Supporting Information

Magnetically separable Fe_3O_4-SO_3H nanoparticles as an efficient solid acid support for the facile synthesis of two types of spiroindole fused dihydropyridine derivatives under solvent free conditions

Kamalesh Debnath, Krishnadipti Singha and Animesh Pramanik*

Department of Chemistry, University of Calcutta, 92, A. P. C. Road, Kolkata-700 009, India;

Fax: +91-33-2351-9755; Tel: +91-33-2484-1647.

E-mail: animesh_in2001@yahoo.co.in

Contents **Page No.**

Reaction Scheme:

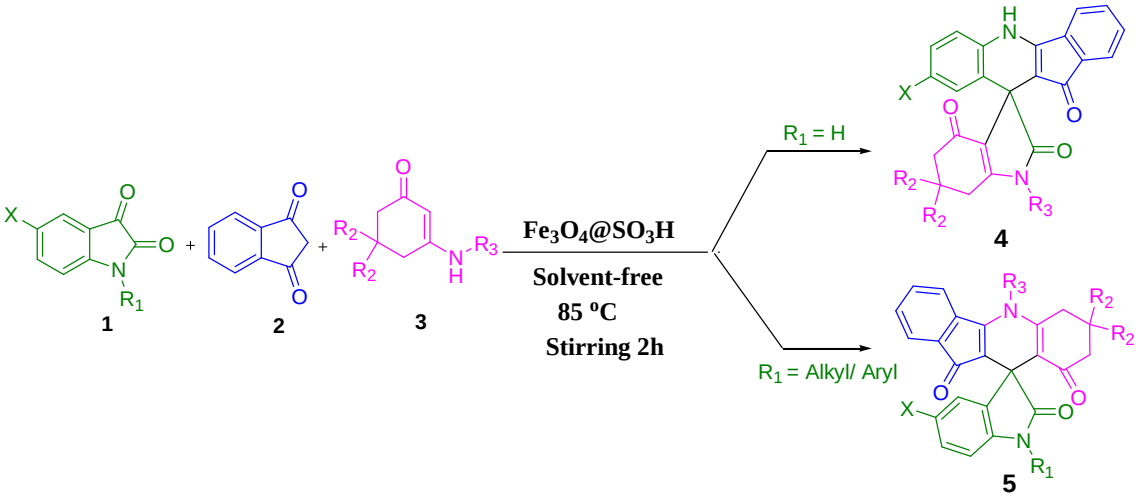
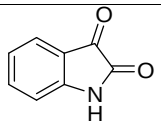
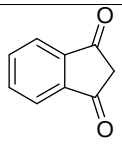
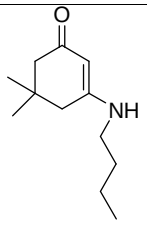
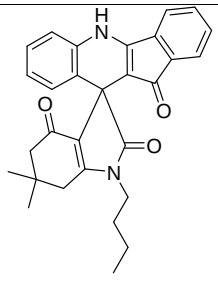
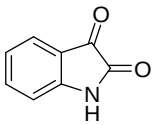
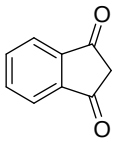
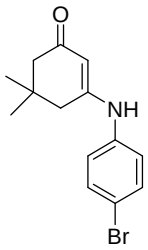
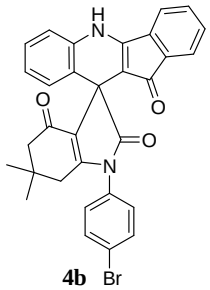
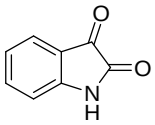
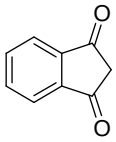
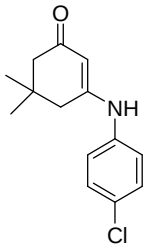
