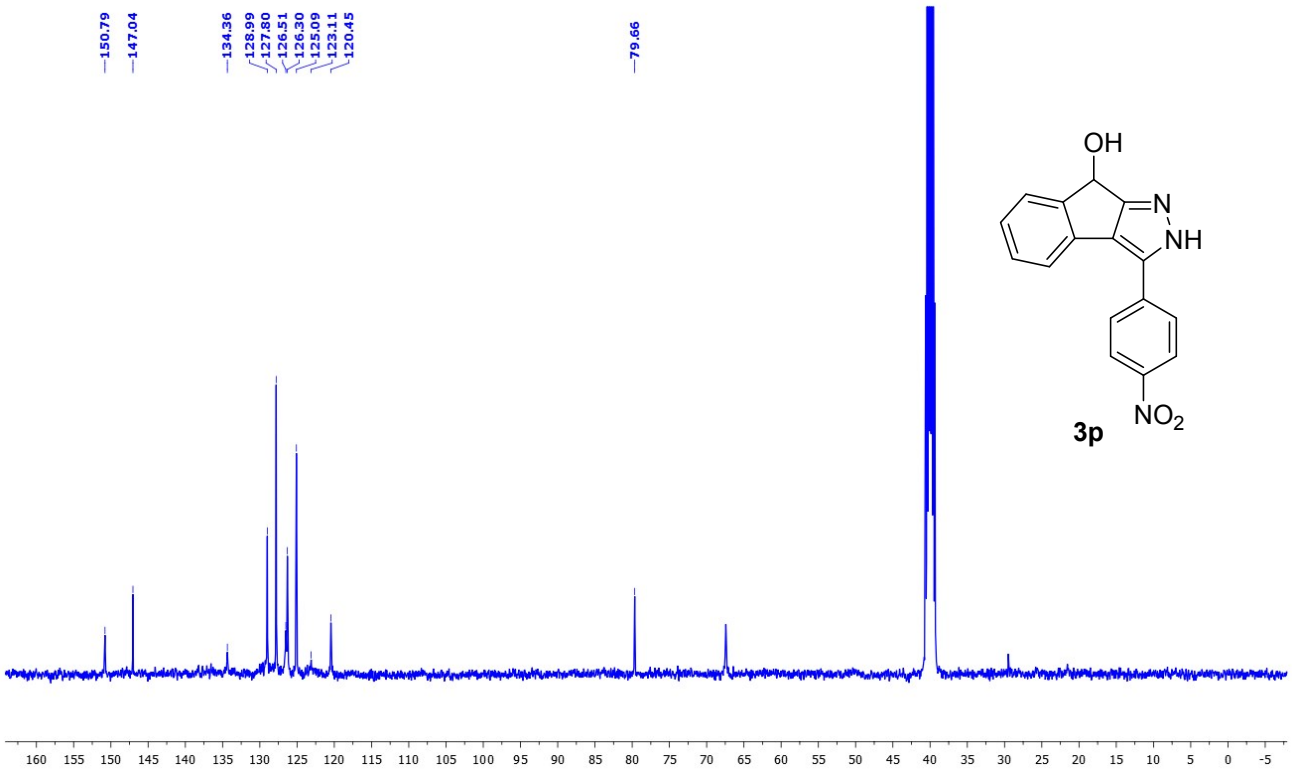
^{13}C NMR spectra of **3o** (101 MHz, $CDCl_3$ + DMSO-d_6):



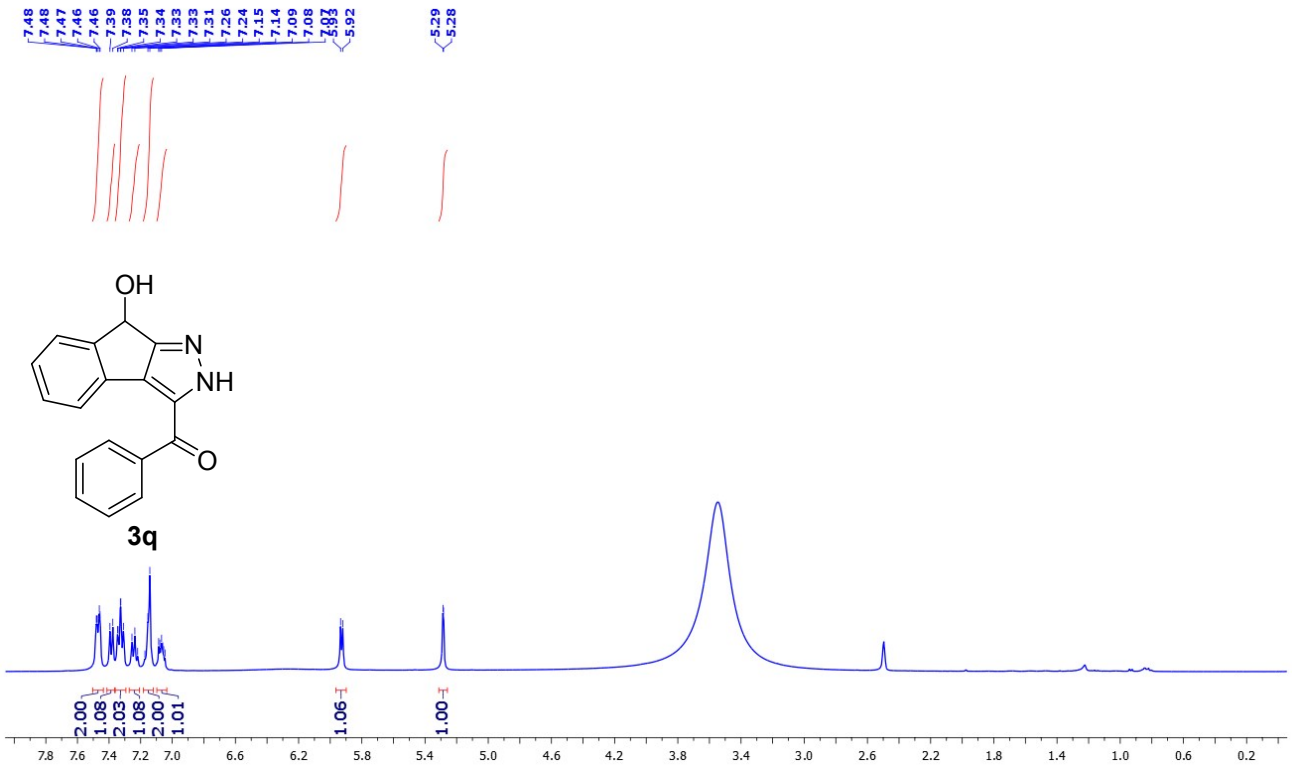
^{1}H NMR spectra of **3p** (400 MHz, DMSO-d_6):



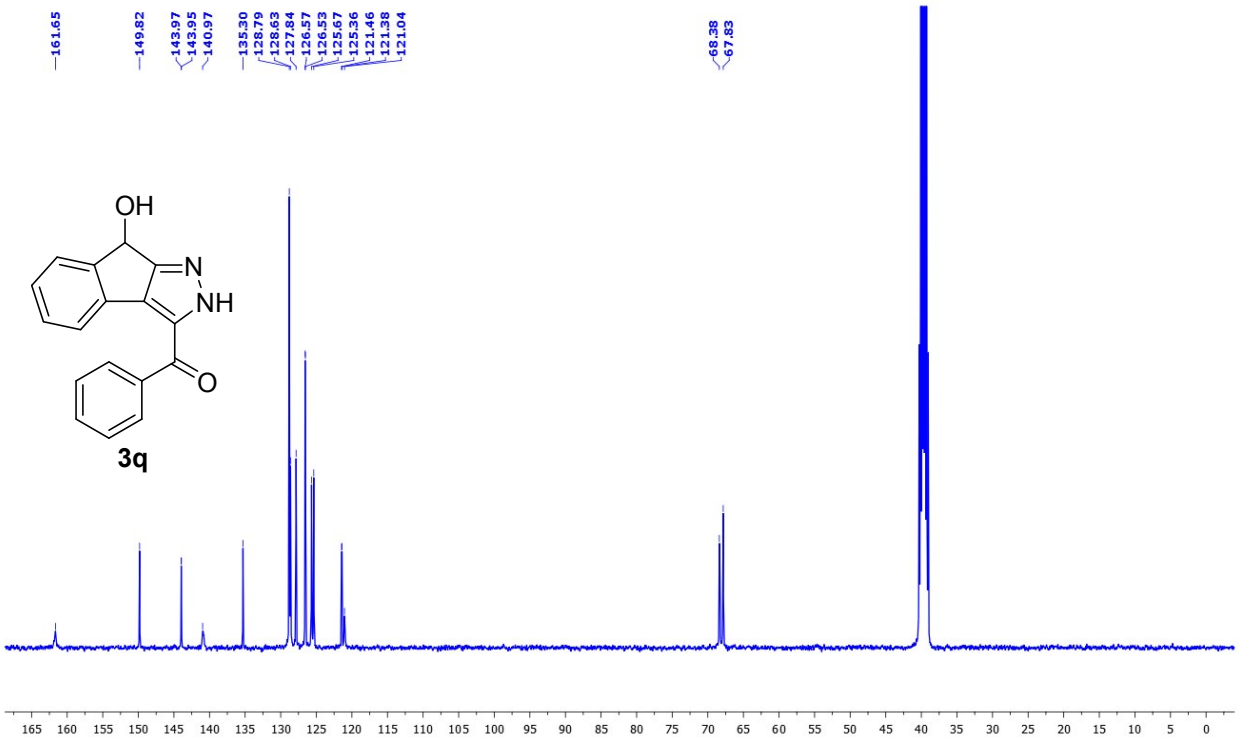
^{13}C NMR spectra of **3p** (101 MHz, DMSO-d_6):



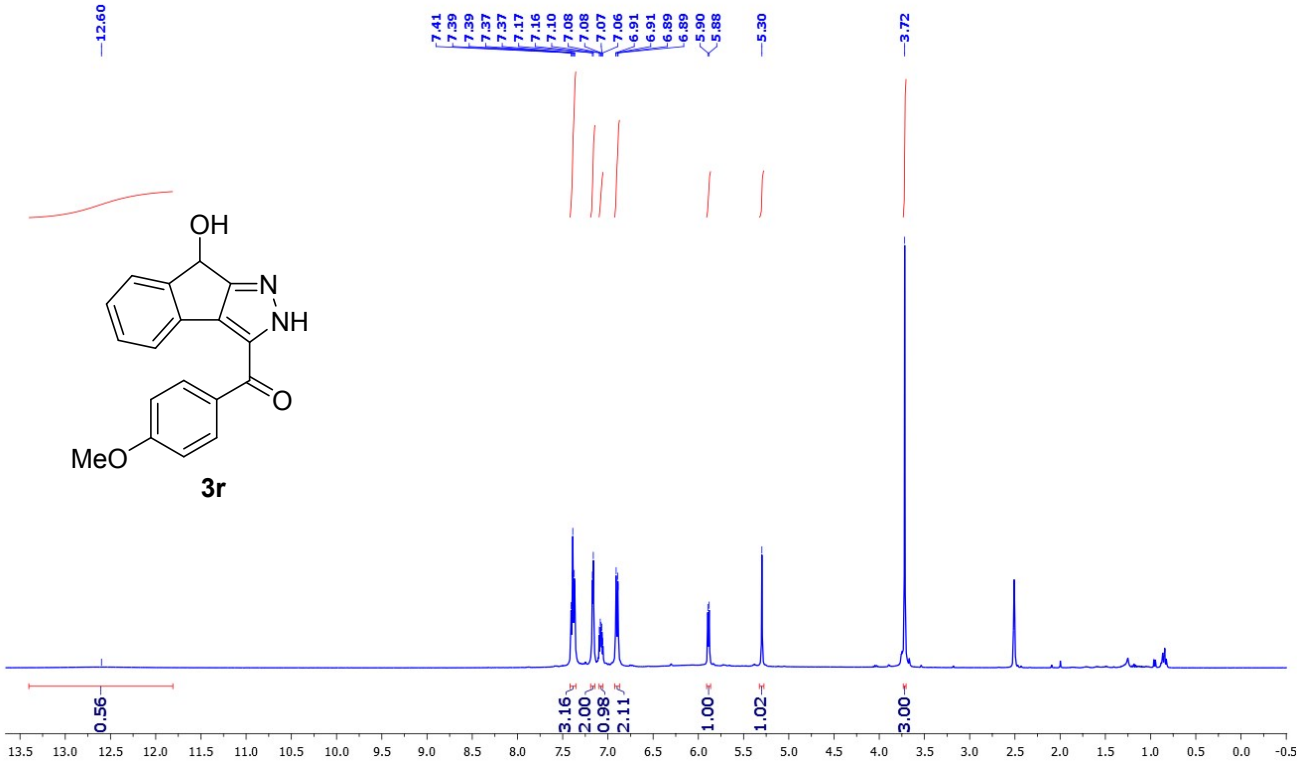
^{1}H NMR spectra of **3q** (400 MHz, DMSO-d_6):



