Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

ZrO_2 nanoparticles as a reusable solid dual acid-base catalyst for facile one-pot synthesis of multi-functionalized spirooxindole derivatives under solvent free condition

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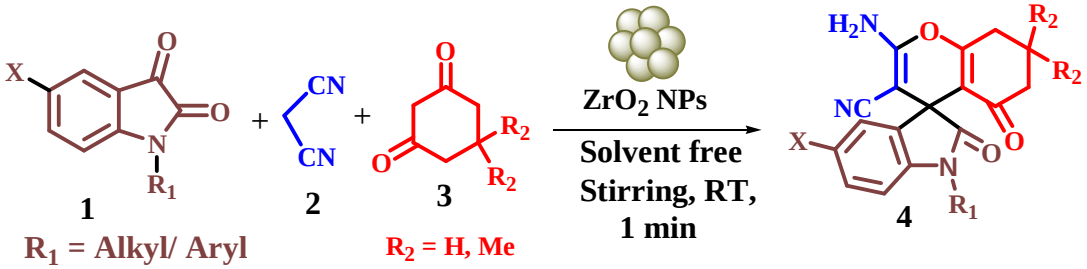
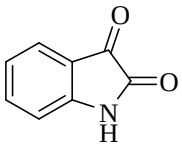
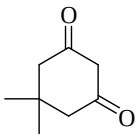
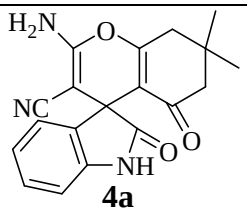
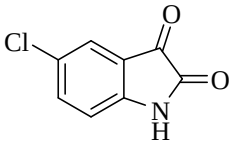
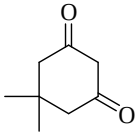
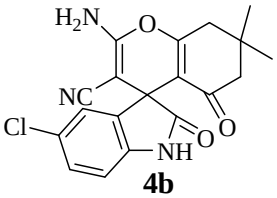
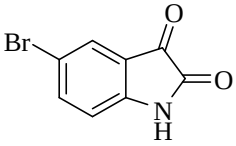
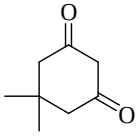
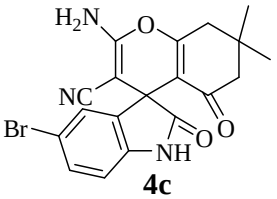
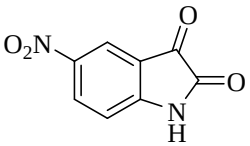
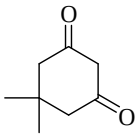
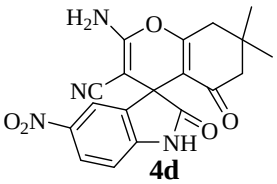
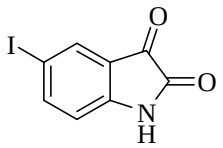
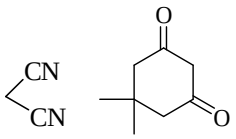
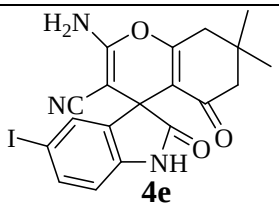
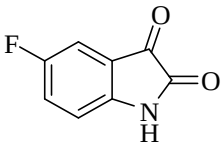
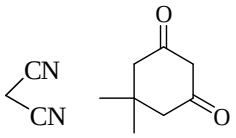
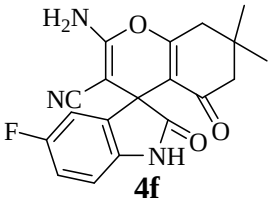
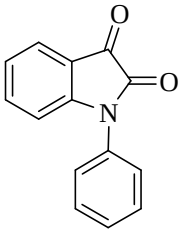
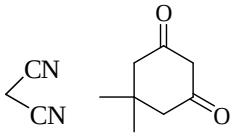
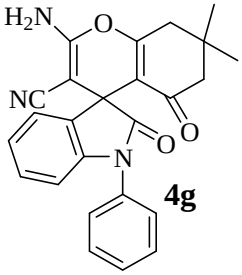
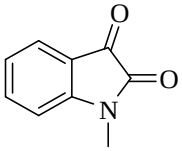
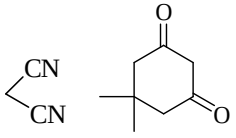
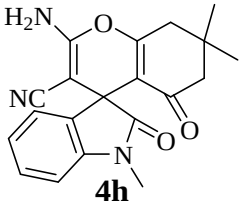
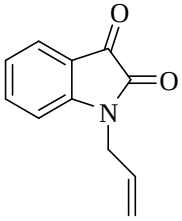
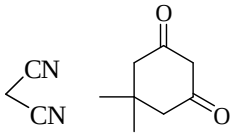
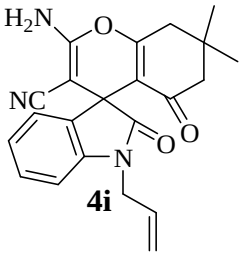
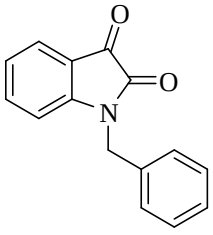
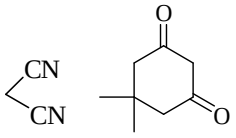
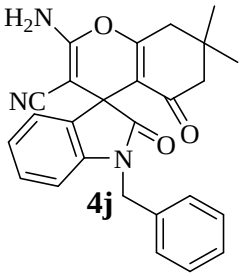
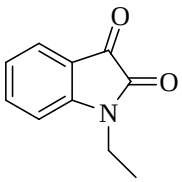
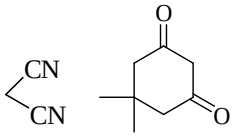
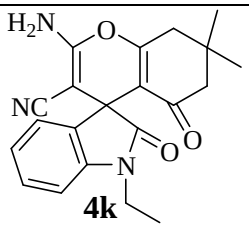
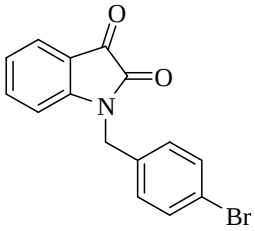
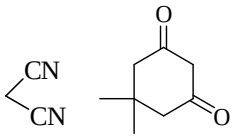
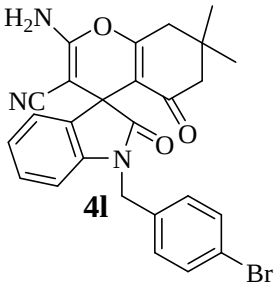
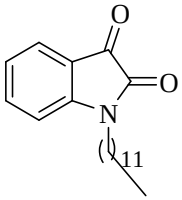
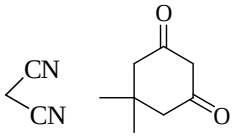
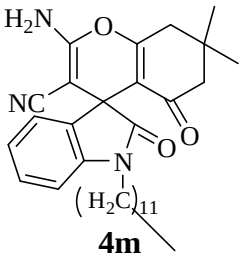
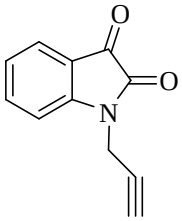
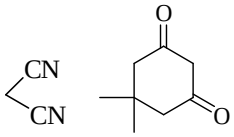
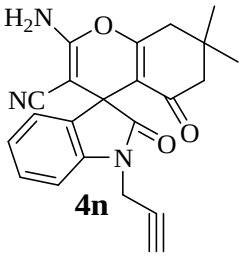
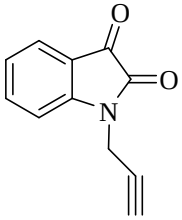
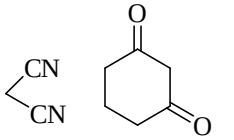
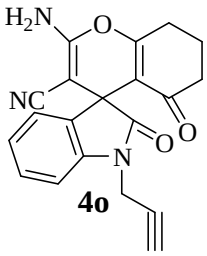
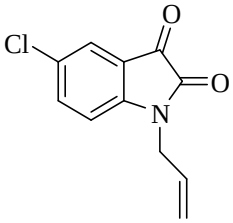
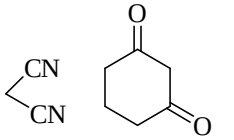
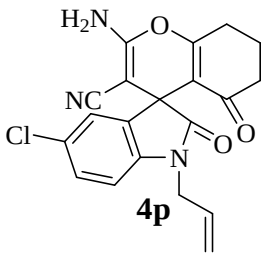
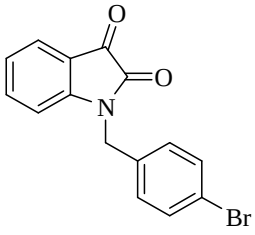
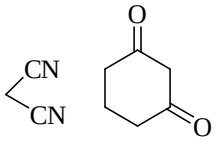
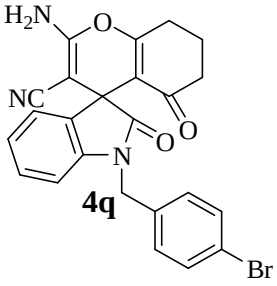
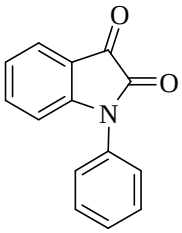
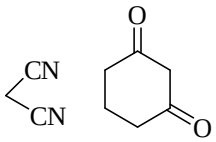
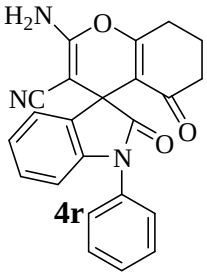
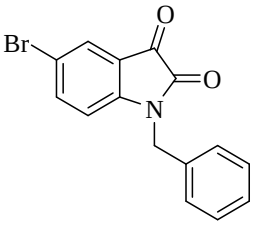
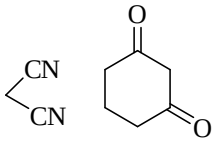
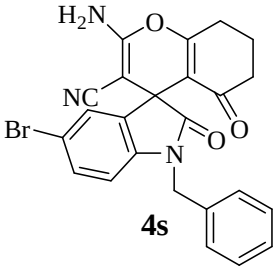


Table S1: Synthesis of spiro[4*H*-pyran-3,3′-oxindoles] compounds **4a-s** through a three-component reaction

Entry	1	2	3	Product (4)	Yield[a] (%)	Melting Point (°C)	References
1				 **4a**	84	288-292	1a
2				 **4b**	88	296-298	1b
3				 **4c**	80	>300	1a
4				 **4d**	81	296-298	1d

5			 **4e**	89	>300	1c
6			 **4f**	85	292-294	1c
7			 **4g**	82	298-300	1d
8			 **4h**	90	258-260	1a
9			 **4i**	92	232-236	—
10			 **4j**	87	270-272	1a

11			 **4k**	88	280-282	1e
12			 **4l**	91	244-246	—
13			 **4m**	86	184-186	—
14			 **4n**	84	228-230	—
15			 **4o**	92	252-254	—
16			 **4p**	88	274-276	—

17			 **4q**	82	258-260	—
18			 **4r**	89	294-296	—
19			 **4s**	90	282-284	—

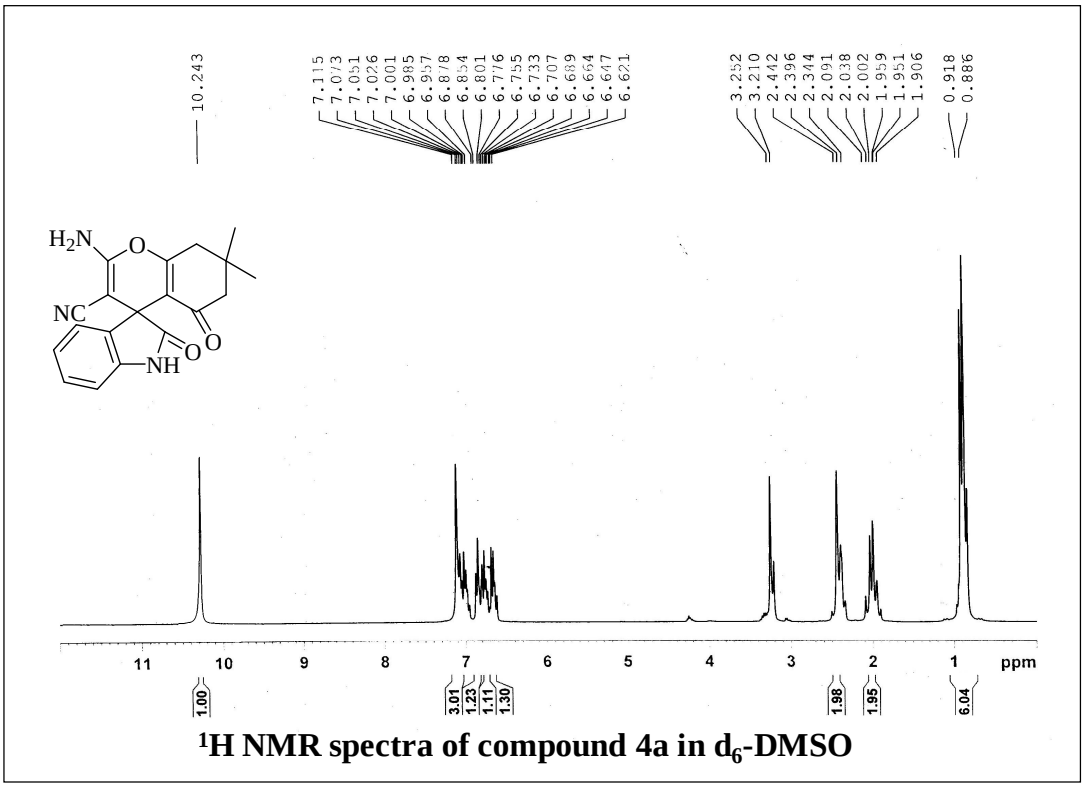
[a]Isolated Yields (%)

References:

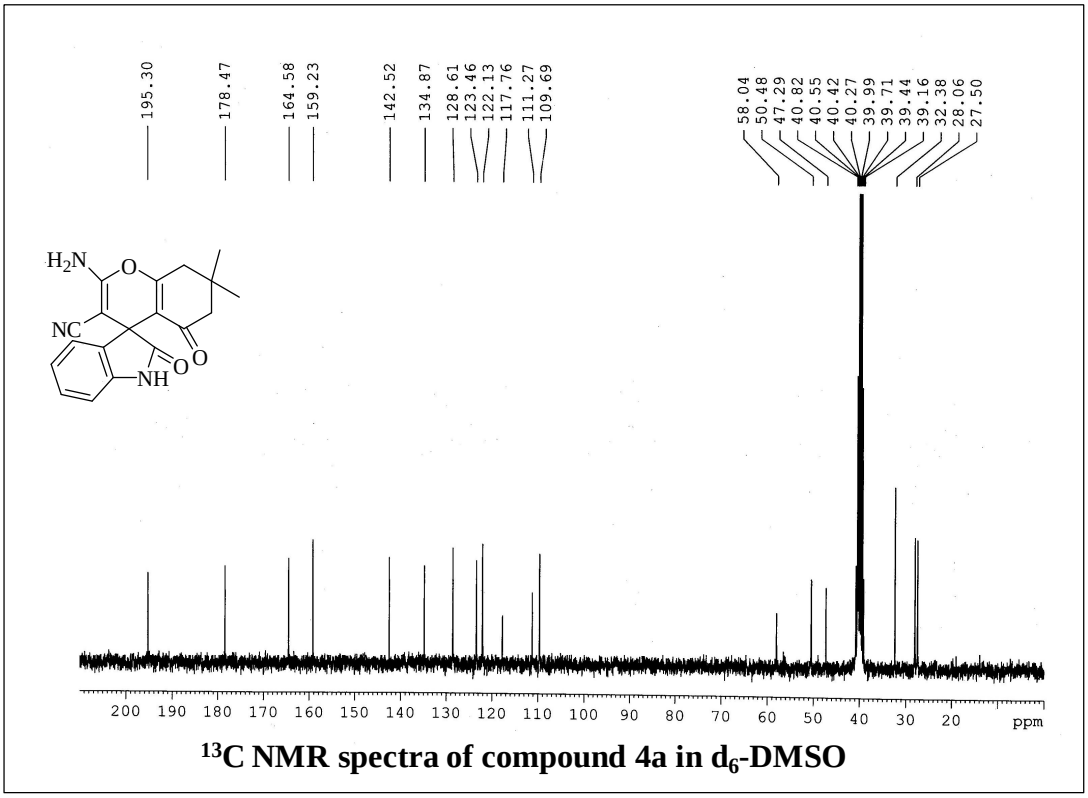
1. (a) A. Mobinikhaledi, N. Foroughifar and M. A. B. Fard, *Synthetic Communications*, 2011, **41**, 441; (b) A. Dandia, V. Parewa, A. K. Jain and K. S. Rathore, *Green Chem.*, 2011, **13**, 2135; (c) S. Riyaz, A. Naidu and P. K. Dubey, *Lett. org. chem.*, 2012, **9**, 101; (d) H. M. Meshram, D. A. Kumar, B. R. V. Prasad and P. R. Goud, *Helvetica Chimica Acta*, 2010, **93**, 648; (e) R. Baharfar and R. Azimi, *Synthetic Communications*, 2014, **44**, 89.

……

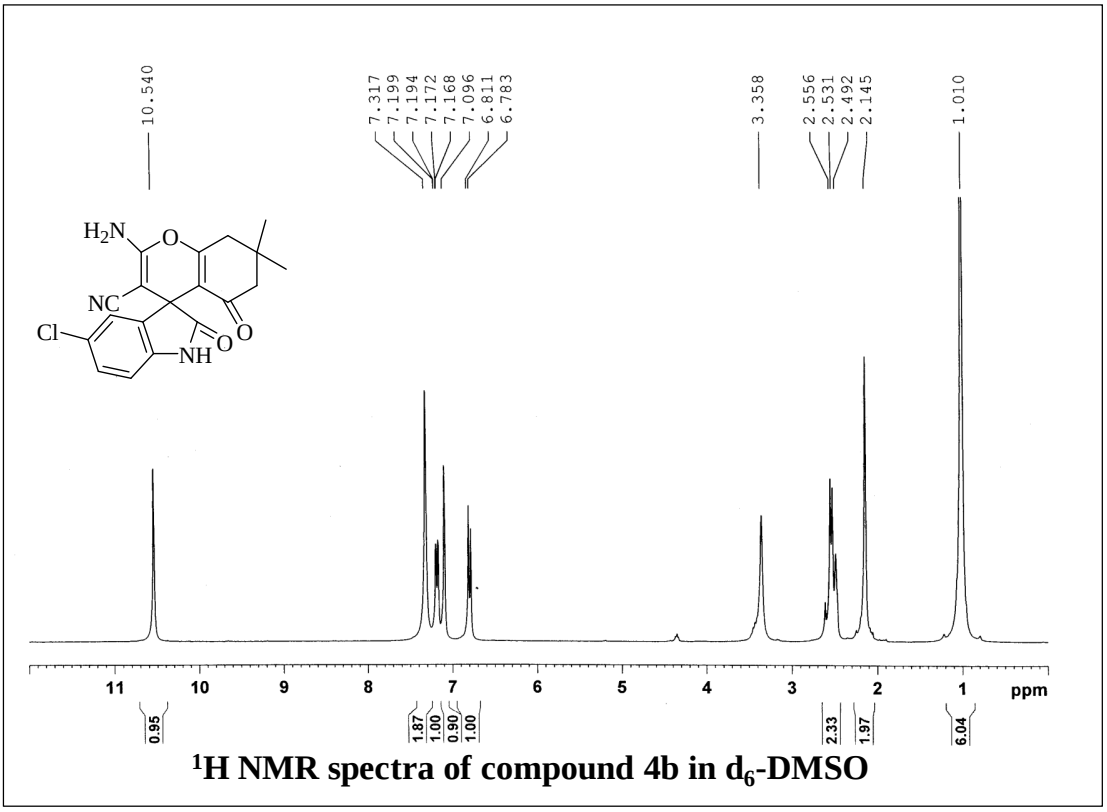
Spectral Data of 4a-s:



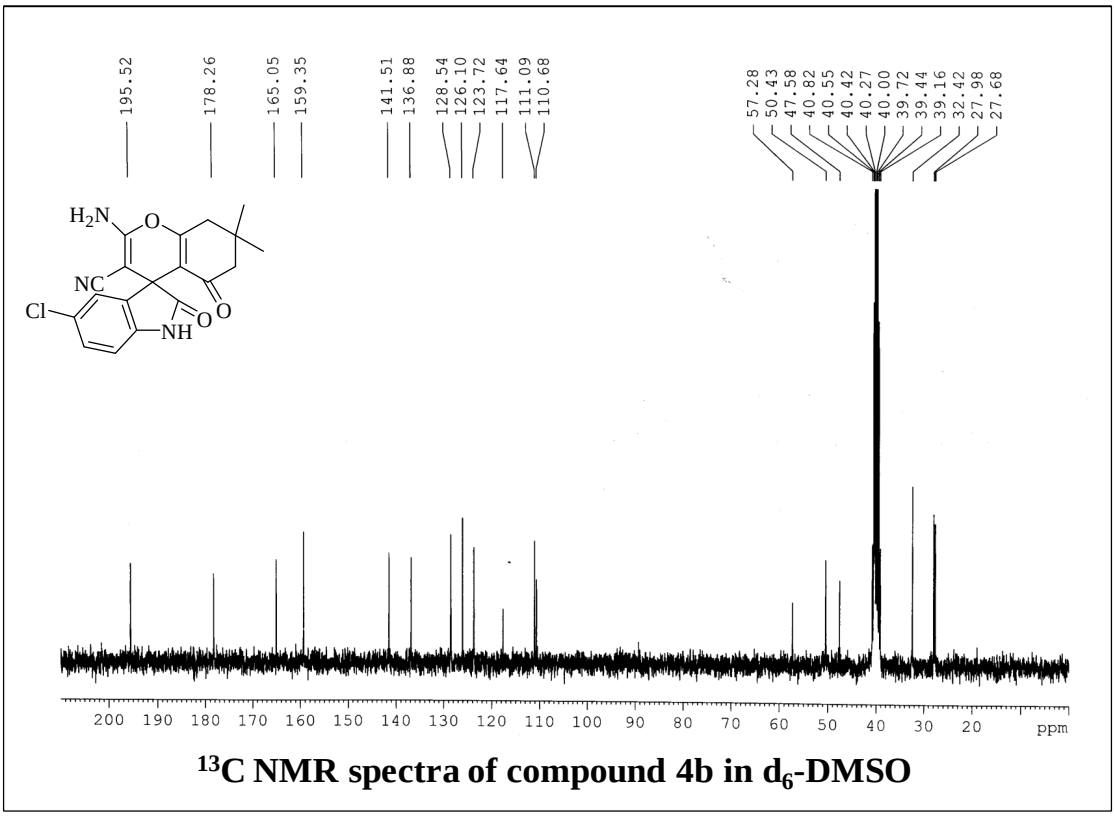
^{1}H NMR spectra of compound 4a in d_6-DMSO



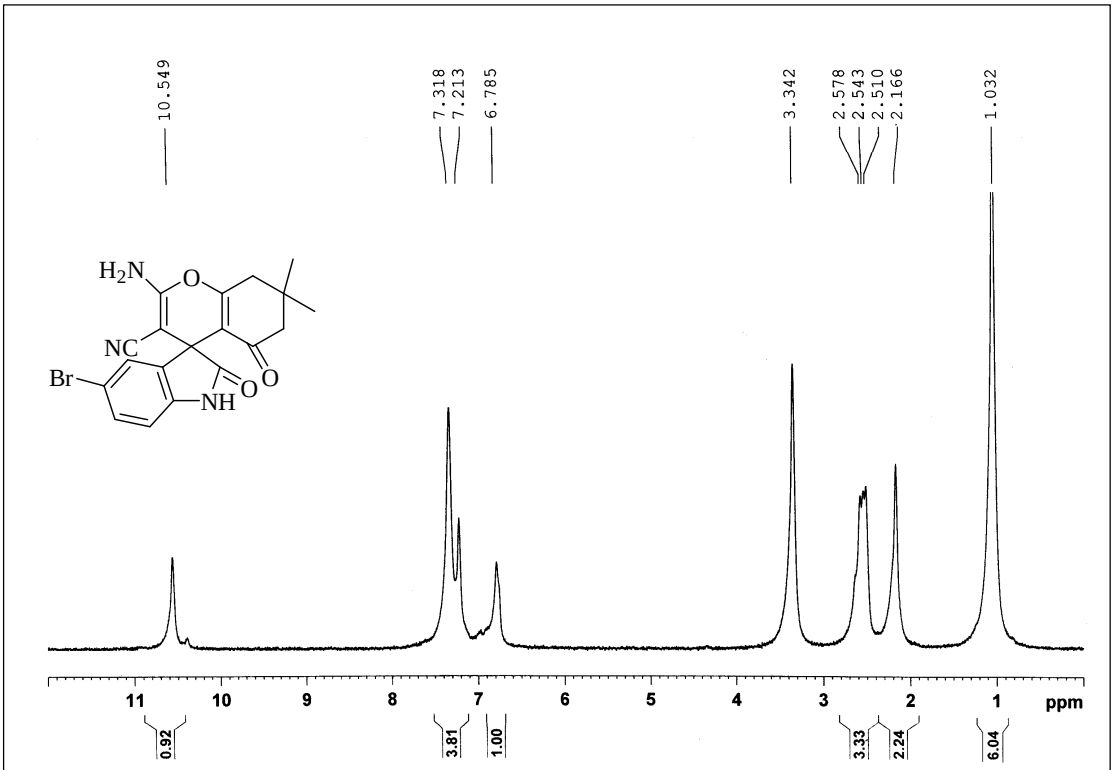
^{13}C NMR spectra of compound 4a in d_6-DMSO



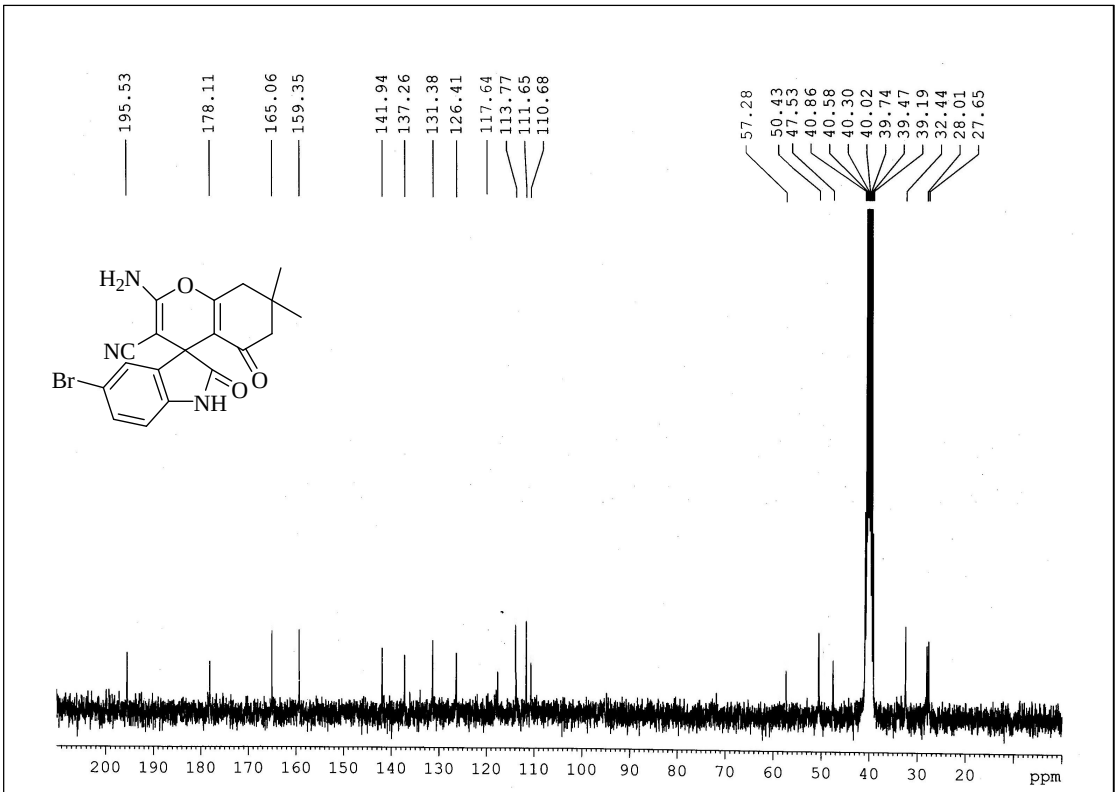
^{1}H NMR spectra of compound 4b in d_6-DMSO



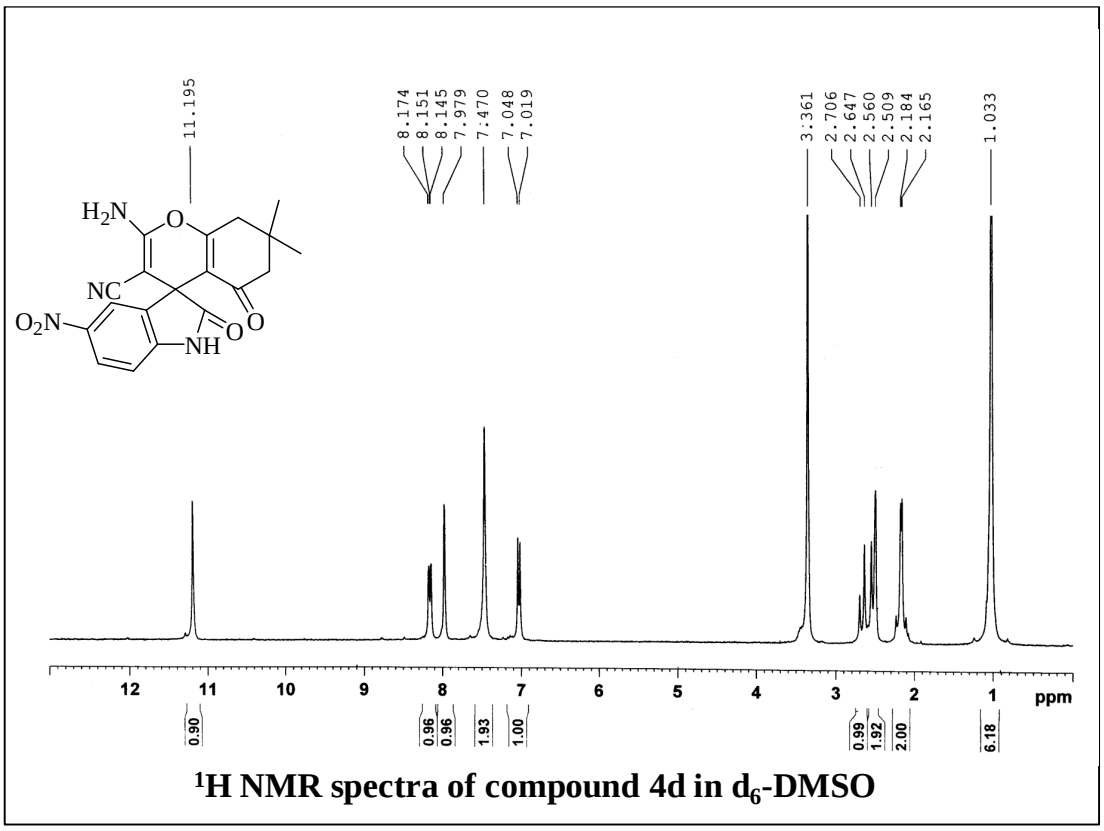
^{13}C NMR spectra of compound 4b in d_6-DMSO



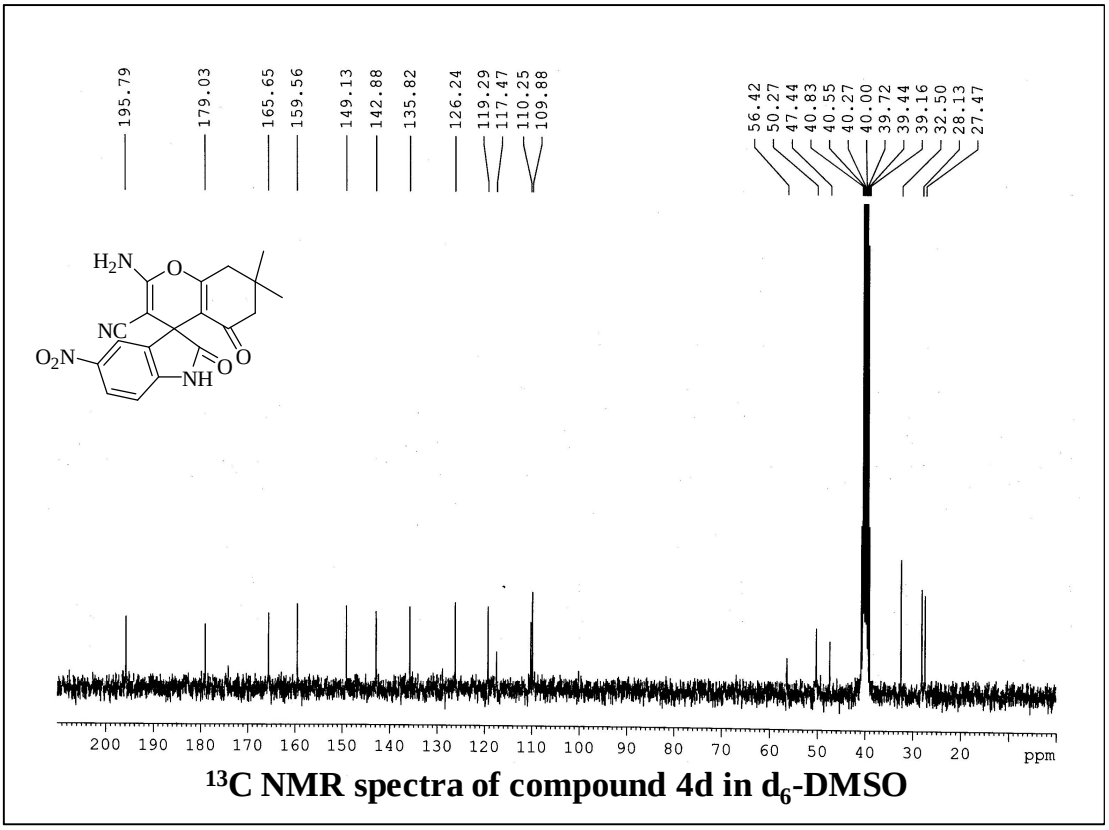
^{1}H NMR spectra of compound 4c in d_6-DMSO