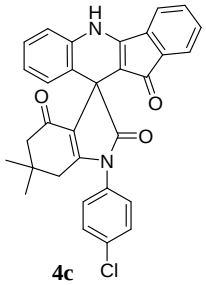
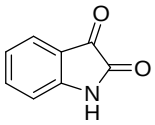
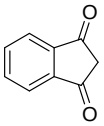
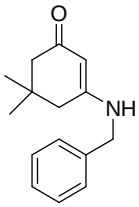
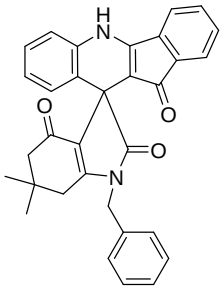
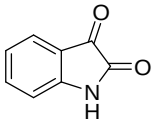
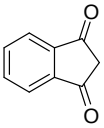
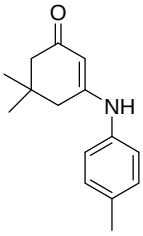
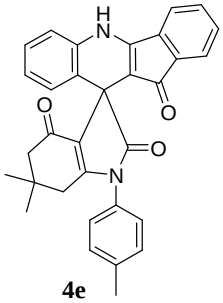
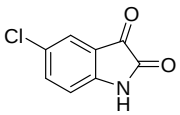
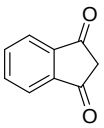
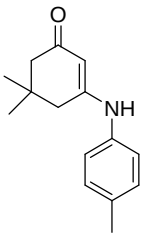
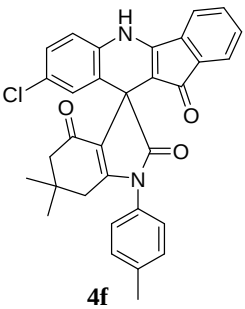
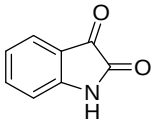
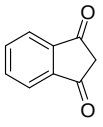
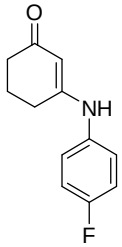
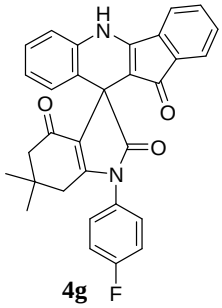
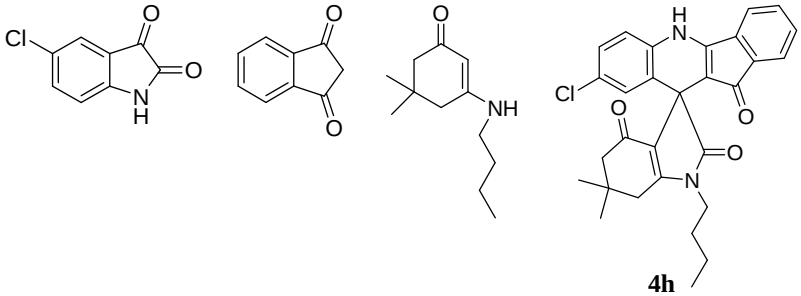
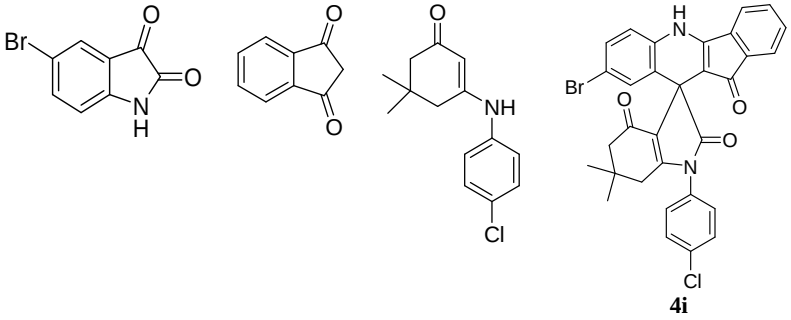
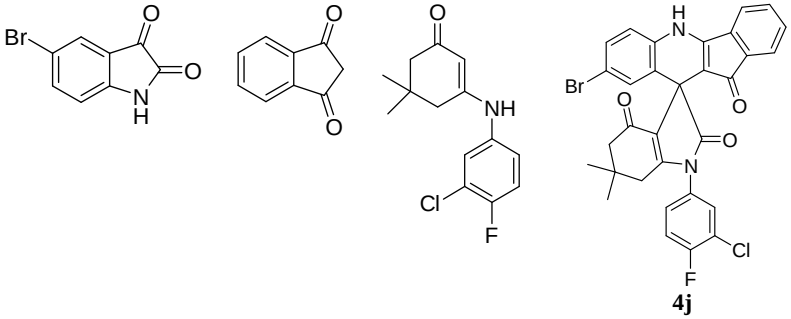
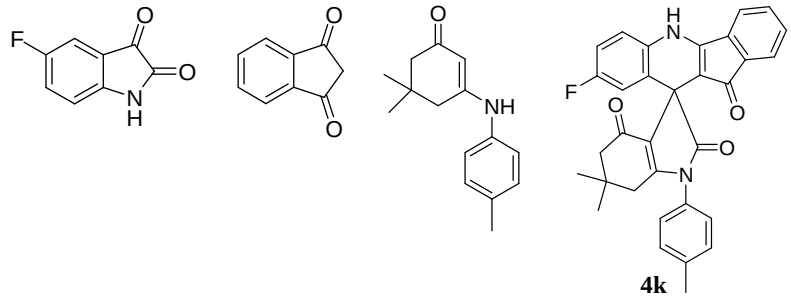
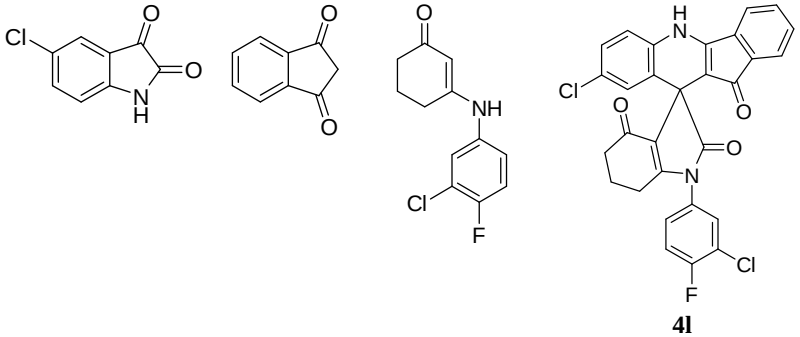
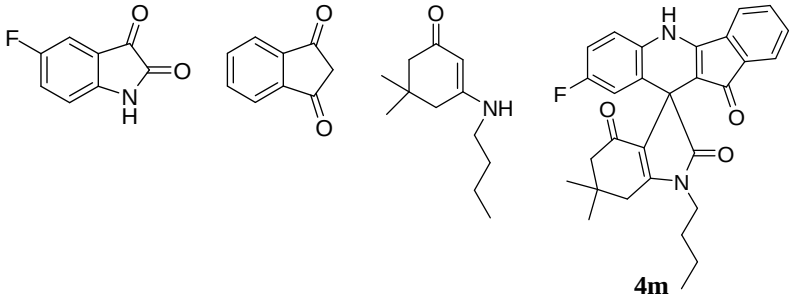
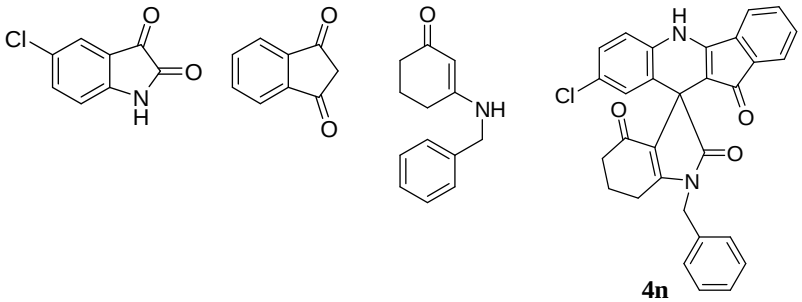
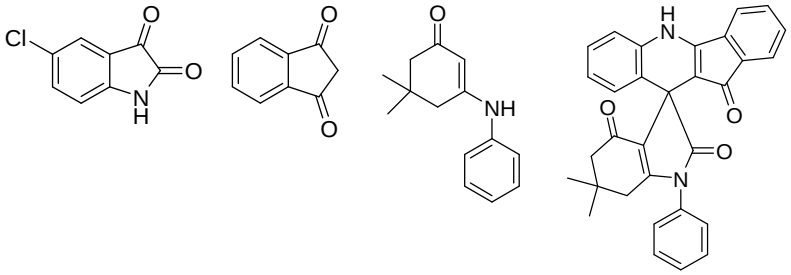