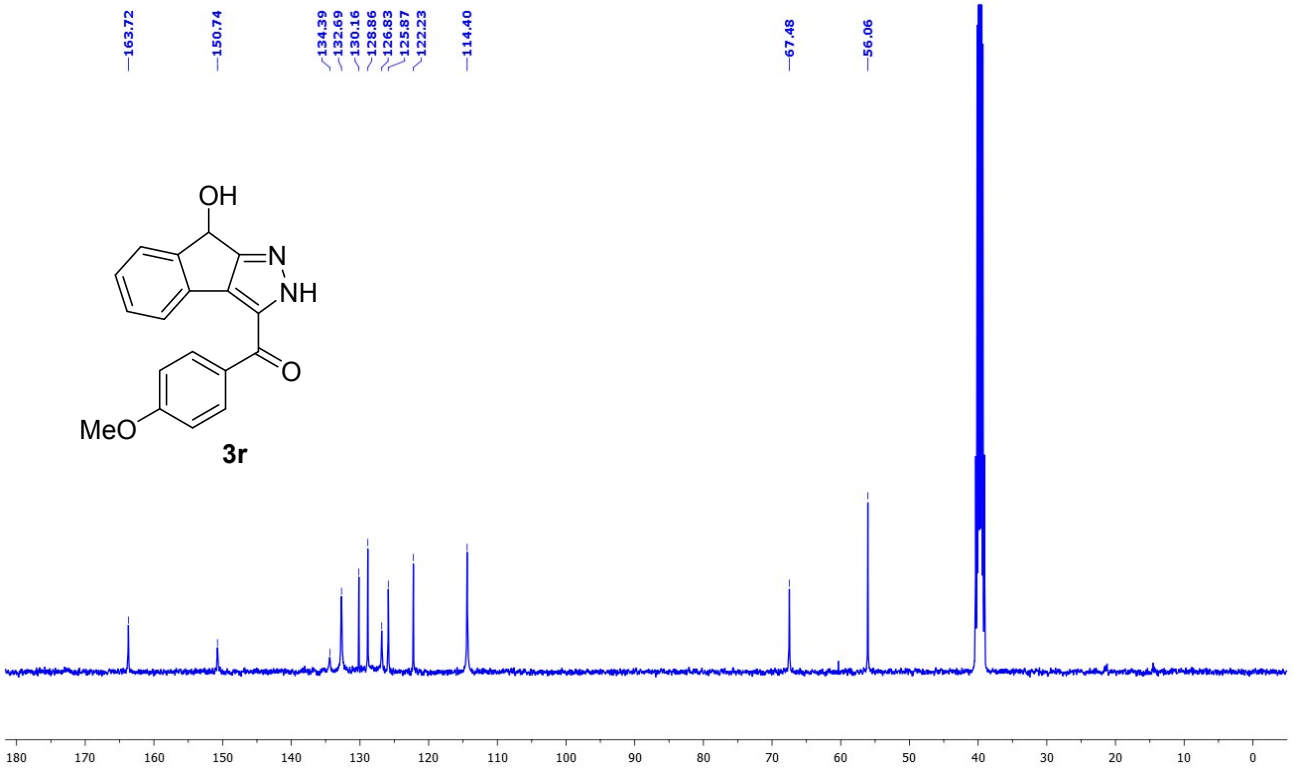
^{13}C NMR spectra of **3q** (101 MHz, DMSO-d_6):



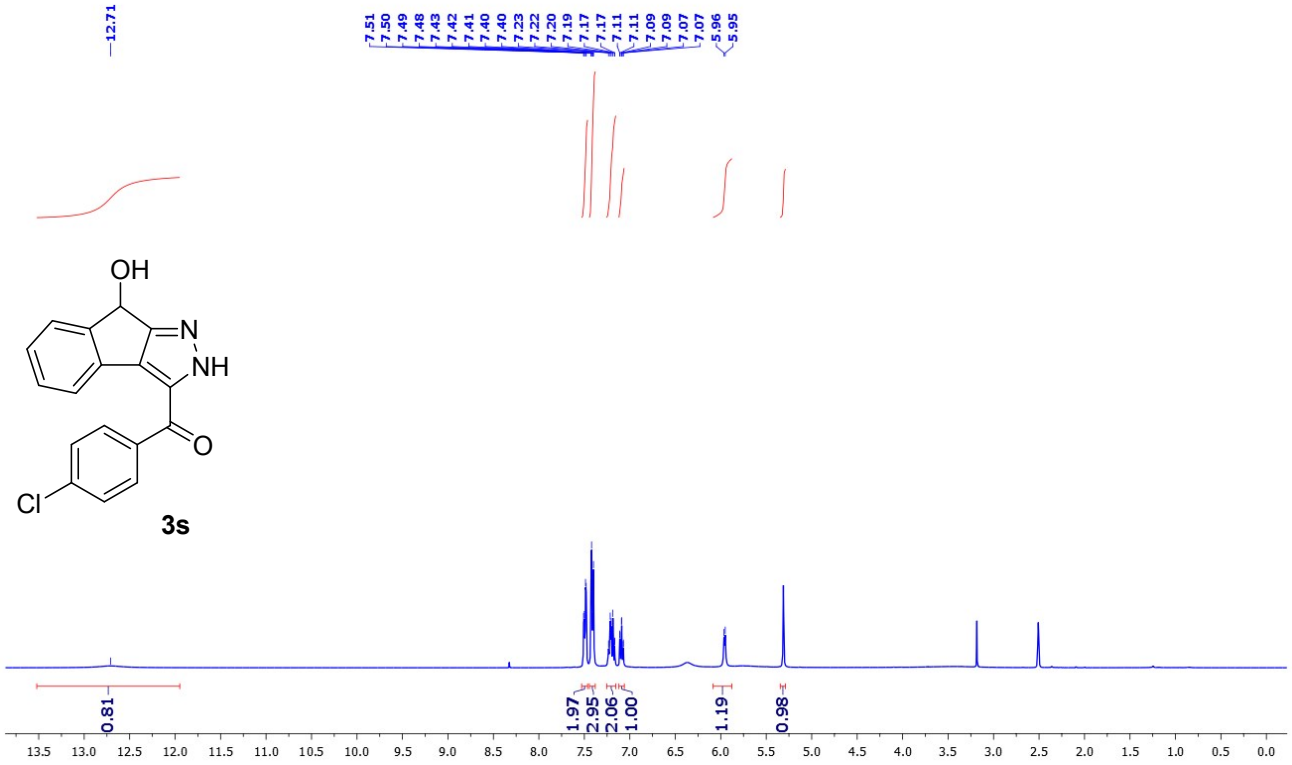
^{1}H NMR spectra of **3r** (400 MHz, DMSO-d_6):



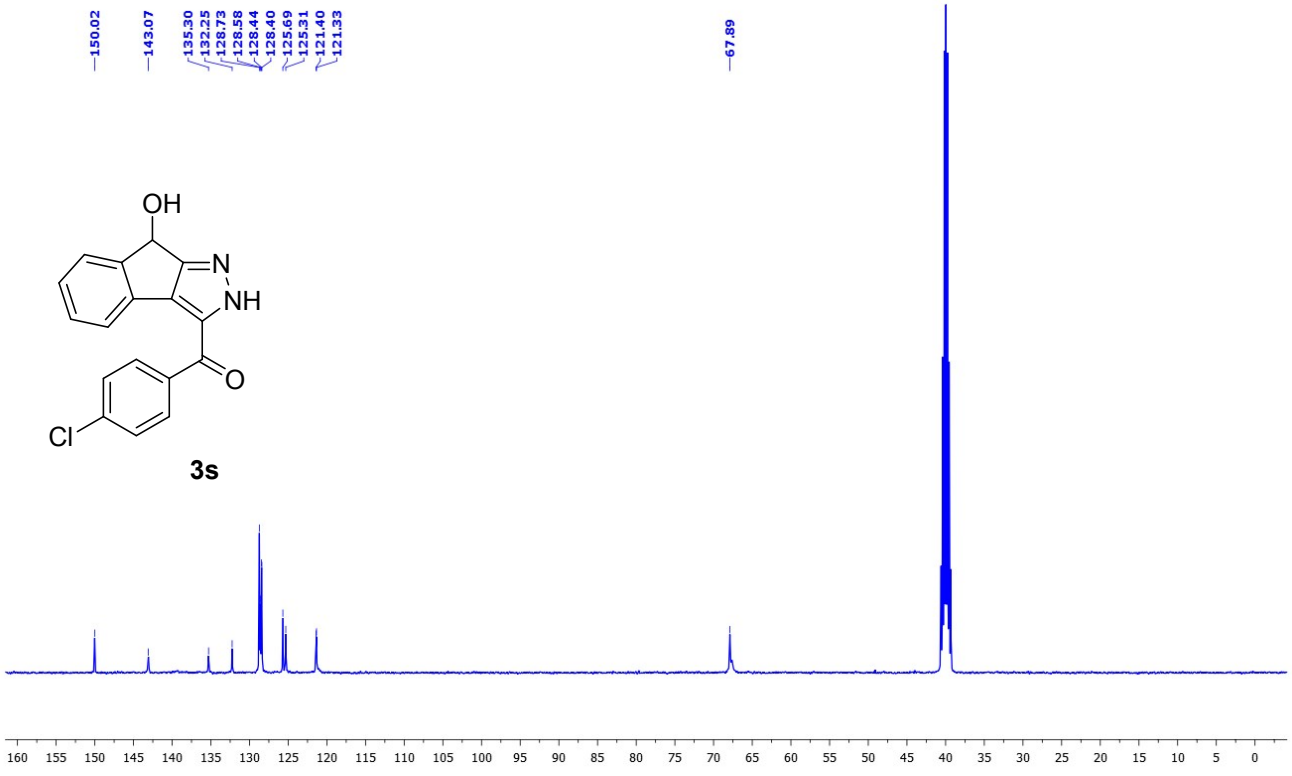
^{13}C NMR spectra of **3r** (101 MHz, DMSO-d_6):