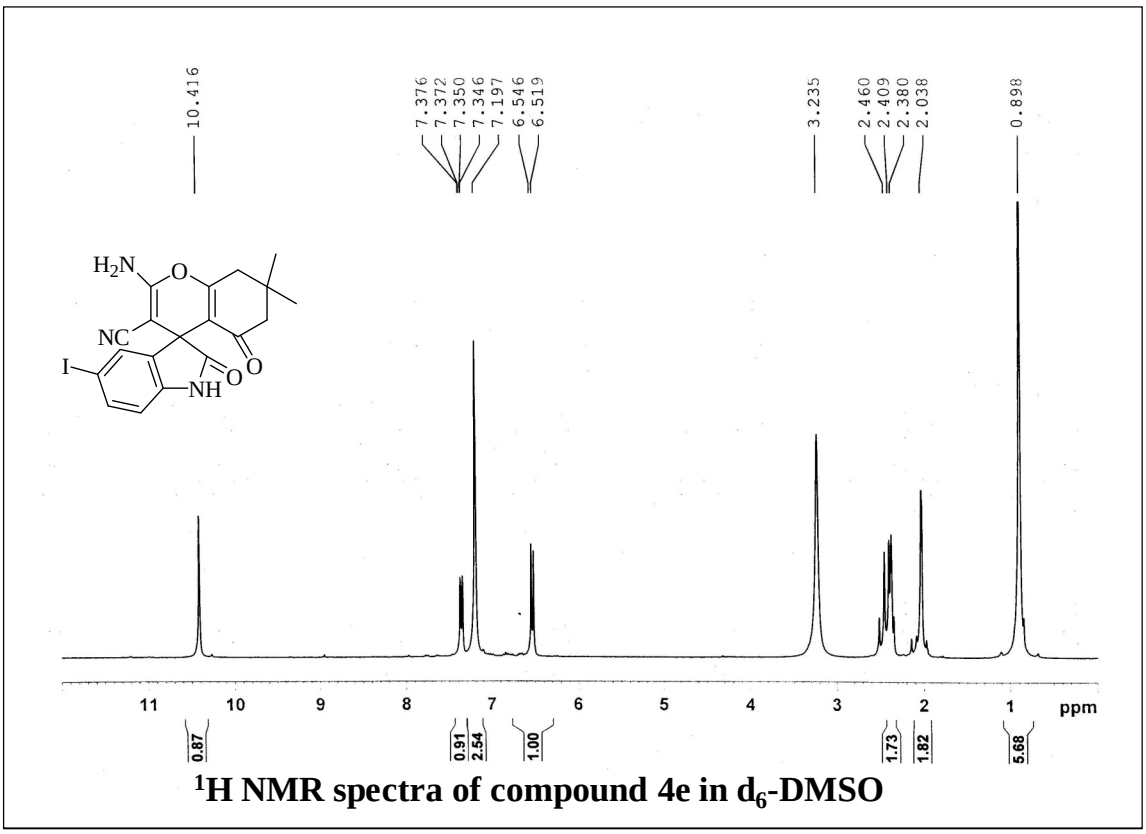
^{13}C NMR spectra of compound 4c in d_6-DMSO



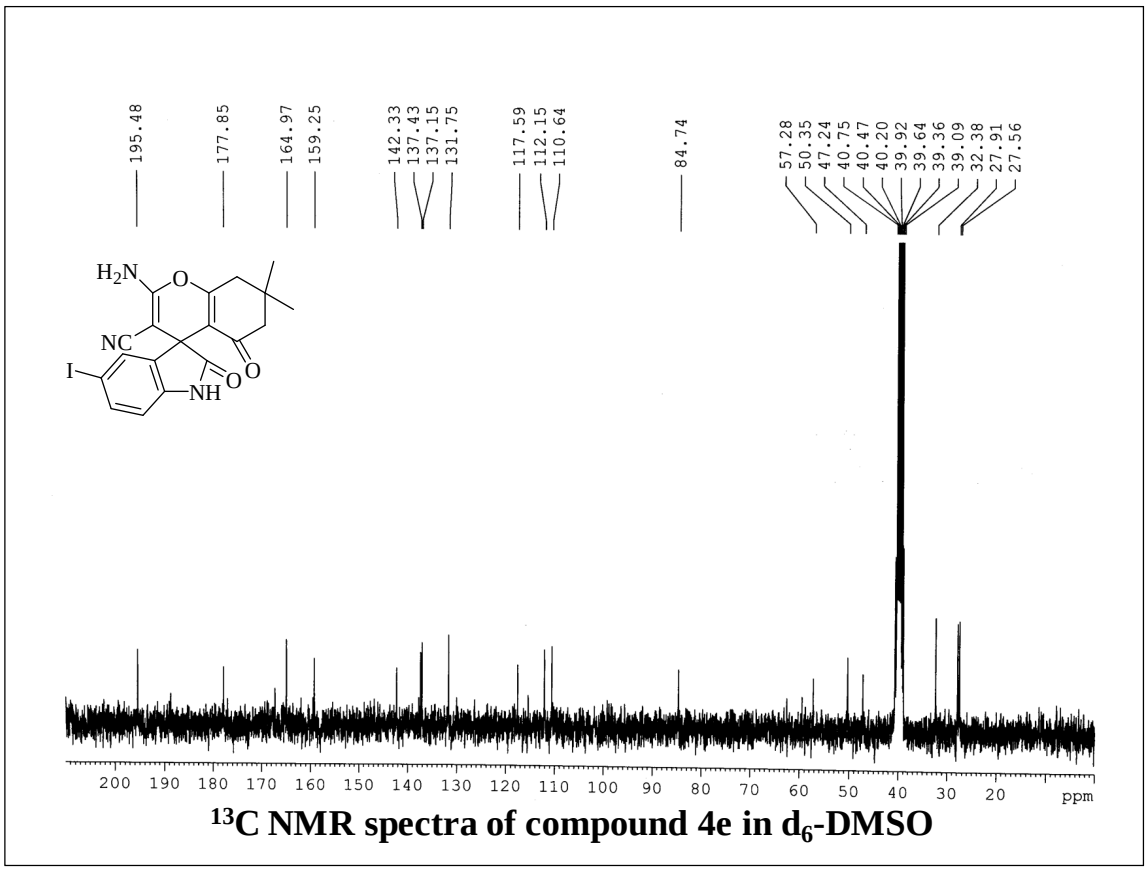
^{1}H NMR spectra of compound 4d in d_6-DMSO



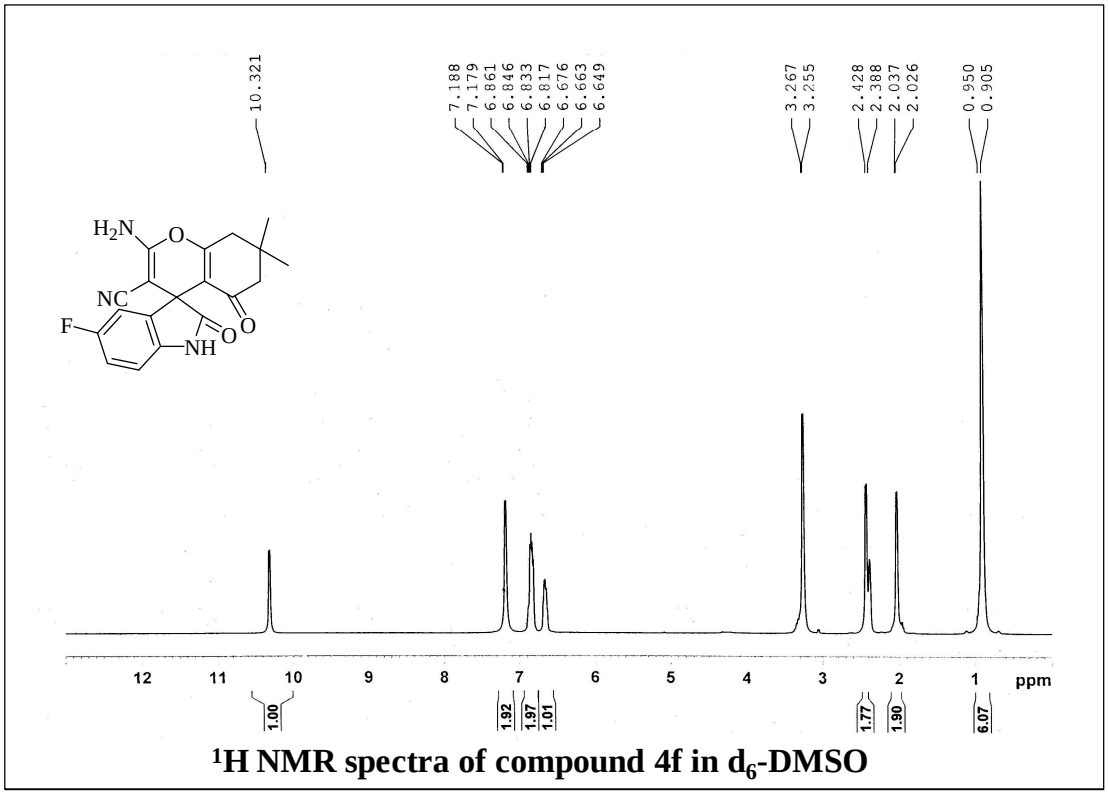
^{13}C NMR spectra of compound 4d in d_6-DMSO



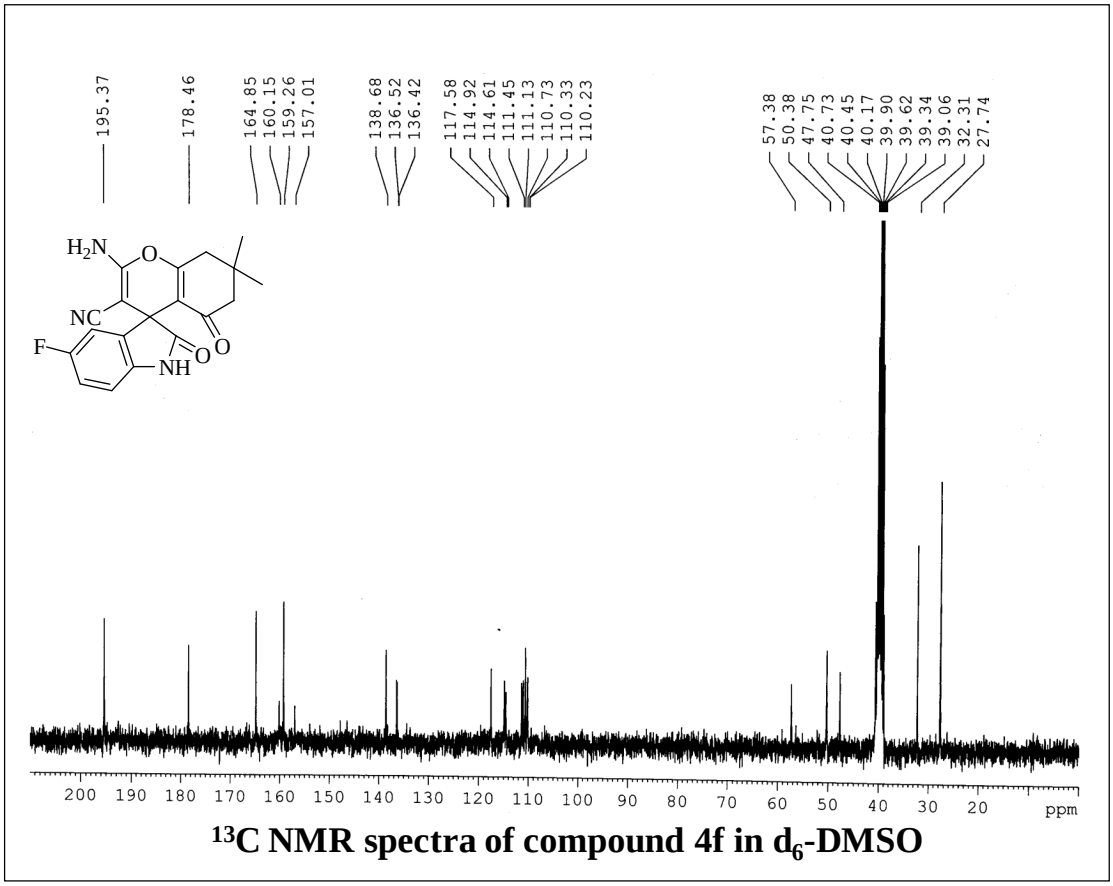
^{1}H NMR spectra of compound 4e in d_6-DMSO



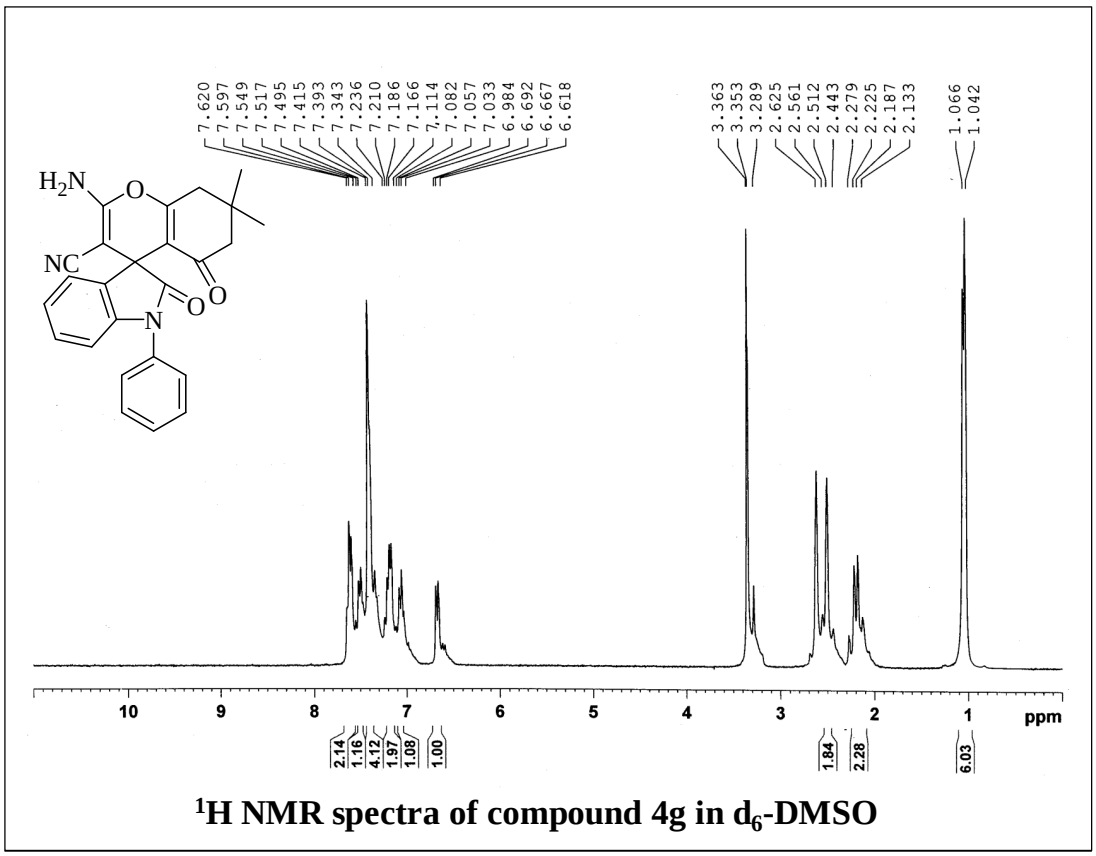
^{13}C NMR spectra of compound 4e in d_6-DMSO



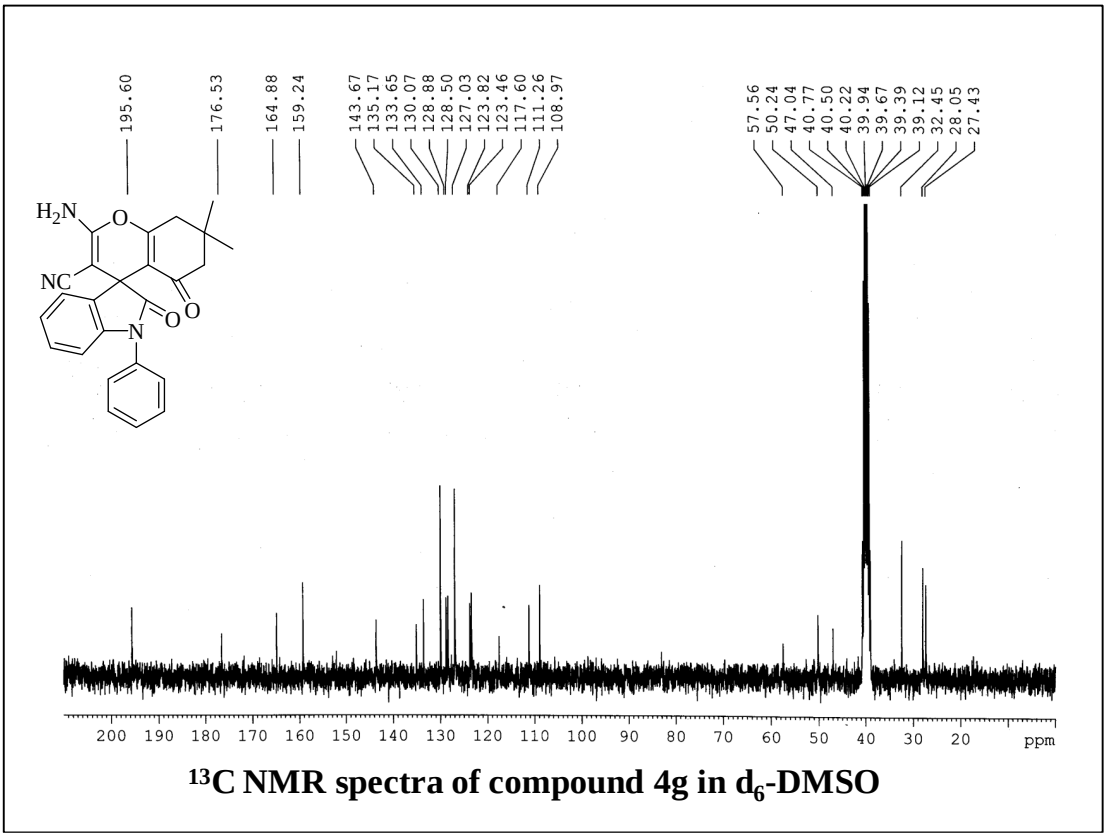
^{1}H NMR spectra of compound 4f in d_6-DMSO



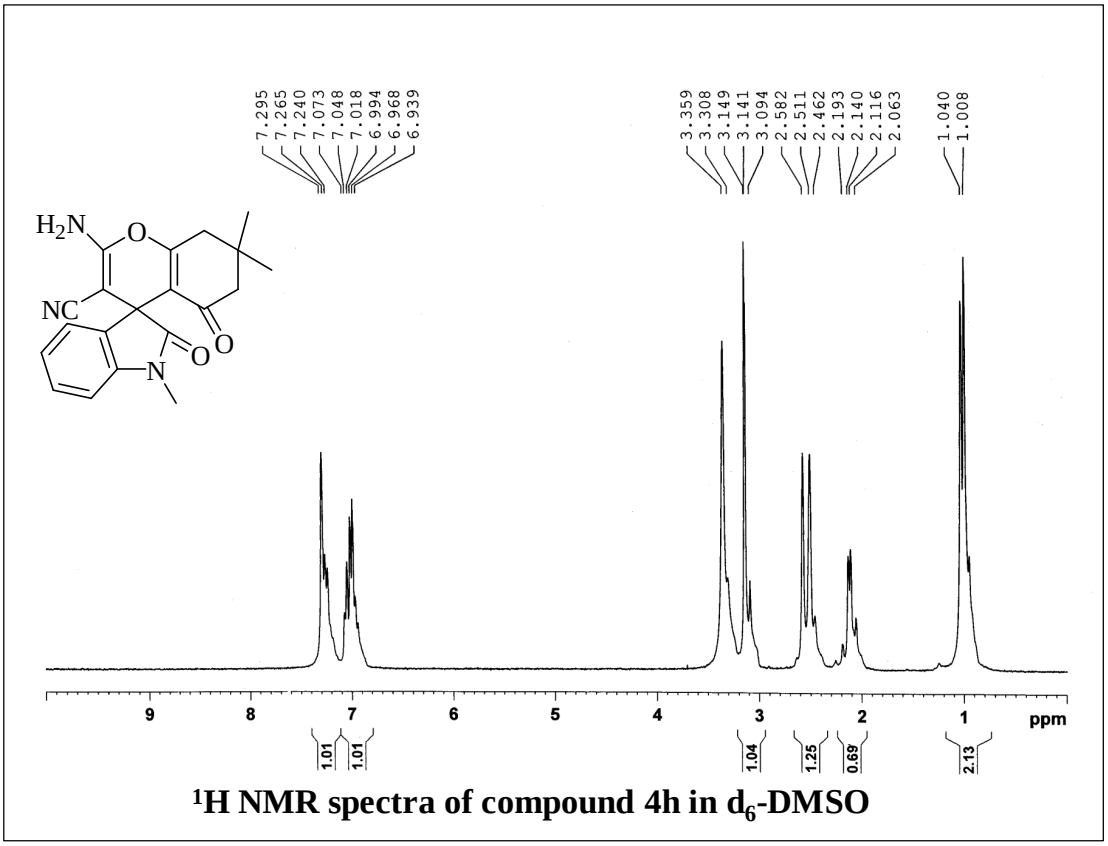
^{13}C NMR spectra of compound 4f in d_6-DMSO



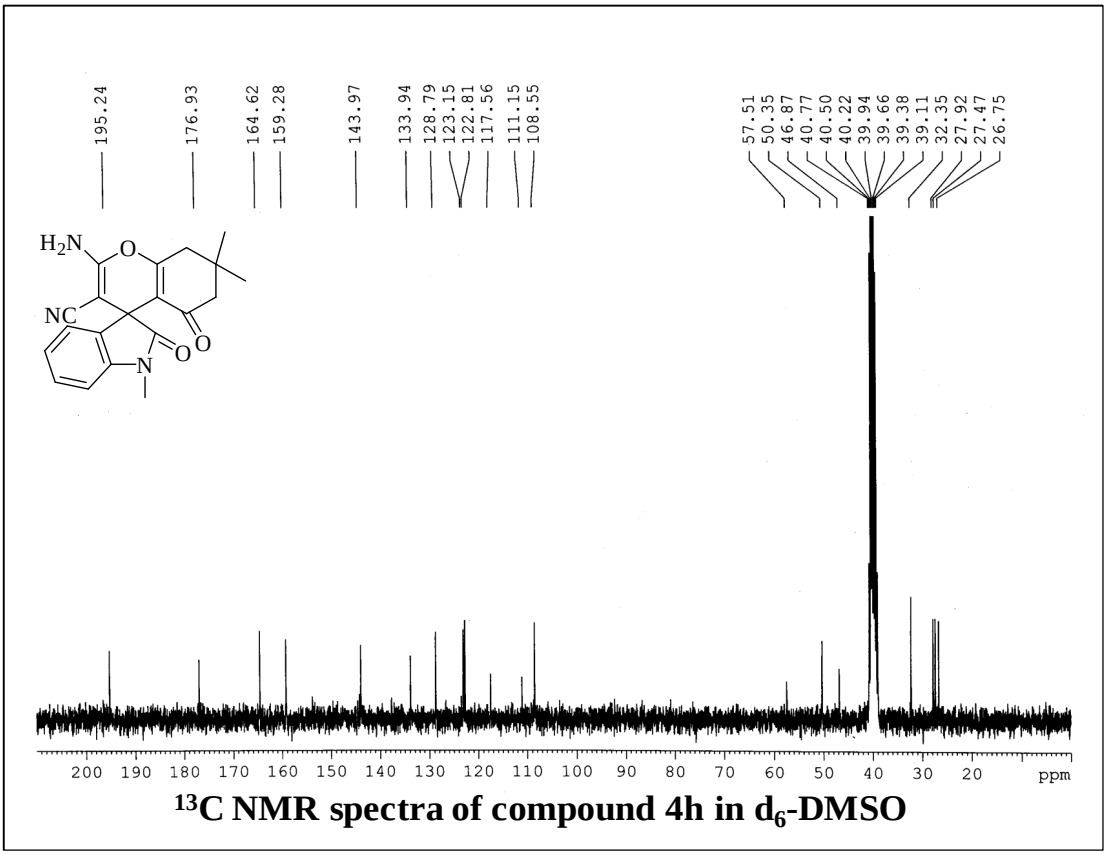
^{1}H NMR spectra of compound 4g in d_6-DMSO



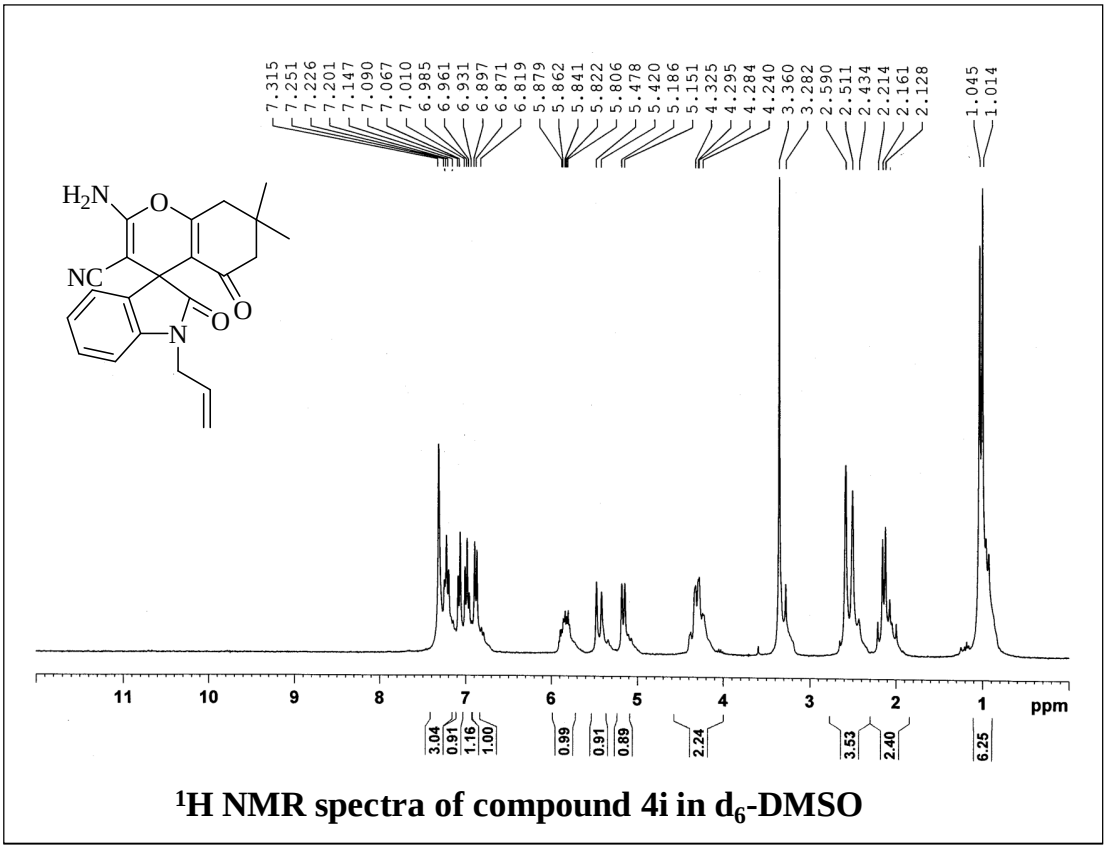
^{13}C NMR spectra of compound 4g in d_6-DMSO



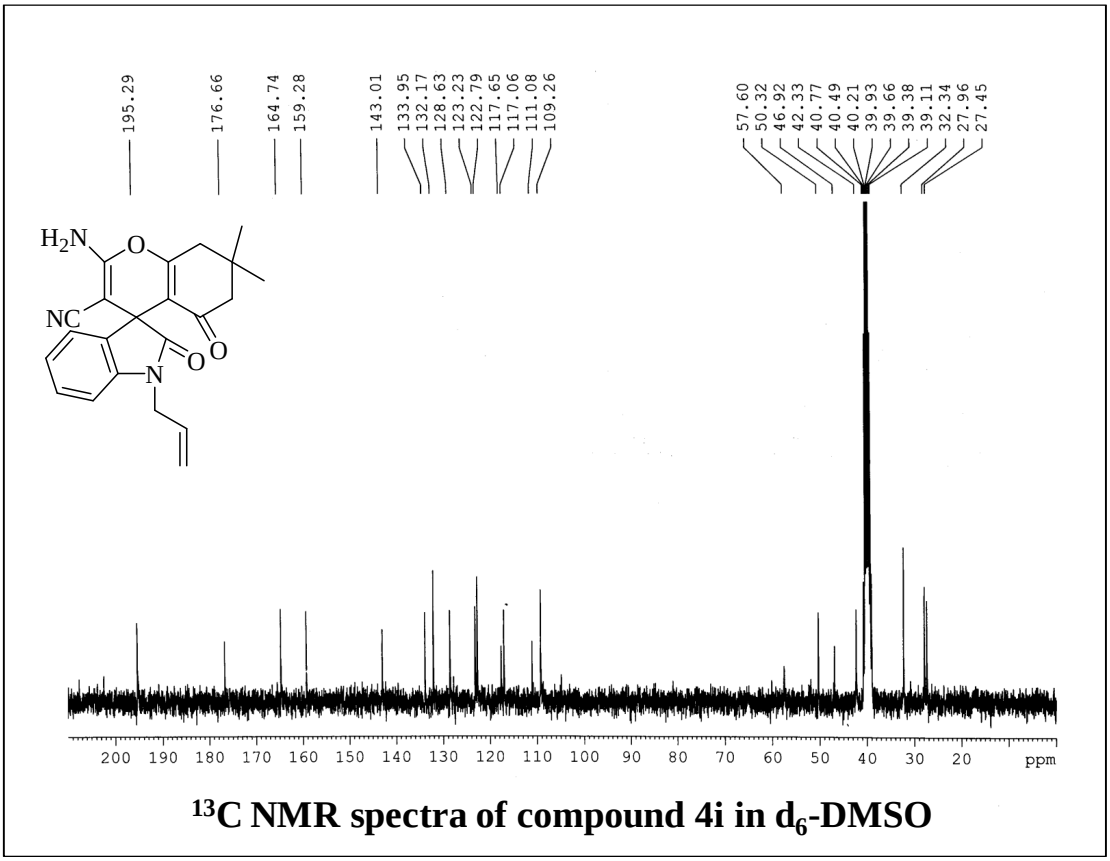
^{1}H NMR spectra of compound 4h in d_6-DMSO



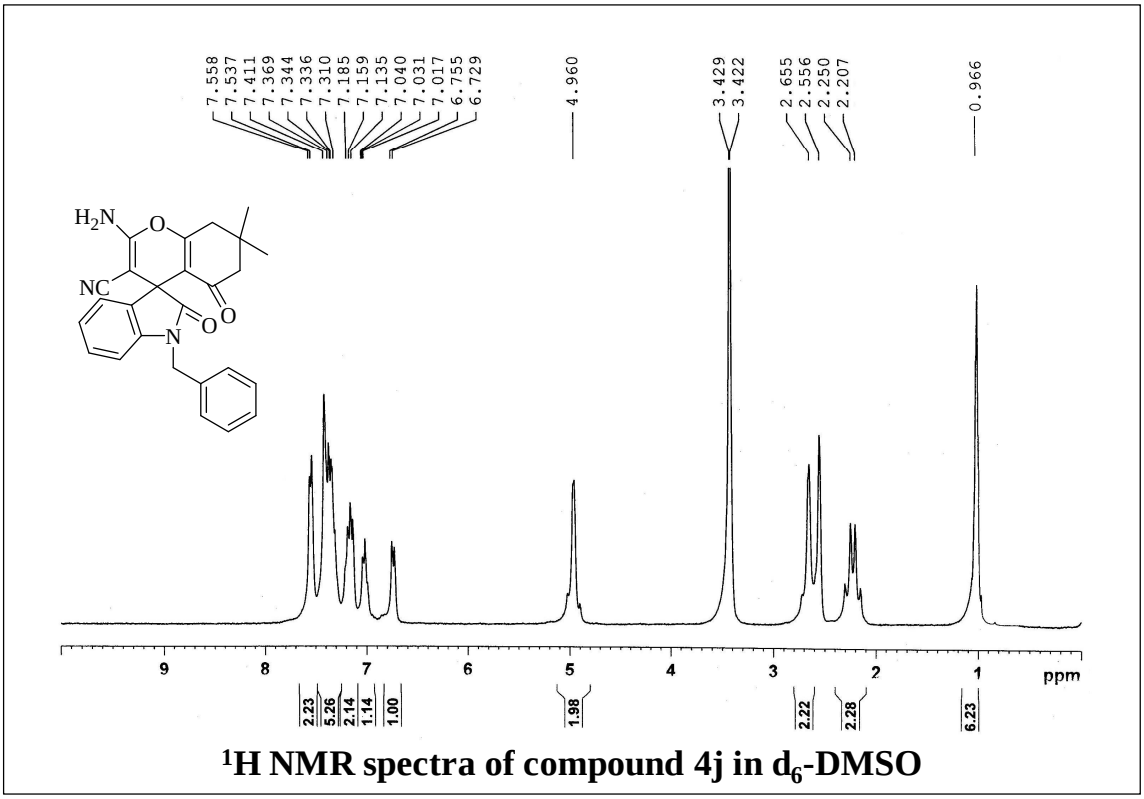
^{13}C NMR spectra of compound 4h in d_6-DMSO



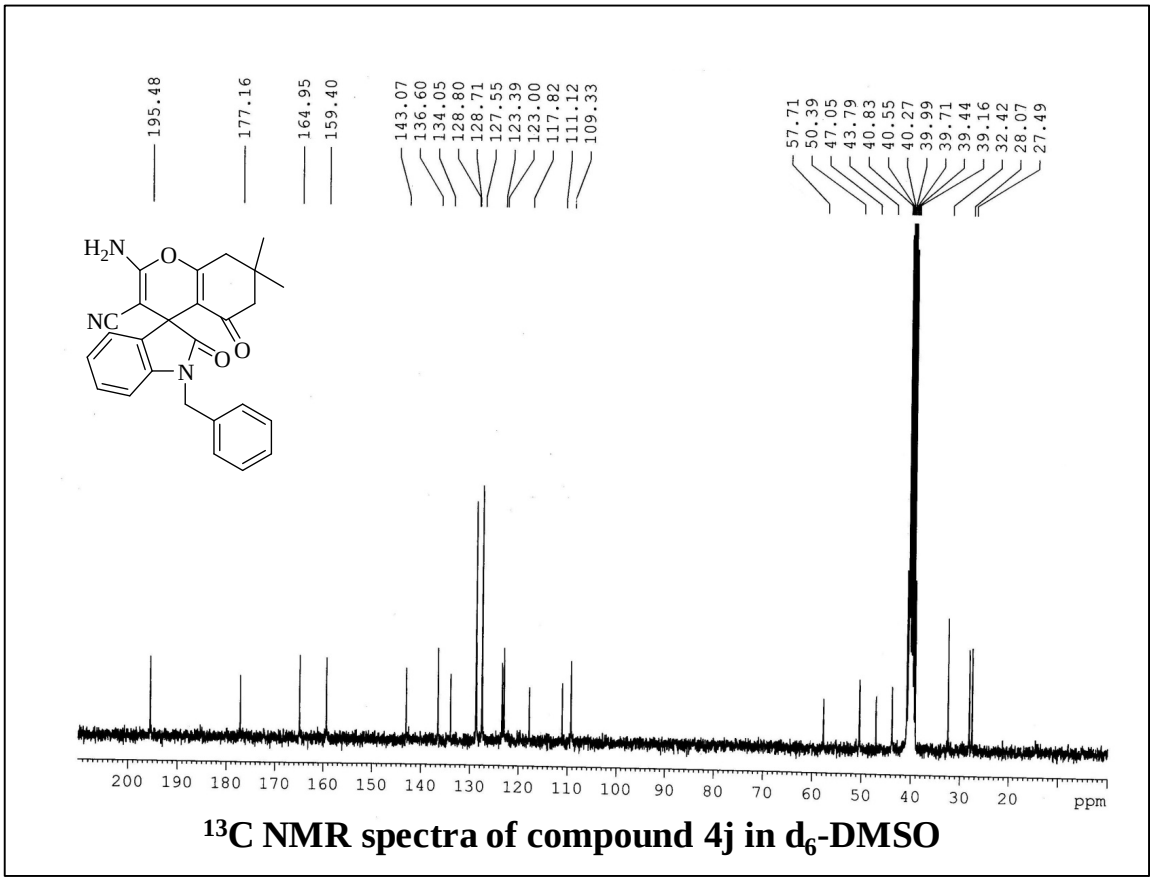
^{1}H NMR spectra of compound 4i in d_6-DMSO