Table S1: Synthesis of spiro[indolo-3,10′-indeno[1,2-*b*]quinolin]-2,4,11′-triones **4a**–**n** through a three-component reaction

Entry	1	2	3	Product (4)	Yield[a] (%)	Melting Point/ Literature m.p[1] (°C)
1				 **4a**	85	>310/335-342
2				 **4b**	80	>310/336-340

3				 **4c**	81	>310/332-338
4				 **4d**	79	>310/>350
5				 **4e**	88	>310/335-342
6				 **4f**	76	>310
7				 **4g**	78	>310

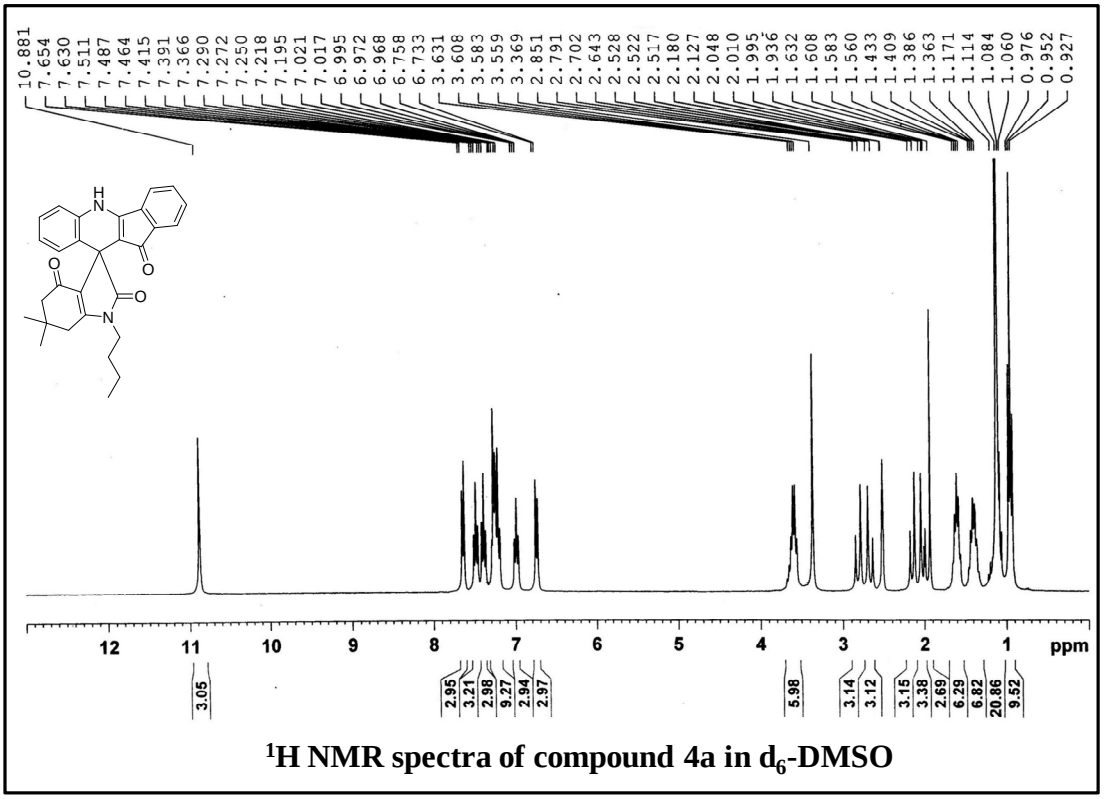
8	 **4h**				87	>310/314-320
9	 **4i**				75	>310
10	 **4j**				74	>310
11	 **4k**				74	>310
12	 **4l**				78	300-302

13	 **4m**				82	>310
14	 **4n**				85	>310
15	 **4o**				86	>310/338-344

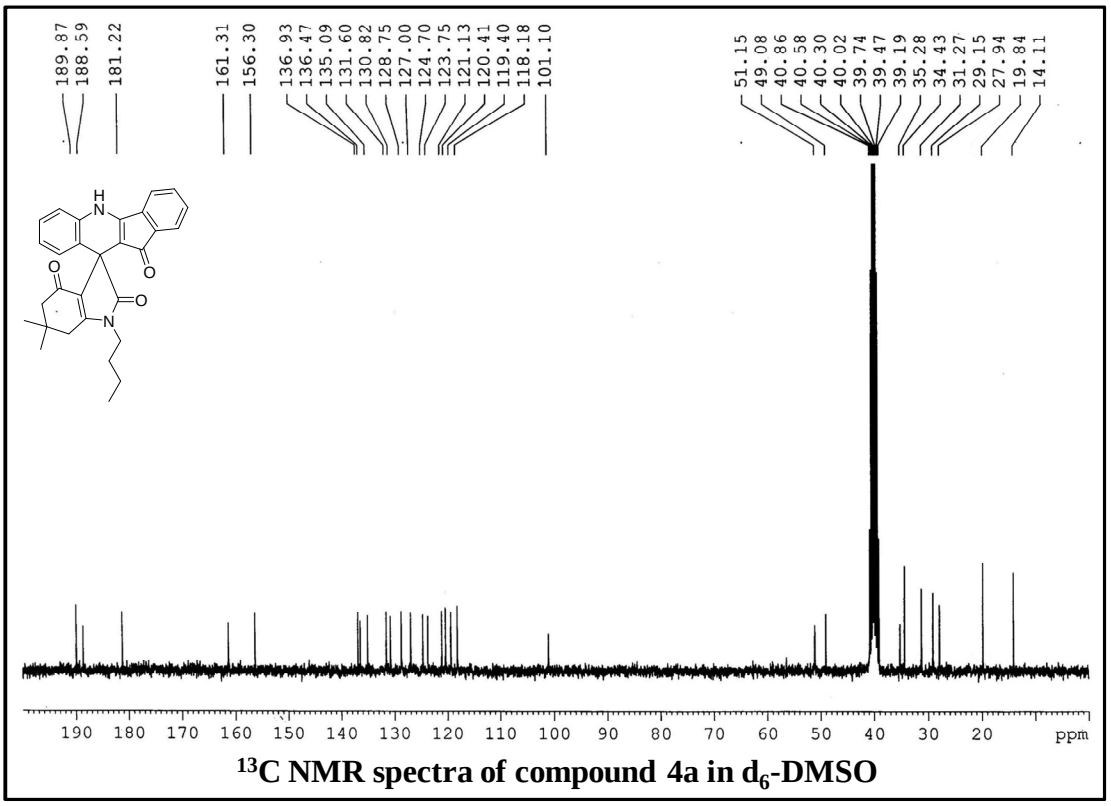
[a]Isolated Yields (%)