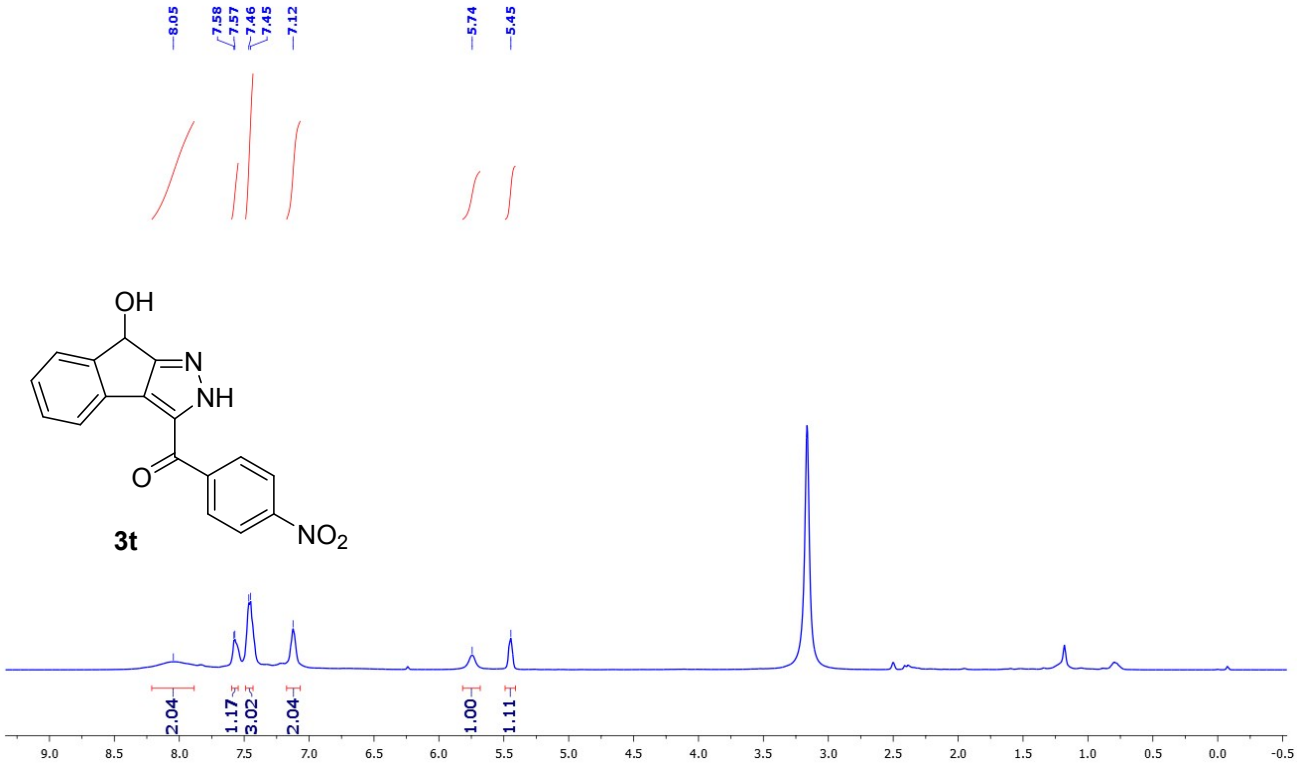
^{1}H NMR spectra of **3s** (400 MHz, DMSO-d_6):



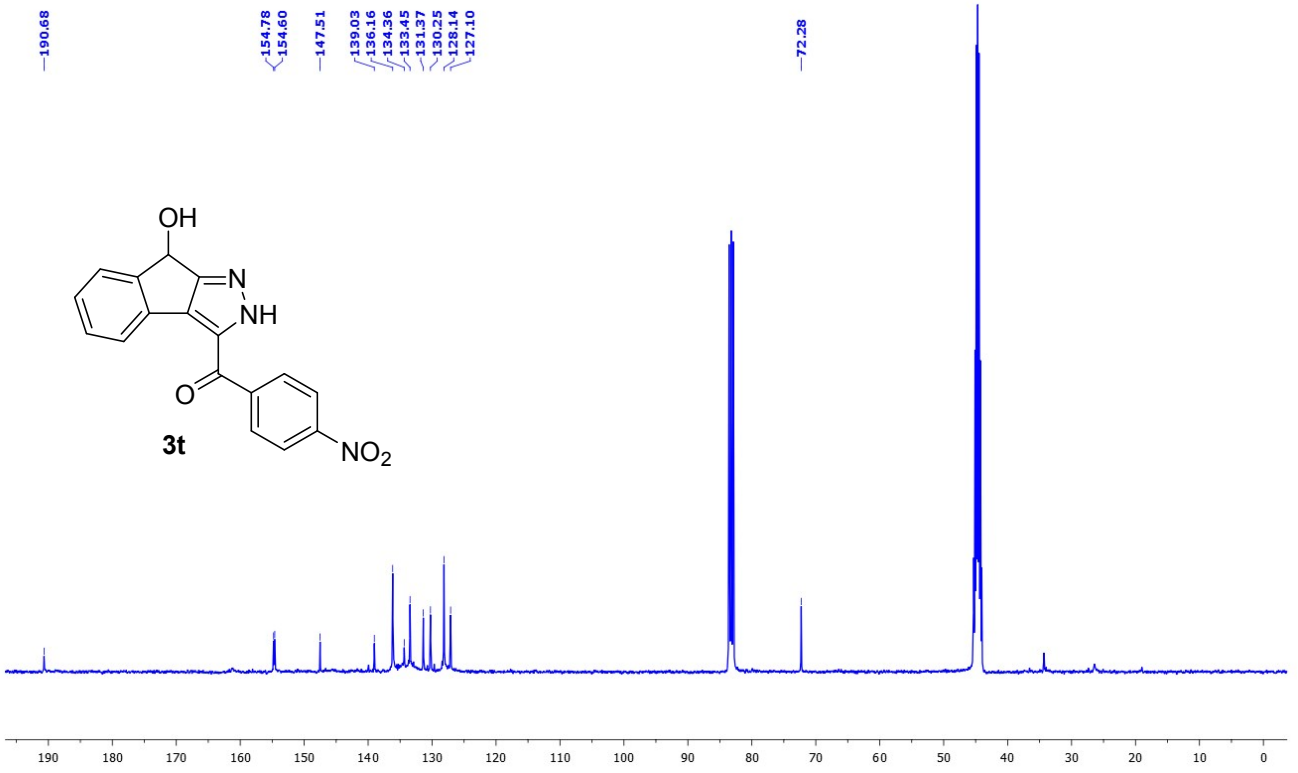
^{13}C NMR spectra of **3s** (101 MHz, DMSO-d_6):



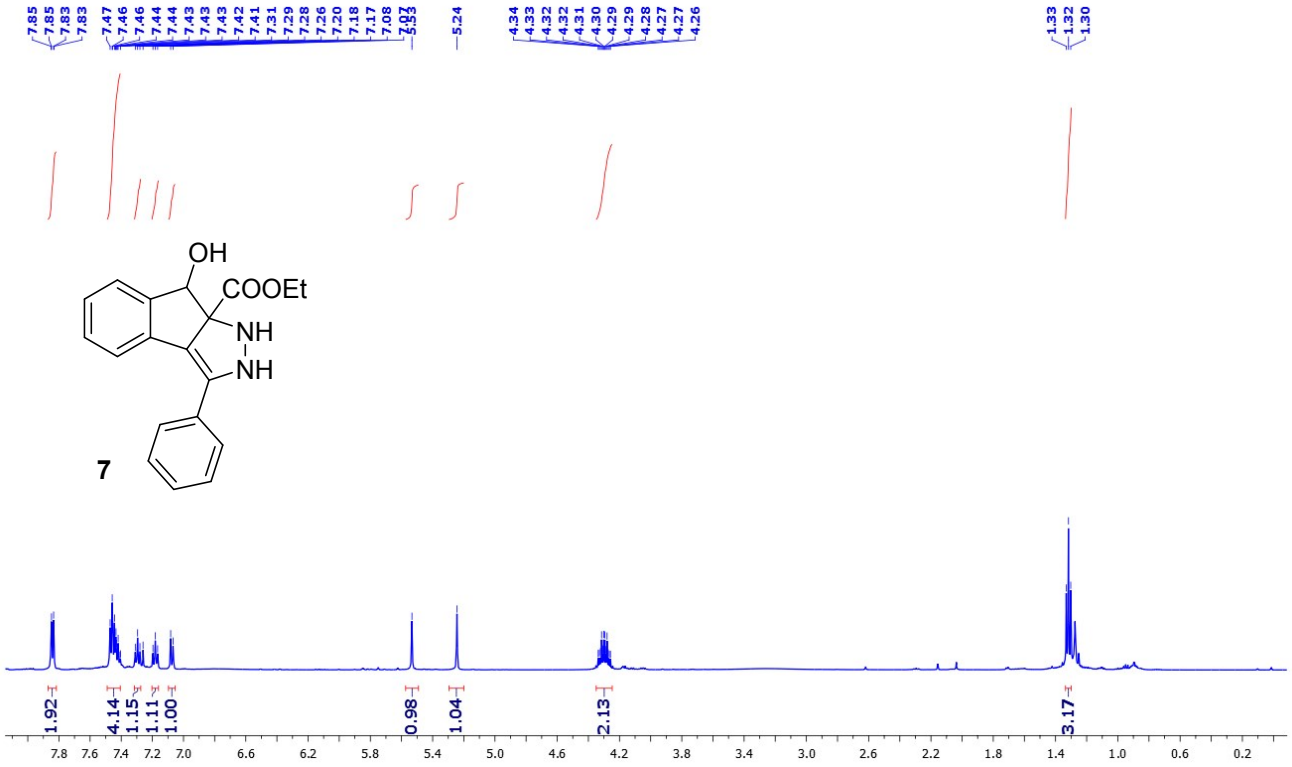
^{1}H NMR spectra of **3t** (400 MHz, DMSO-d_6):



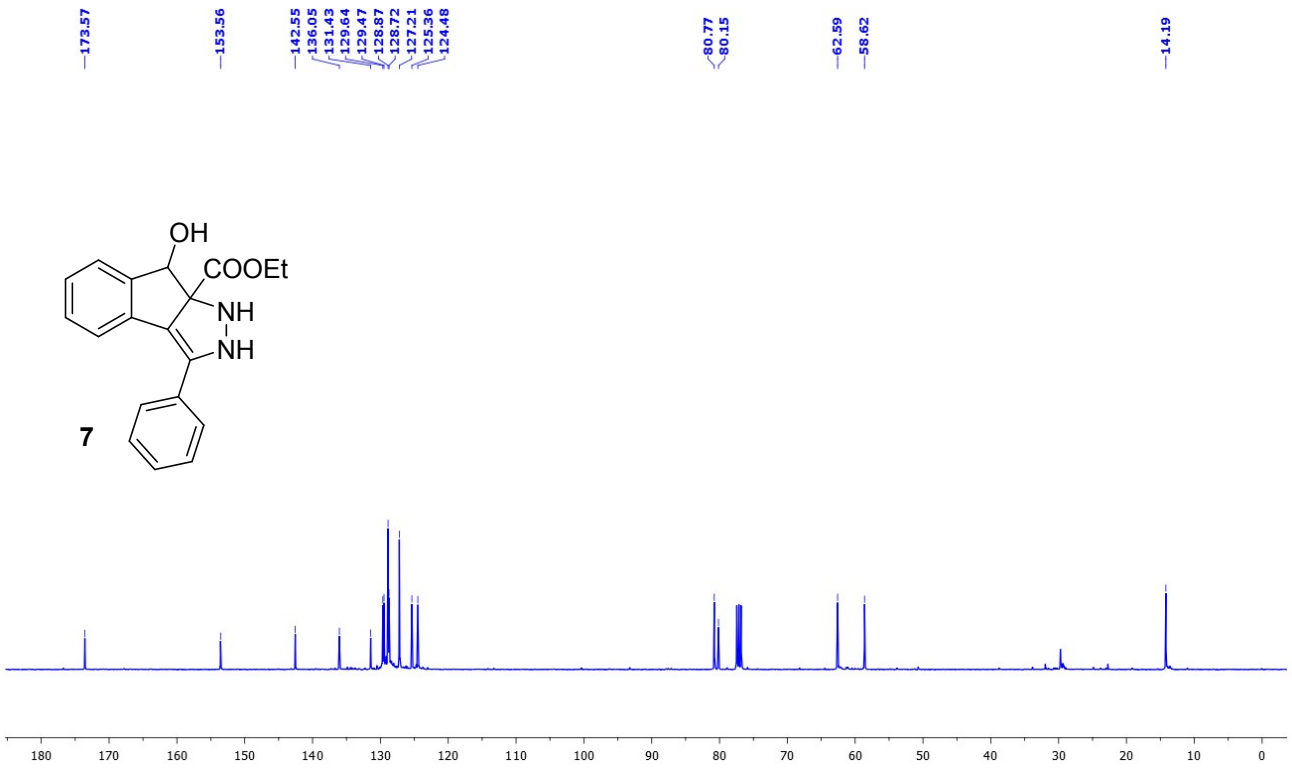
^{13}C NMR spectra of **3t** (101 MHz, $CDCl_3$ + DMSO-d_6):