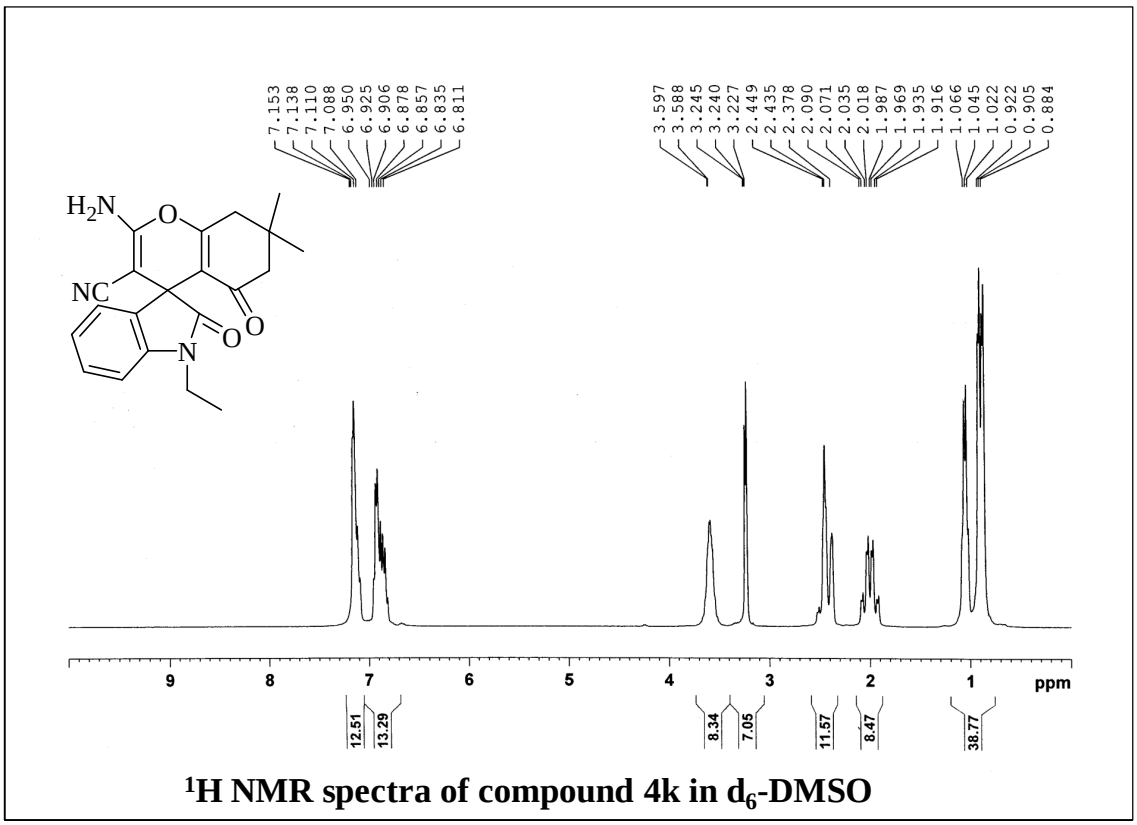
^{13}C NMR spectra of compound 4i in d_6-DMSO



^{1}H NMR spectra of compound 4j in d_6-DMSO



^{13}C NMR spectra of compound 4j in d_6-DMSO



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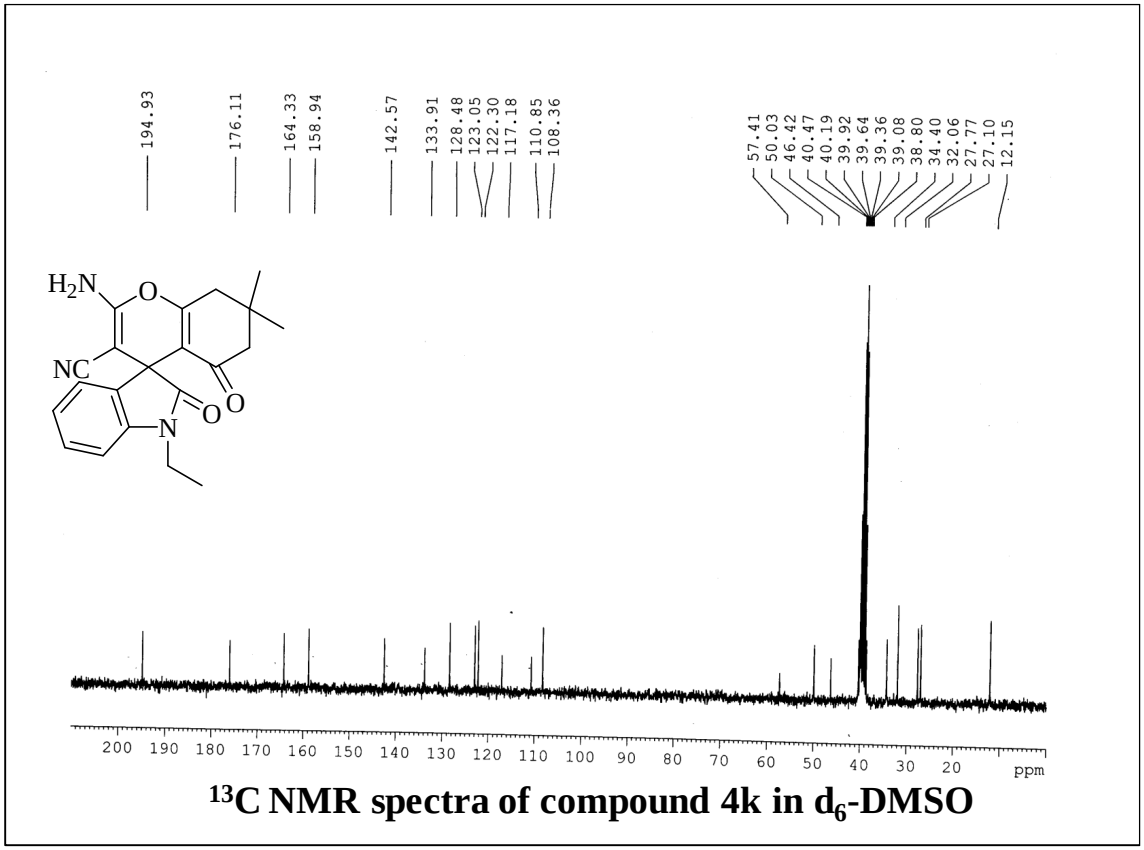

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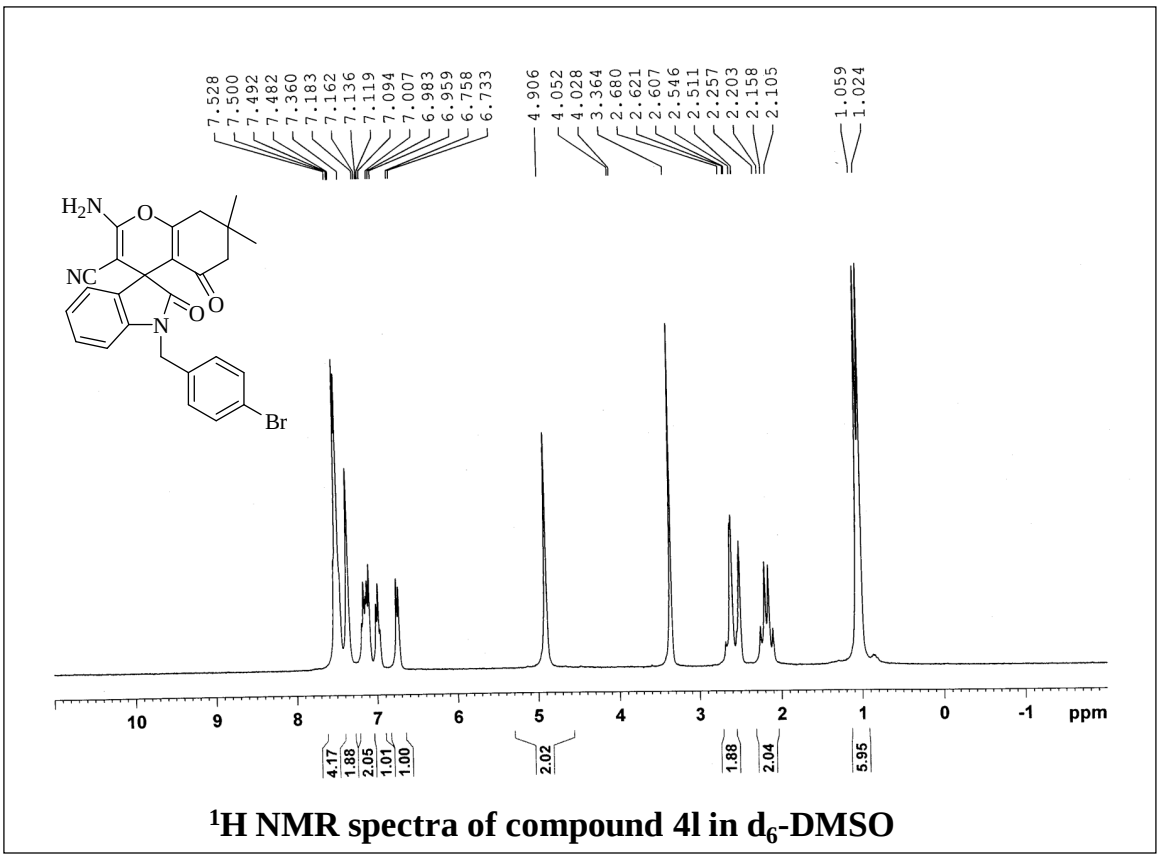

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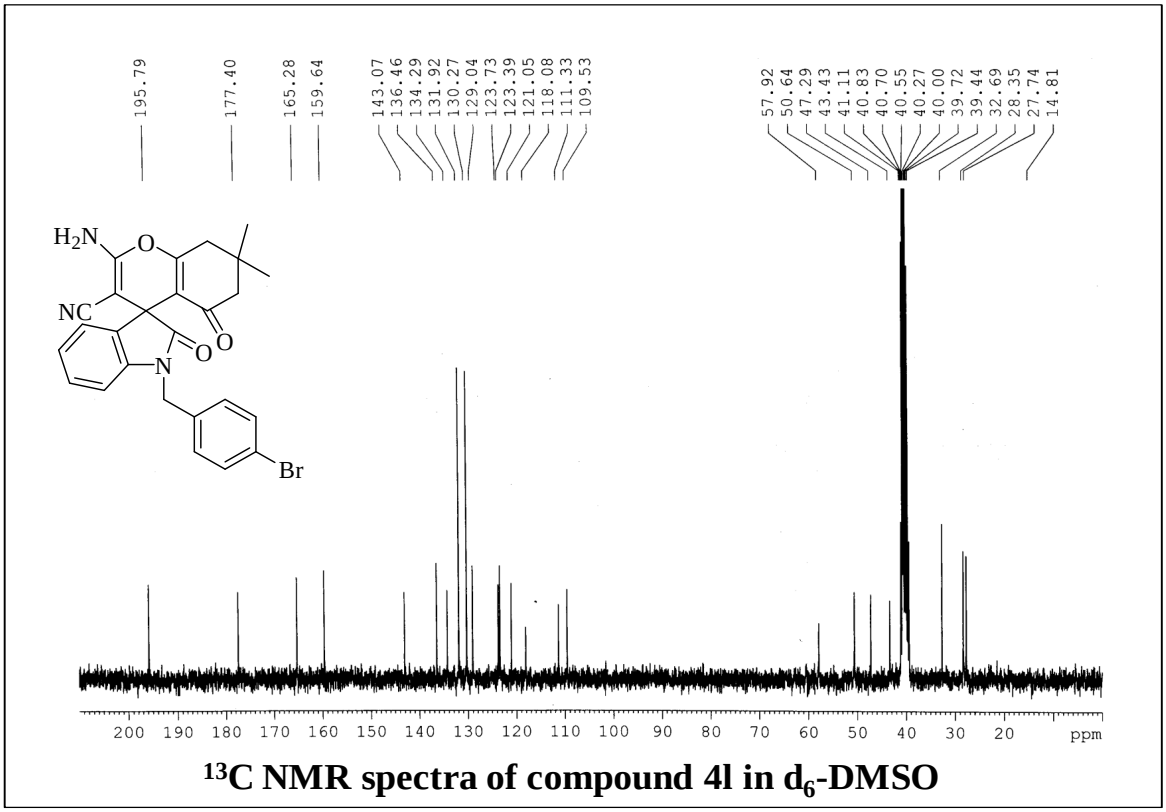

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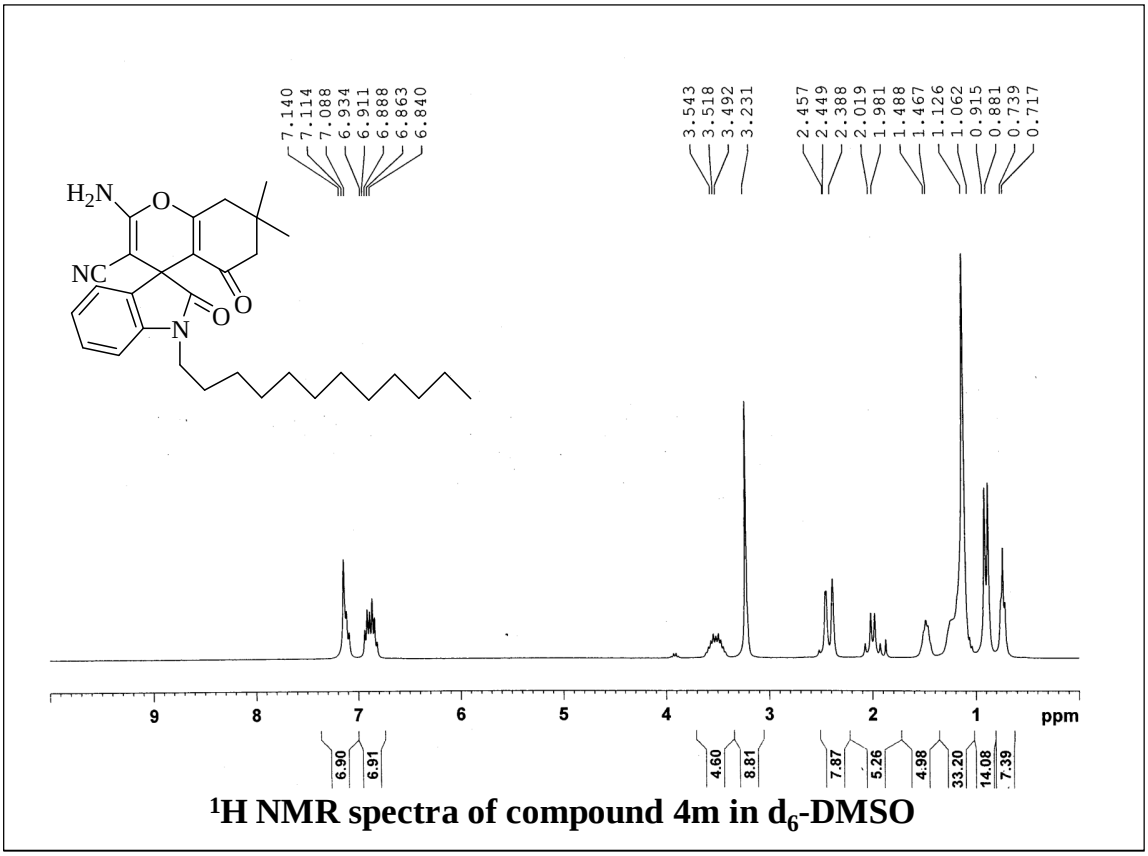
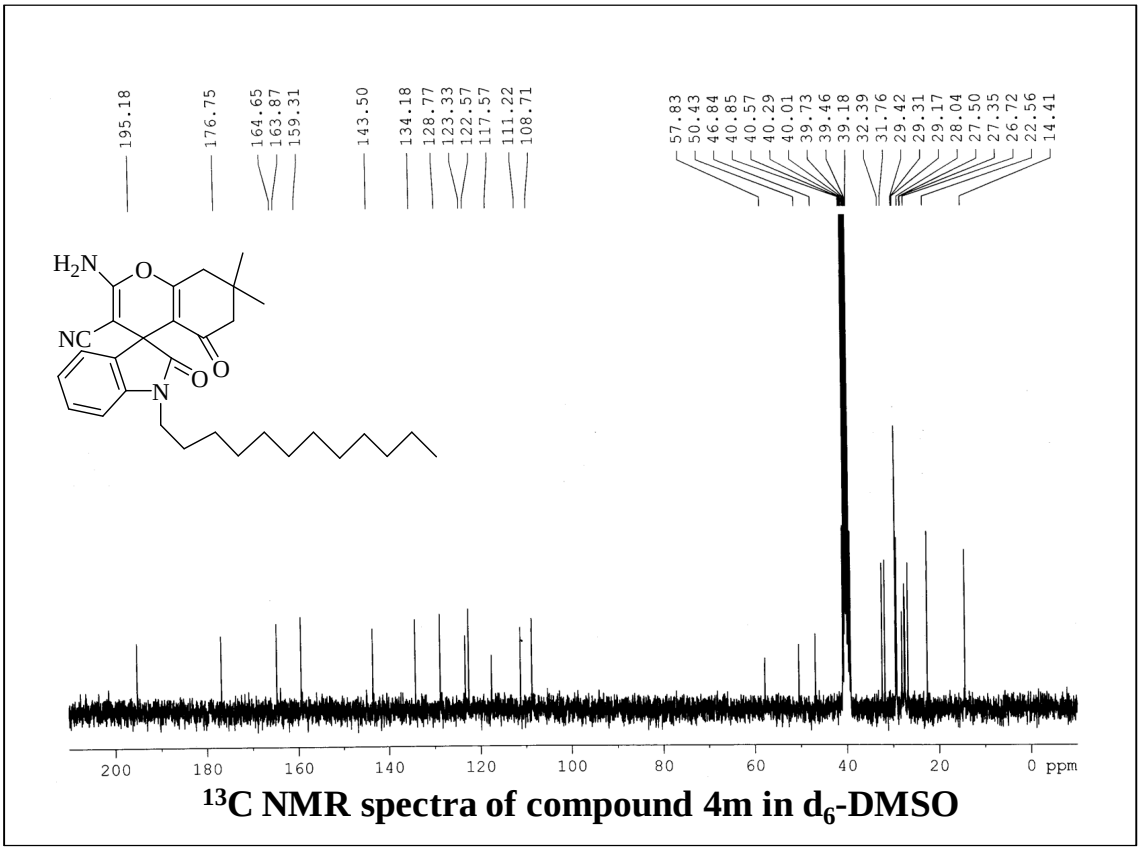
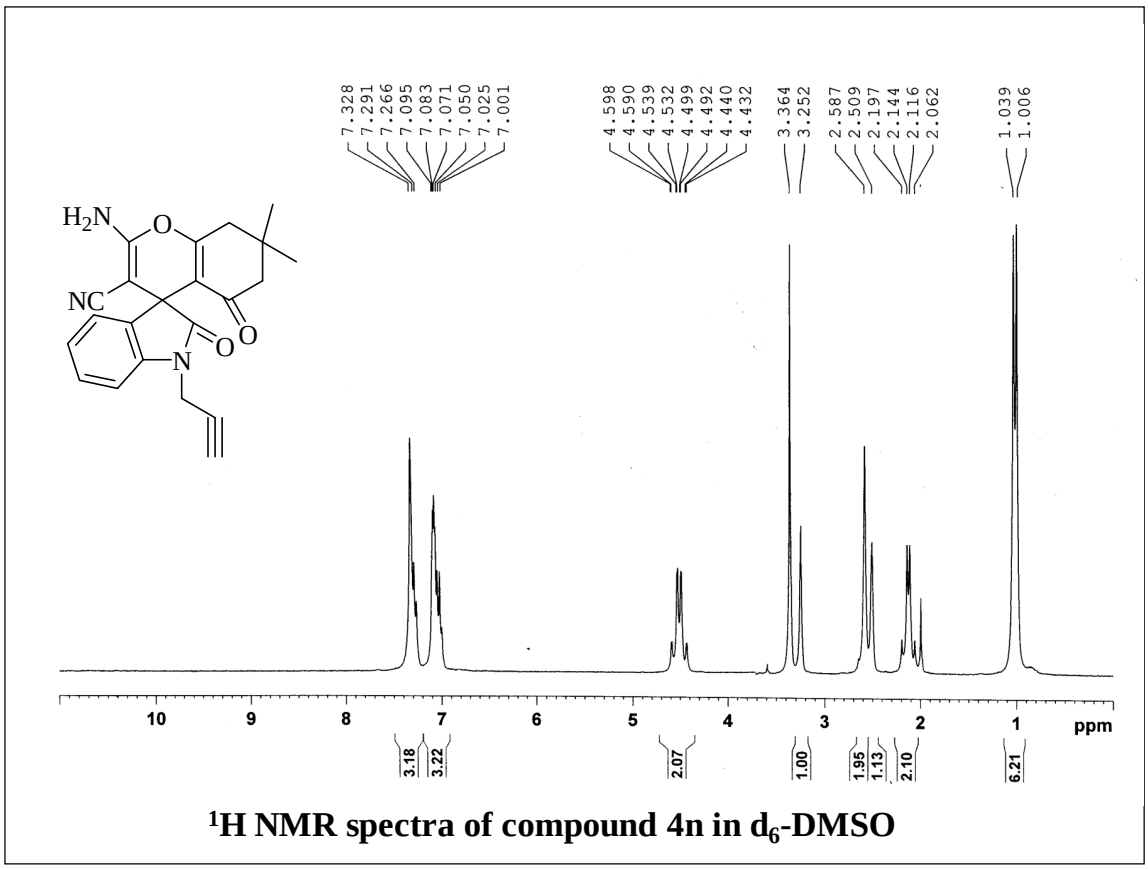


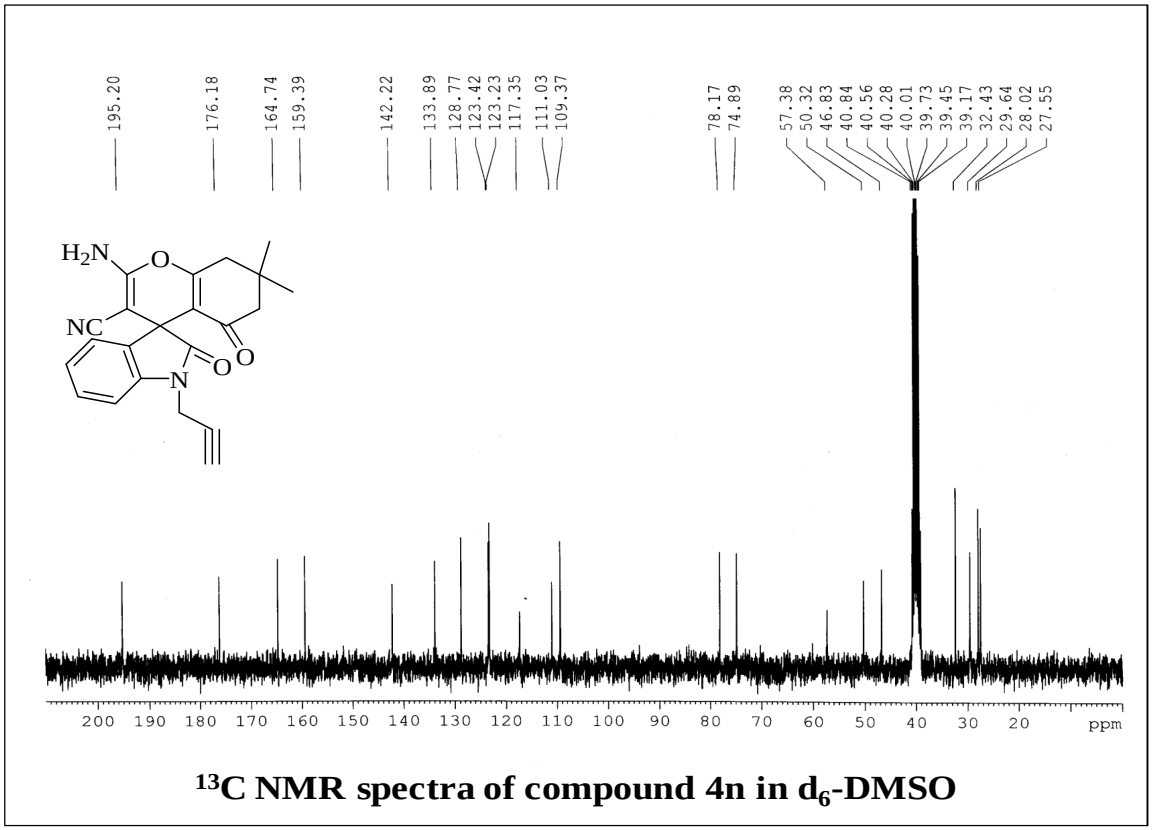
^{1}H NMR spectra of compound 4m in d_6-DMSO



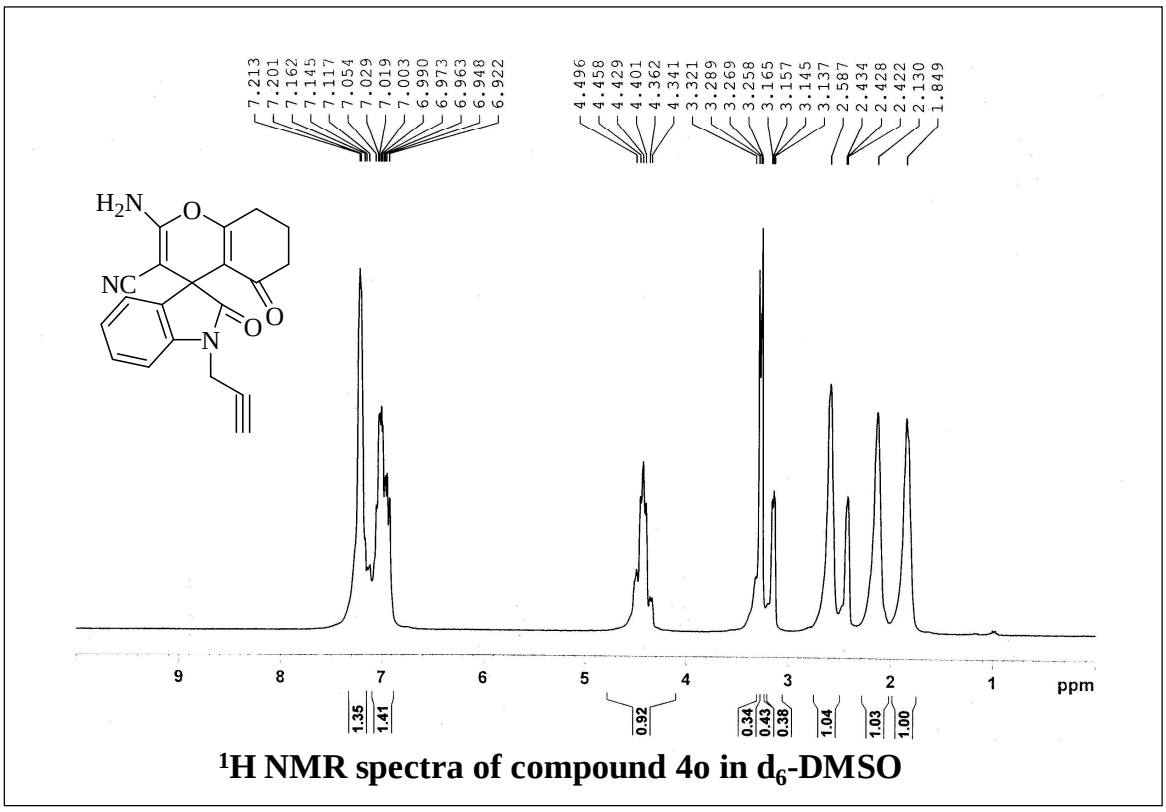
^{13}C NMR spectra of compound 4m in d_6-DMSO



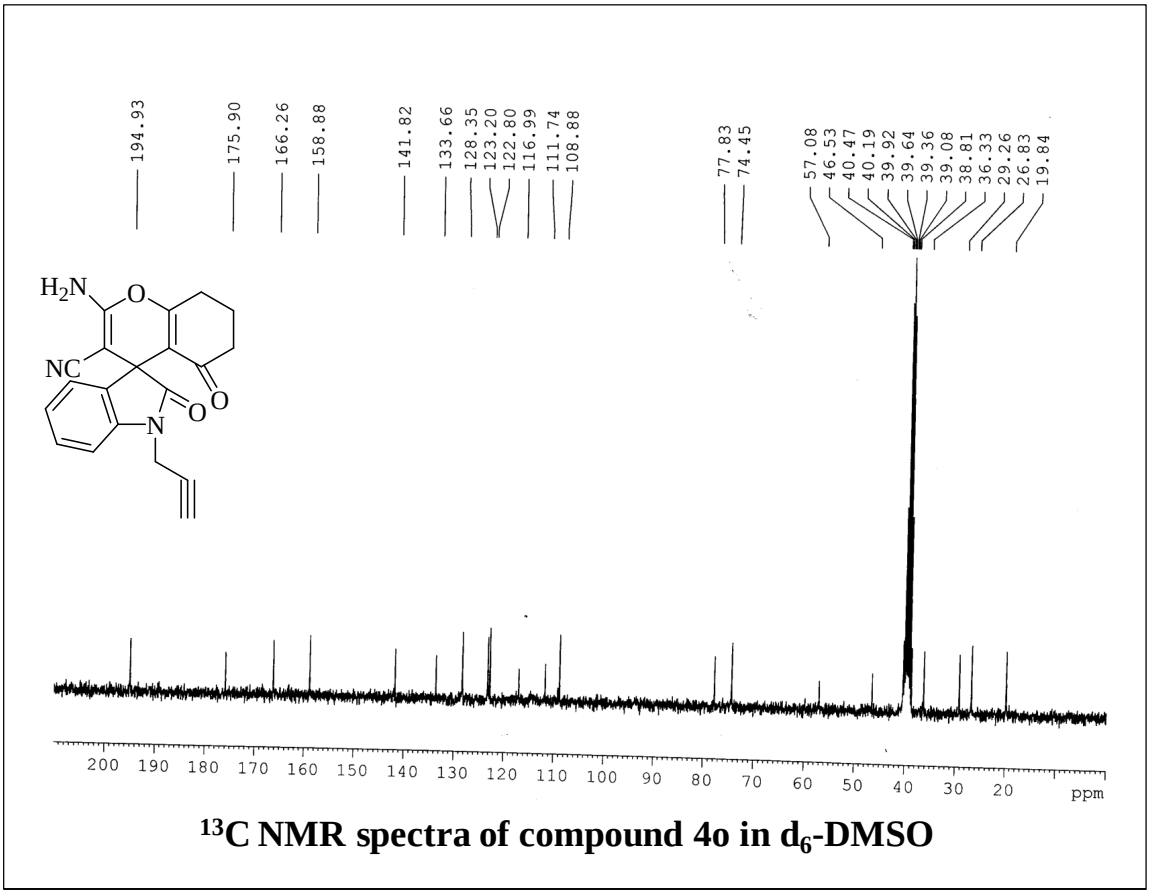
^{1}H NMR spectra of compound 4n in d_6-DMSO



^{13}C NMR spectra of compound 4n in d_6-DMSO



^{1}H NMR spectra of compound 4o in d_6-DMSO



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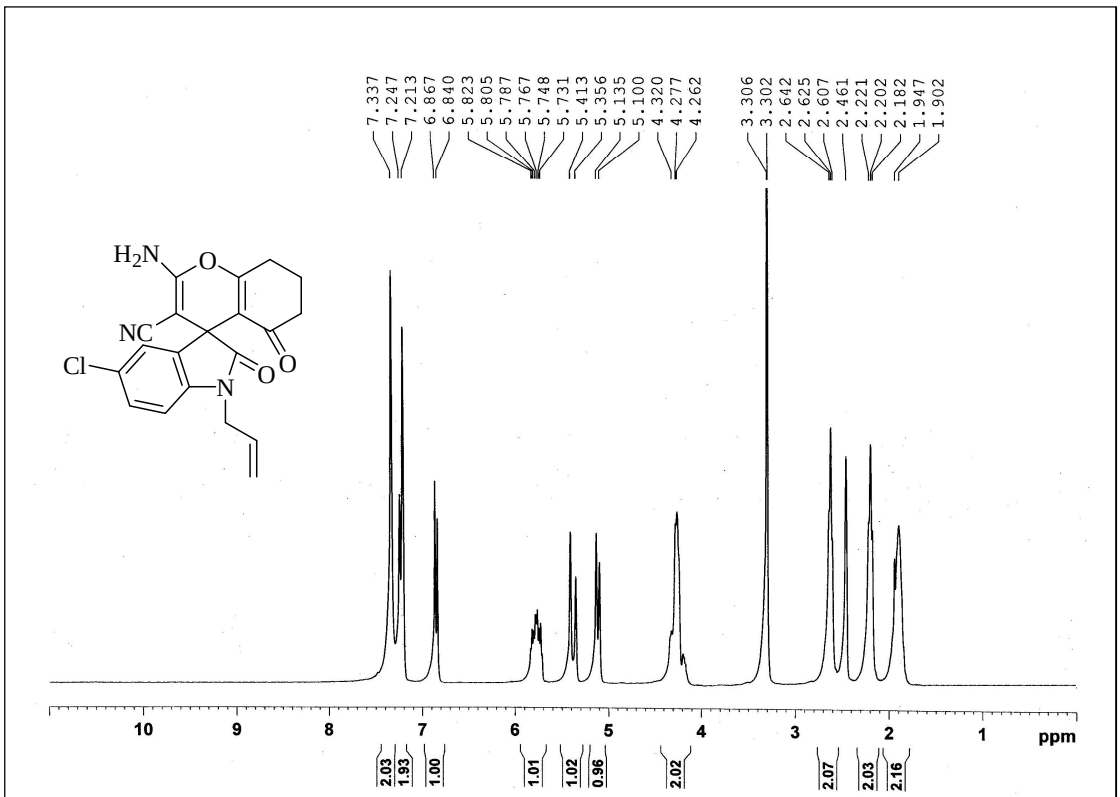
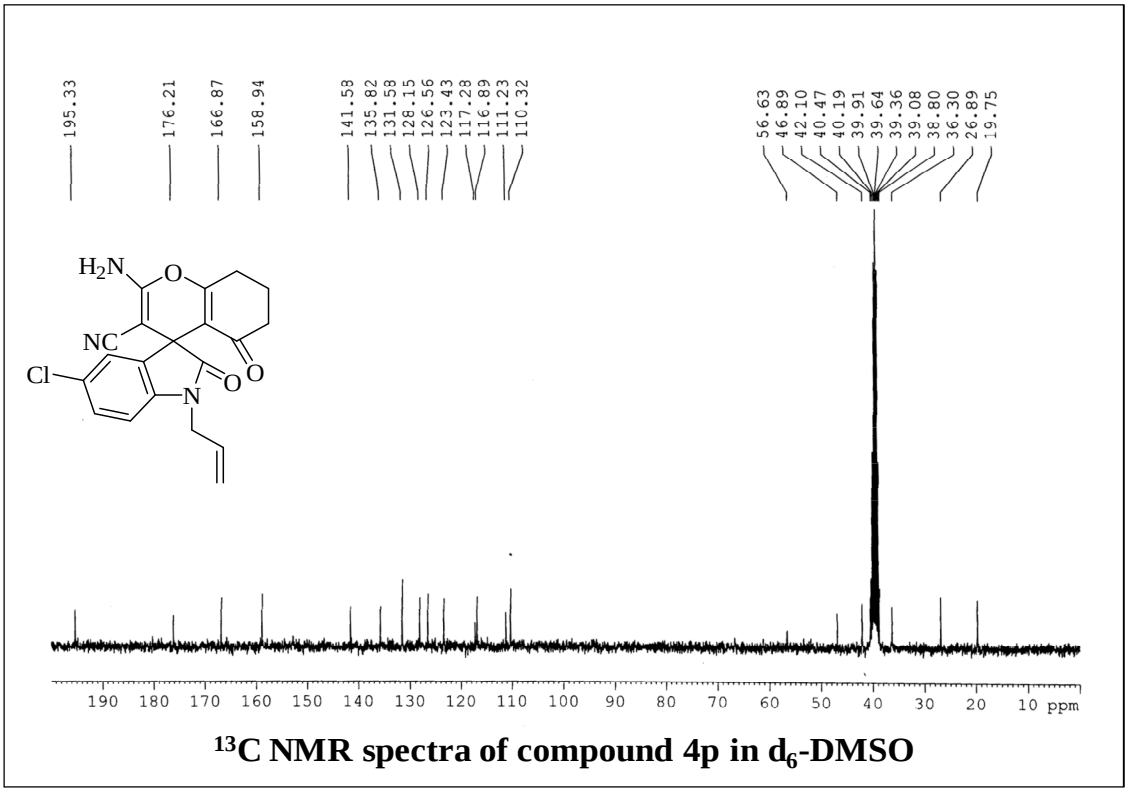
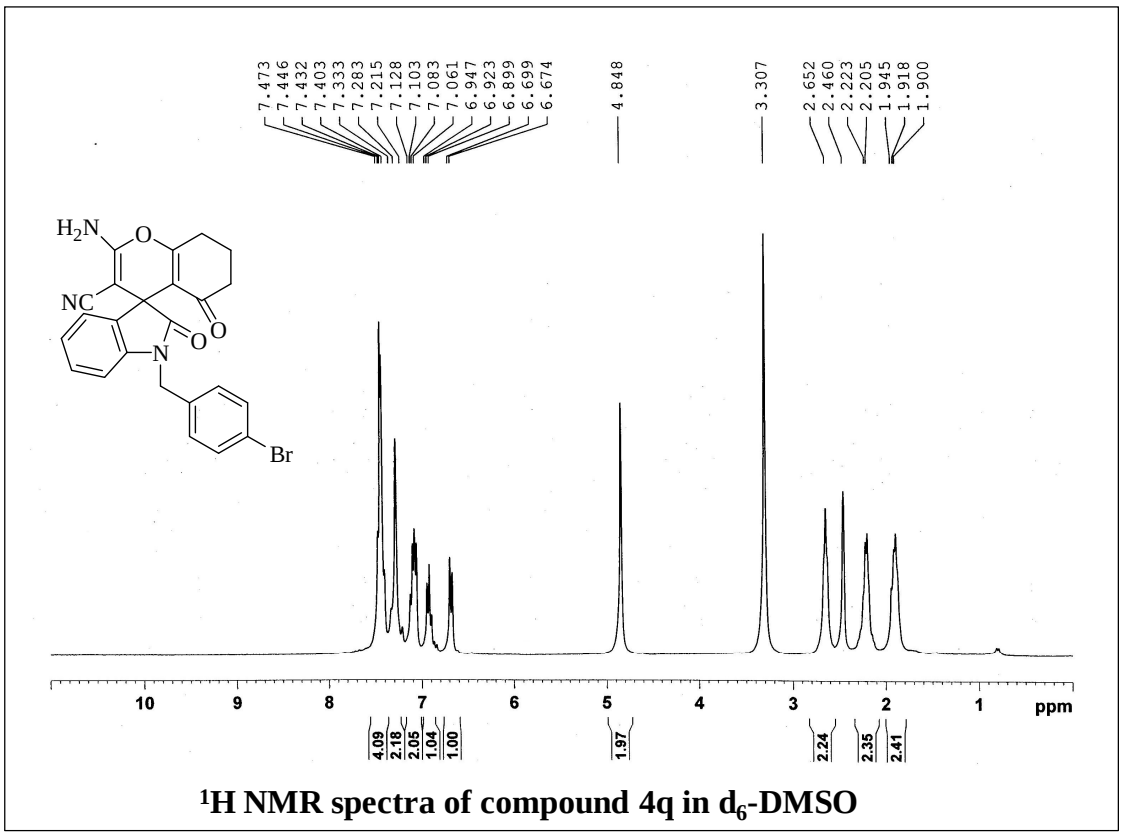