1 A. Mondal, M. Brown and C. Mukhopadhyay, *RSC Adv.*, 2014, **4**, 36890.

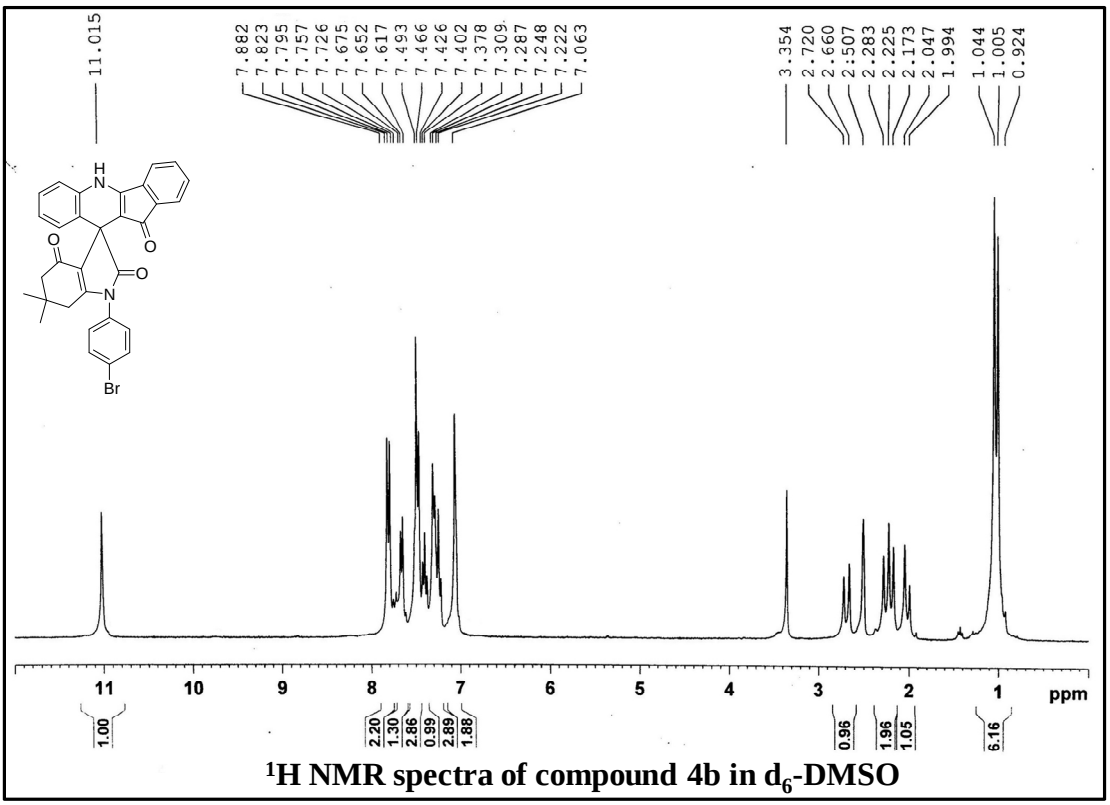
Spectral Data of 4a-n:



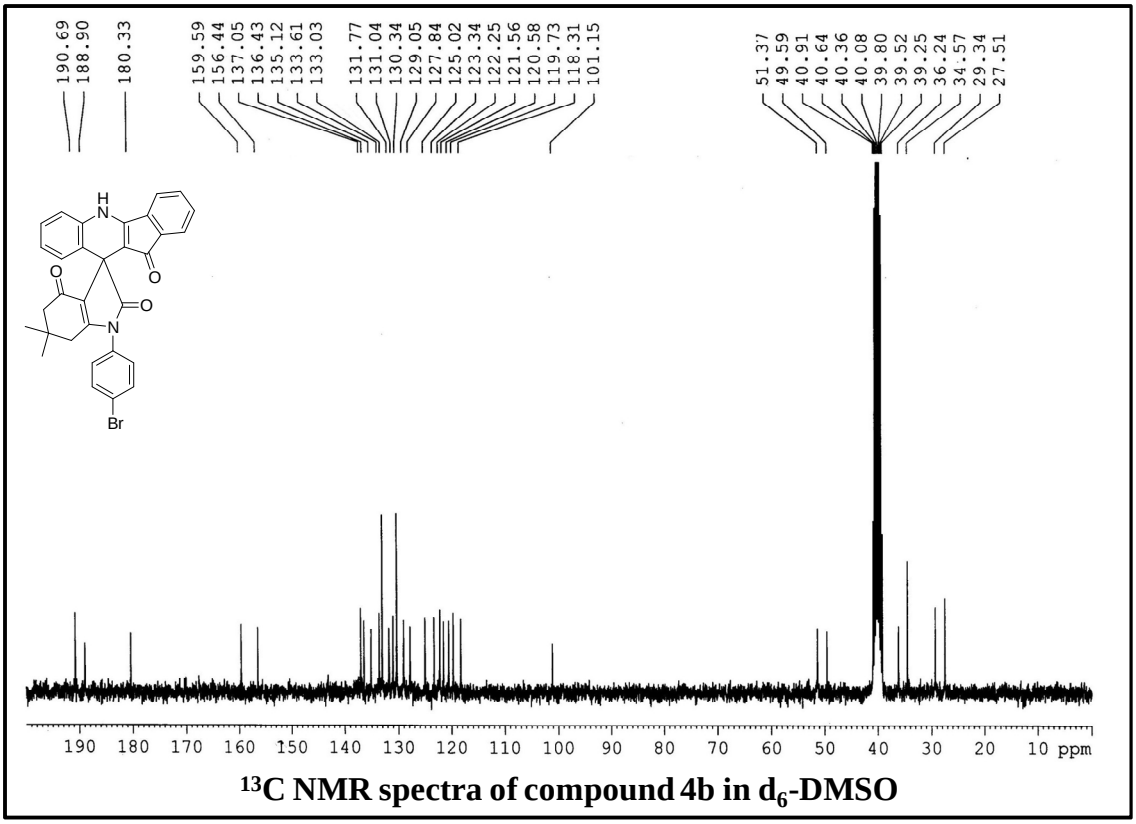
^{1}H NMR spectra of compound 4a in d_6-DMSO