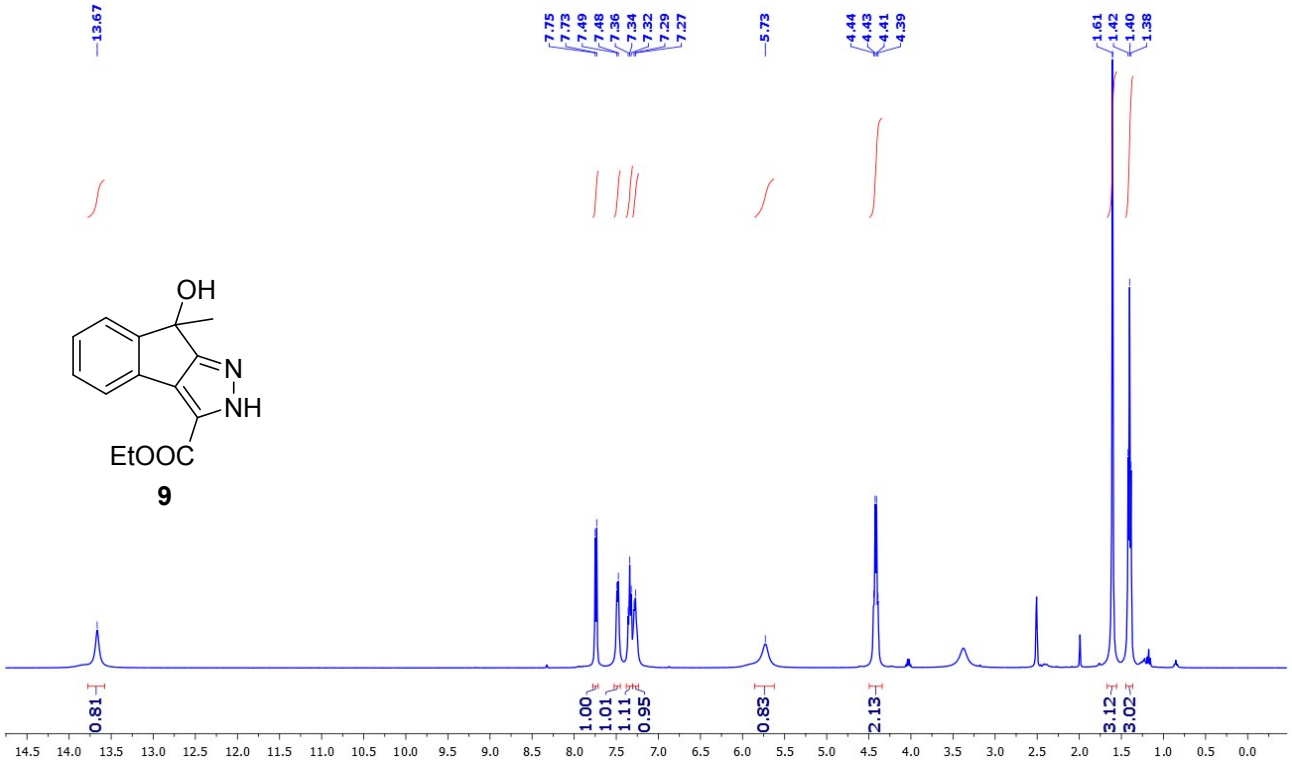
^{1}H NMR spectra of **7** (500 MHz, $CDCl_3$):



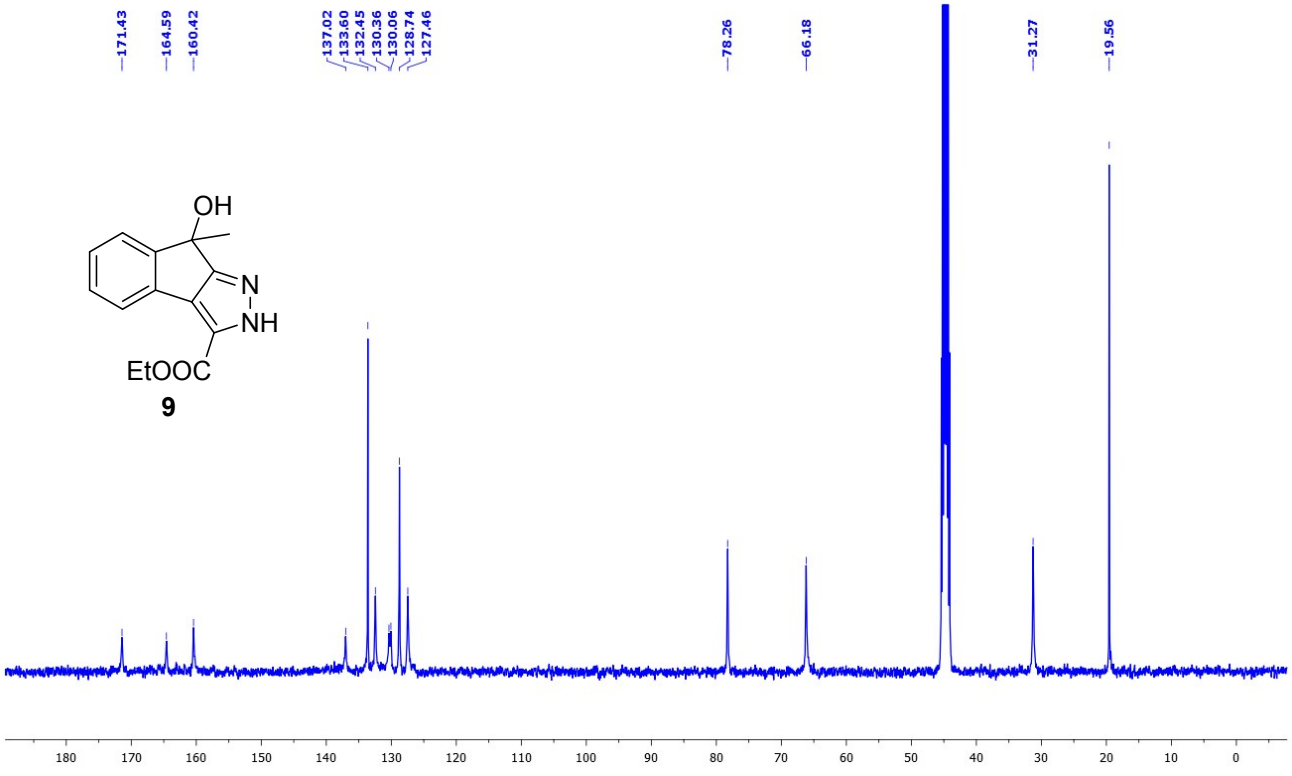
^{13}C NMR spectra of **7** (101 MHz, $CDCl_3$):



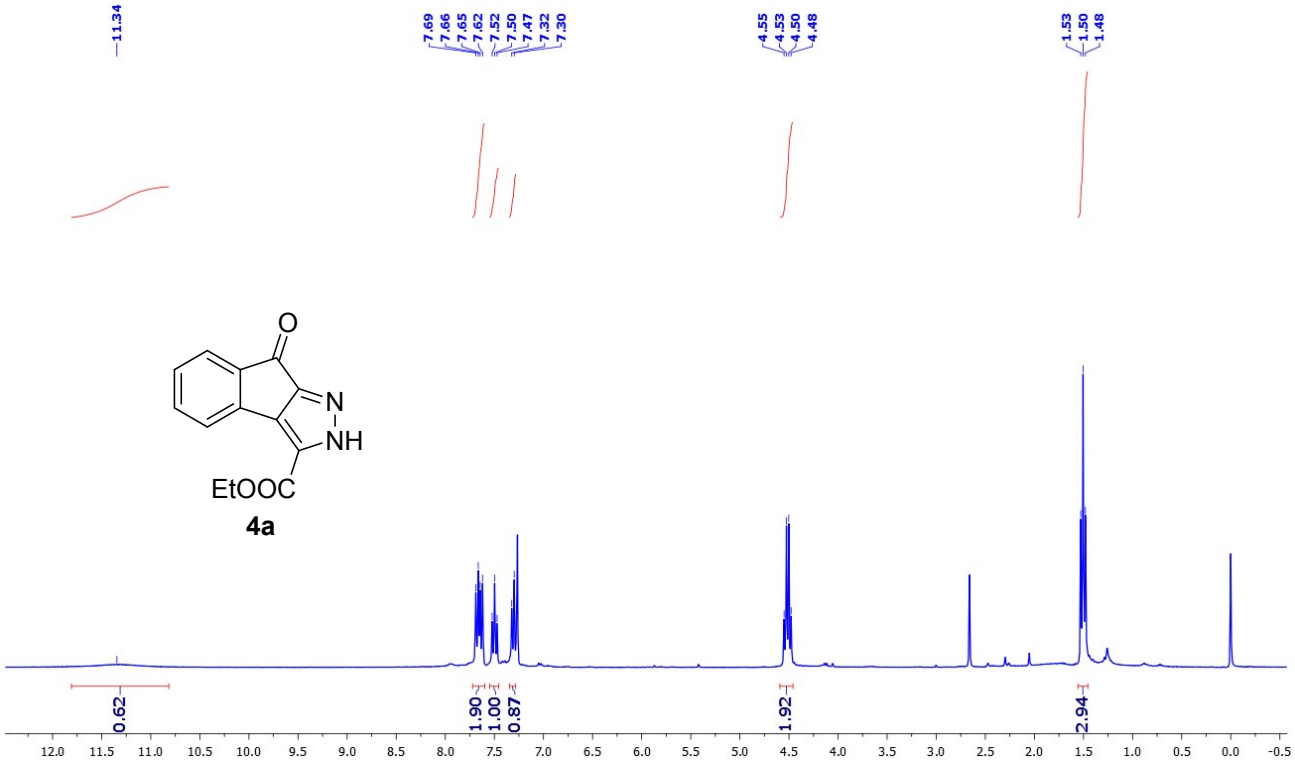
^{1}H NMR spectra of **9** (400 MHz, DMSO-d_6):