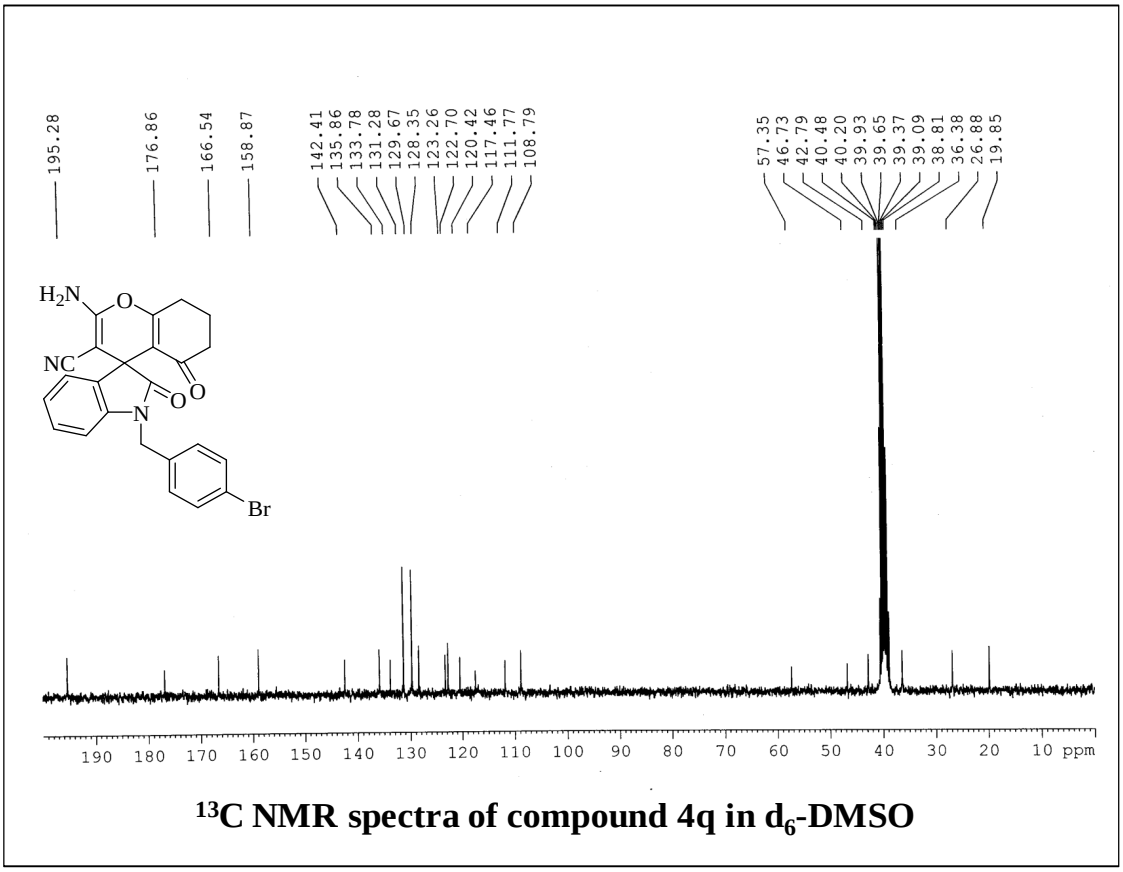
^{1}H NMR spectra of compound 4p in d_6-DMSO



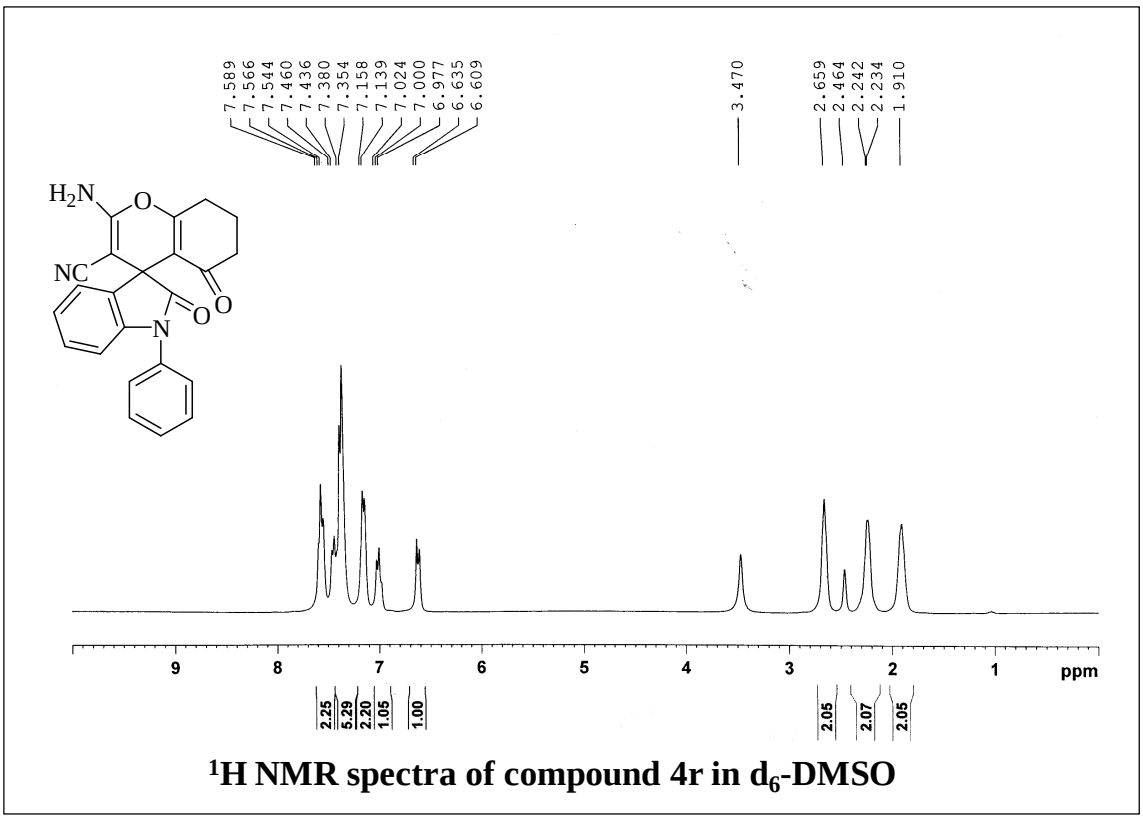
^{13}C NMR spectra of compound 4p in d_6-DMSO



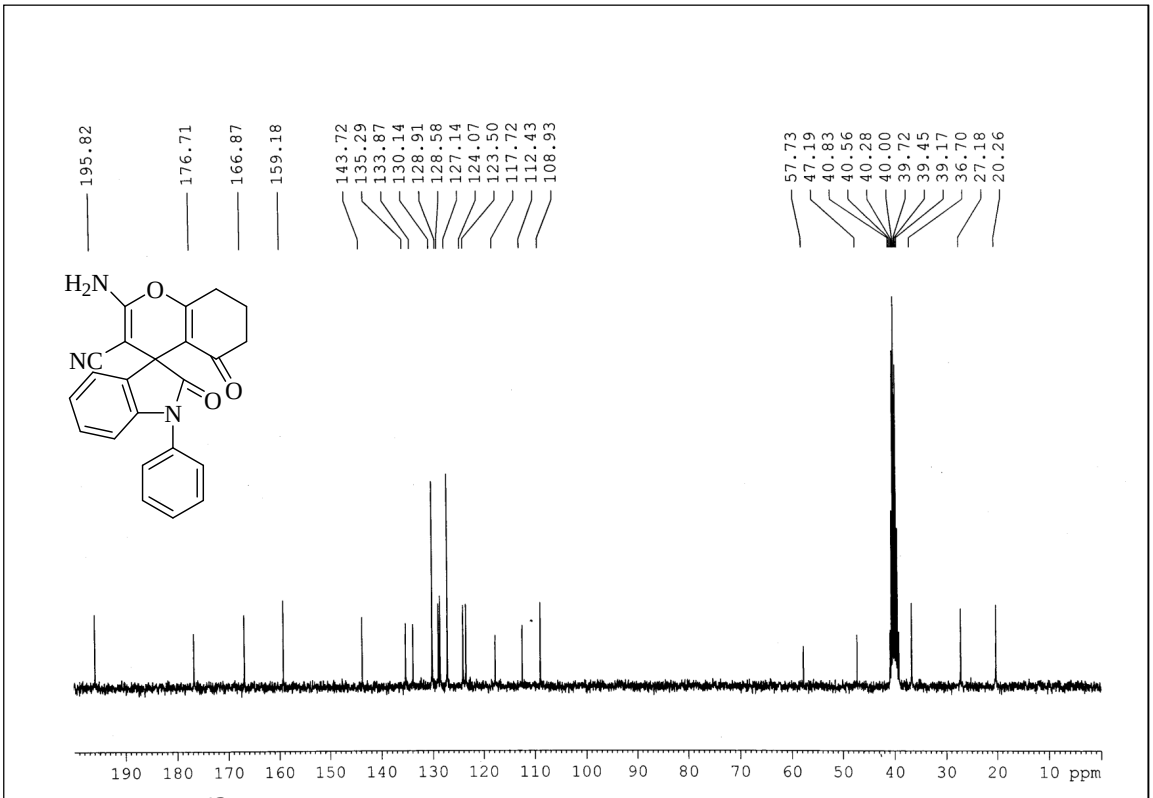
^{1}H NMR spectra of compound 4q in d_6-DMSO



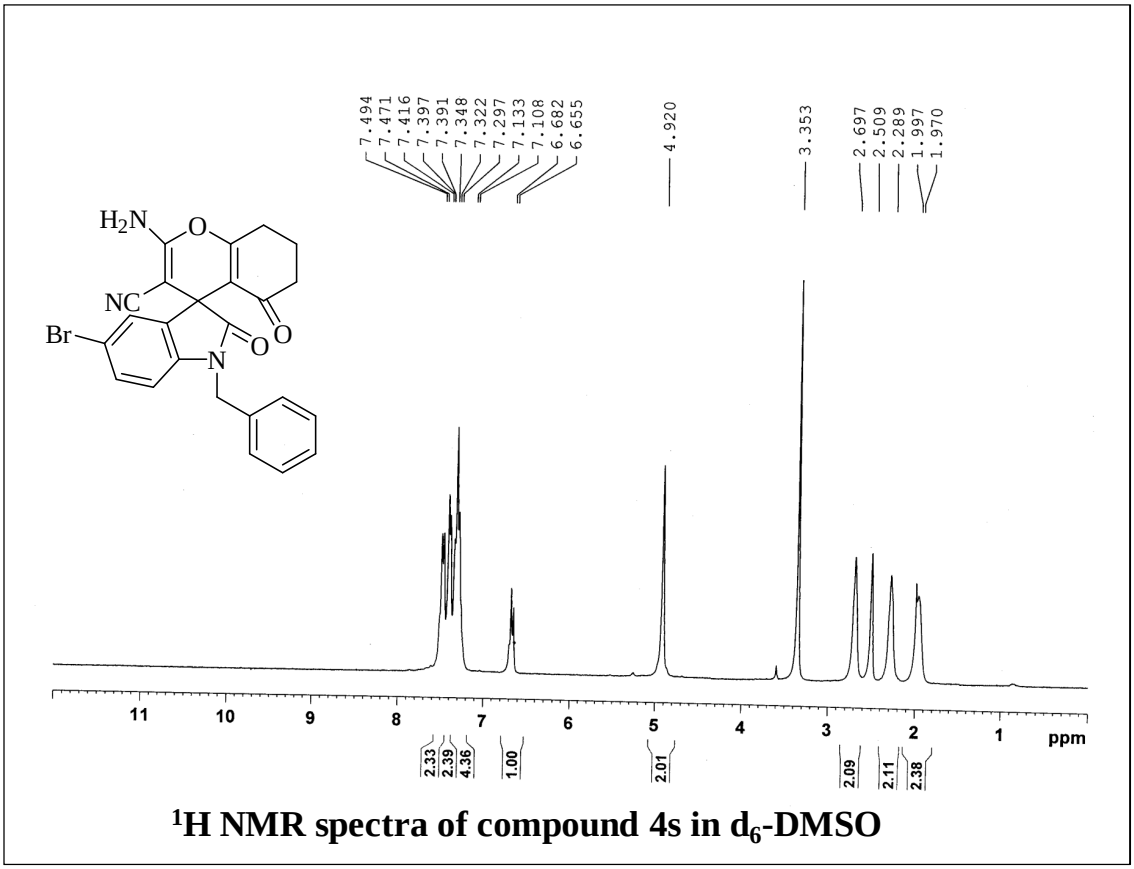
^{13}C NMR spectra of compound 4q in d_6-DMSO



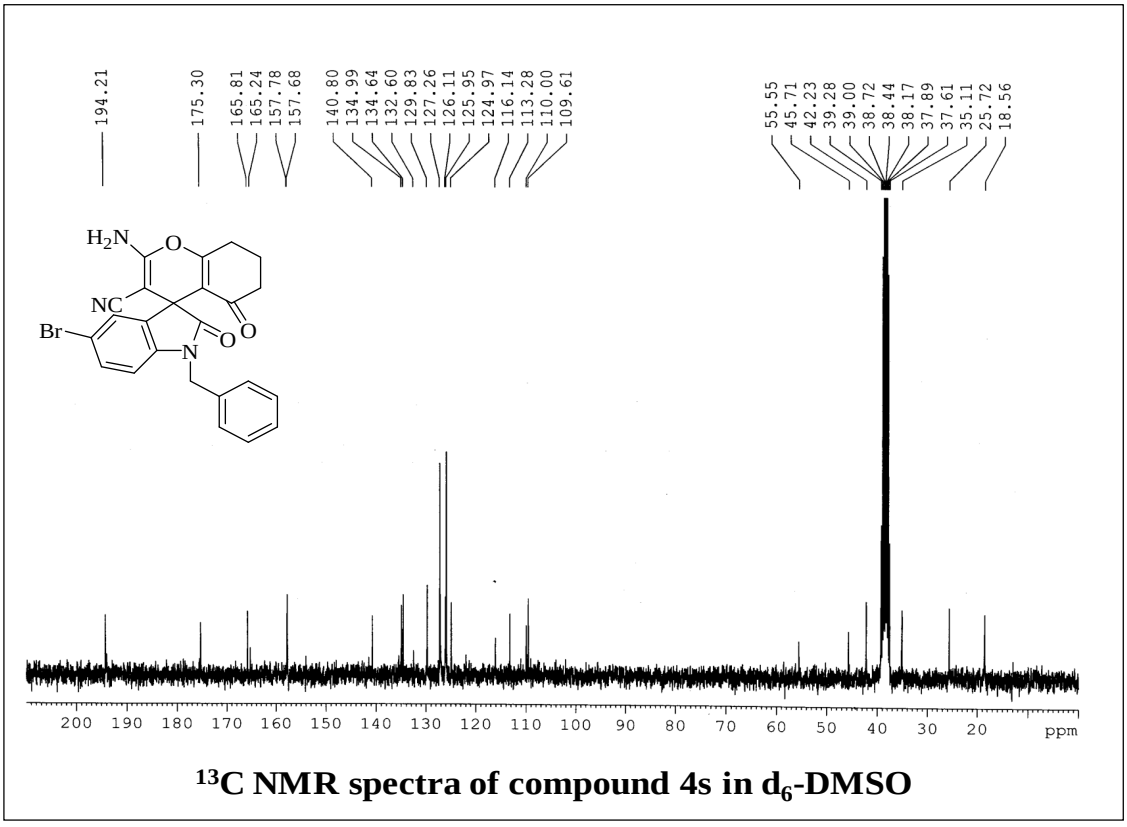
^{1}H NMR spectra of compound 4r in d_6-DMSO



^{13}C NMR spectra of compound 4r in d_6-DMSO



^{1}H NMR spectra of compound 4s in d_6-DMSO



^{13}C NMR spectra of compound 4s in d_6-DMSO

Reaction Scheme:

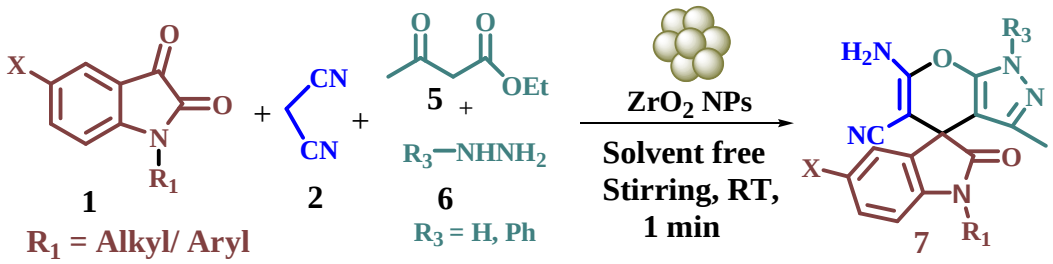
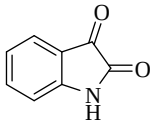
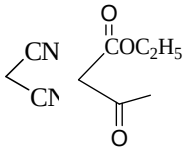
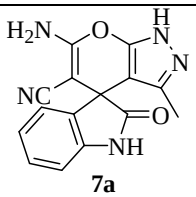
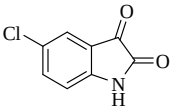
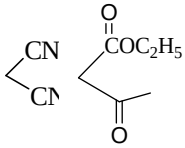
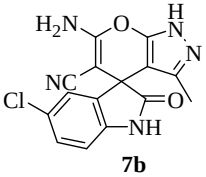
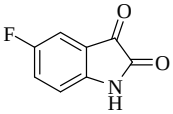
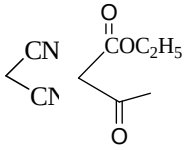
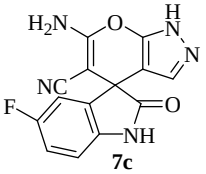
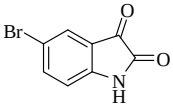
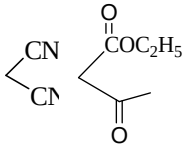
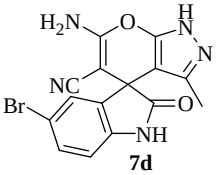
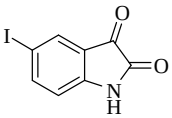
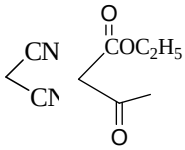
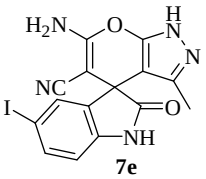
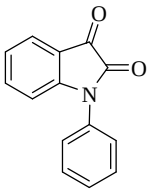
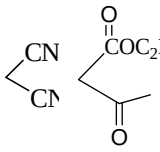
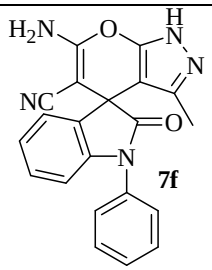
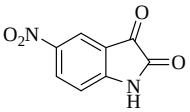
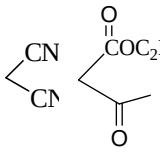
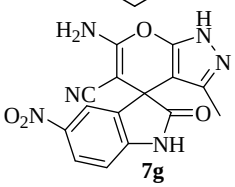
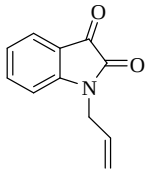
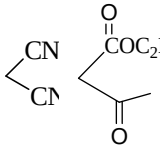
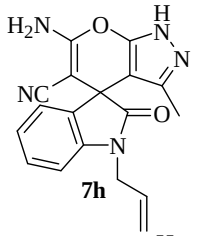
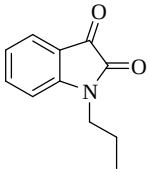
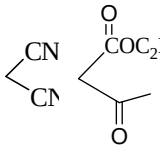
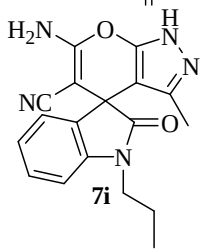
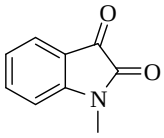
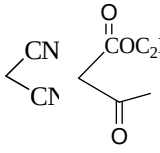
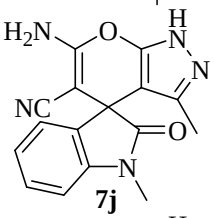
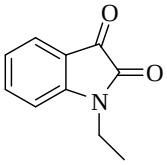
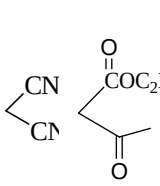
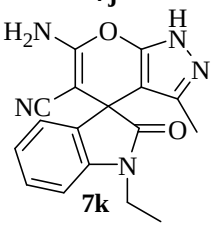
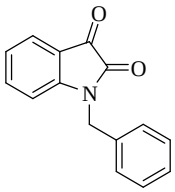
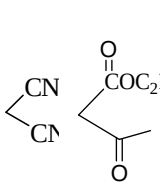
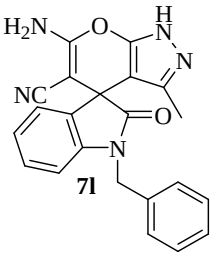
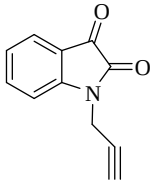
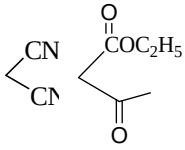
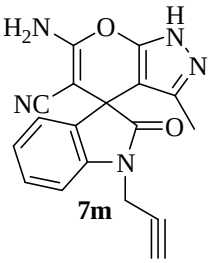
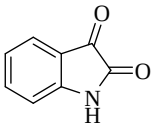
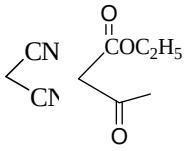
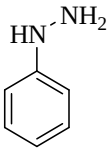
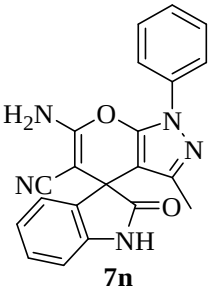
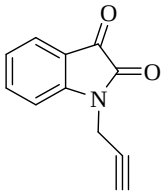
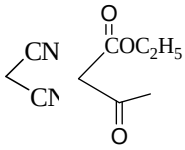
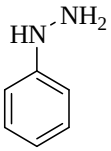
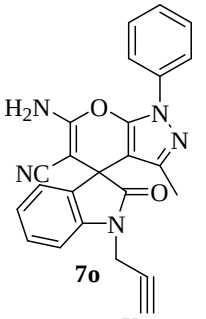
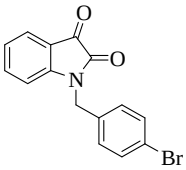
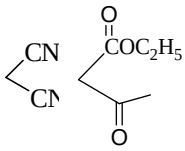
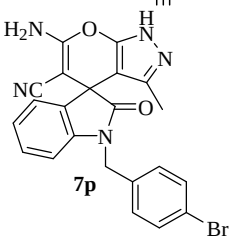
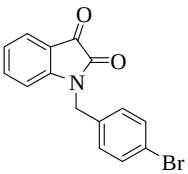
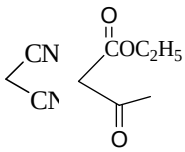
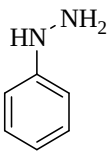
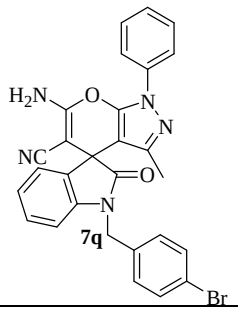
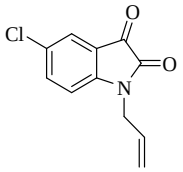
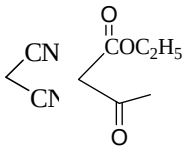
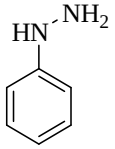
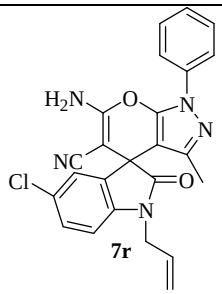
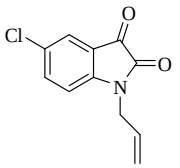
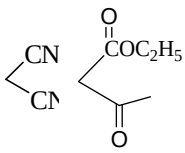
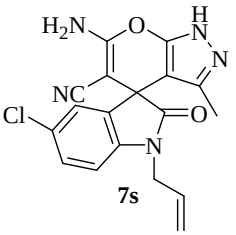
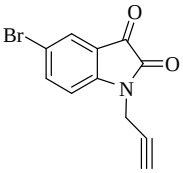
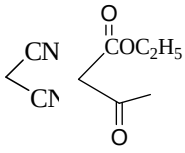
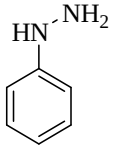
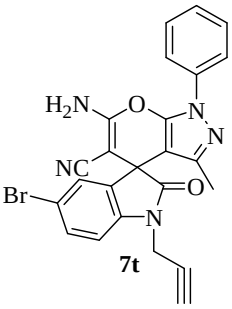
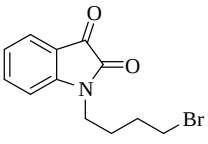
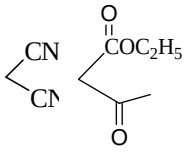
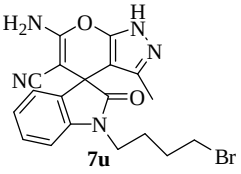
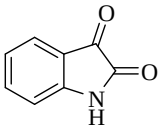
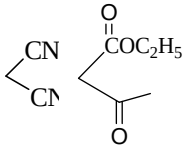
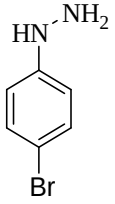
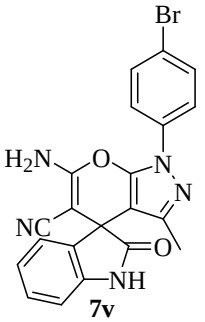
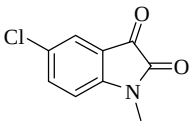
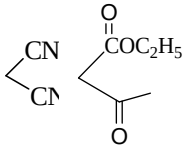
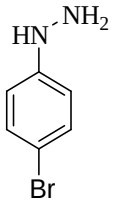
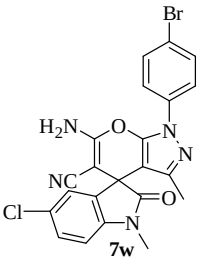


Table S2: Synthesis of spiro[indoline-3,4′(1*H*′)-pyrano-[2,3-*c*]pyrazol-2-one compounds **7a-w** through a four-component reaction

Entry	1	2	3	4	Product (7)	Yield[a] (%)	Melting Point(°C)	Reference
1				H_2N-NH_2	 **7a**	90	278-280	2a
2				H_2N-NH_2	 **7b**	86	294-296	2a
3				H_2N-NH_2	 **7c**	87	278-280	2a
4				H_2N-NH_2	 **7d**	84	282-284	2a
5				H_2N-NH_2	 **7e**	92	>300	2b

6			H_2N-NH_2	 **7f**	80	228-232	–
7			H_2N-NH_2	 **7g**	83	240-244	2b
8			H_2N-NH_2	 **7h**	90	244-246	–
9			H_2N-NH_2	 **7i**	84	250-254	2c
10			H_2N-NH_2	 **7j**	86	262-264	2b
11			H_2N-NH_2	 **7k**	92	260-262	2b
12			H_2N-NH_2	 **7l**	88	254-258	2b

13			H_2N-NH_2	 **7m**	89	258-262	–
14				 **7n**	94	224-226	2a
15				 **7o**	83	140-142	–
16			H_2N-NH_2	 **7p**	87	158-162	–
17				 **7q**	85	190-192	–

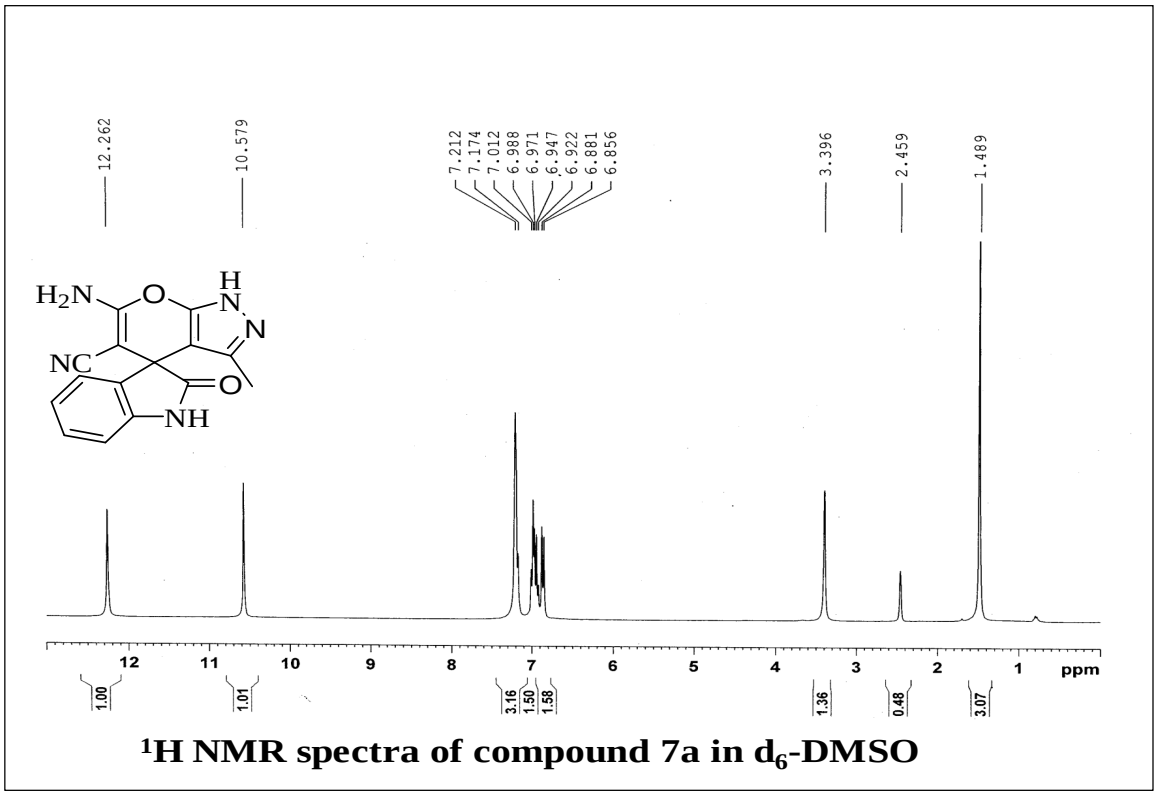
18				 **7r**	78	178-180	–
19			H_2N-NH_2	 **7s**	86	272-274	–
20				 **7t**	82	196-198	–
21			H_2N-NH_2	 **7u**	88	200-204	–
22				 **7v**	80	228-232	–
23				 **7w**	84	198-202	–

[a]Isolated Yields (%)

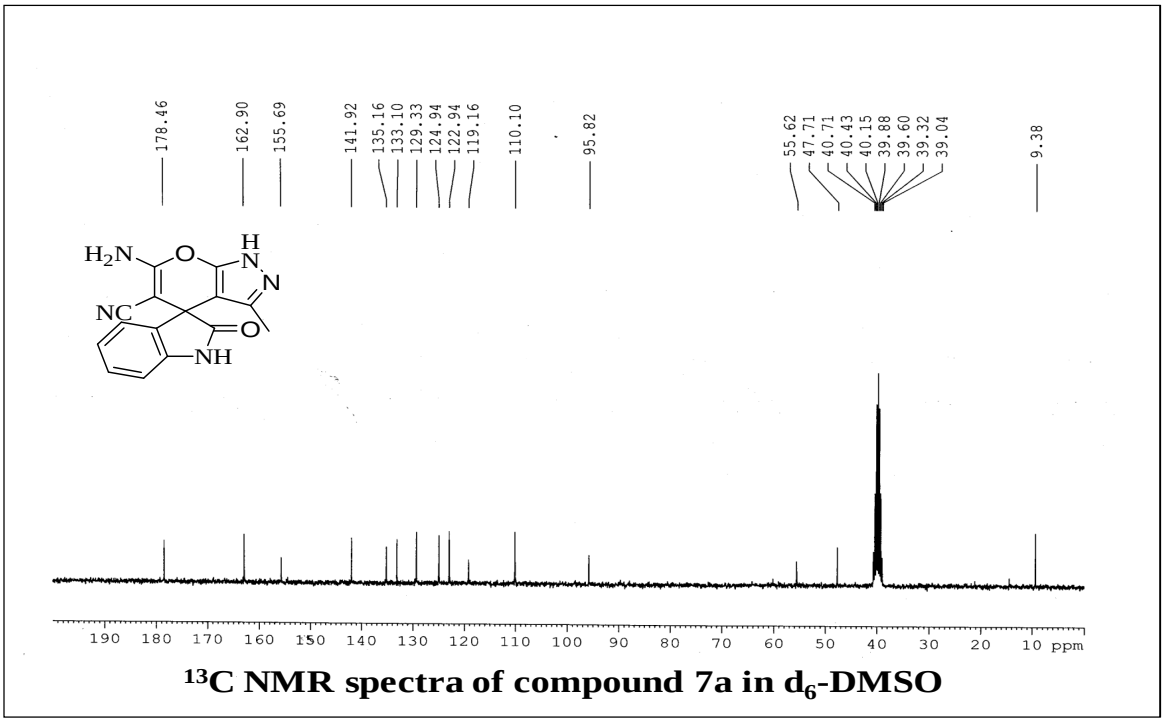
Reference:

2. (a) P. Rai, M. Srivastava, J. Singh and J. Singh, *New J. Chem.*, 2014, **38**, 3181; (b) D. M. Pore, P. G. Hegade, D. S. Gaikwad, P. B. Patil and J. D. Patil, *Lett. org. chem.*, 2014, **11**, 131; (c) Y. M. Litvinov, A. A. Shestopalov, L. A. Rodinovskaya and A. M. Shestopalov, *J. Comb. Chem.* 2009**, 11**, 914.