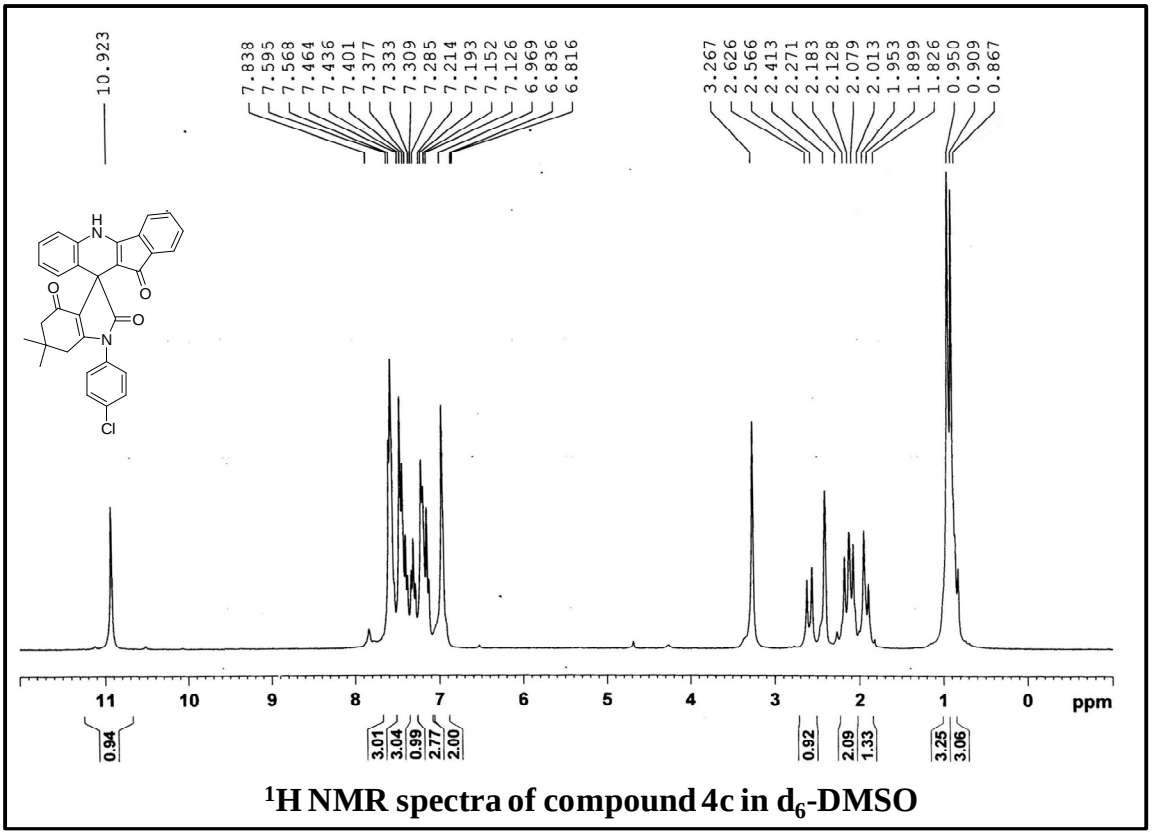
^{13}C NMR spectra of compound 4a in d_6-DMSO



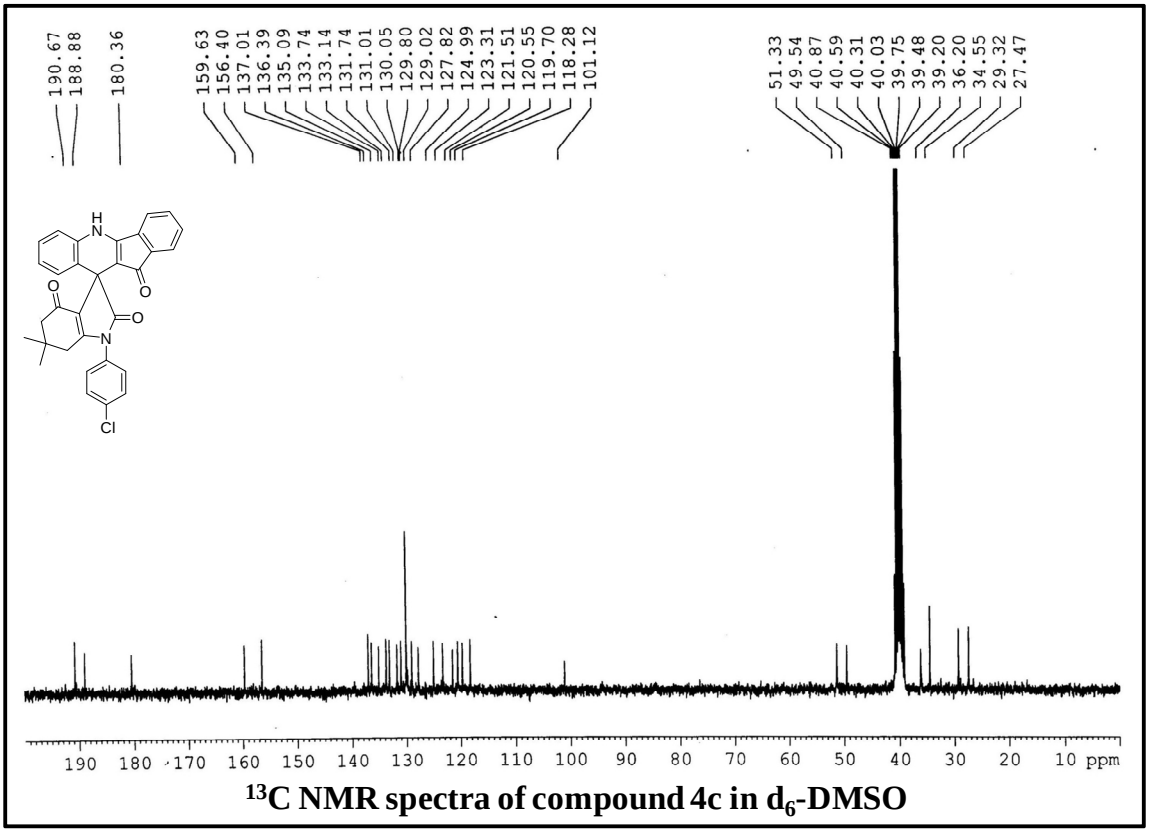
^{1}H NMR spectra of compound 4b in d_6-DMSO