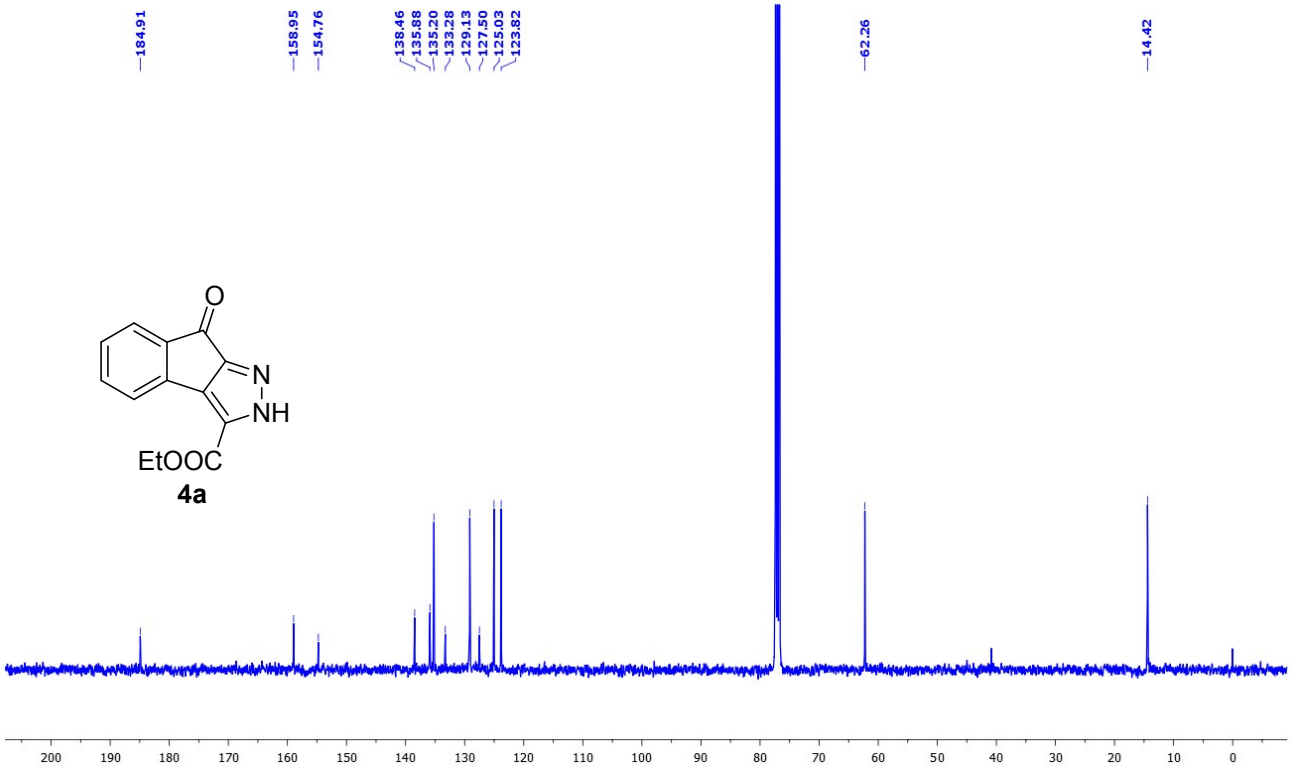
^{13}C NMR spectra of **9** (101 MHz, DMSO-d_6):



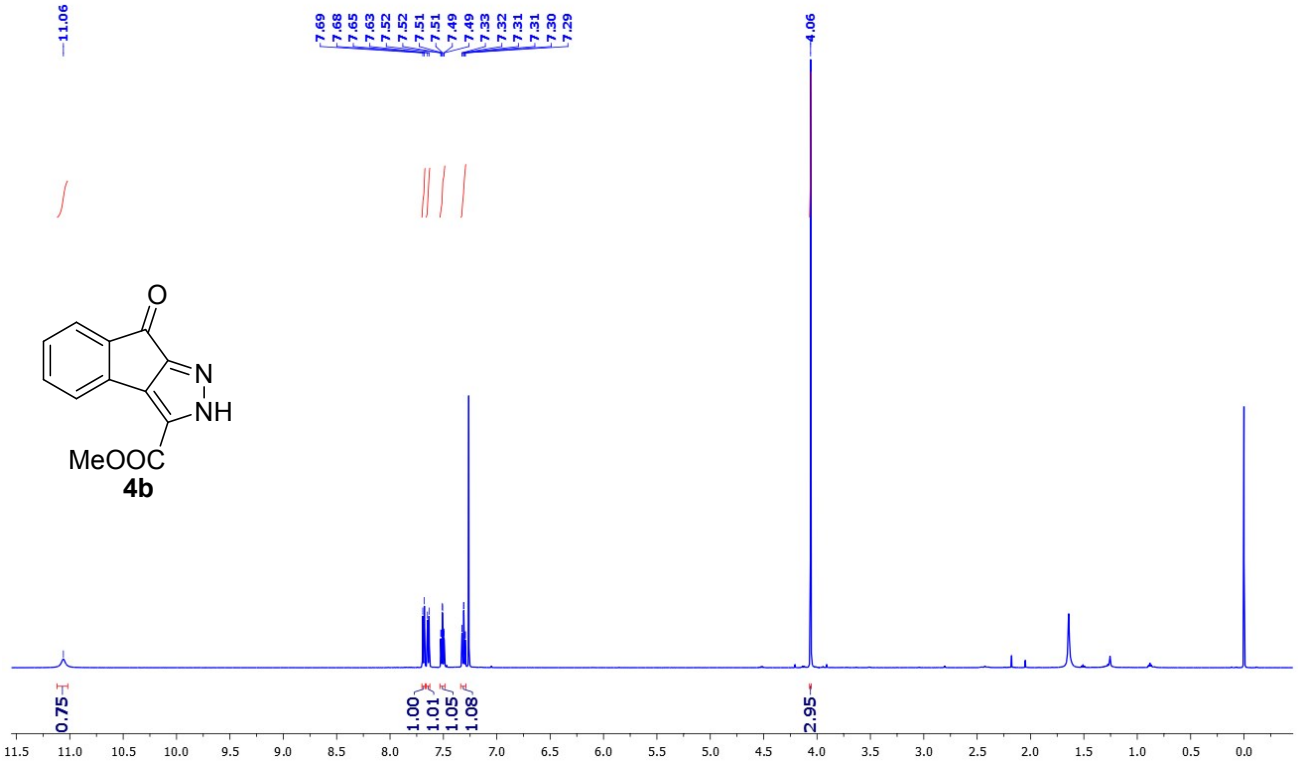
^{1}H NMR spectra of **4a** (400 MHz, $CDCl_3$):



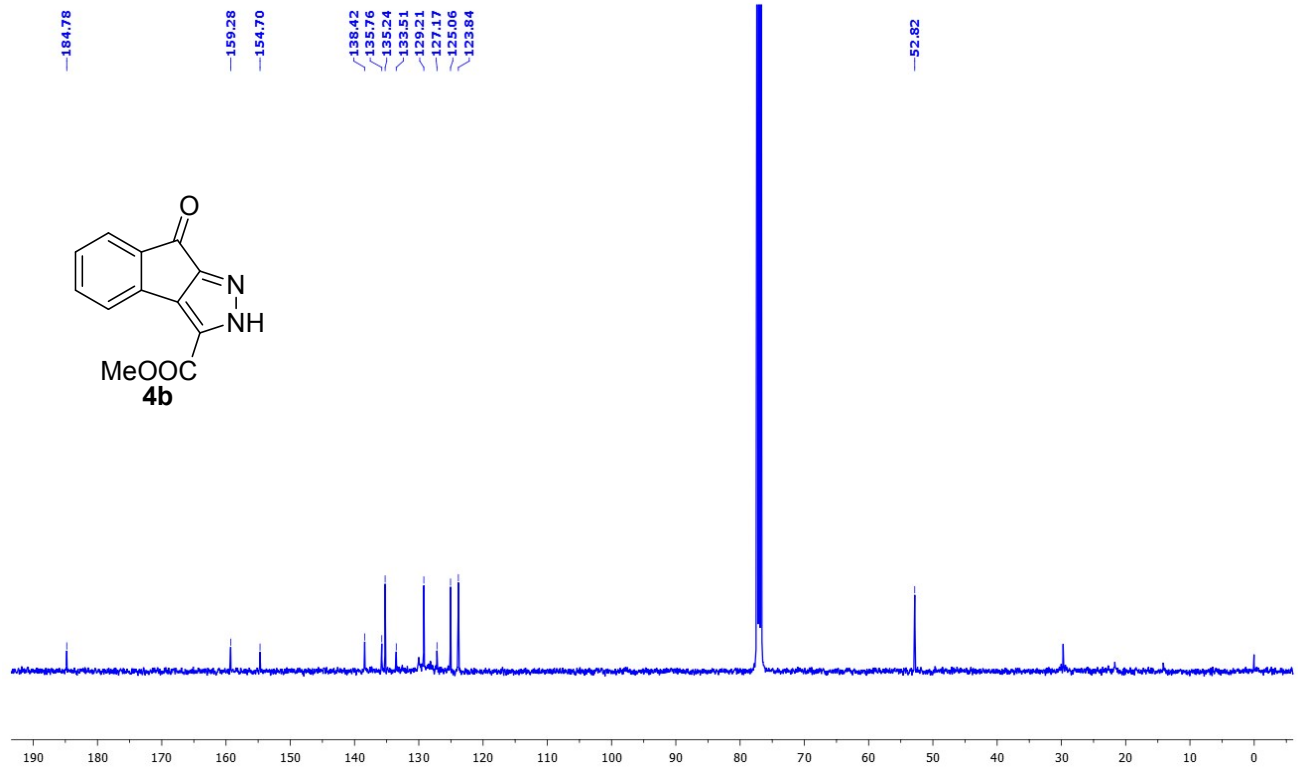
^{13}C NMR spectra of **4a** (101 MHz, $CDCl_3$):



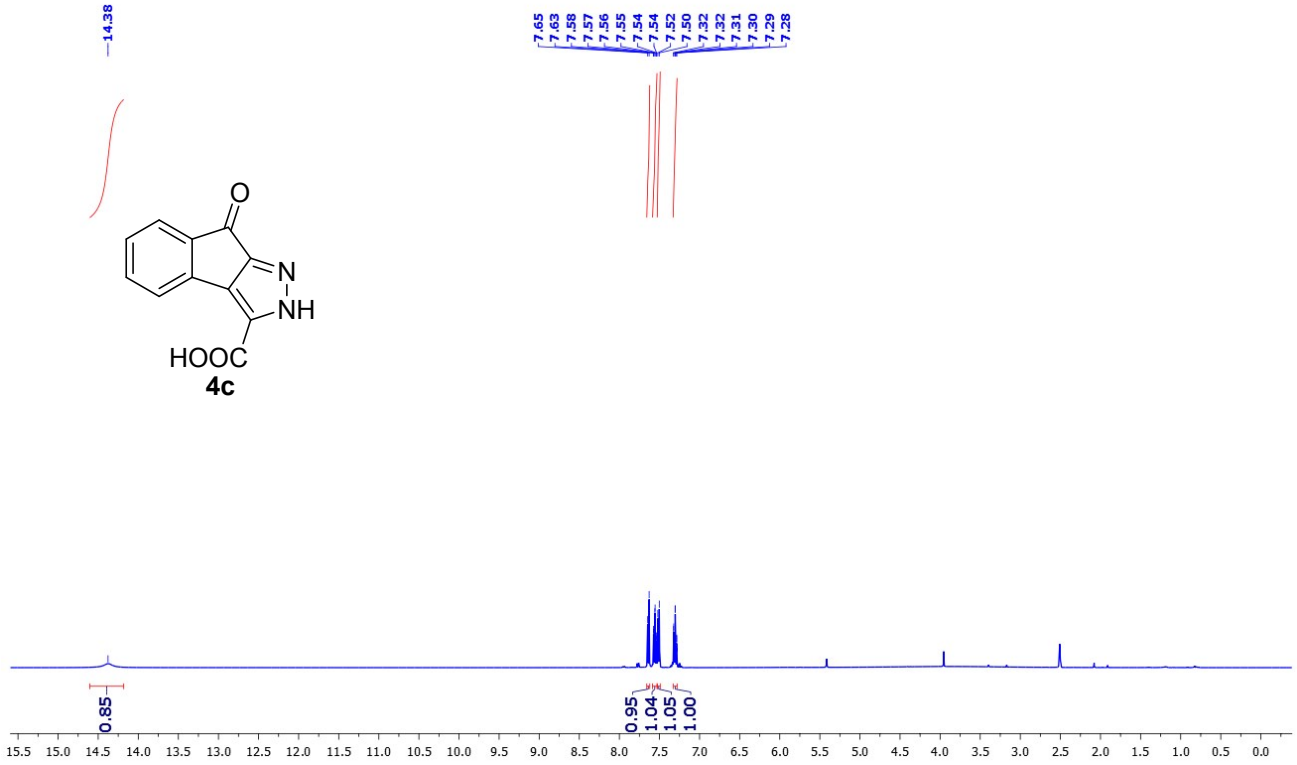
^{1}H NMR spectra of **4b** (500 MHz, $CDCl_3$):