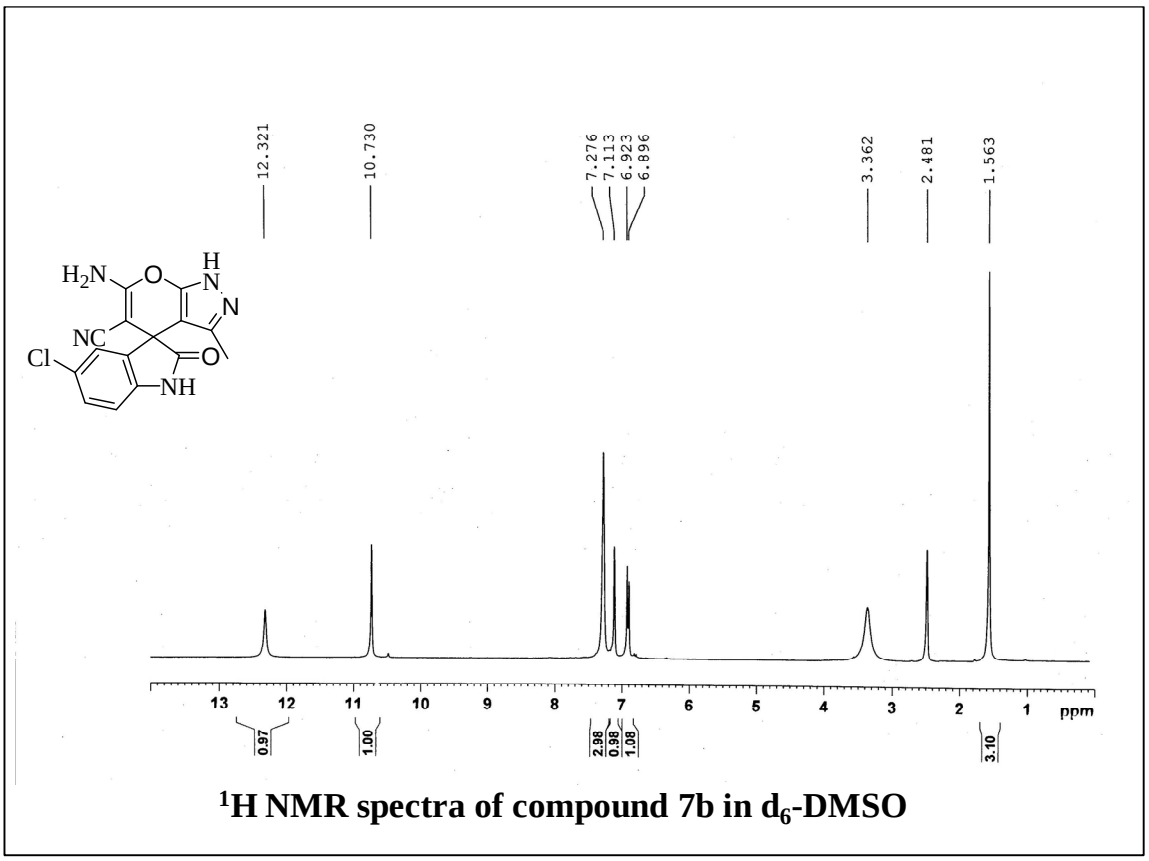
Spectral Data of 7a-w:



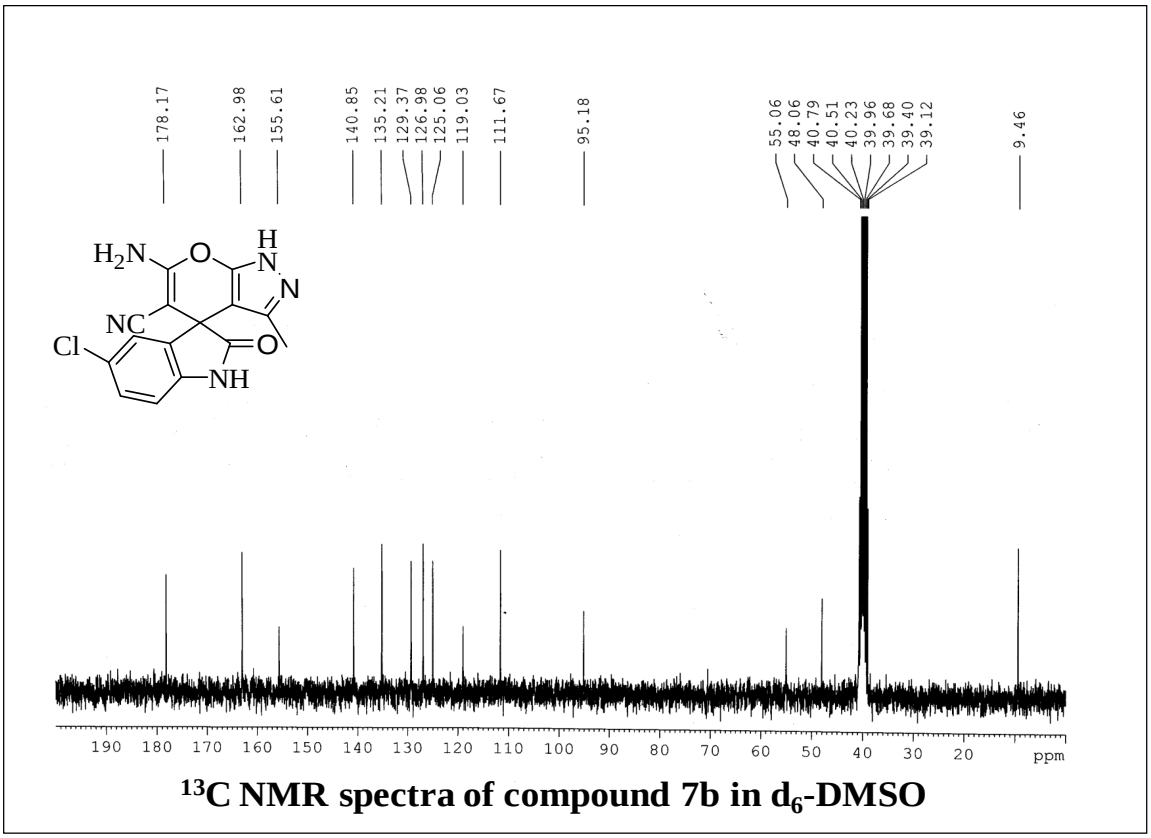
^{1}H NMR spectra of compound 7a in d_6-DMSO



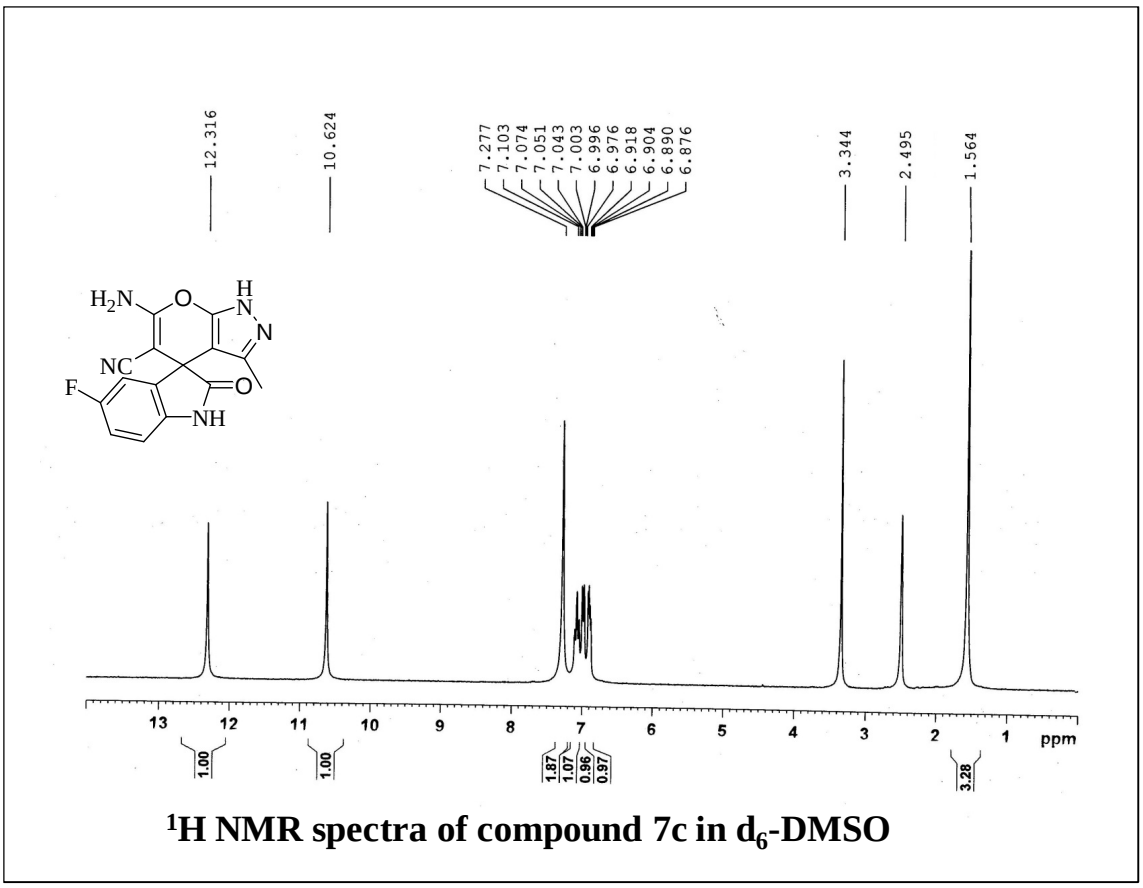
^{13}C NMR spectra of compound 7a in d_6-DMSO



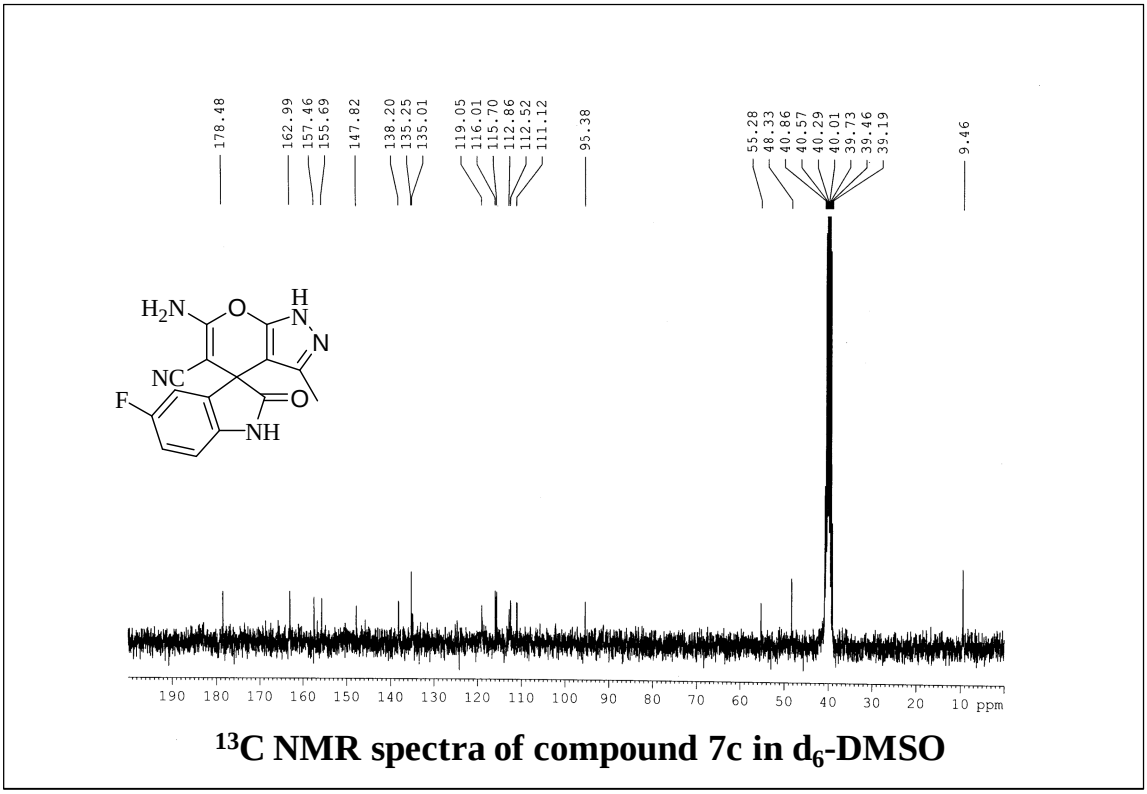
^{1}H NMR spectra of compound 7b in d_6-DMSO



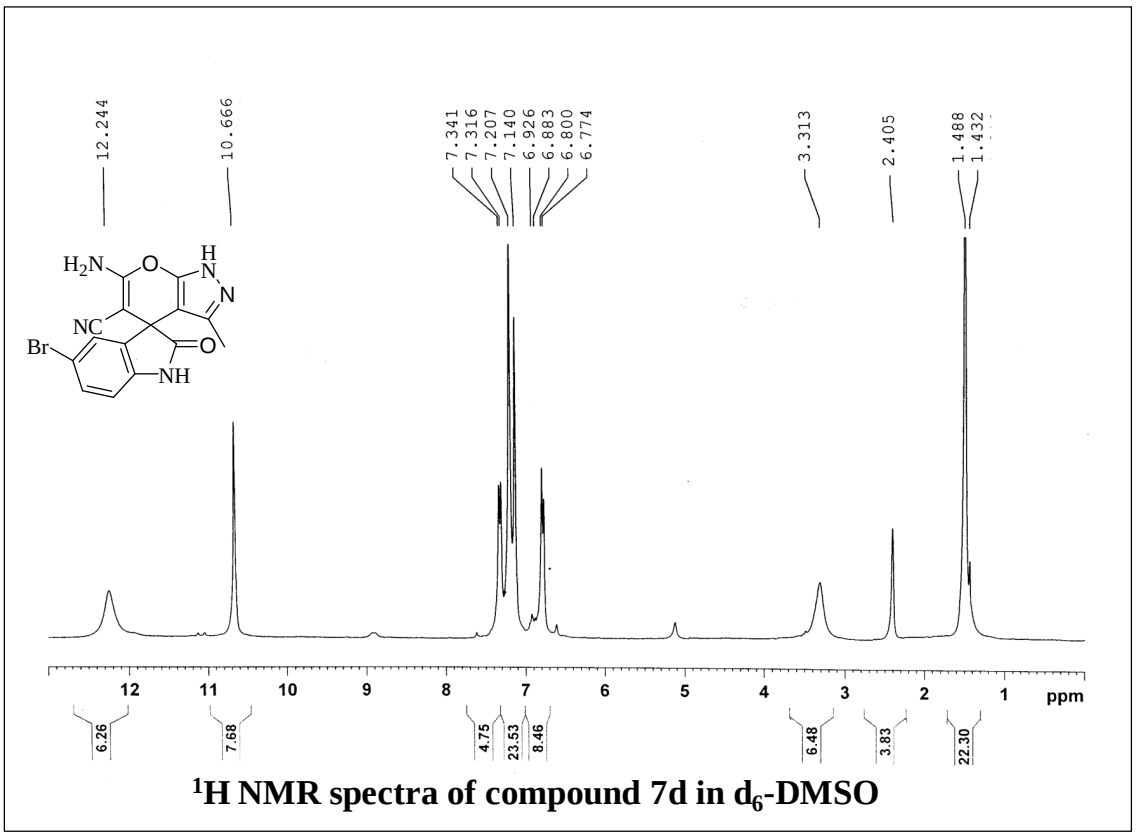
^{13}C NMR spectra of compound 7b in d_6-DMSO



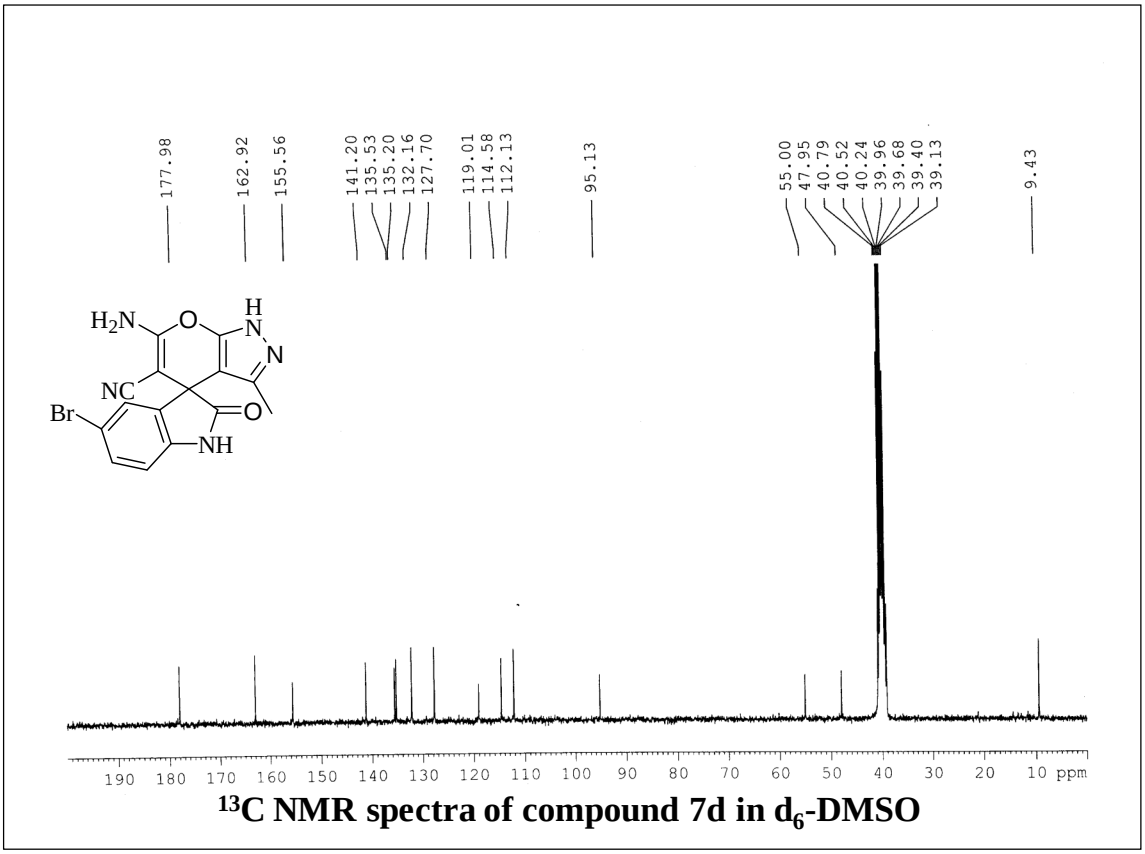
^{1}H NMR spectra of compound 7c in d_6-DMSO



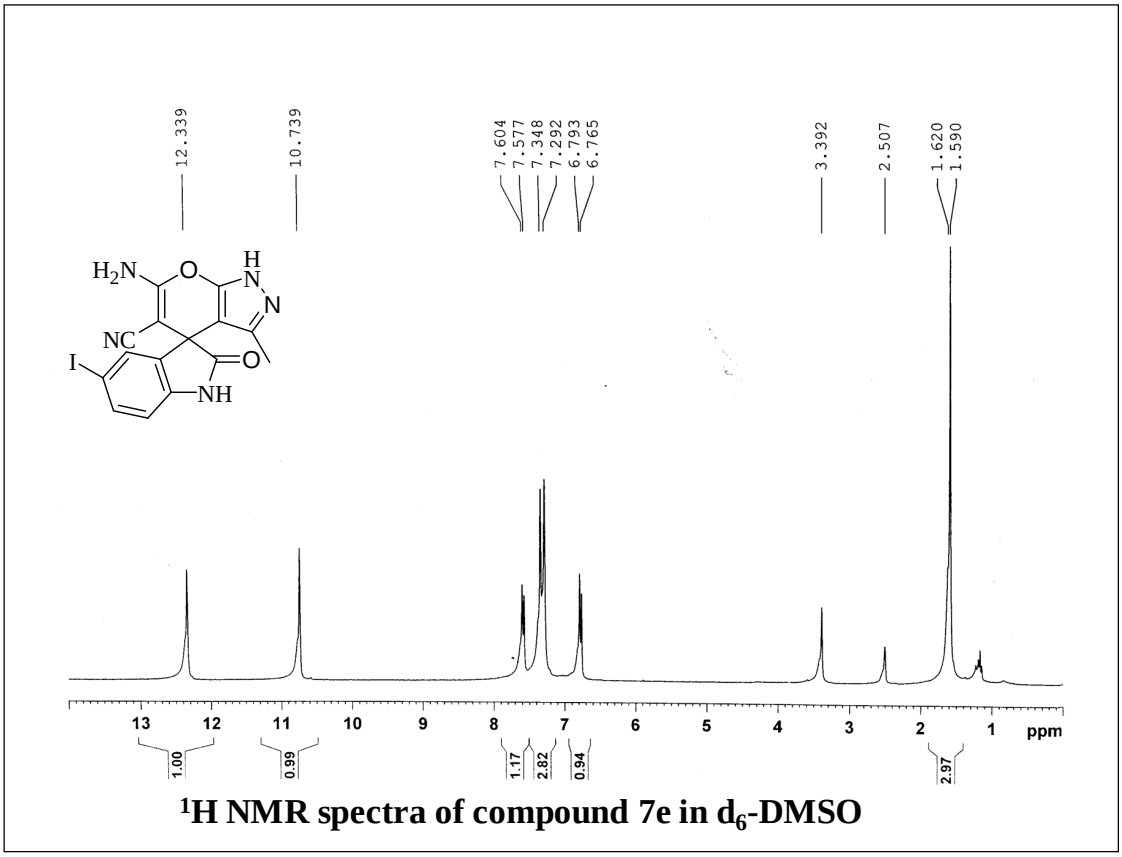
^{13}C NMR spectra of compound 7c in d_6-DMSO



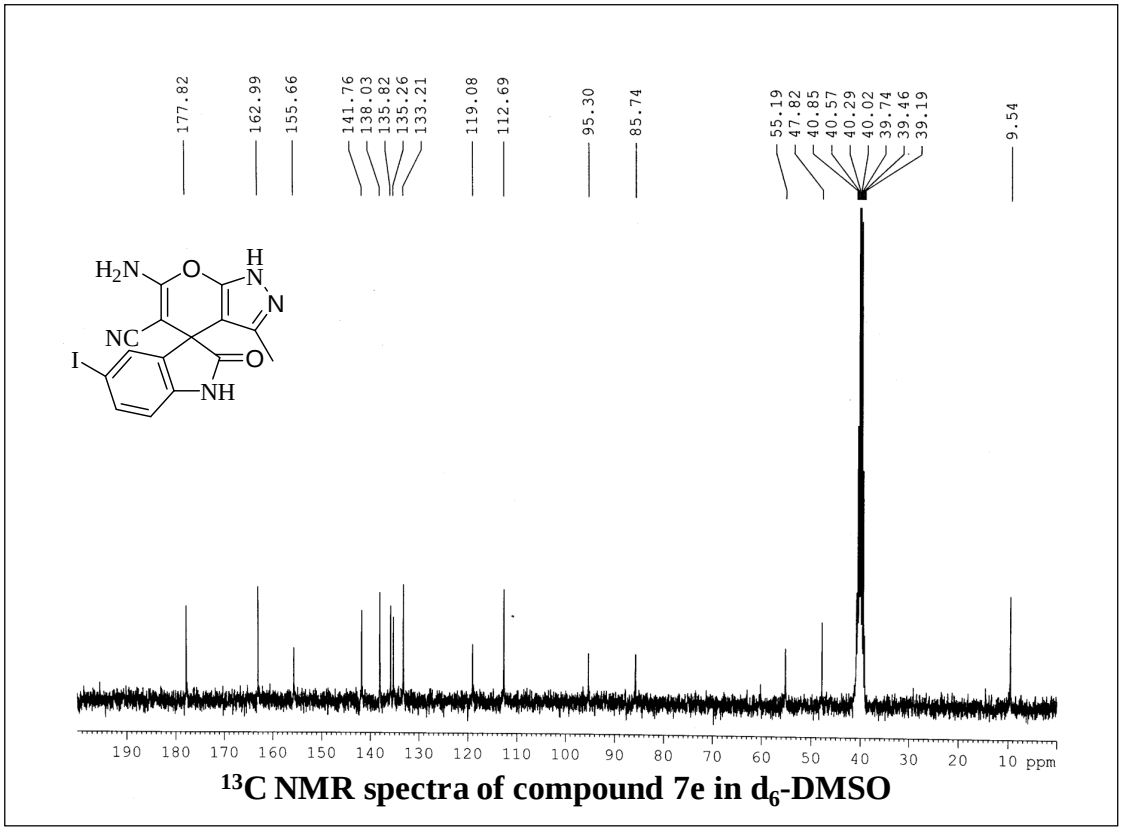
^{1}H NMR spectra of compound 7d in d_6-DMSO



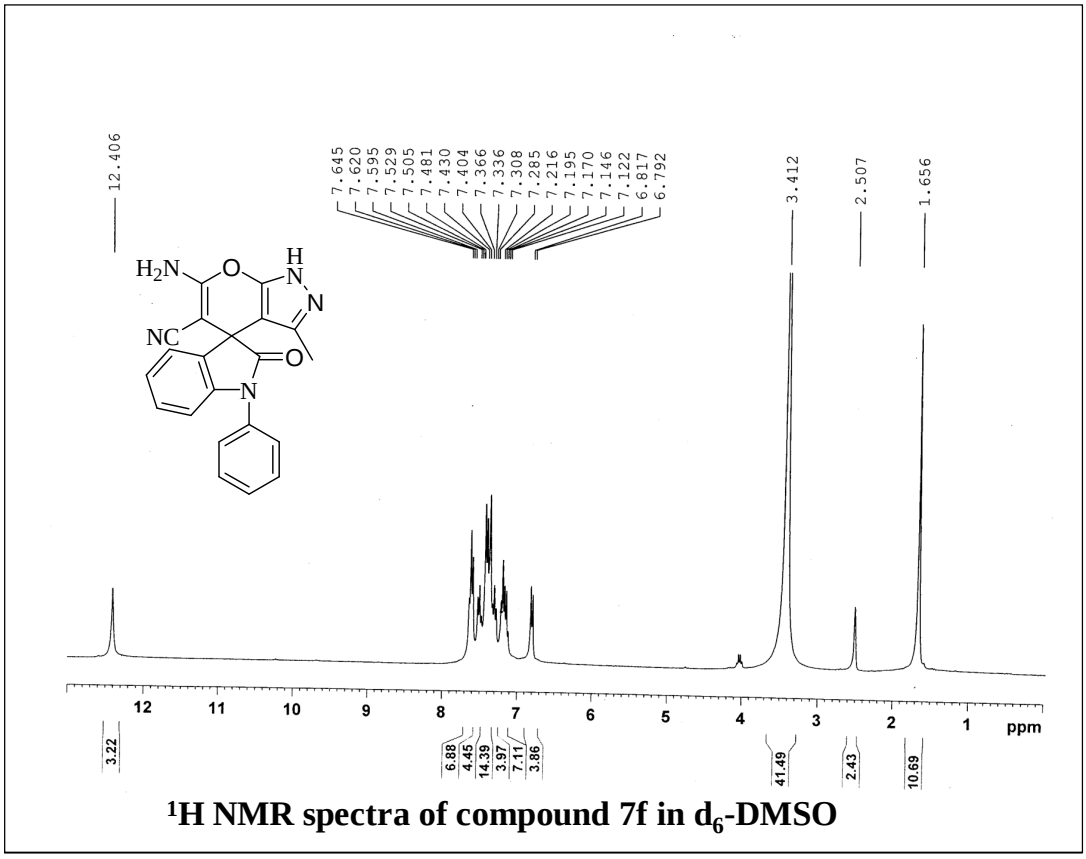
^{13}C NMR spectra of compound 7d in d_6-DMSO



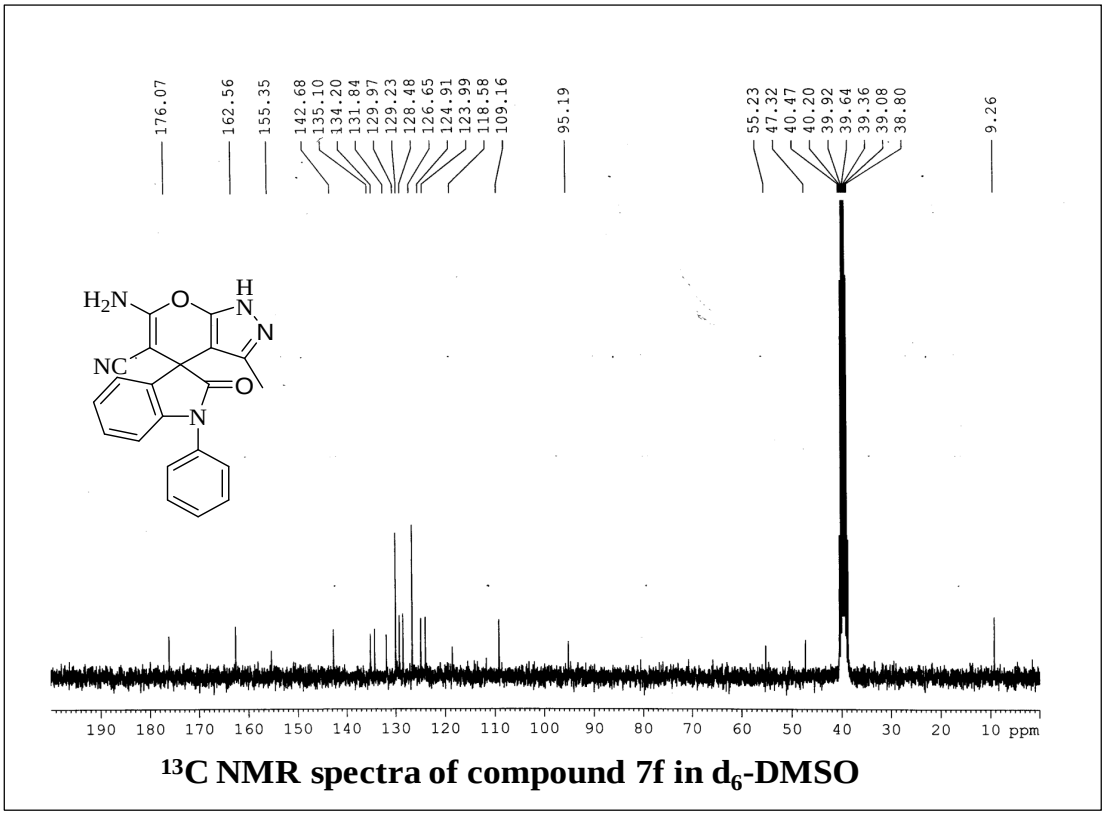
^{1}H NMR spectra of compound 7e in d_6-DMSO



^{13}C NMR spectra of compound 7e in d_6-DMSO



^{1}H NMR spectra of compound 7f in d_6-DMSO



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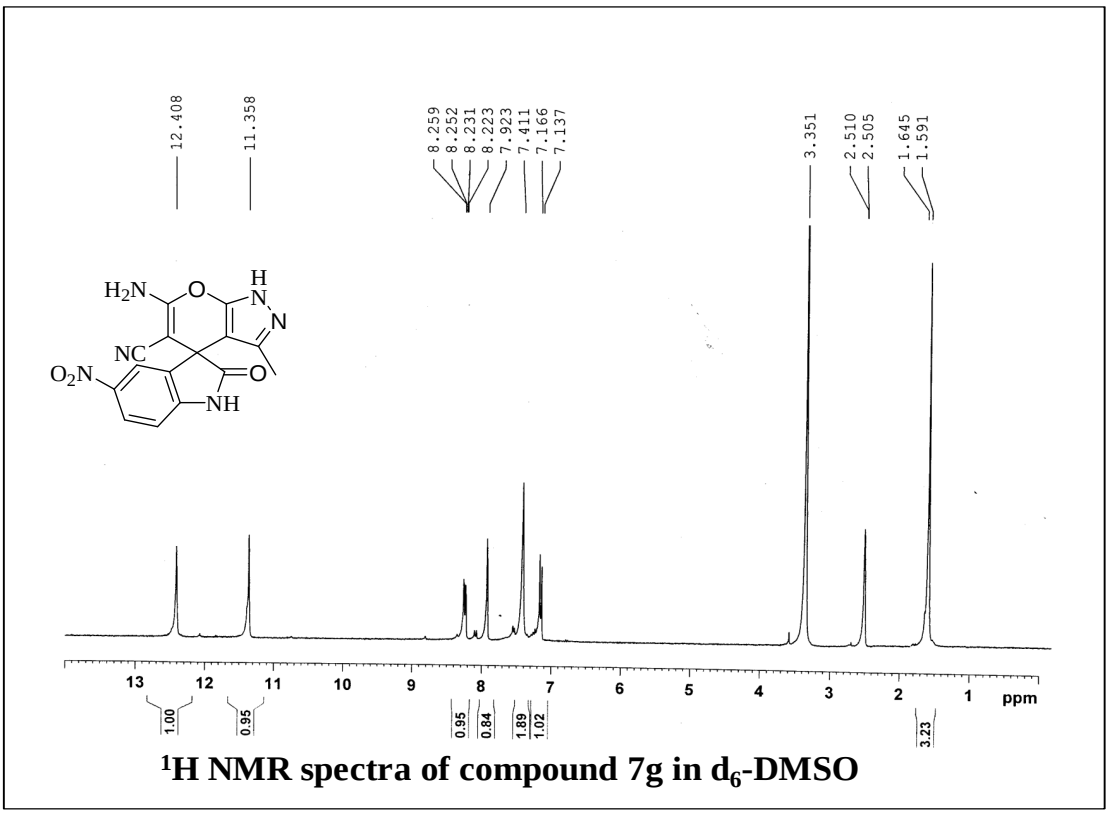