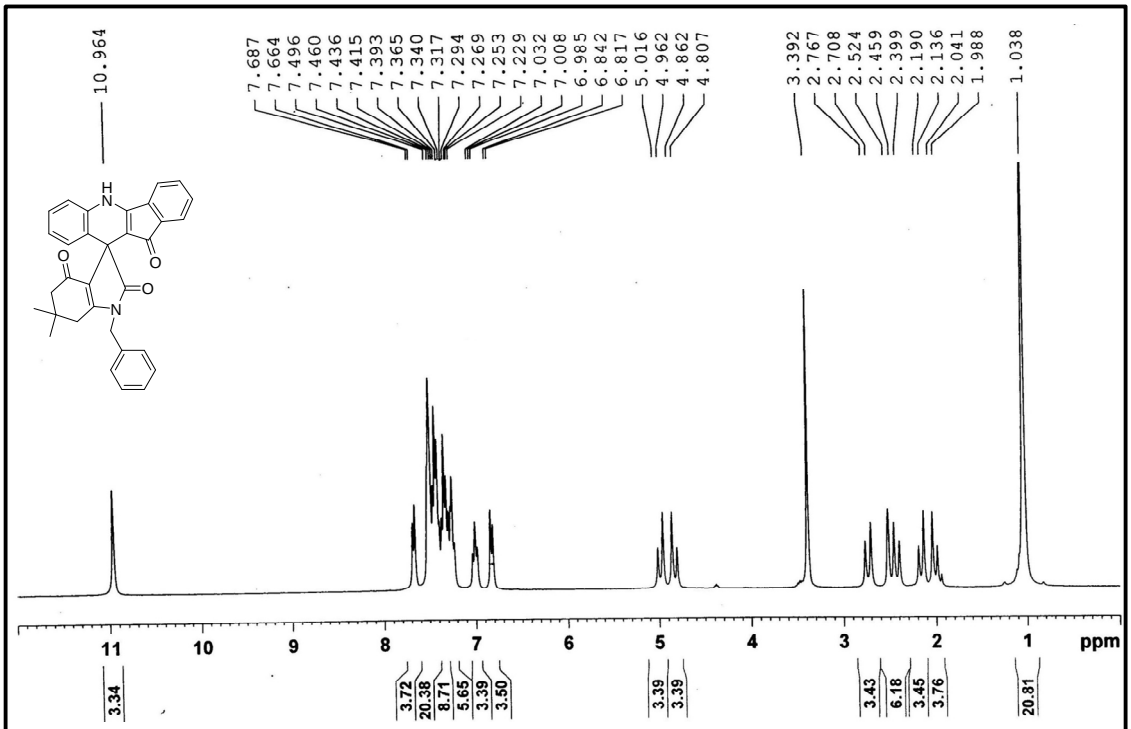
^{13}C NMR spectra of compound 4b in d_6-DMSO



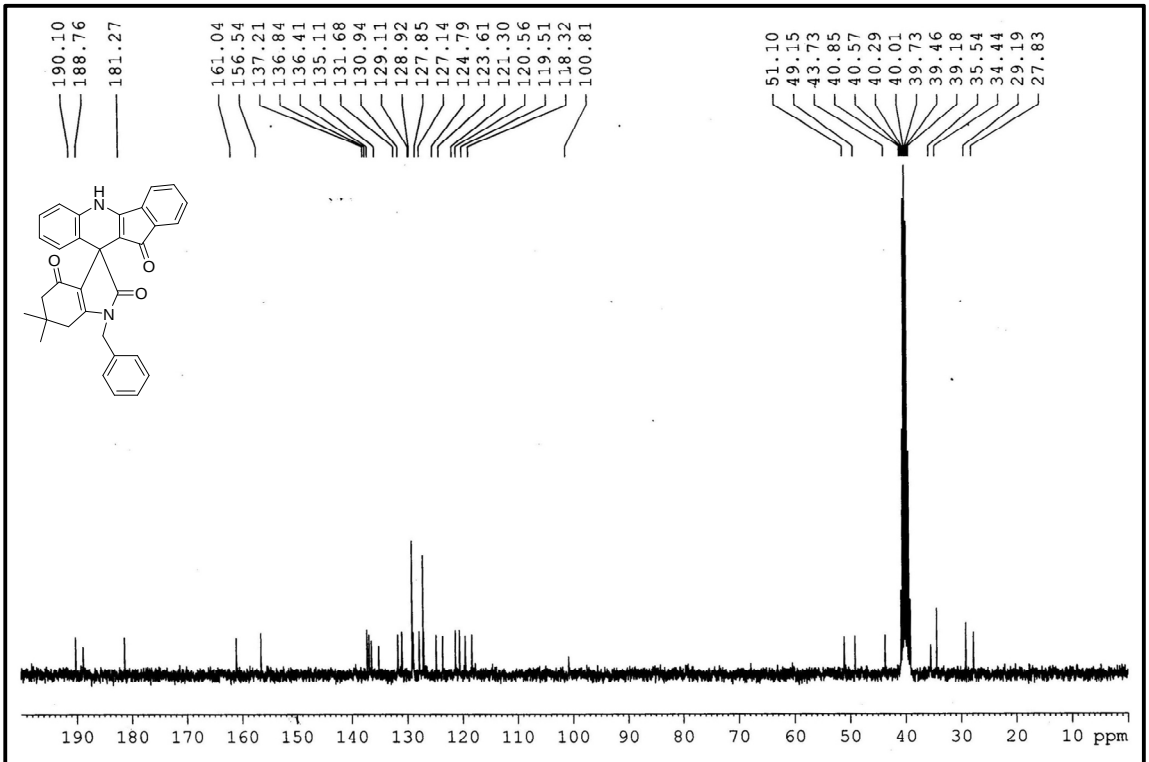
^{1}H NMR spectra of compound 4c in d_6-DMSO