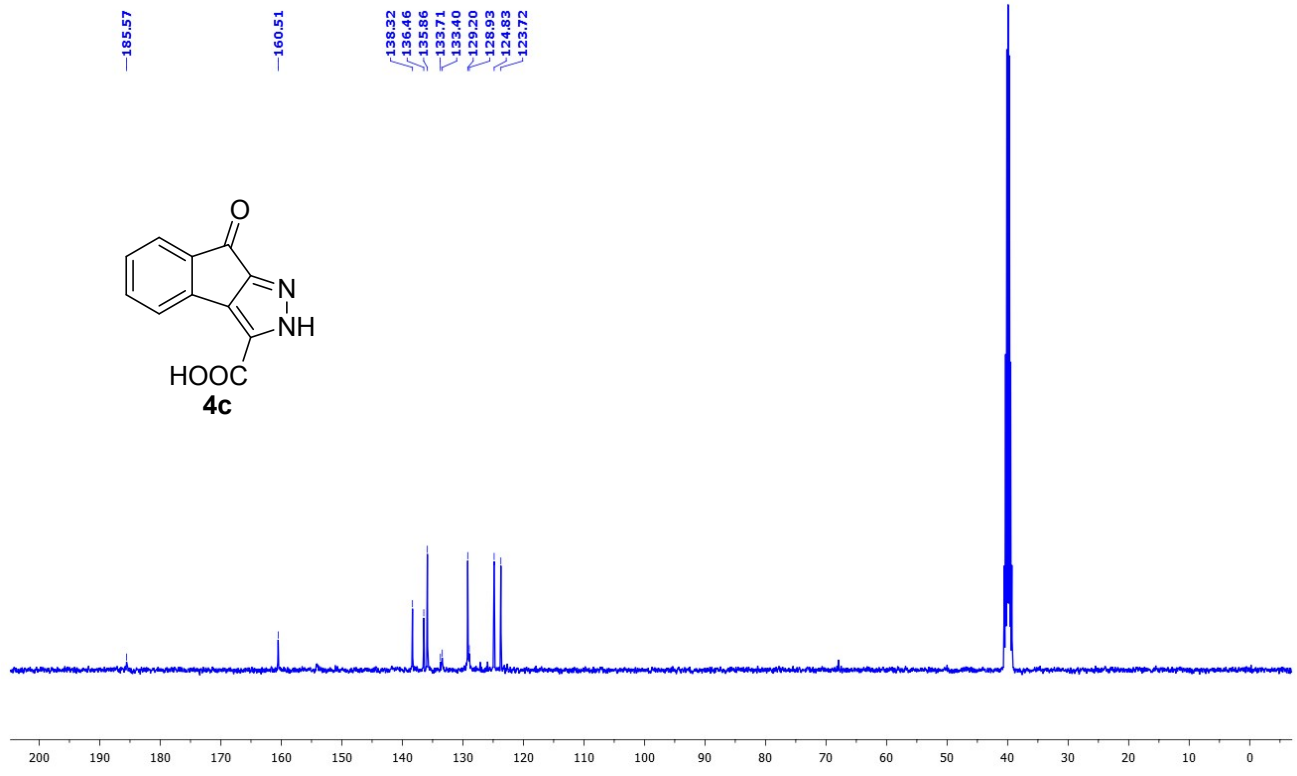
^{13}C NMR spectra of **4b** (101 MHz, $CDCl_3$):



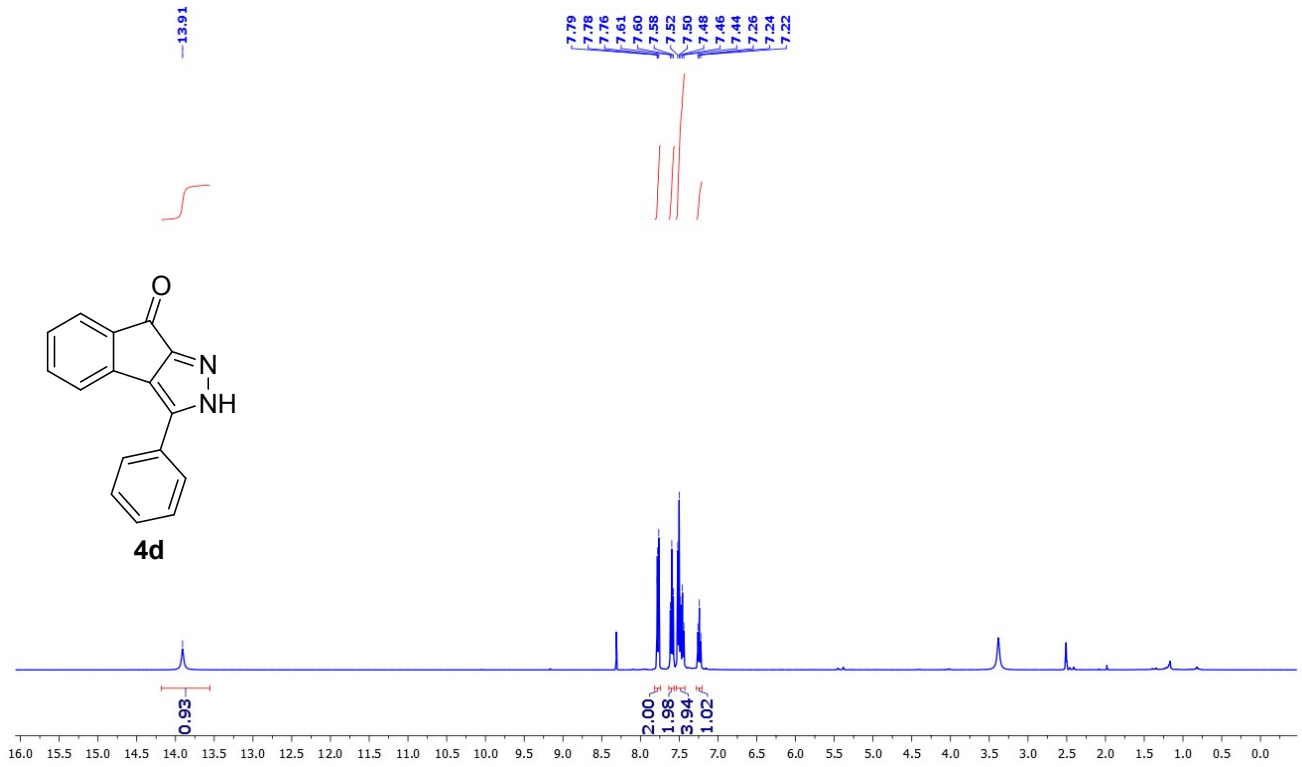
^{1}H NMR spectra of **4c** (400 MHz, DMSO-d_6):



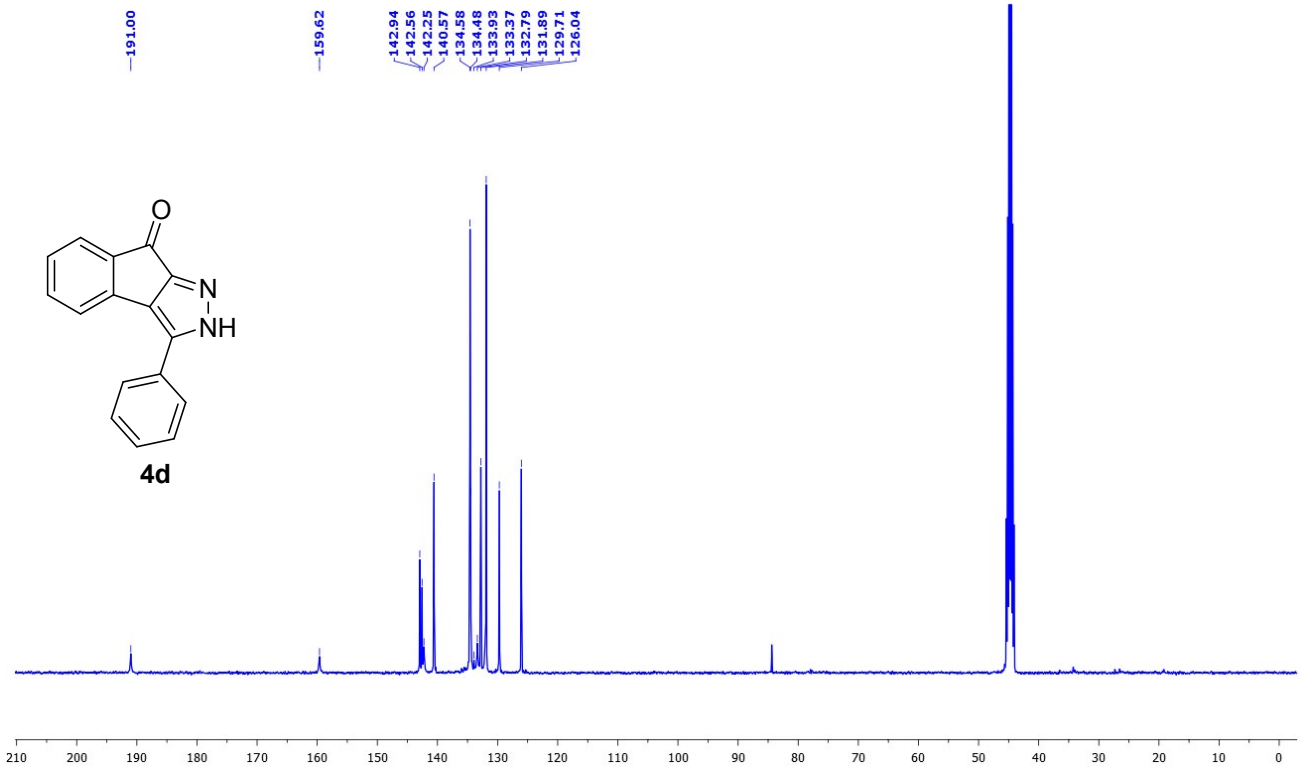
^{13}C NMR spectra of **4c** (101 MHz, DMSO-d_6):