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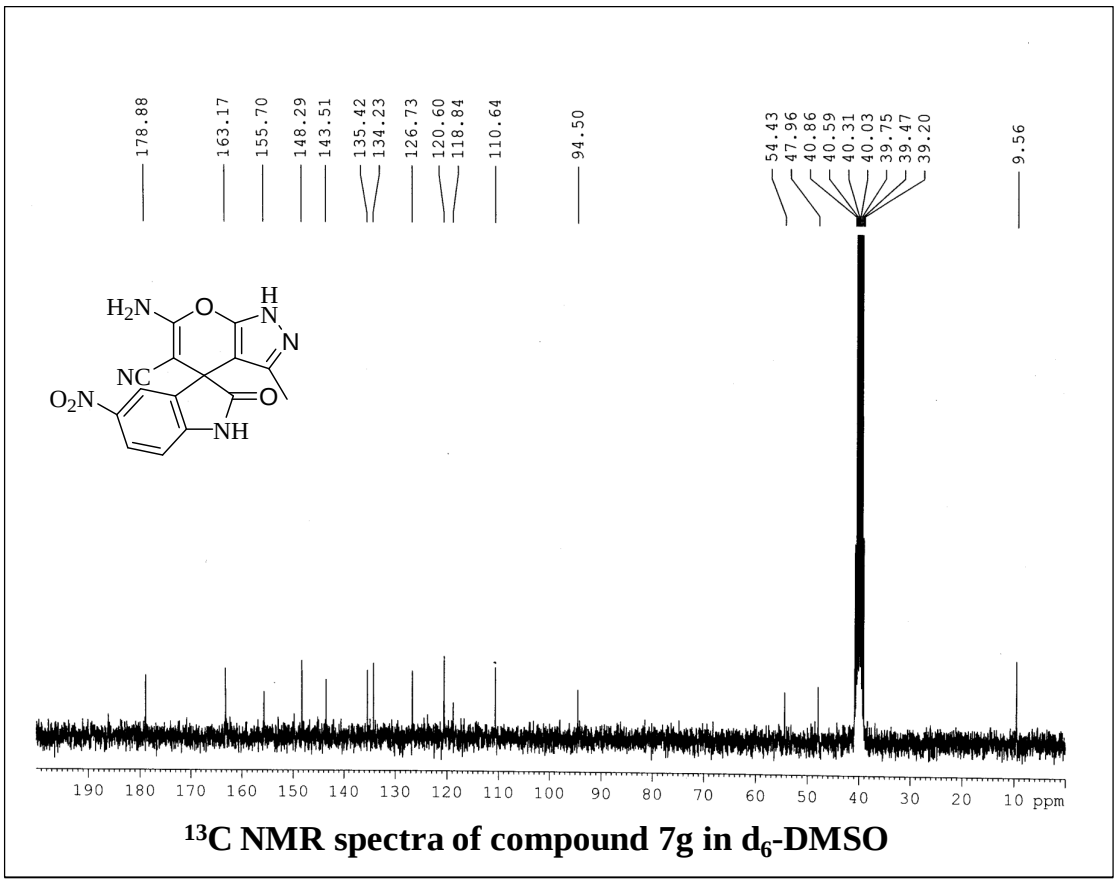
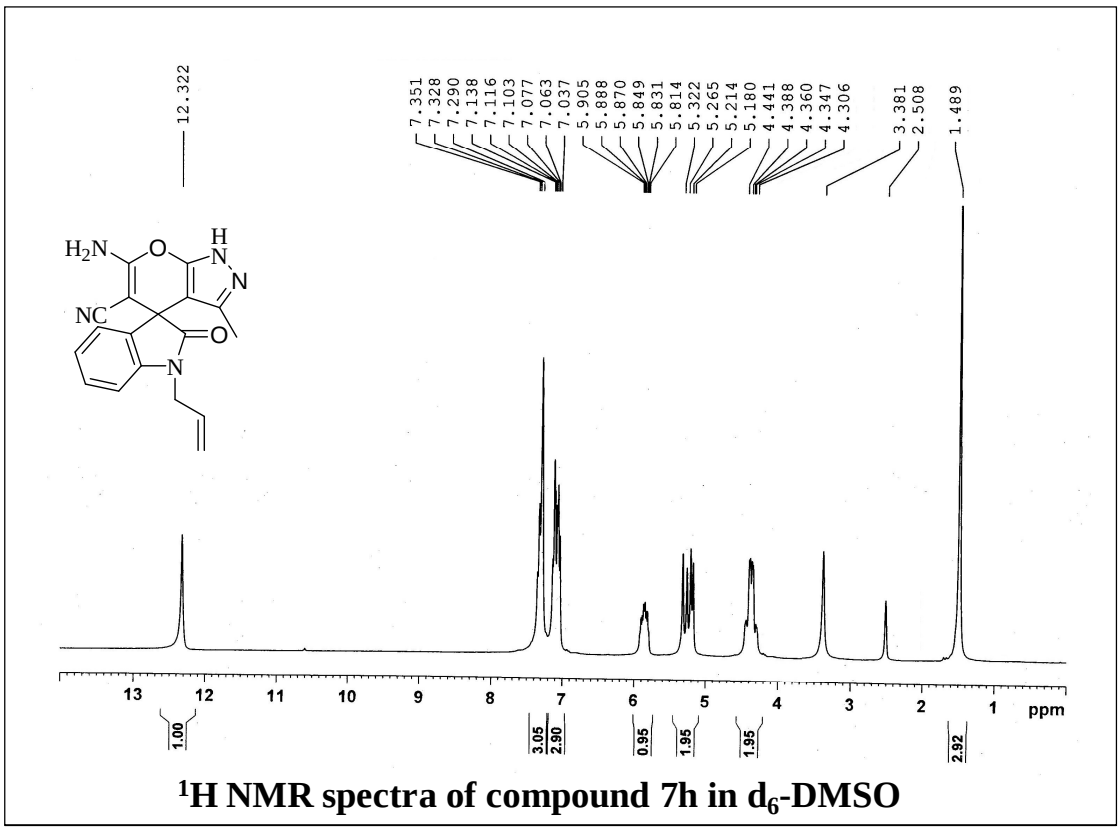
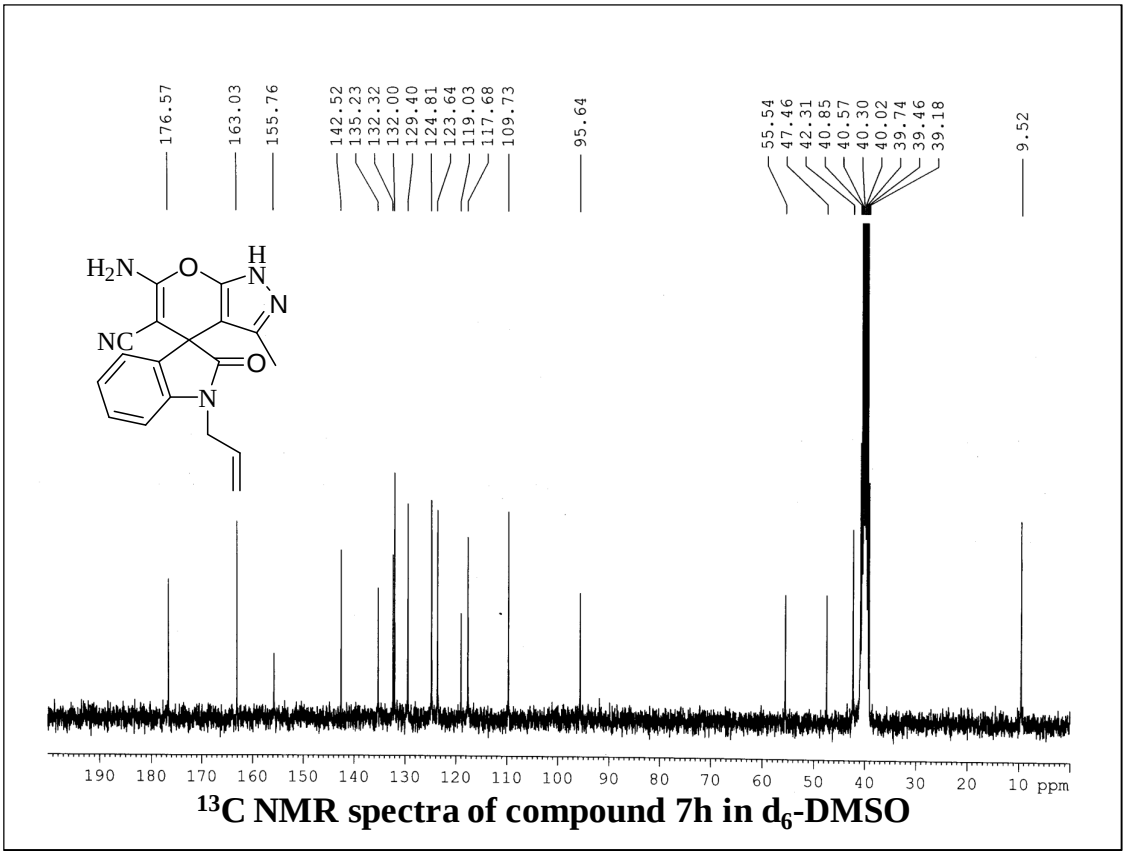


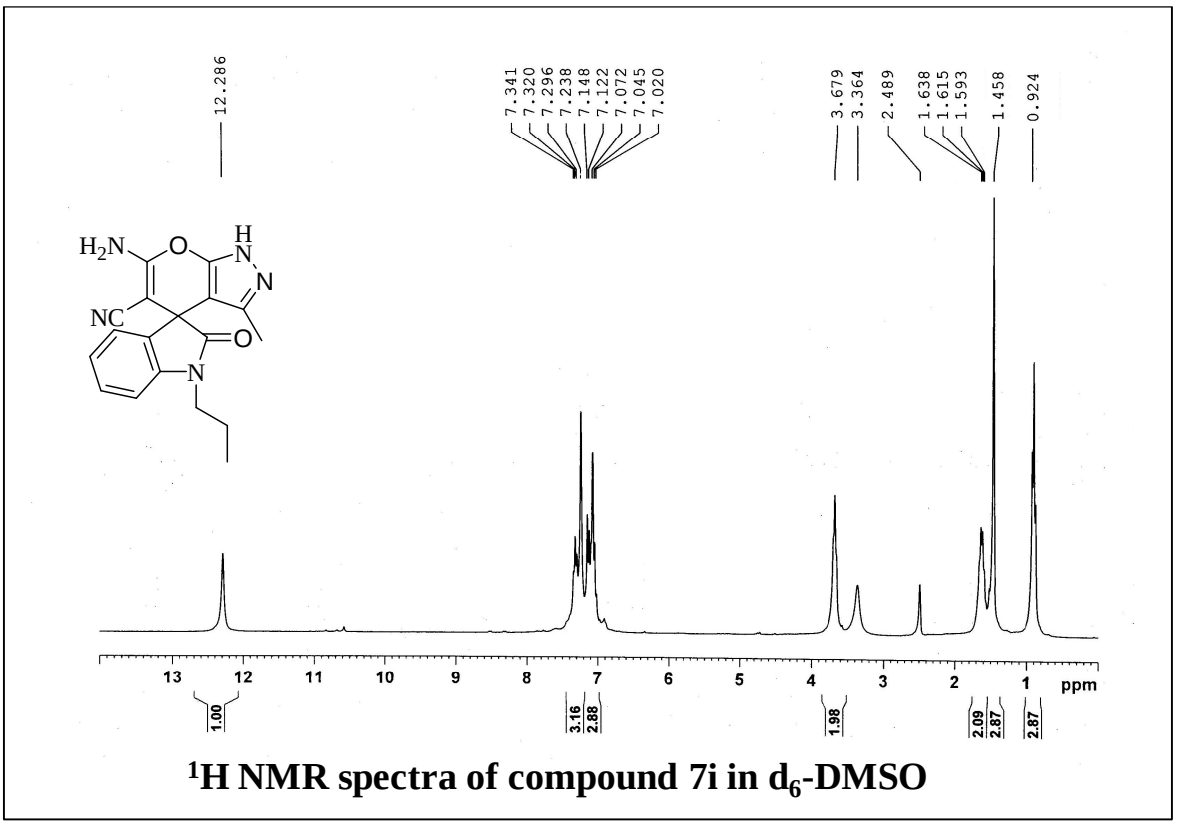
^{13}C NMR spectra of compound 7g in d_6-DMSO



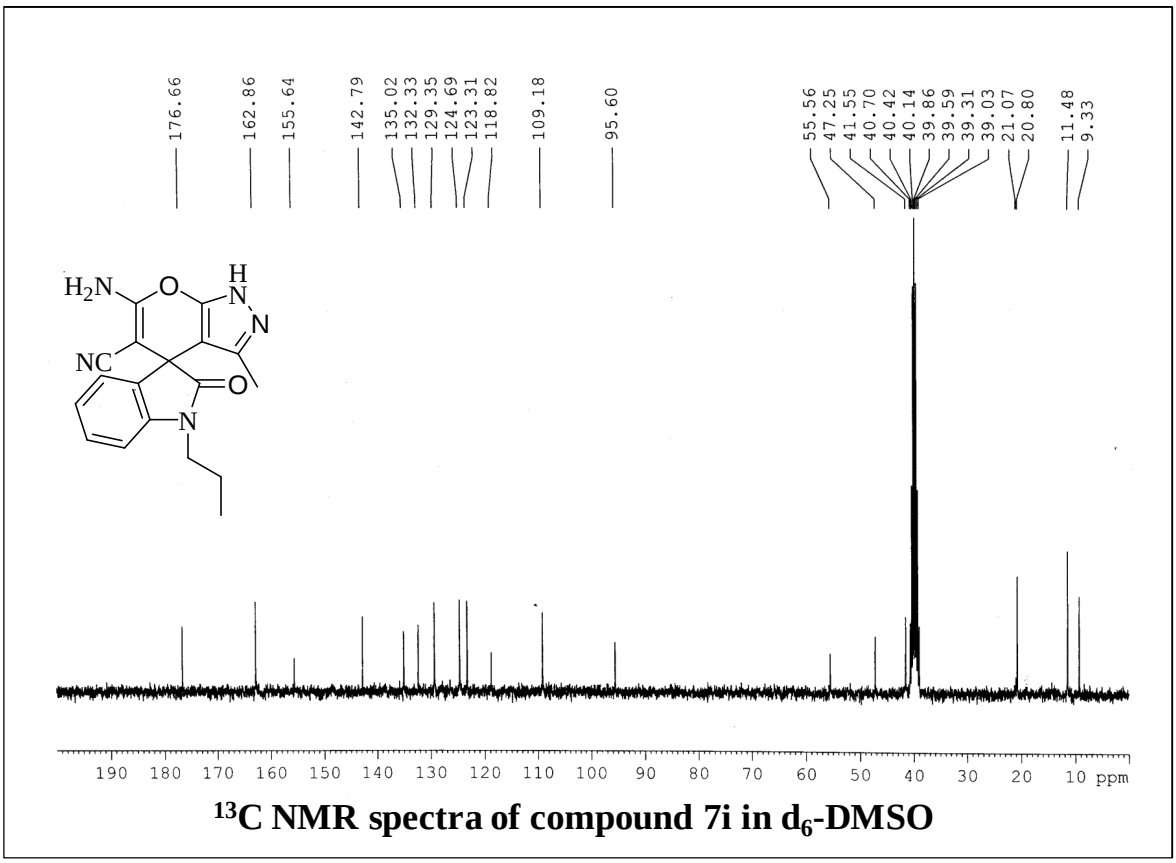
^{1}H NMR spectra of compound 7h in d_6-DMSO



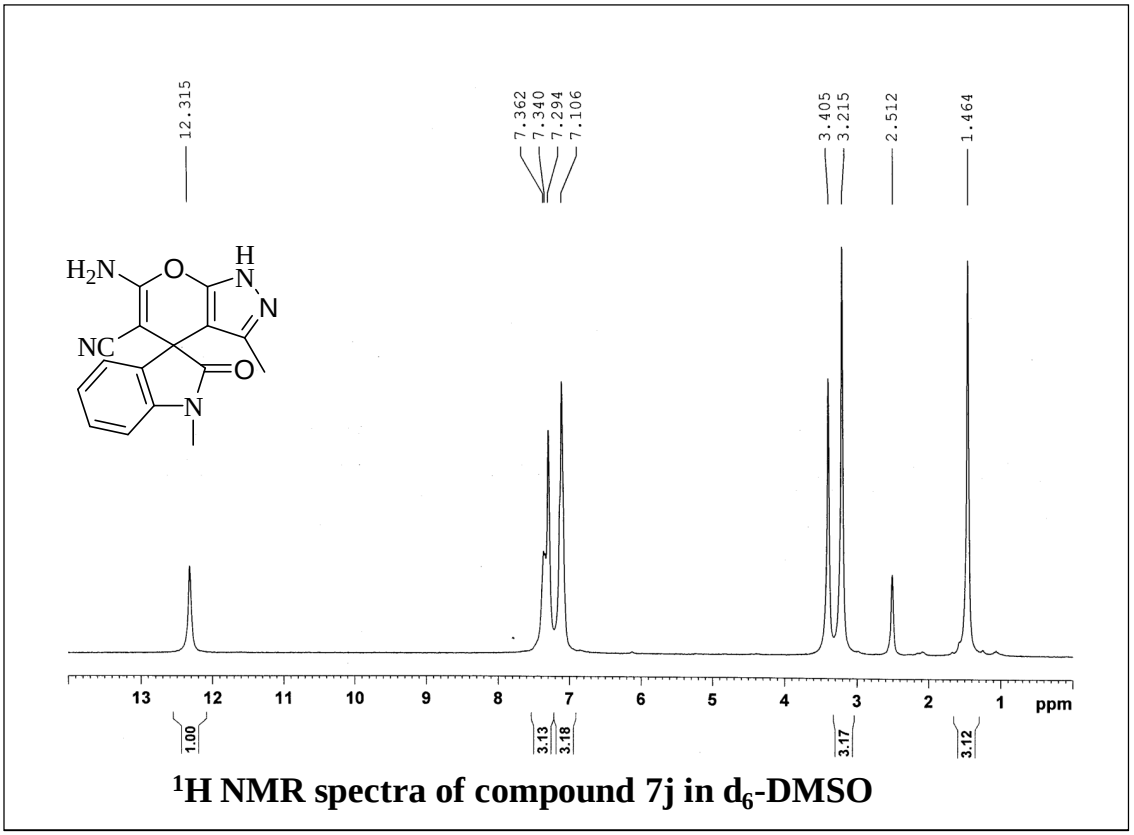
^{13}C NMR spectra of compound 7h in d_6-DMSO



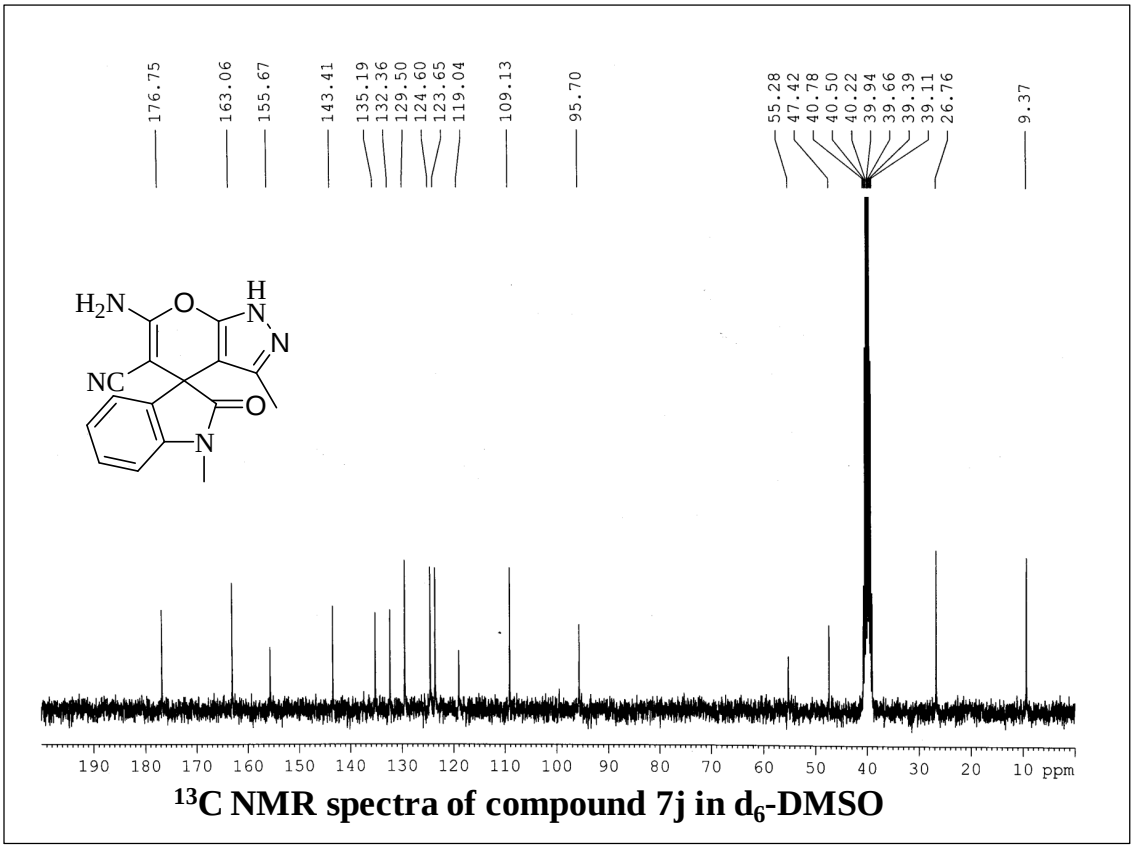
^{1}H NMR spectra of compound 7i in d_6-DMSO



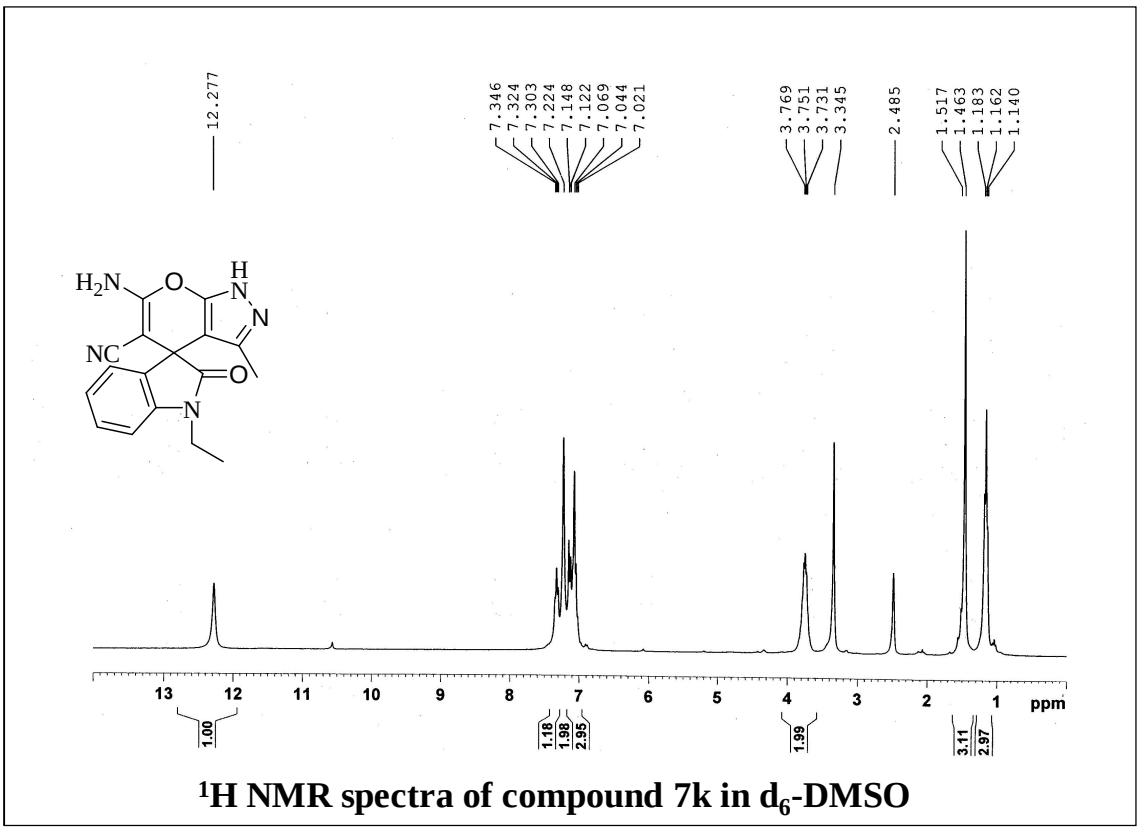
^{13}C NMR spectra of compound 7i in d_6-DMSO



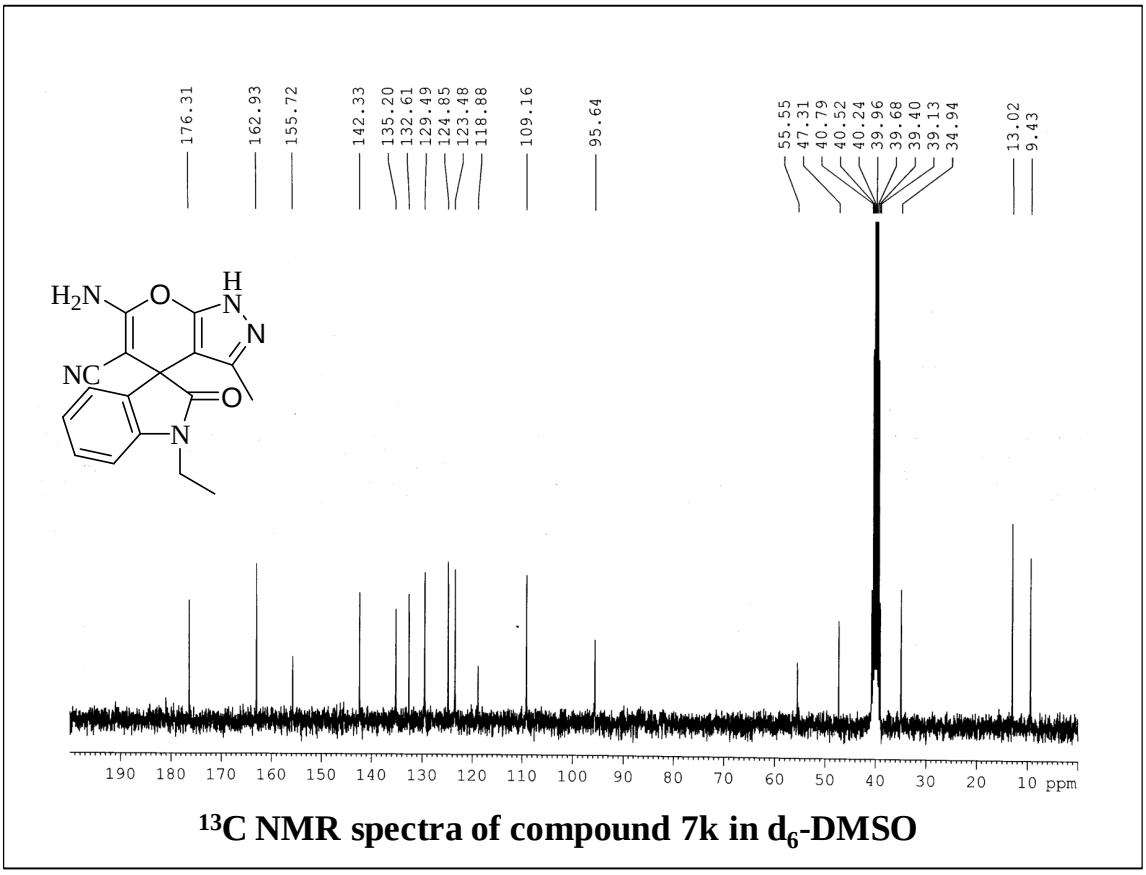
^{1}H NMR spectra of compound 7j in d_6-DMSO



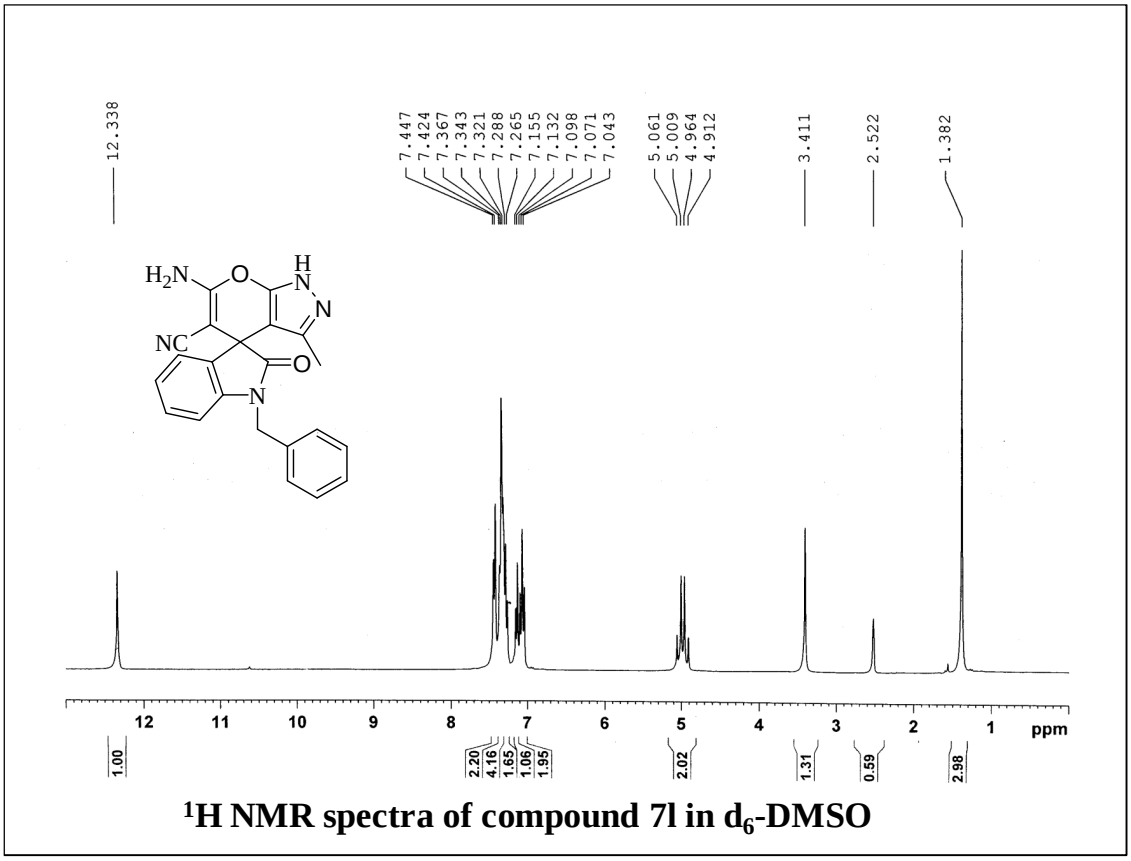
^{13}C NMR spectra of compound 7j in d_6-DMSO



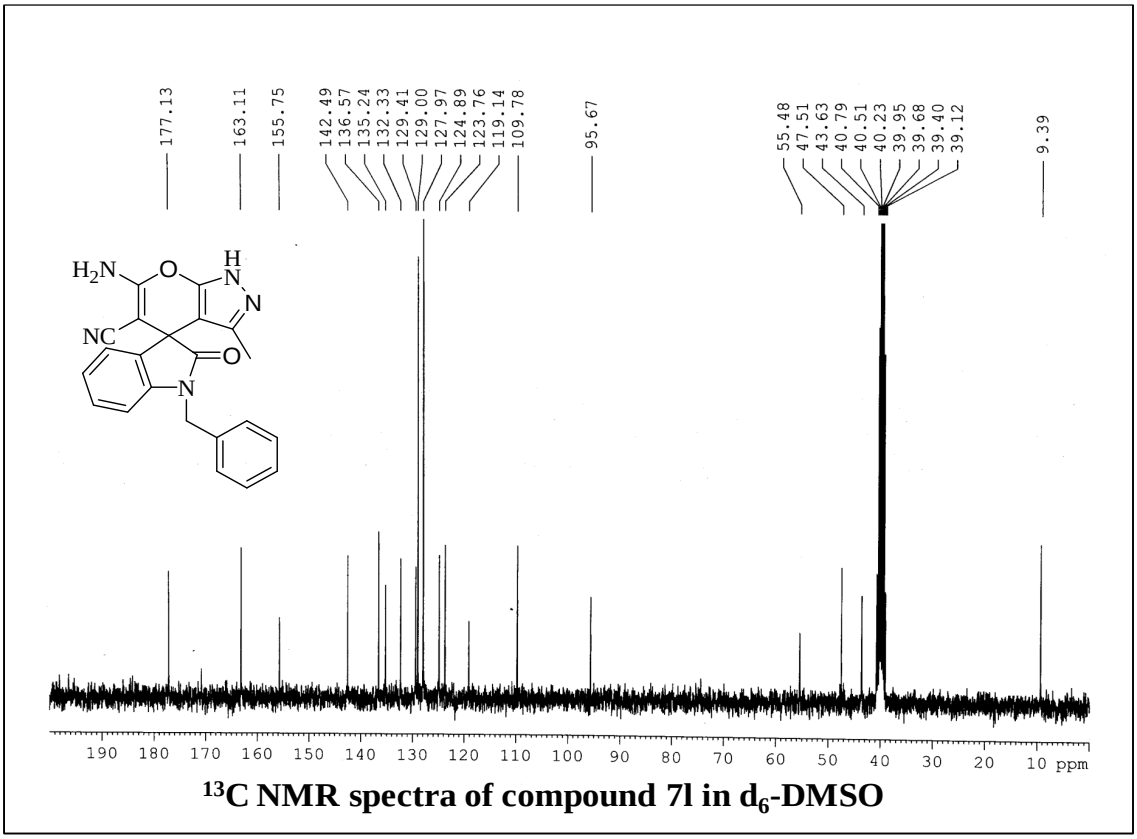
^{1}H NMR spectra of compound 7k in d_6-DMSO