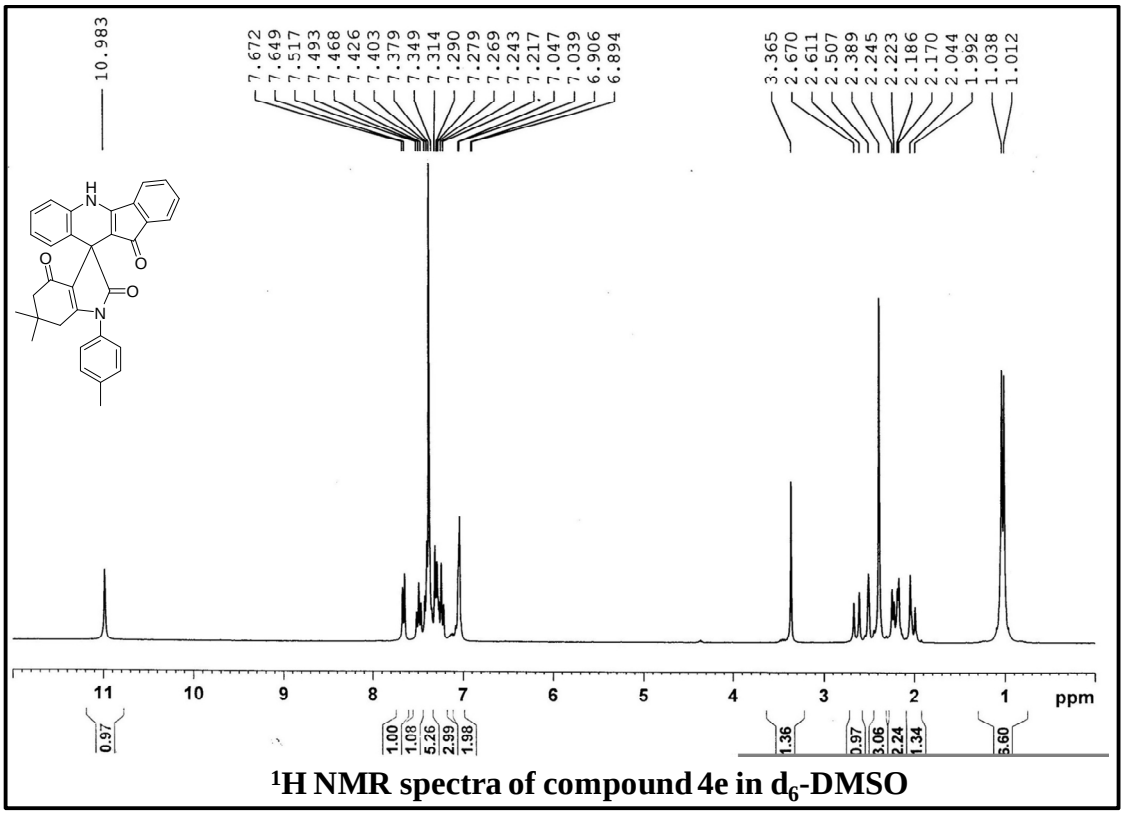
^{13}C NMR spectra of compound 4c in d_6-DMSO



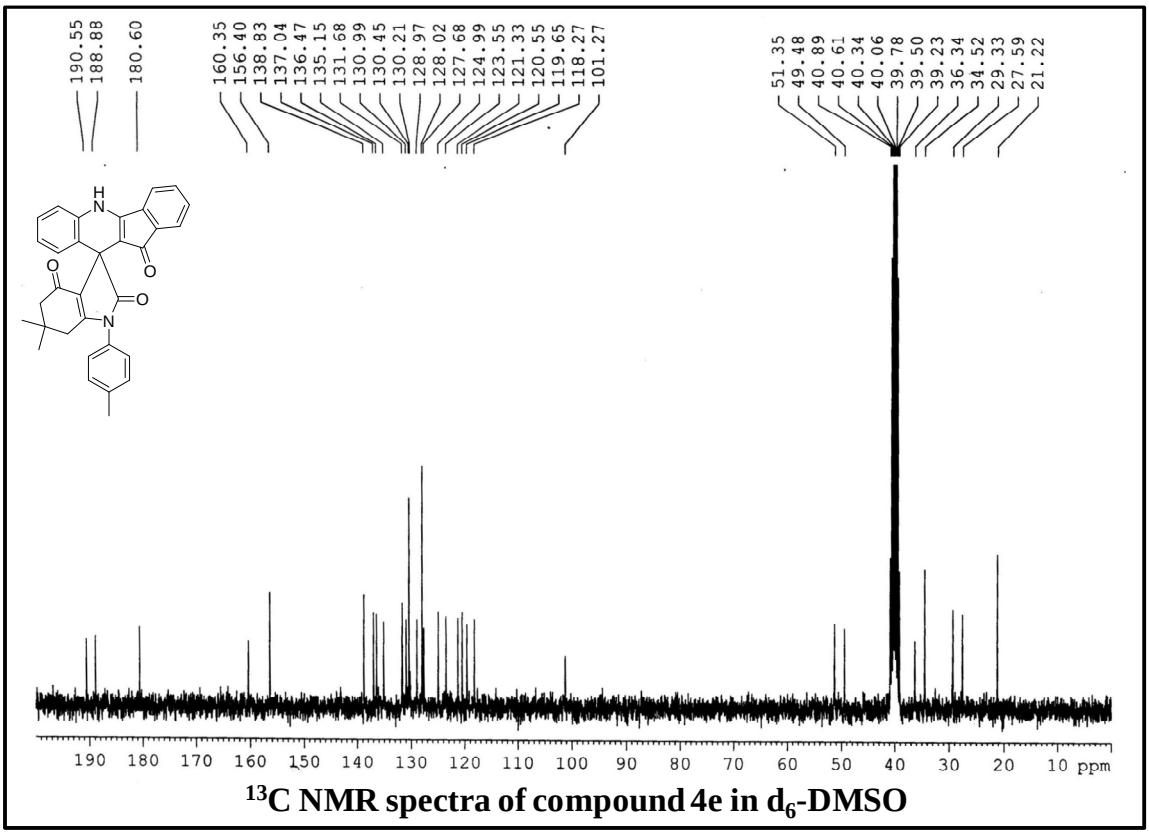
^{1}H NMR spectra of compound 4d in d_6-DMSO