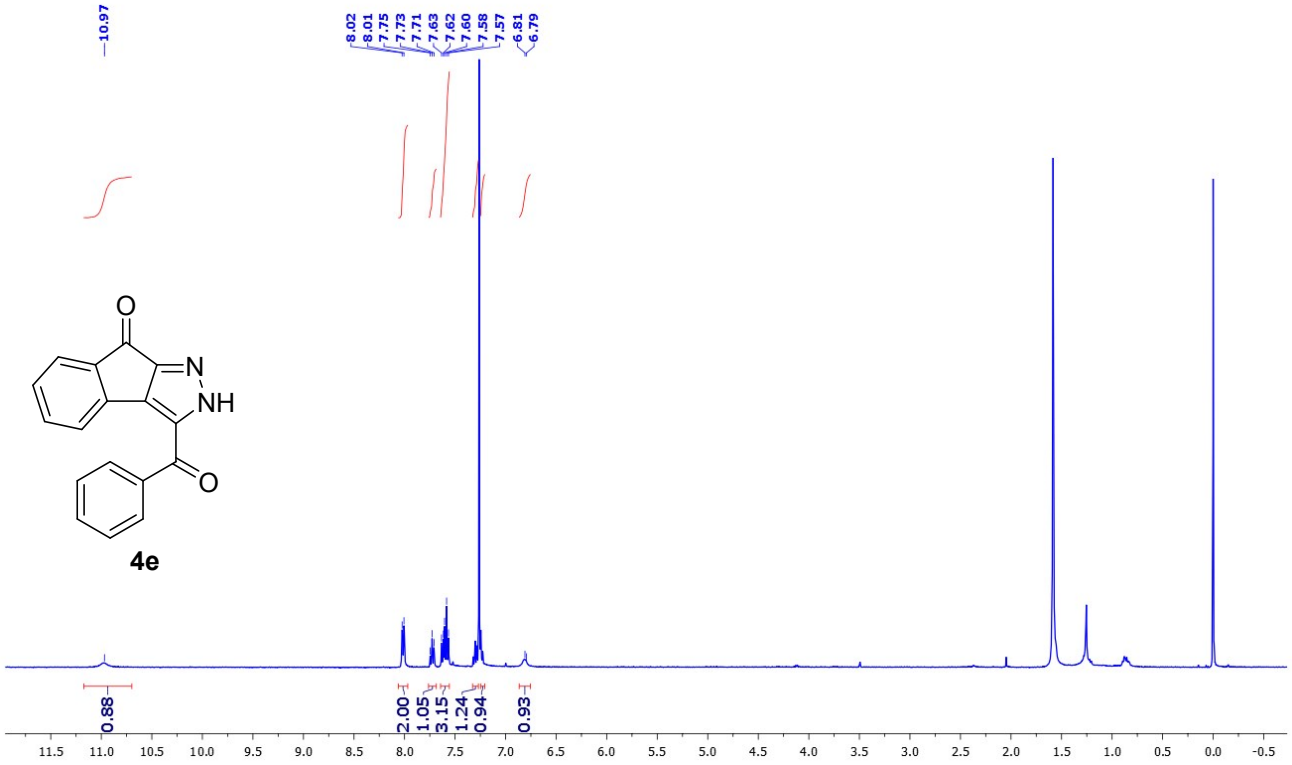
^{1}H NMR spectra of **4d** (400 MHz, $CDCl_3$ + DMSO-d_6):



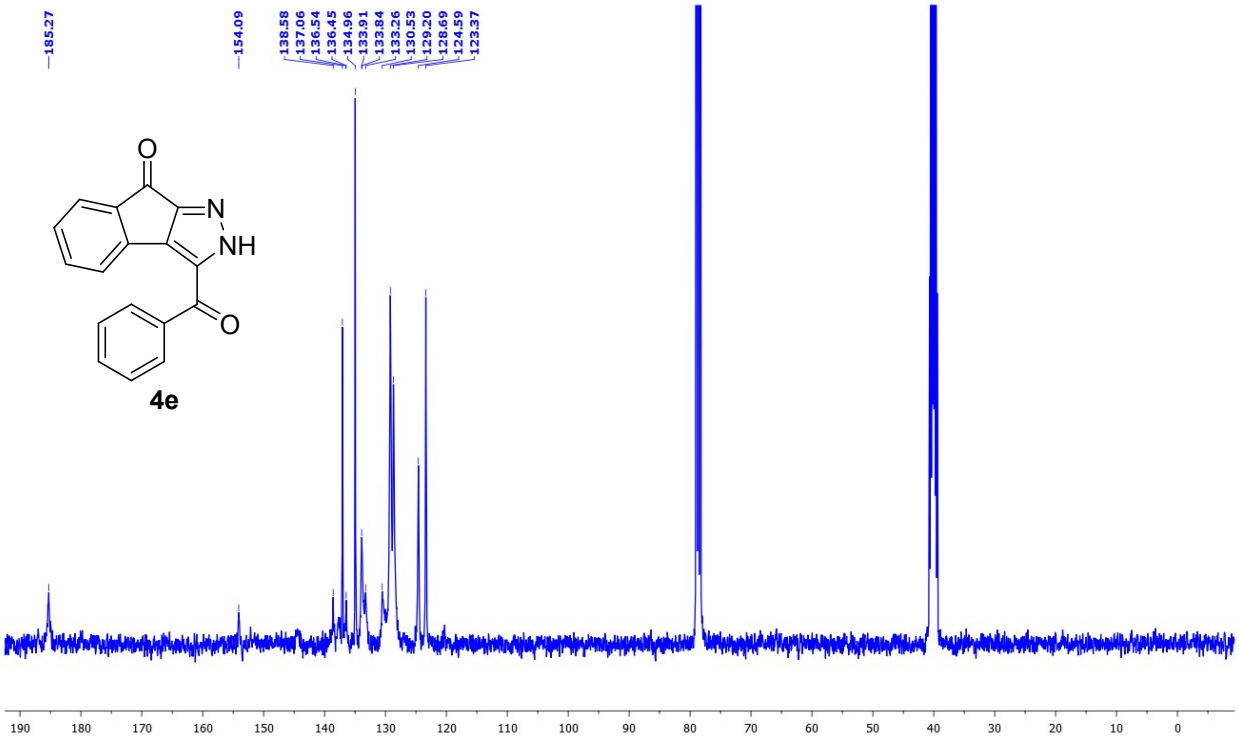
^{13}C NMR spectra of **4d** (101 MHz, DMSO-d_6):



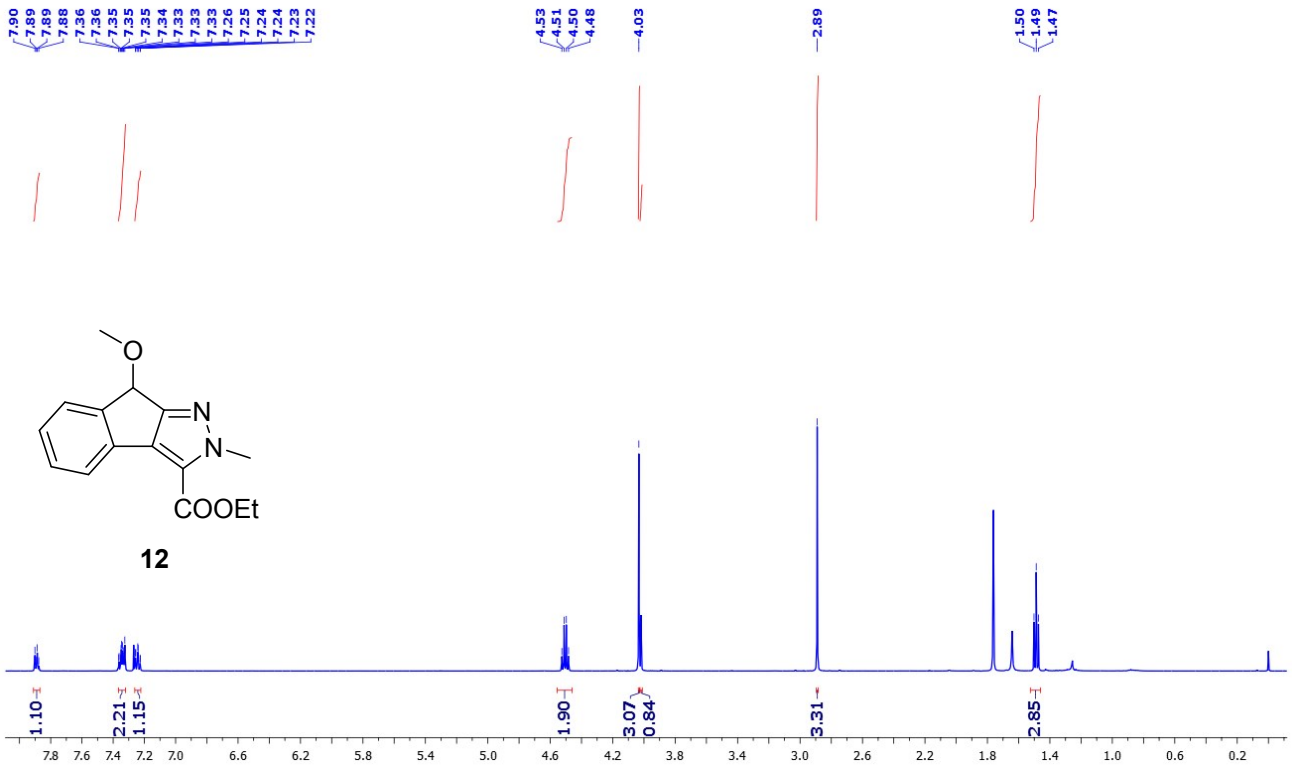
^{1}H NMR spectra of **4e** (400 MHz, $CDCl_3$):



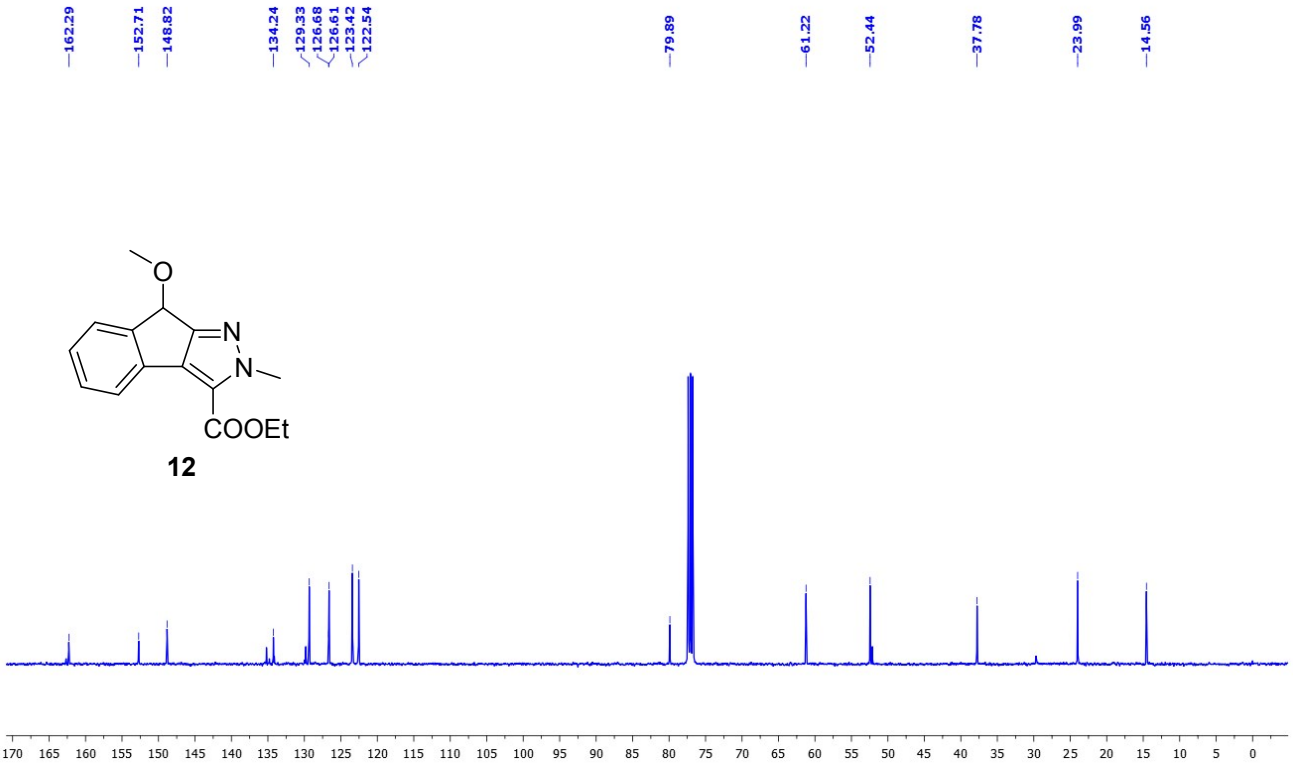
^{13}C NMR spectra of **4e** (101 MHz, $CDCl_3$+DMSO-d_6):