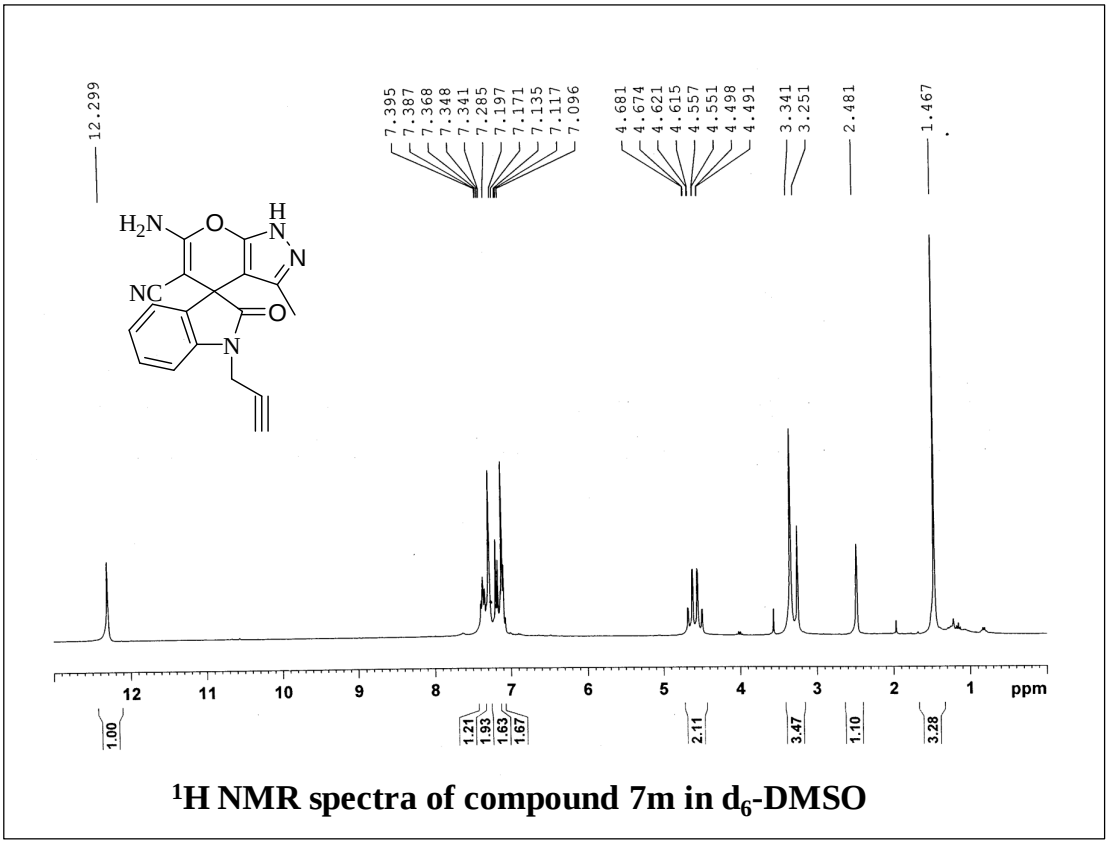
^{13}C NMR spectra of compound 7k in d_6-DMSO



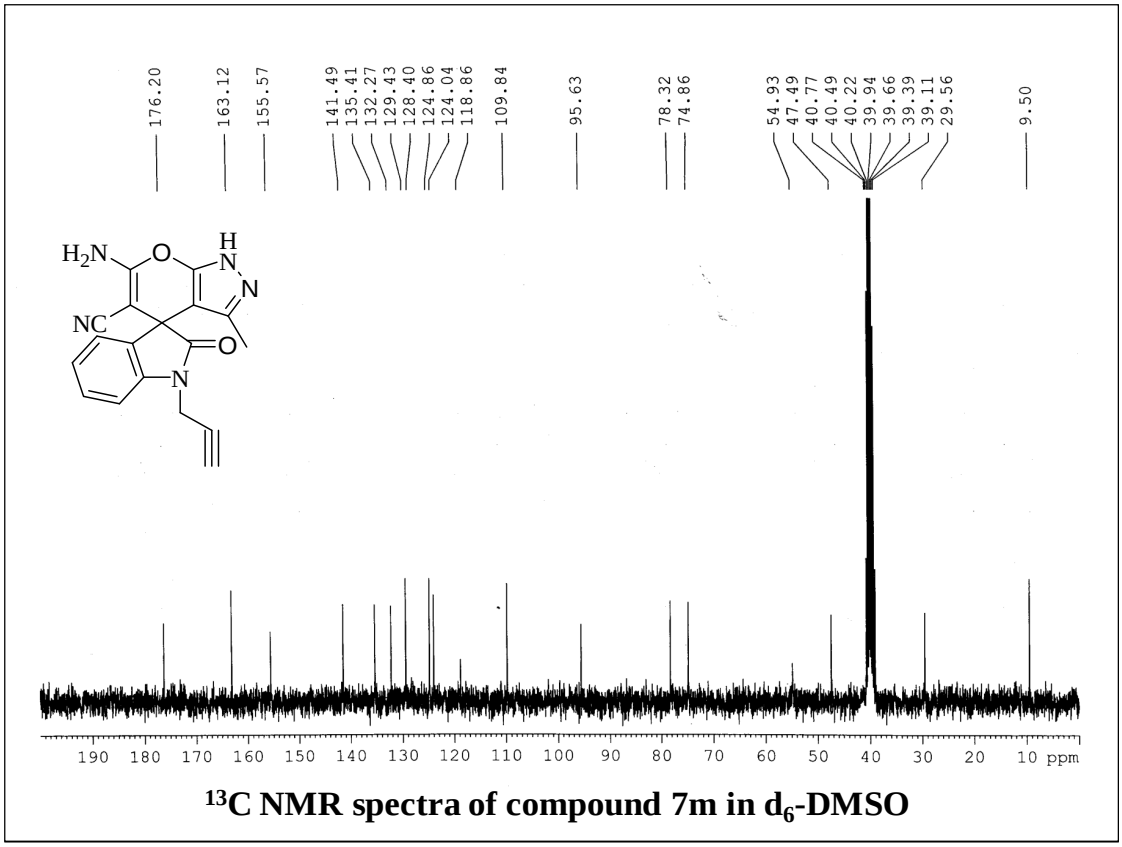
^{1}H NMR spectra of compound 7l in d_6-DMSO



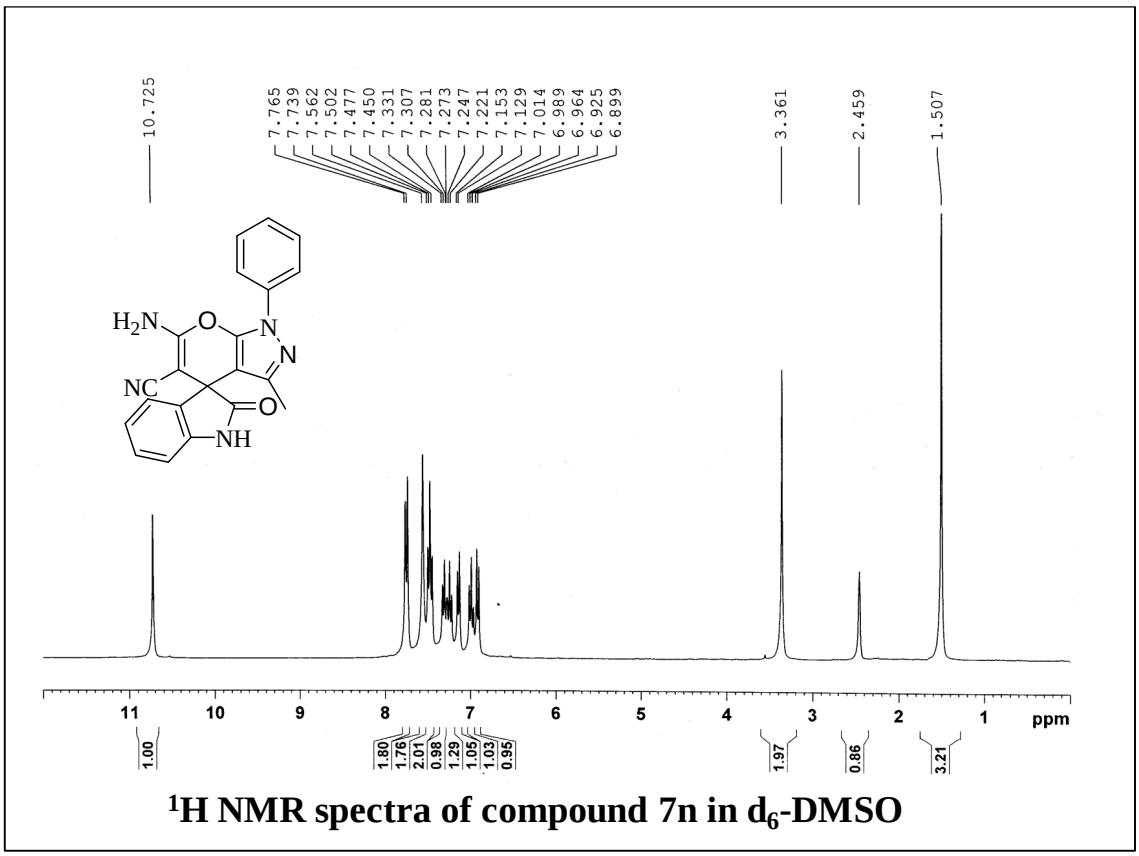
^{13}C NMR spectra of compound 7l in d_6-DMSO



^{1}H NMR spectra of compound 7m in d_6-DMSO



^{13}C NMR spectra of compound 7m in d_6-DMSO



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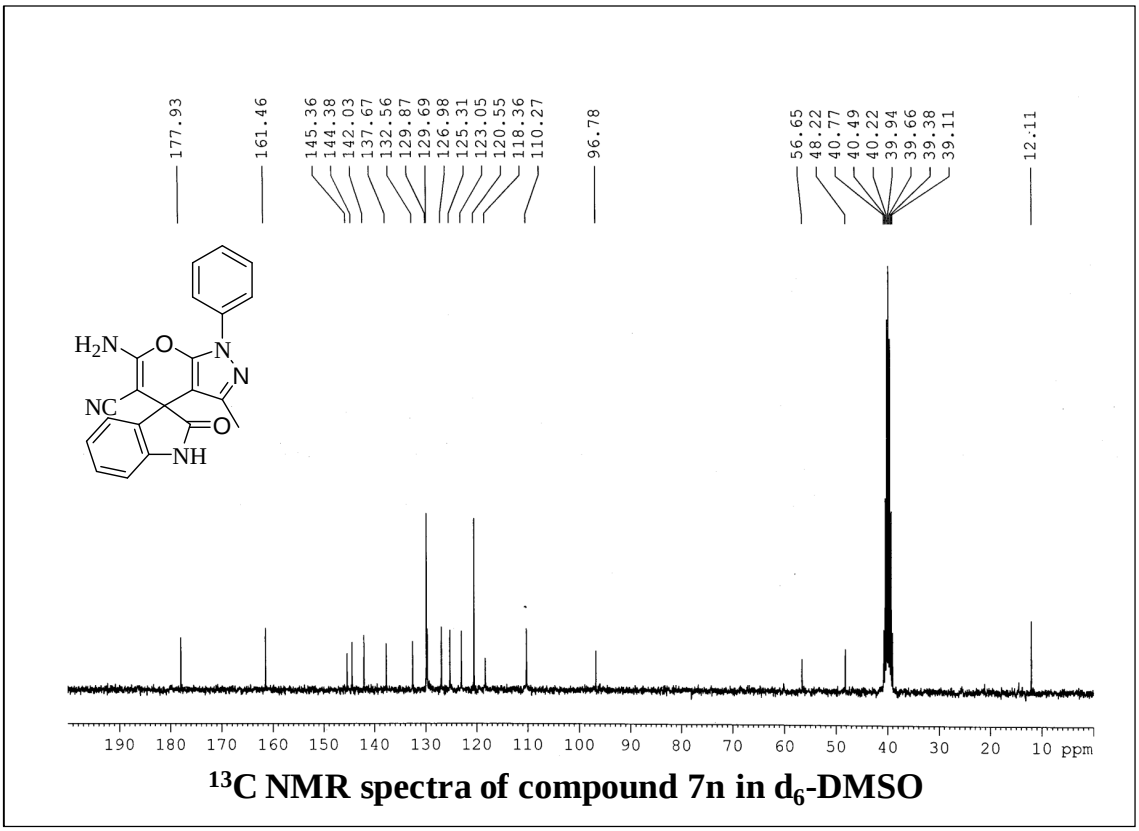
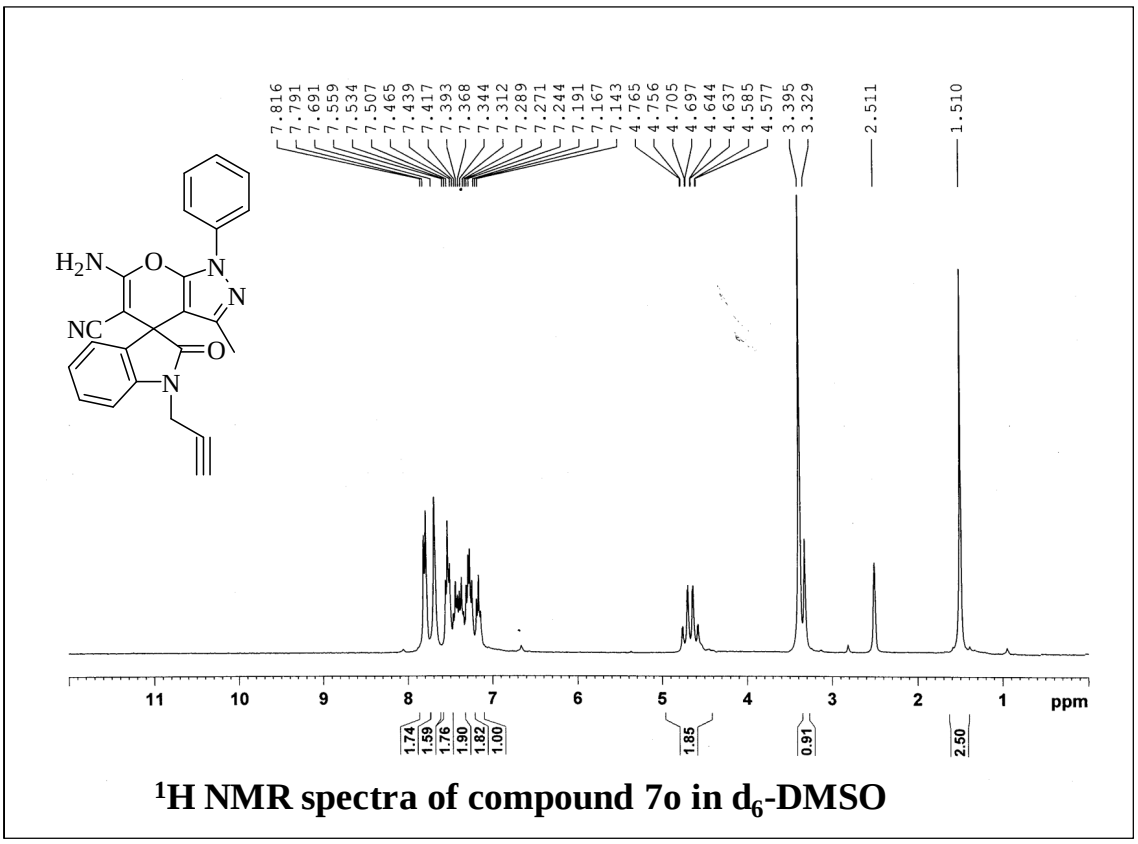
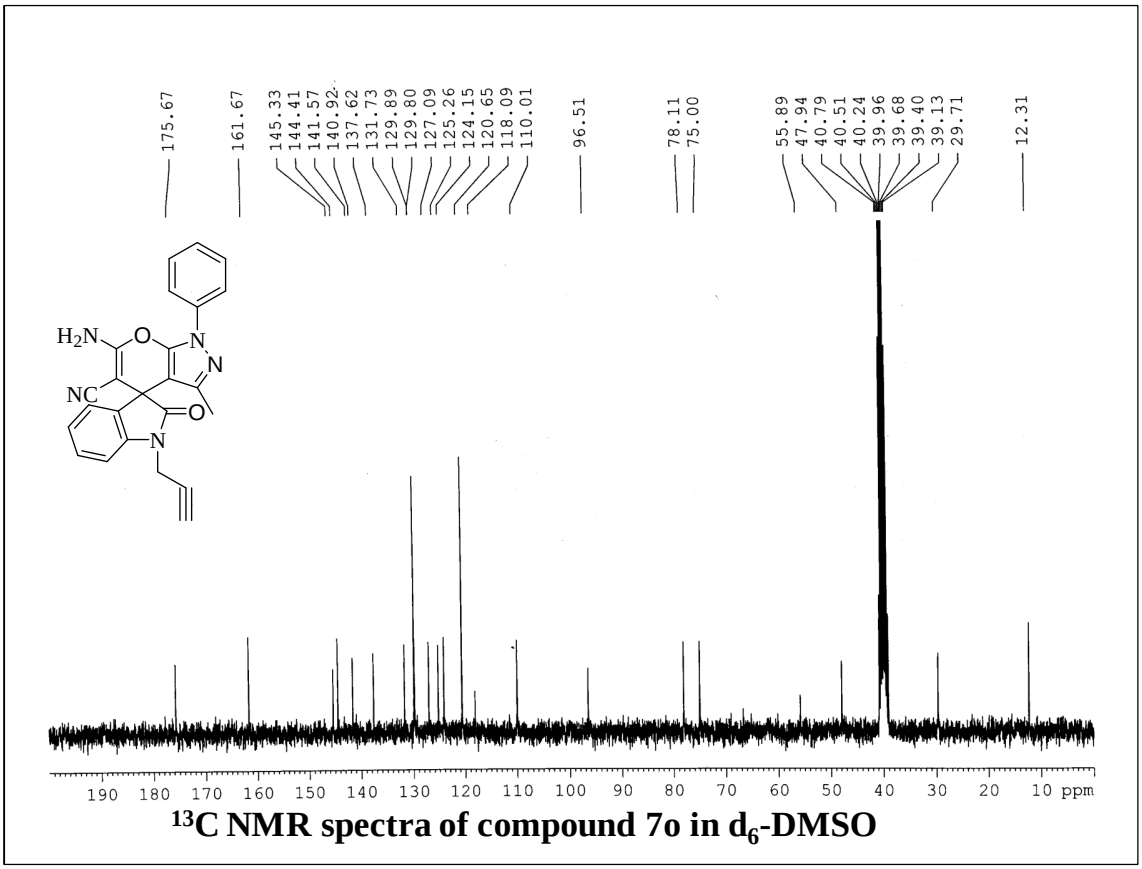


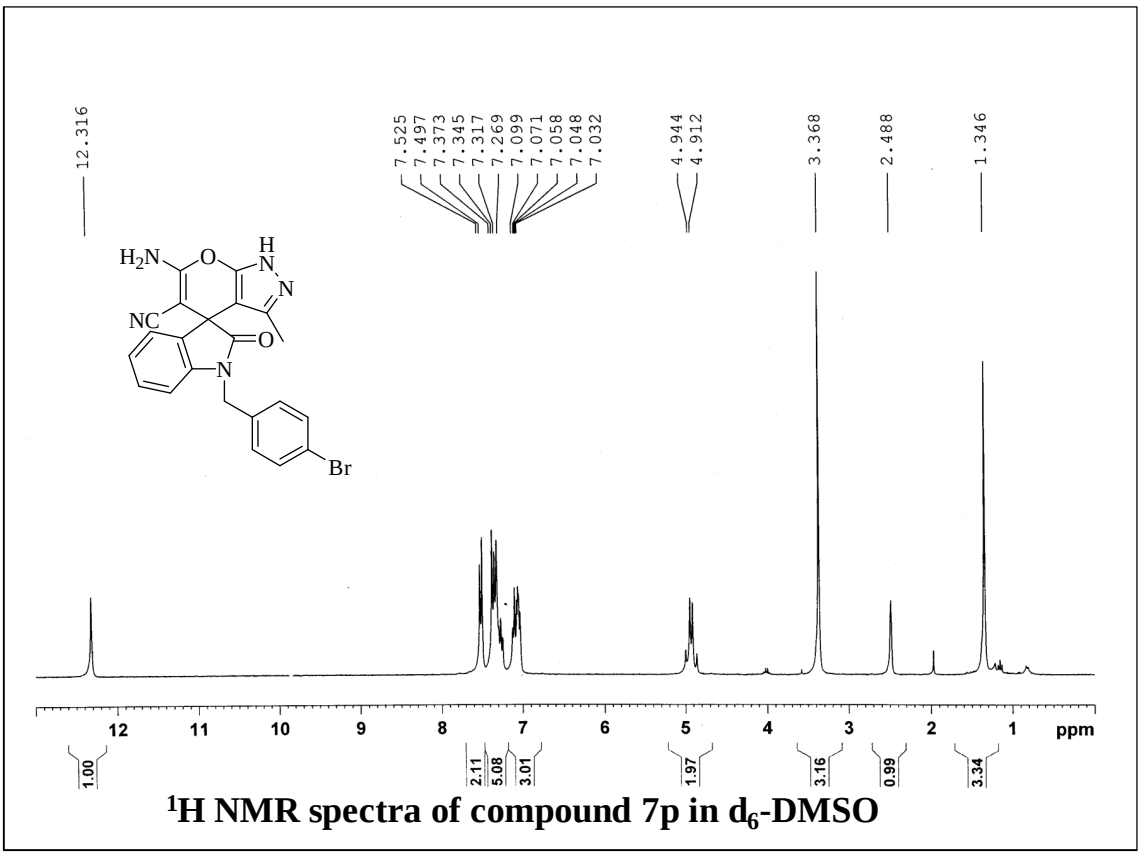
^{13}C NMR spectra of compound 7n in d_6-DMSO



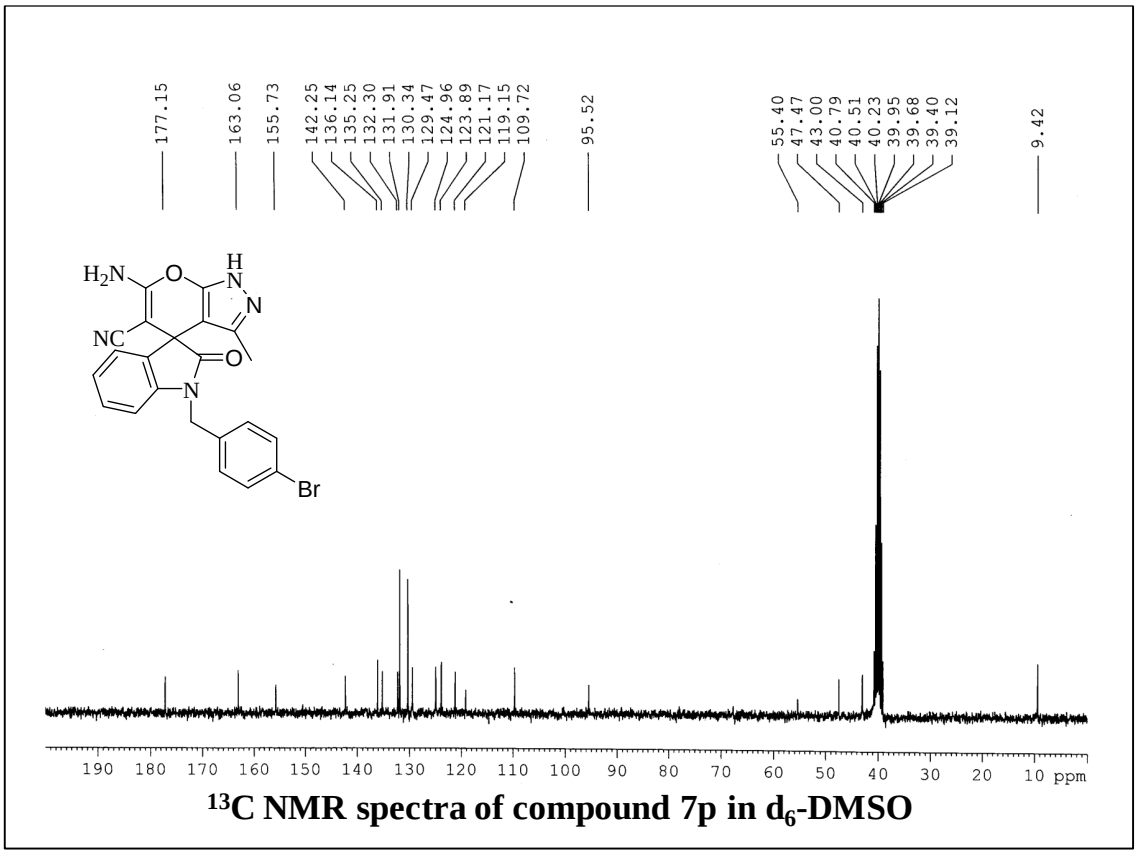
^{1}H NMR spectra of compound 7o in d_6-DMSO



^{13}C NMR spectra of compound 7o in d_6-DMSO



^{1}H NMR spectra of compound 7p in d_6-DMSO



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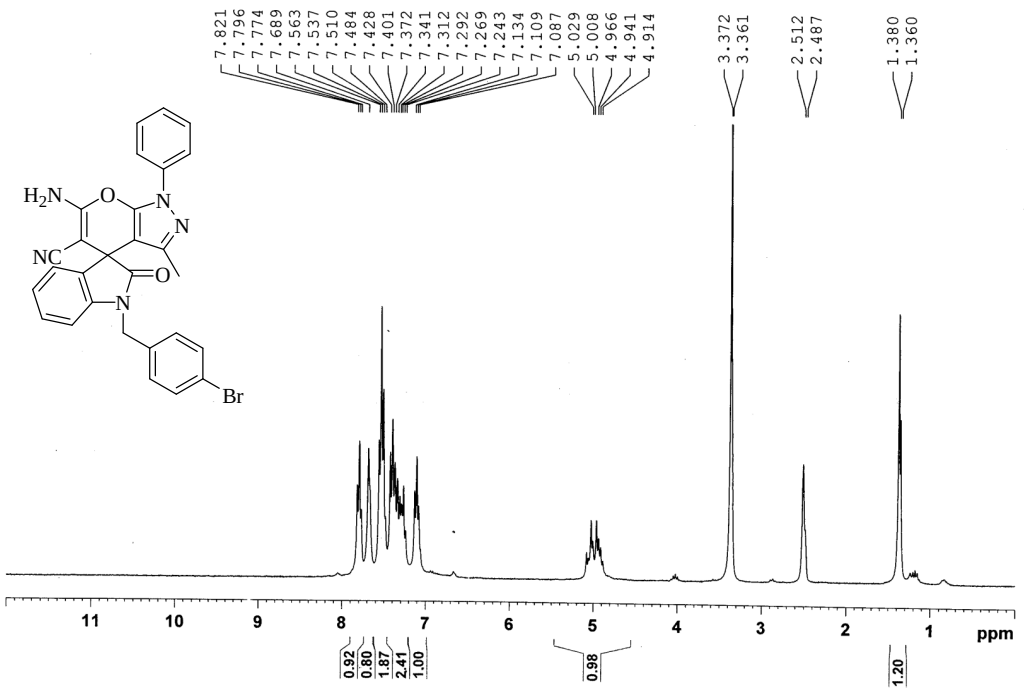
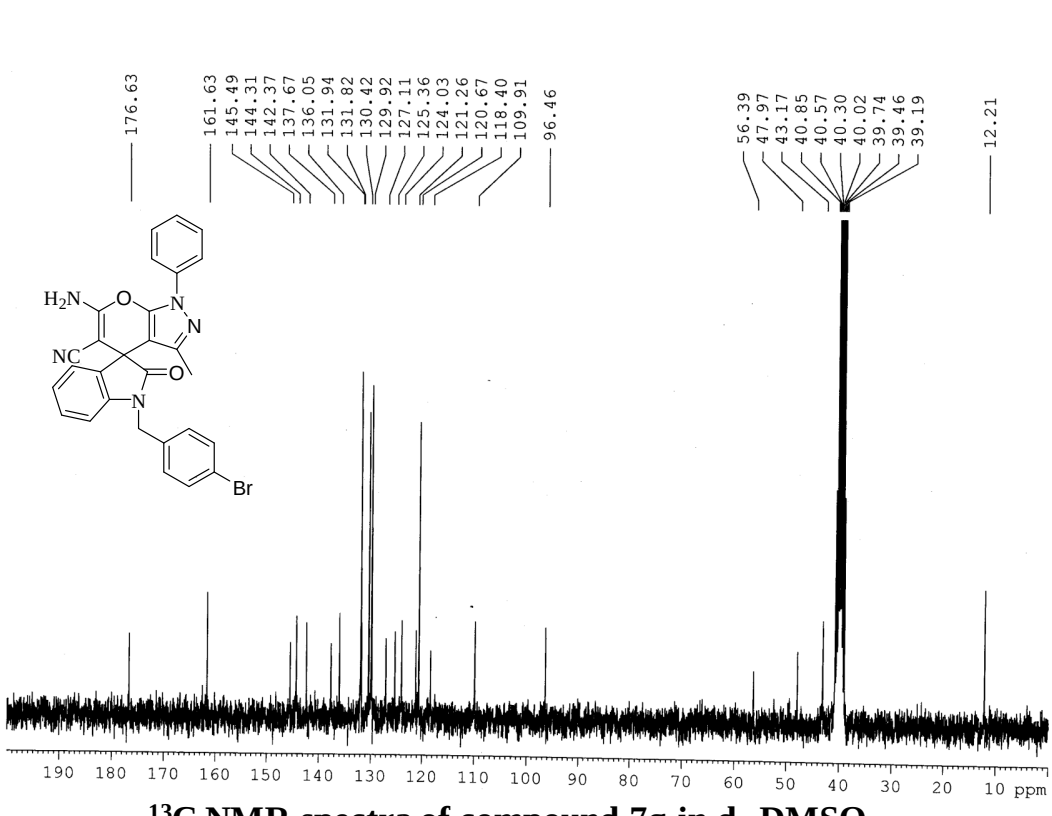


^{1}H NMR spectra of compound 7q in d_6-DMSO



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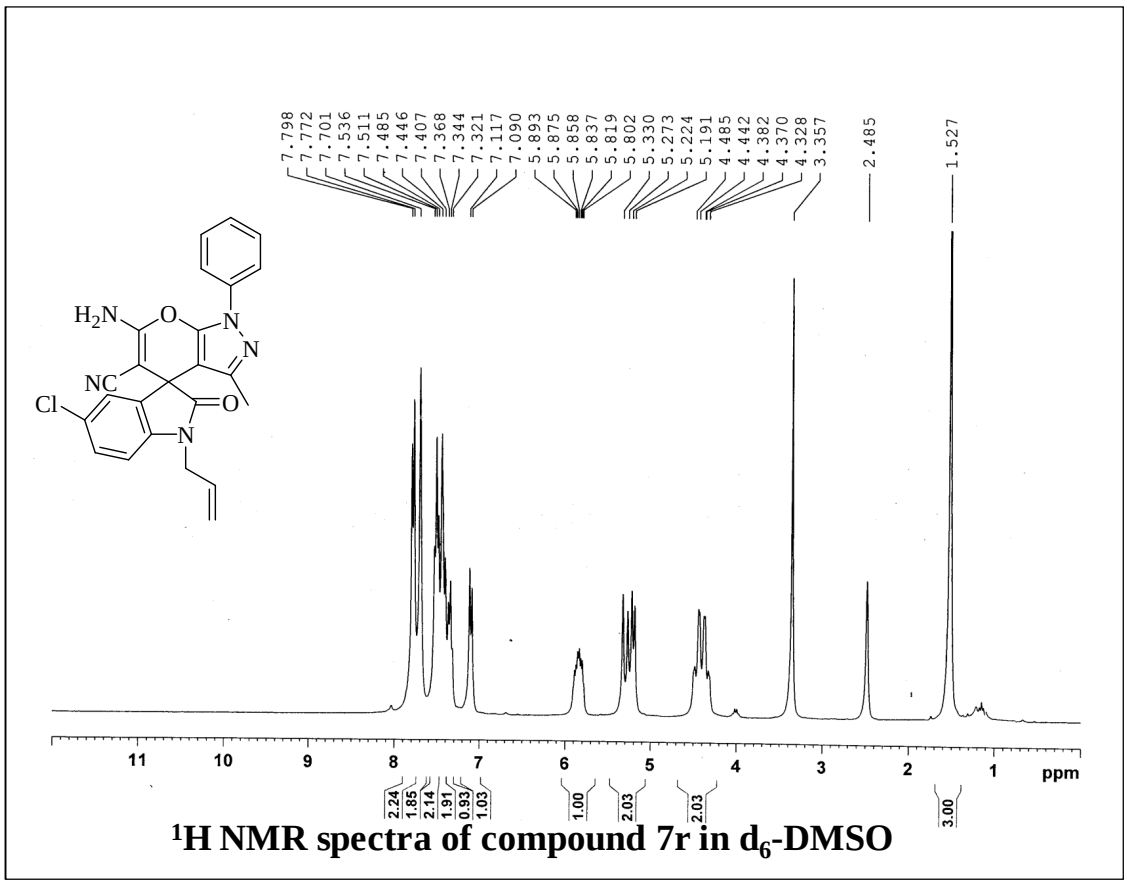

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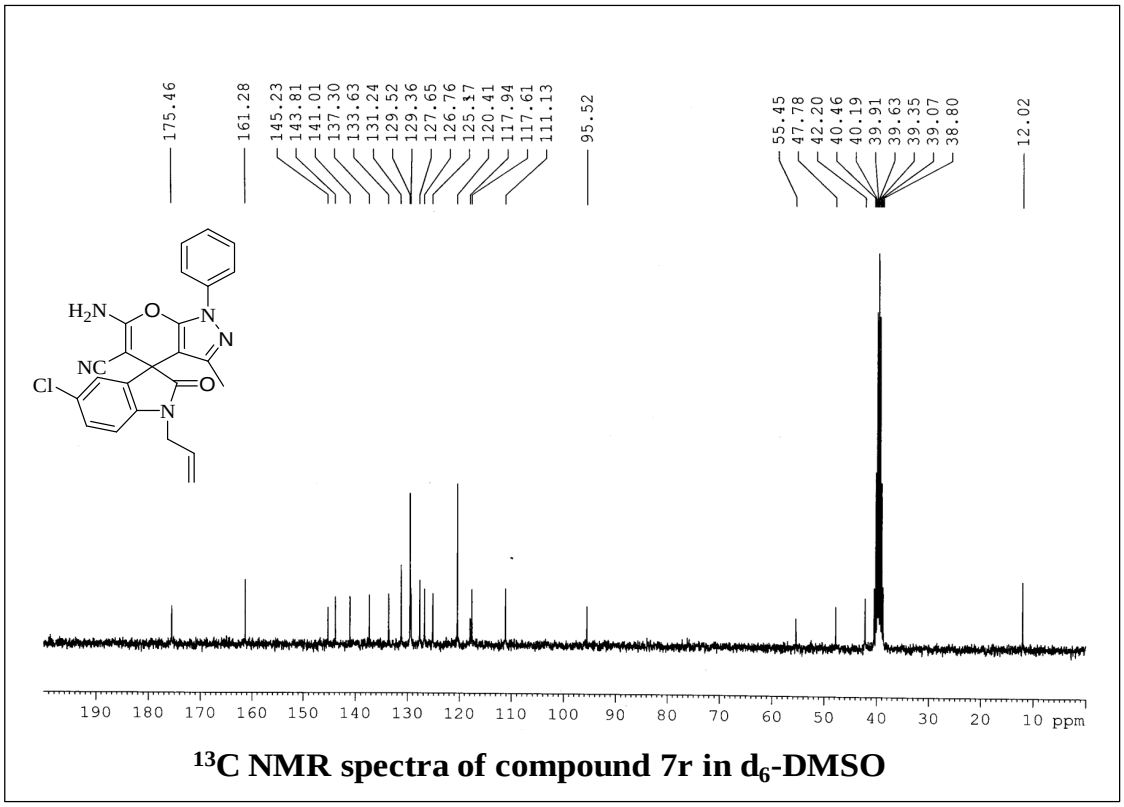
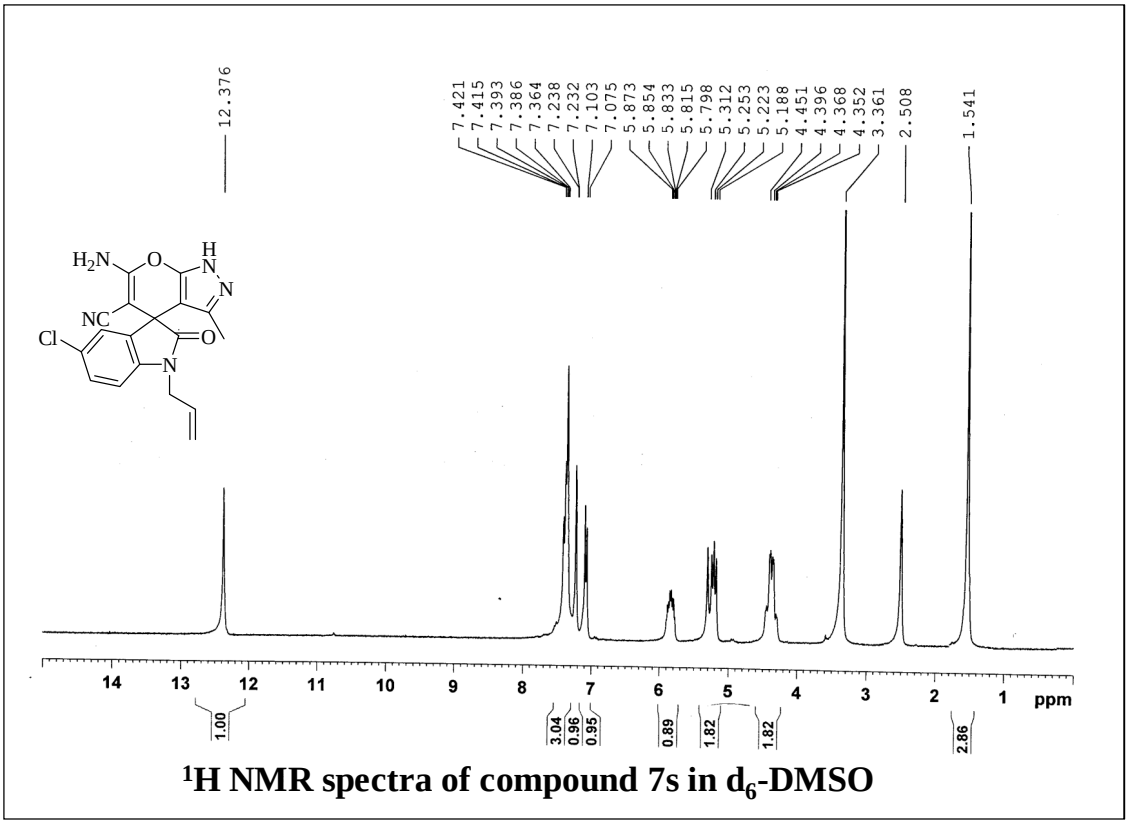
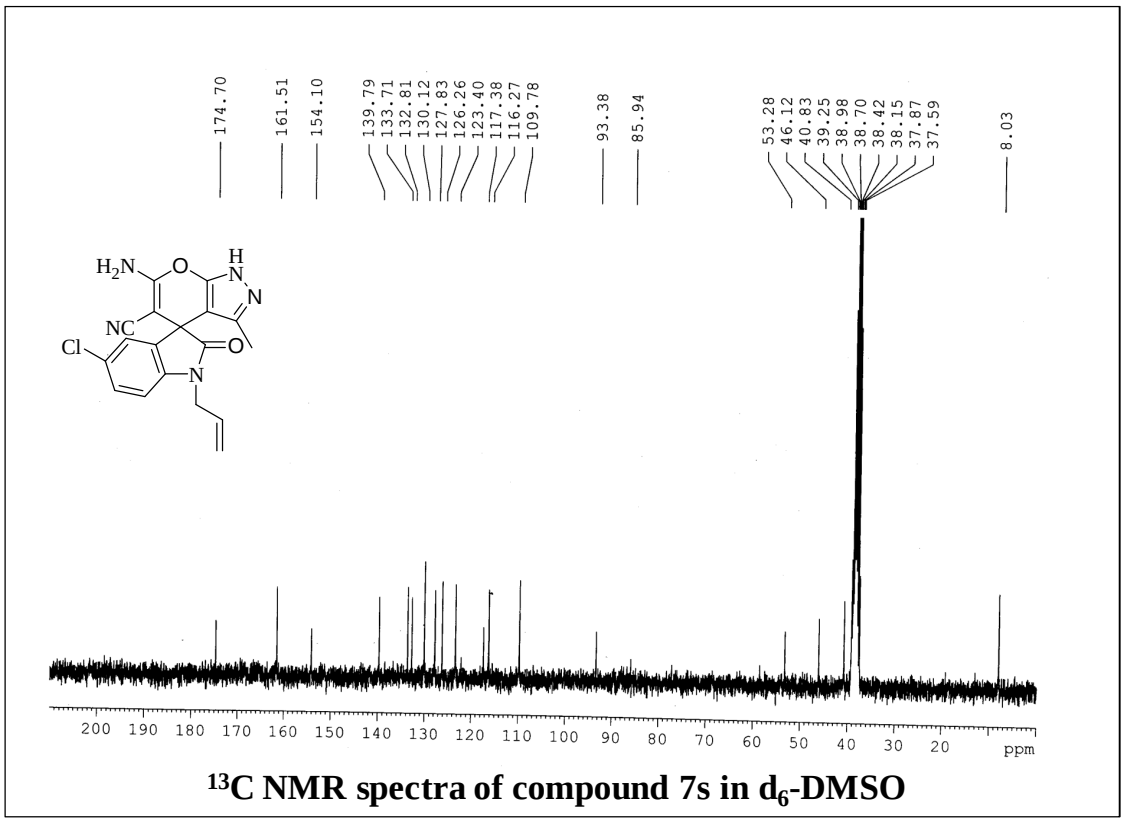


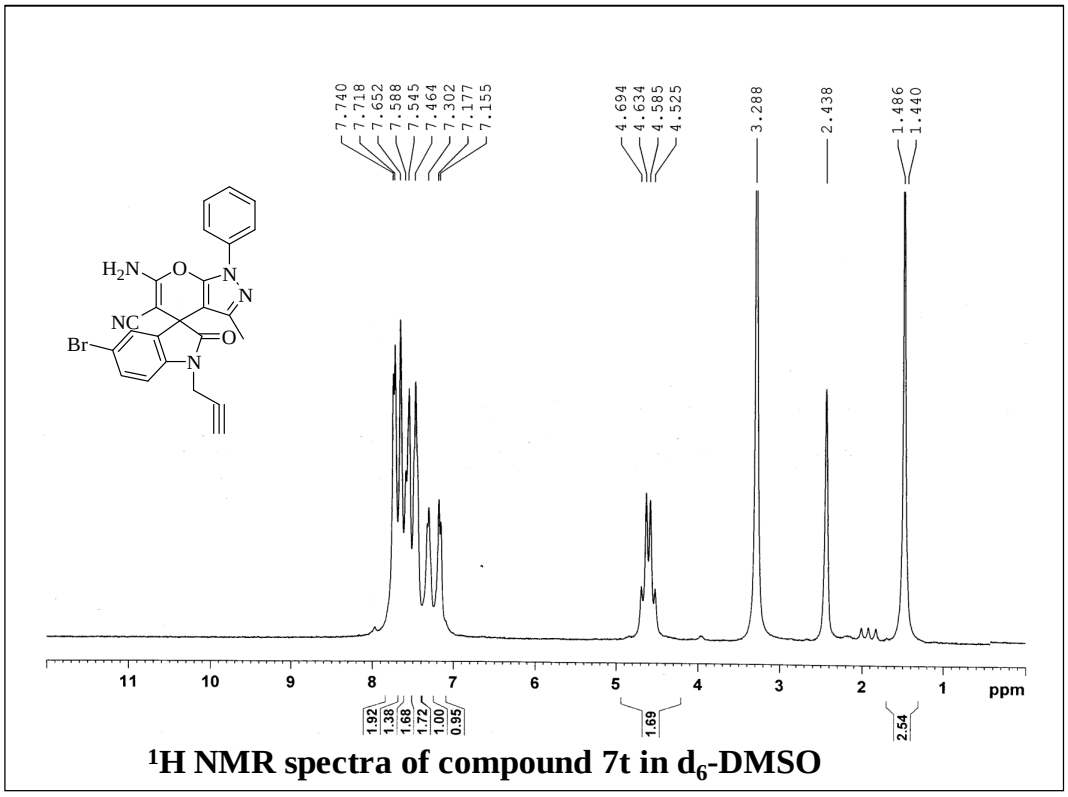
^{13}C NMR spectra of compound 7r in d_6-DMSO



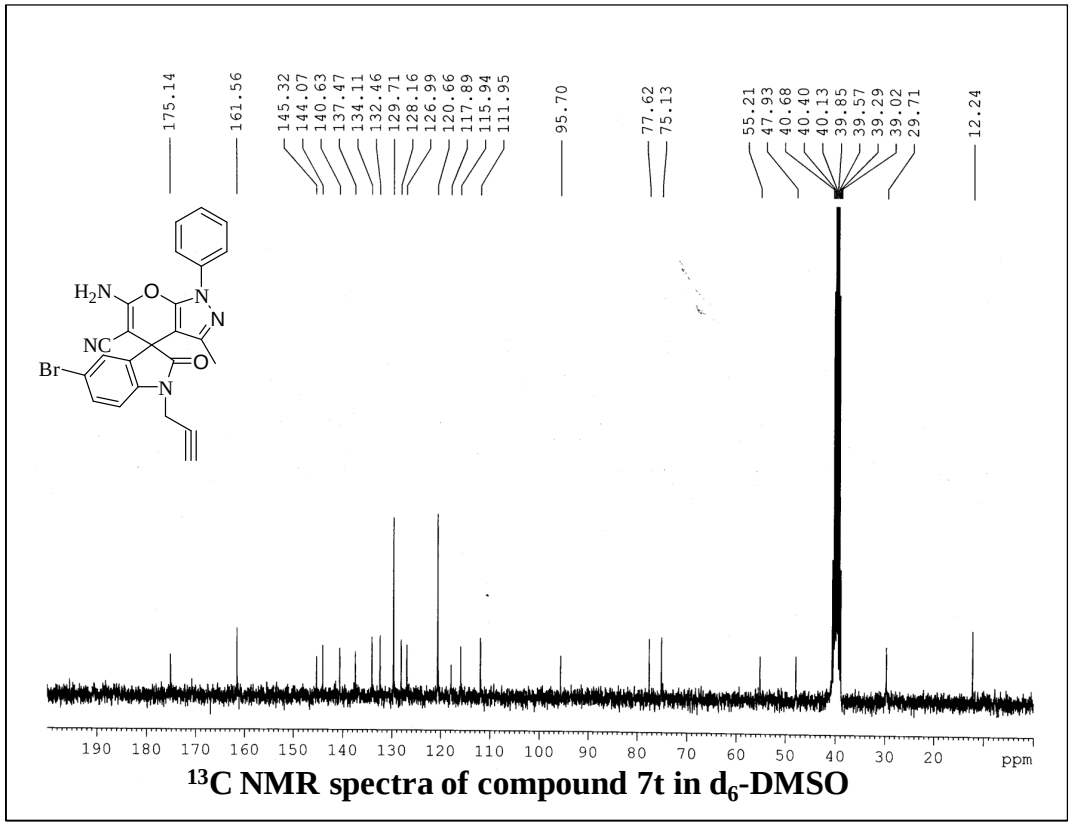
^{1}H NMR spectra of compound 7s in d_6-DMSO



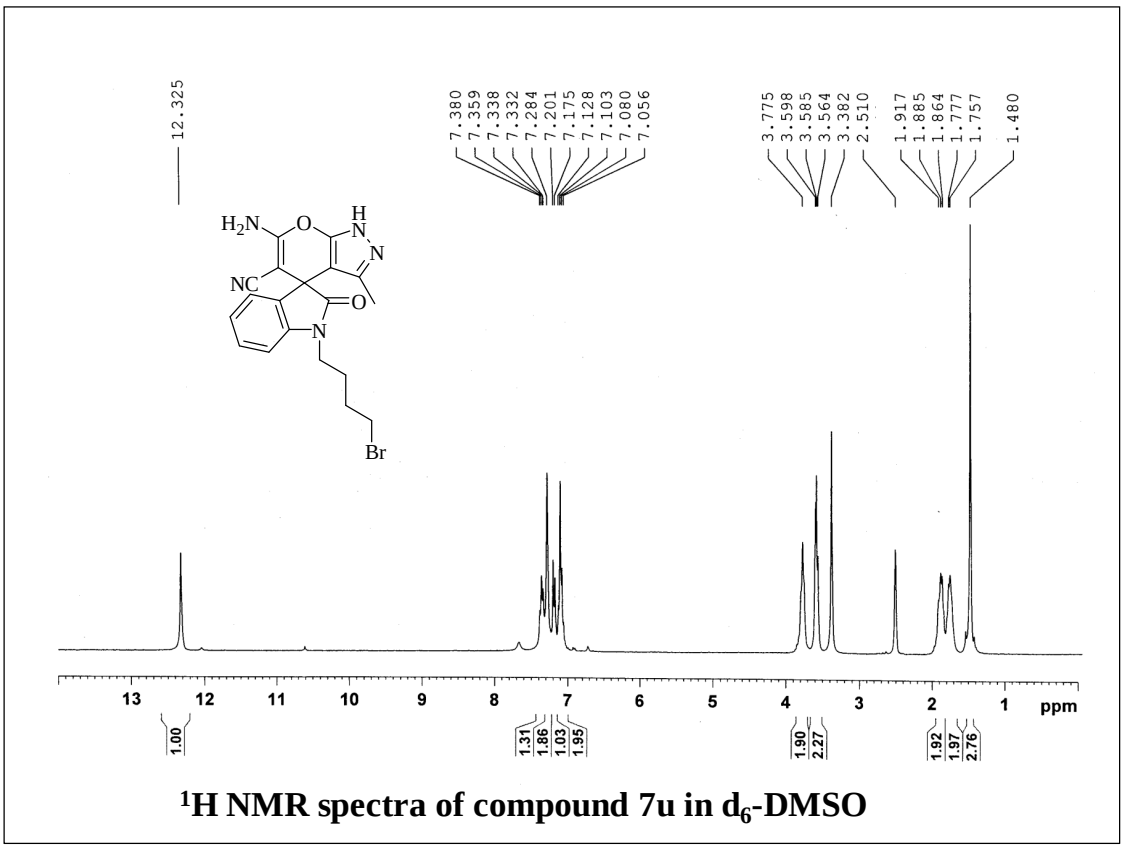
^{13}C NMR spectra of compound 7s in d_6-DMSO



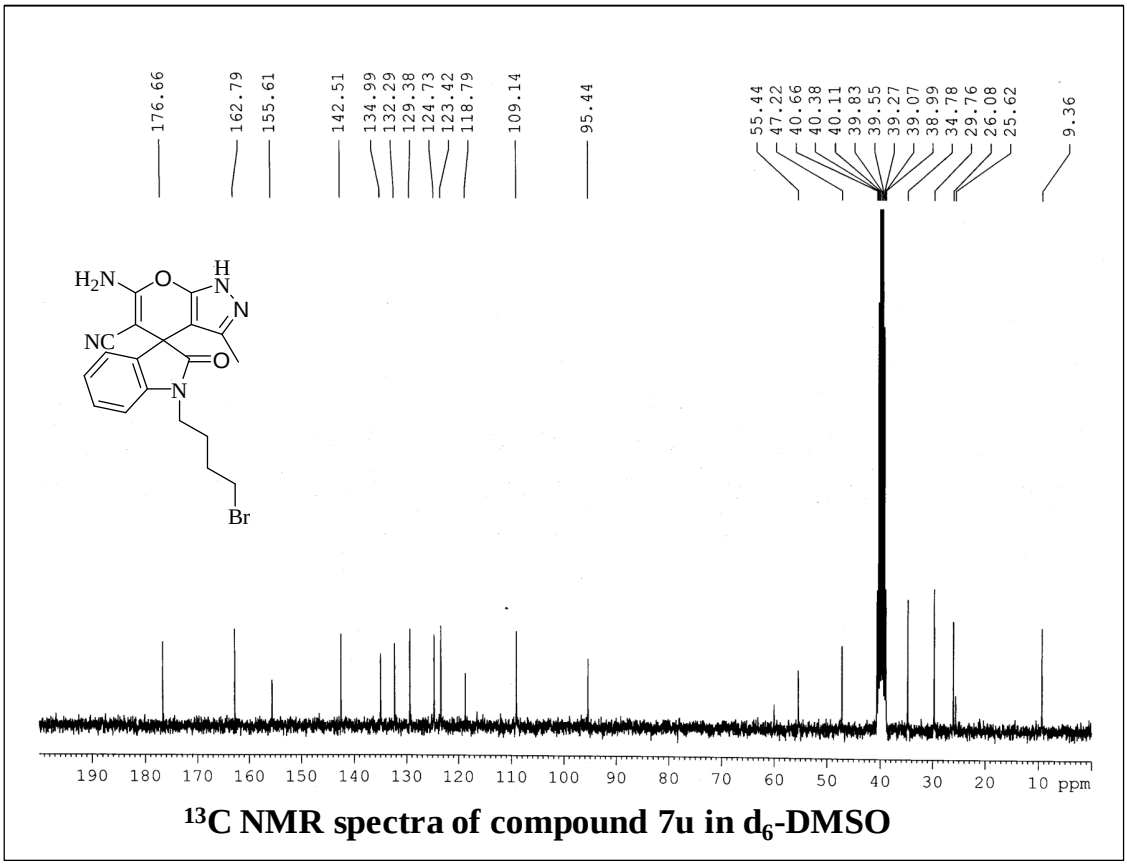
^{1}H NMR spectra of compound 7t in d_6-DMSO



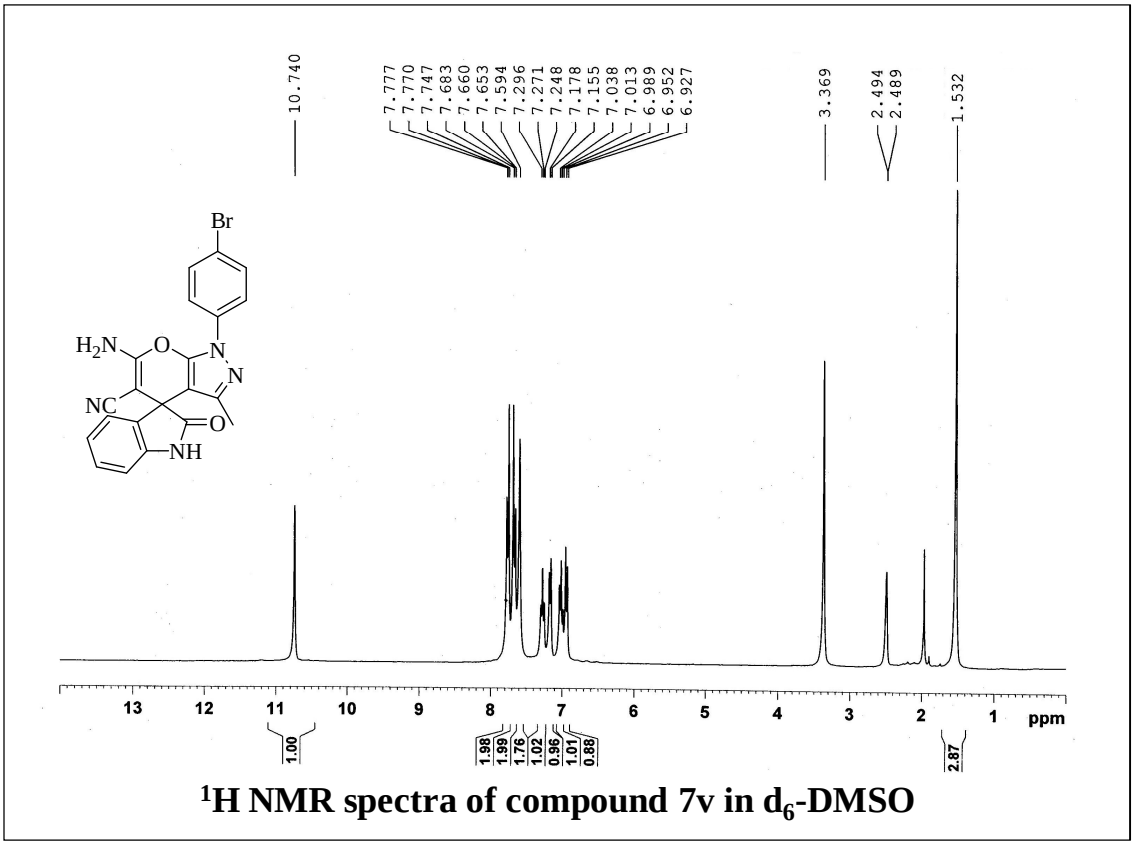
^{13}C NMR spectra of compound 7t in d_6-DMSO



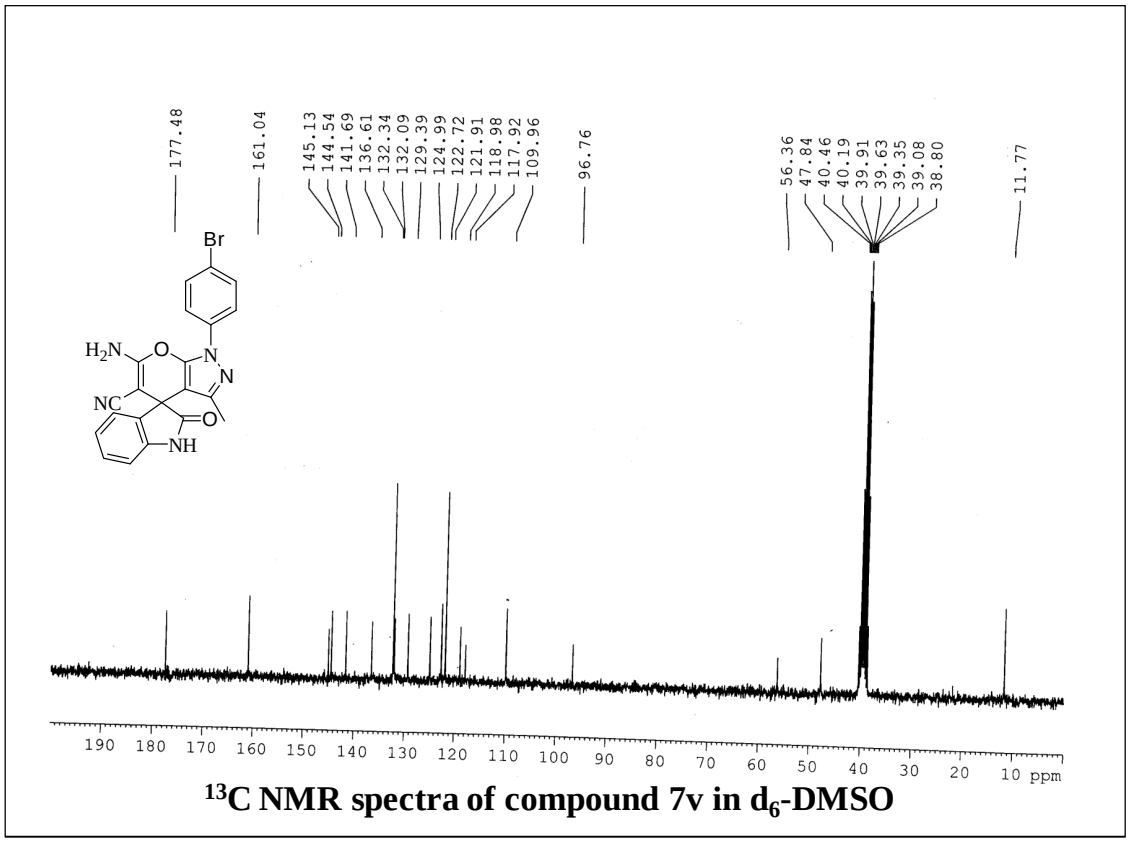
^{1}H NMR spectra of compound 7u in d_6-DMSO



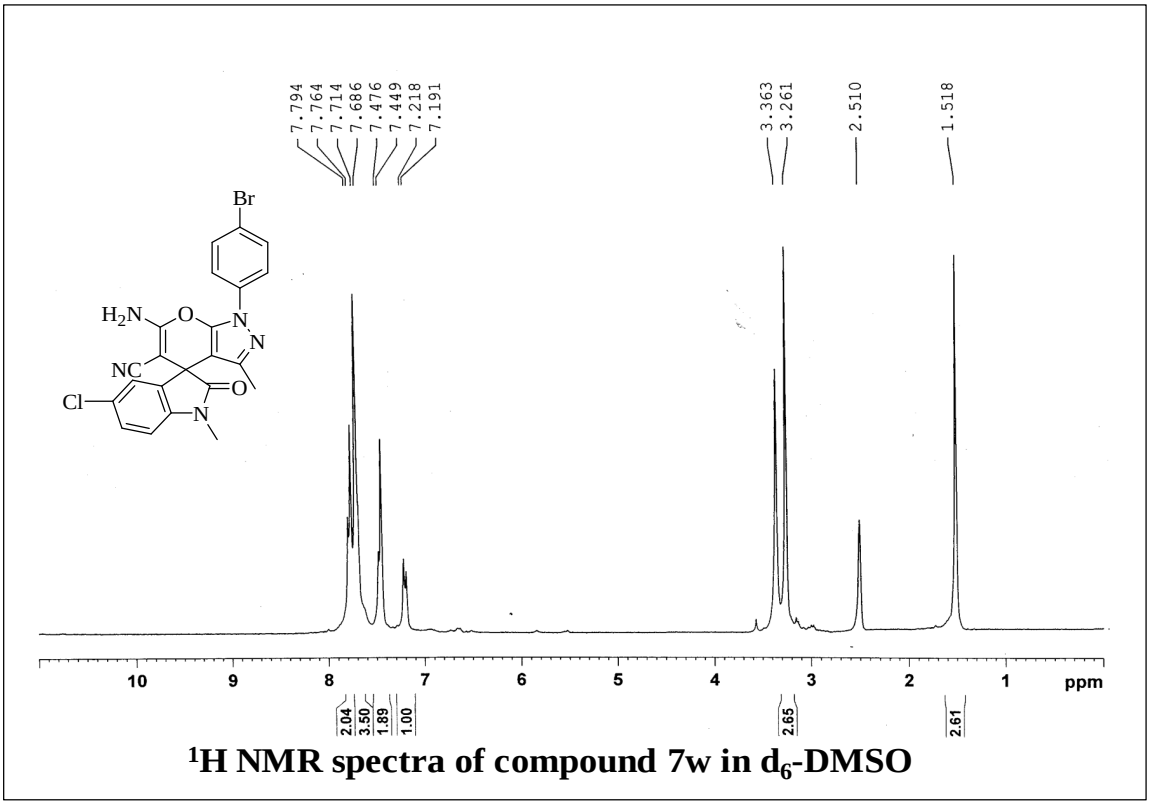
^{13}C NMR spectra of compound 7u in d_6-DMSO



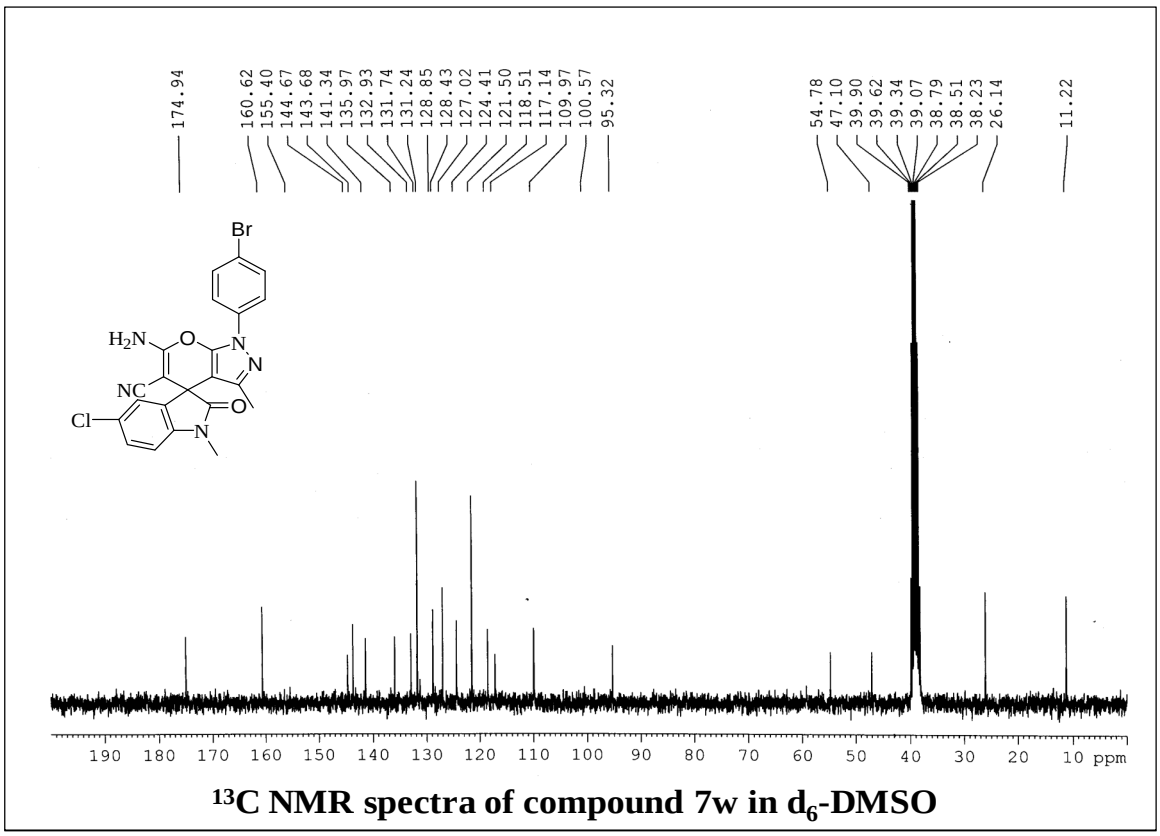
^{1}H NMR spectra of compound 7v in d_6-DMSO



^{13}C NMR spectra of compound 7v in d_6-DMSO



^{1}H NMR spectra of compound 7w in d_6-DMSO



^{13}C NMR spectra of compound 7w in d_6-DMSO

Preparation of the Catalyst:

Preparation of ZrO_2 nano particle: A solution of $ZrO_2Cl_2.8H_2O$ was condensed under a basic medium (pH ~ 10) at 0–5 °C and the solution was stirred for 24 h at 100°C. The colloidal particles were recovered by centrifugation, washed several times with water, dried and finally, the NPs were calcined at 500 °C for 4 h.[3]

UV-Vis spectrum: In the UV-Vis spectrum (Fig. S1) of freshly prepared ZrO_2 nanoparticles taken in solid state, a maxima was observed at 259 nm, which is equivalent to a band gap of 4.76 eV.[3]

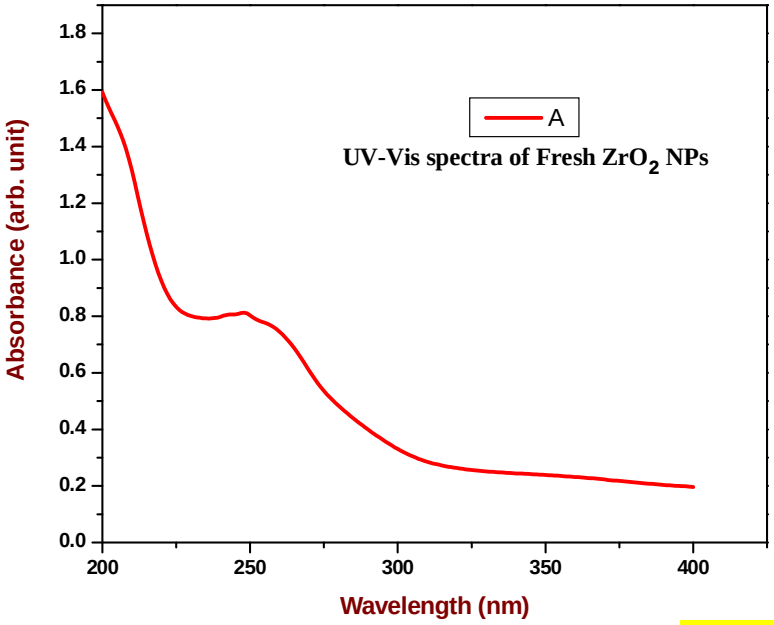


Fig. S1 UV-Vis spectrum of ZrO_2 nanoparticles in solid state

Infrared spectra: The infrared spectrum of fresh ZrO_2 was depicted in Fig. S2a. The fresh ZrO_2 showed a characteristic broad band at 3453cm^{-1} and a broad band between 1600-1635 cm^{-1}, which are assigned to the O–H modes of chemisorbed water and/or terminated hydroxides at the surface of the nanoparticles.[4,5] The infrared spectra of reused catalyst after five runs is depicted in Fig. S2b. It is important to note that all corresponding peaks are intact without any major

change in characteristics peak which indicates that structure of catalyst doesn't change even after 5 cycles.

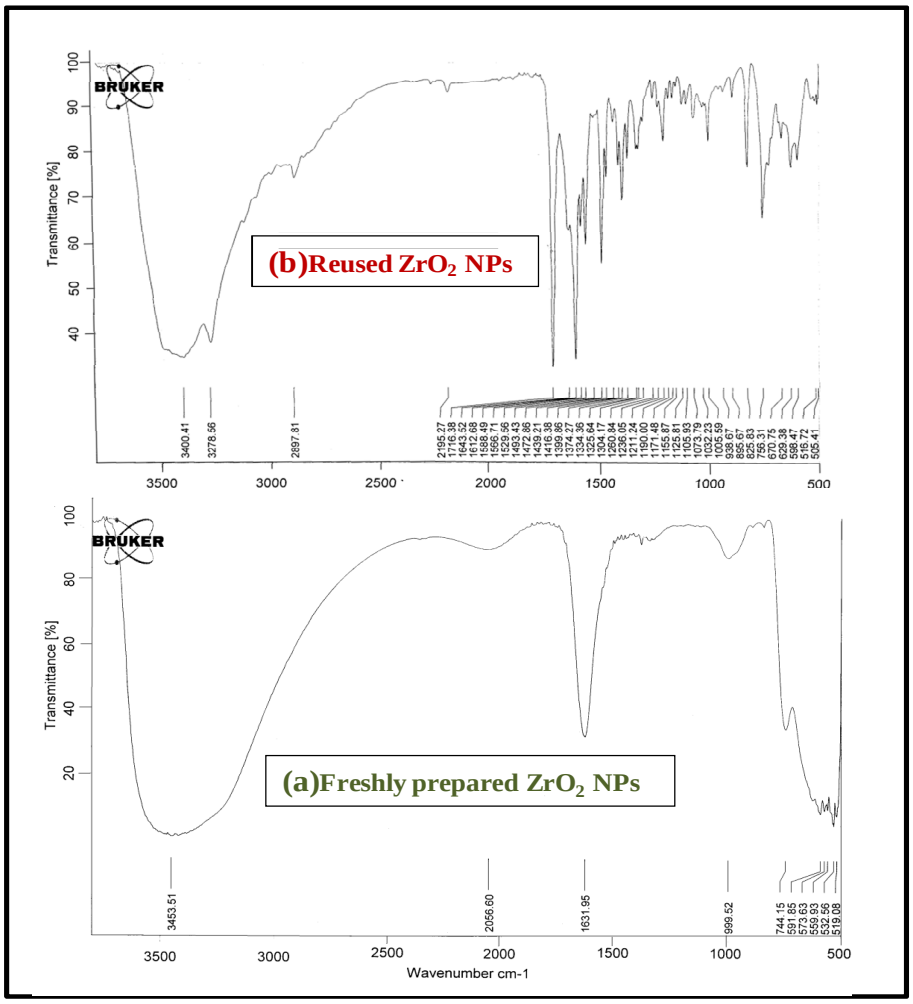


Fig. S2 (**a**) FT-IR spectra of fresh ZrO_2 NPs and (**b**) reused ZrO_2 NPs after 5th cycle

References:

3. A. Saha, S. Payra and S. Banerjee, *Green Chem.*, 2015, **17**, 2859.

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5. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1997.

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