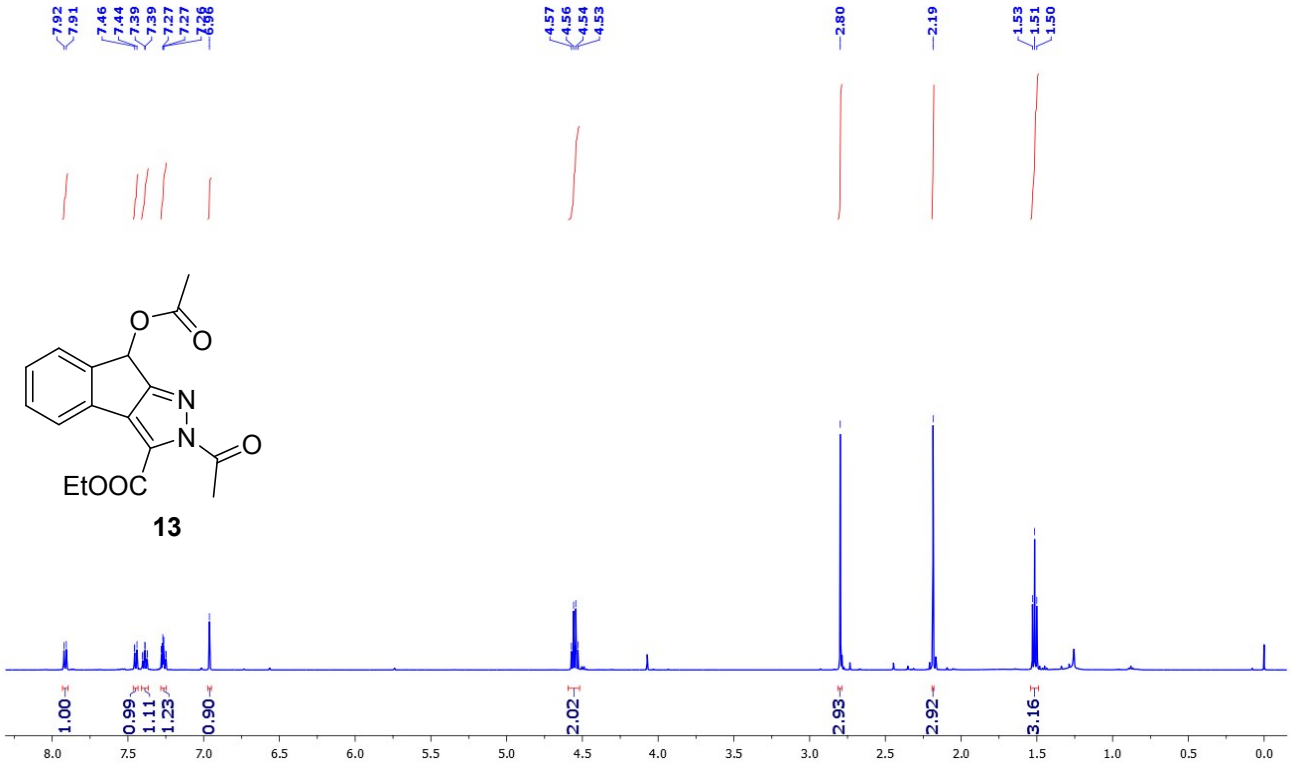
^{1}H NMR spectra of **12** (500 MHz, $CDCl_3$):



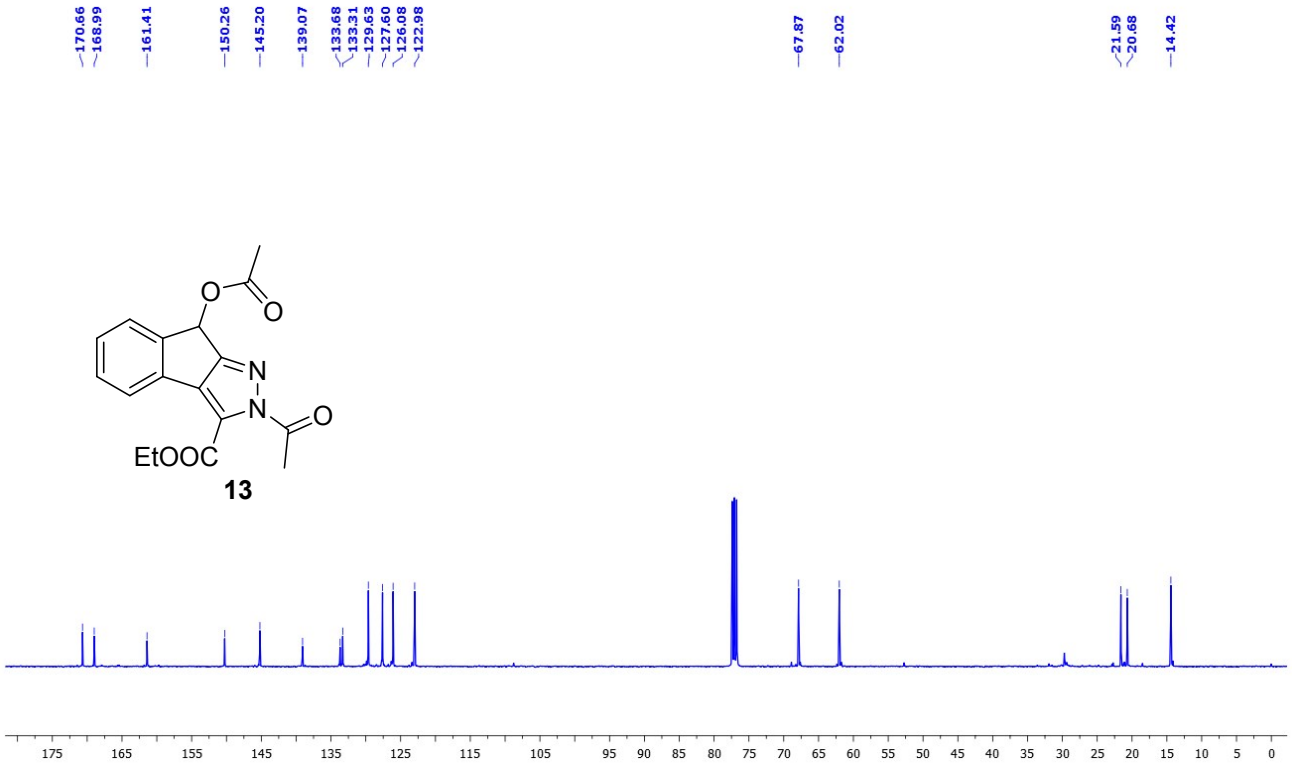
^{13}C NMR spectra of **12** (101 MHz, $CDCl_3$):



^{1}H NMR spectra of **13** (500 MHz, $CDCl_3$):



^{13}C NMR spectra of **13** (101 MHz, $CDCl_3$):



X-ray Crystallographic Data of compounds **3h.**

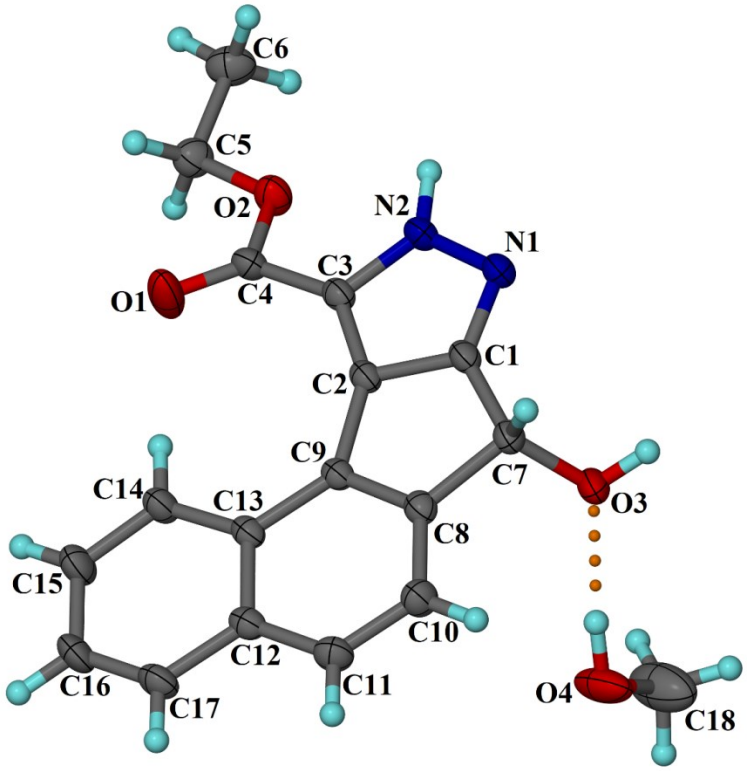


Figure caption: ORTEP diagram of **3h** compound with the atom-numbering. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radius. Dotted line indicates hydrogen bond between the compound and solvent of crystallization methanol that is trapped in the crystal lattice and present in 1:1 stoichiometric ratio (compound: solvent) in the asymmetric unit of the crystal. CCDC deposition number 2033884 contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

Table 1. Crystallographic details of **3h** compound.

Datablock: 3h

Bond precision: C-C = 0.0031 A Wavelength=0.71073

Cell: a=8.755(3) b=9.844(3) c=10.982(4)
alpha=111.200(12) beta=98.323(12) gamma=105.109(11)
Temperature: 293 K

	Calculated	Reported
Volume	821.3(5)	821.3(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C17 H14 N2 O3, C H4 O	C17 H14 N2 O3, C H4 O
Sum formula	C18 H18 N2 O4	C18 H18 N2 O4
Mr	326.34	326.34
Dx,g cm-3	1.320	1.320
Z	2	2
Mu (mm-1)	0.094	0.094
F000	344.0	344.0
F000'	344.17	
h,k,lmax	10,11,13	10,11,13
Nref	2901	2893
Tmin,Tmax	0.965,0.976	0.583,0.746
Tmin'	0.965	

Correction method= # Reported T Limits: Tmin=0.583 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 24.999

R(reflections)= 0.0482(2287) wR2(reflections)= 0.1386(2893)

S = 1.046 Npar= 232

Data collection and Structure solution details: Single crystal X-ray data for **3h** compound were collected at room temperature on a Bruker D8 QUEST equipped with a four-circle kappa diffractometer and Photon 100 detector. An Iμs microfocus Mo source (λ=0.71073Å) supplied the multi-mirror monochromated incident beam. A combination of Phi and Omega scans were used to collect the necessary data and unit cell dimensions were determined using 9909reflections. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS97[2] and refinement was carried out by full-matrix least-squares technique using SHELXL-2014/7.[2-3] Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were

positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97 Å, and with U_{iso}(H) = 1.2U_{eq} (C) or 1.5U_{eq} for methyl atoms. Solvent of crystallization methanol was trapped in the crystal lattice and present in 1:1 stoichiometric ratio (compound: solvent) in the asymmetric unit of the crystal. The N bound and O bound H atoms were located from the difference Fourier map. Structures with CCDC deposition number2033884contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. SHELXS97 and SHELXL Version 2014/7, http://shelx.uni-ac.gwdg.de/SHELX/index.php
3. Muller, P, Herbst-Imer, R, Spek, A. L, Schneider, T. R, and Sawaya, M. R. Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. Muller, P. Ed. 2006 Oxford University Press: Oxford, New York, pp. 57–91.