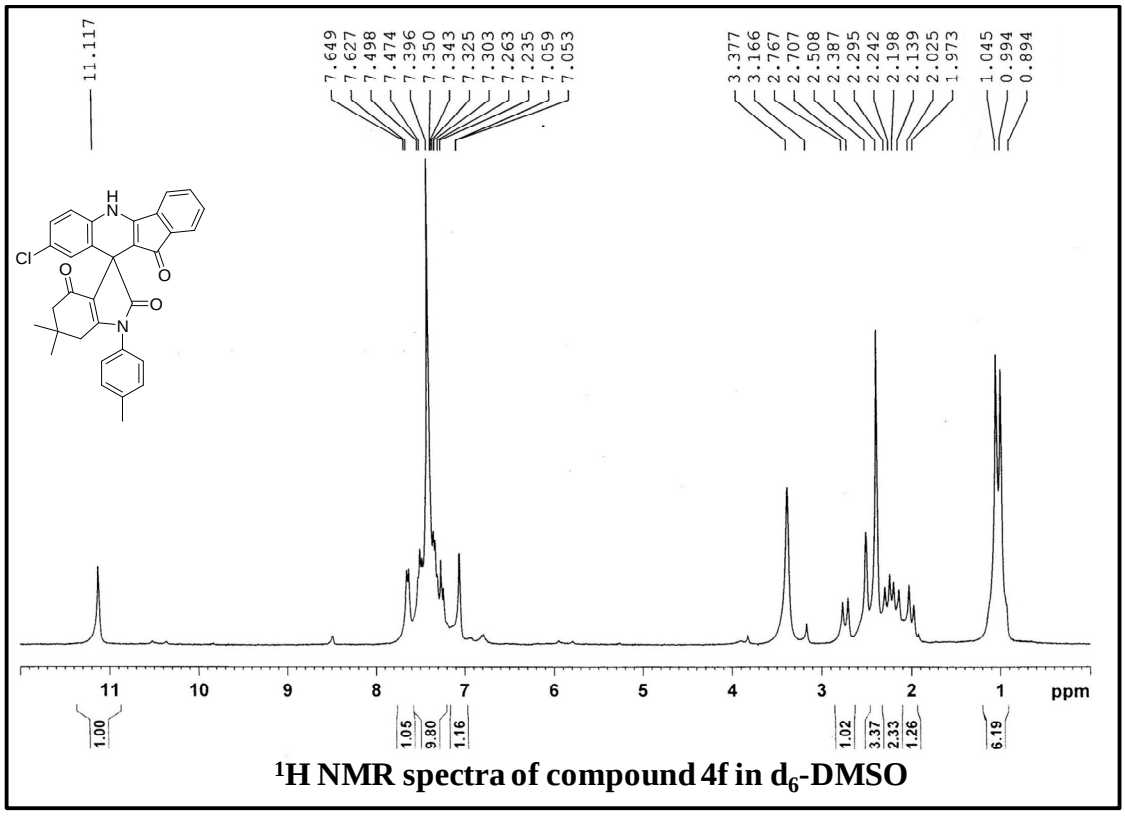
^{13}C NMR spectra of compound 4d in d_6-DMSO



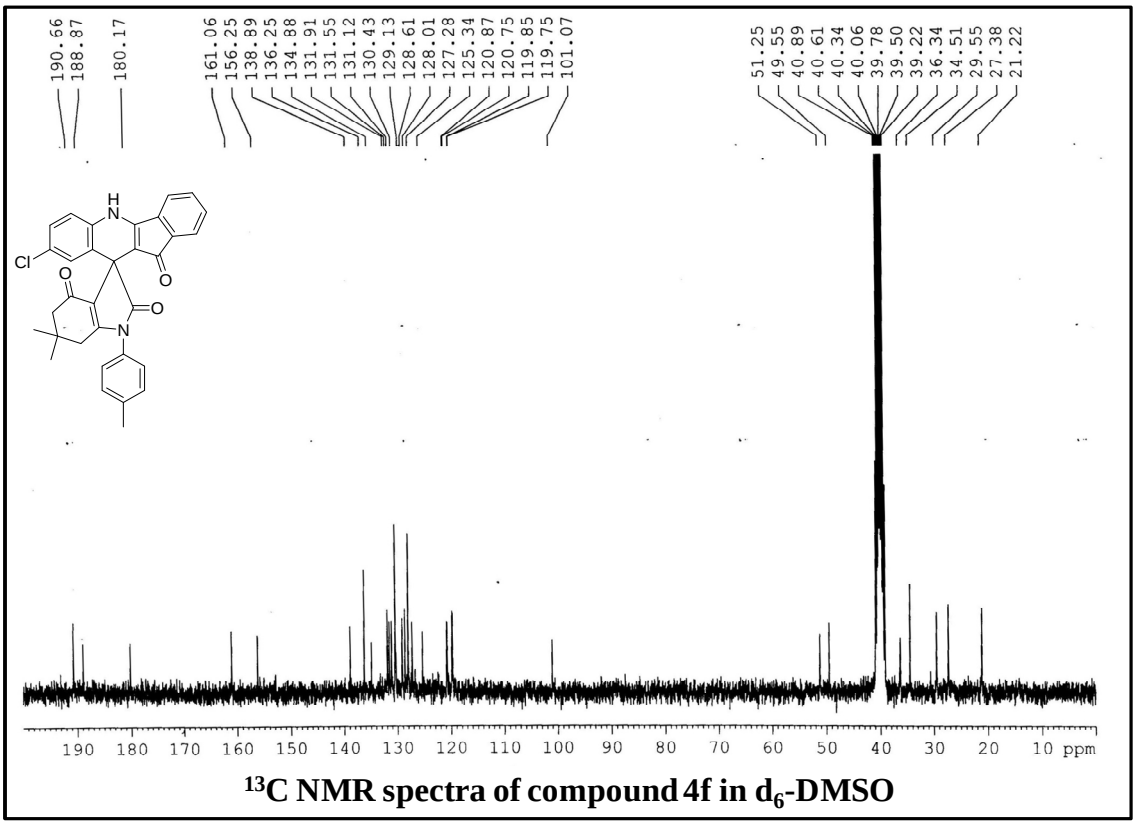
^{1}H NMR spectra of compound 4e in d_6-DMSO



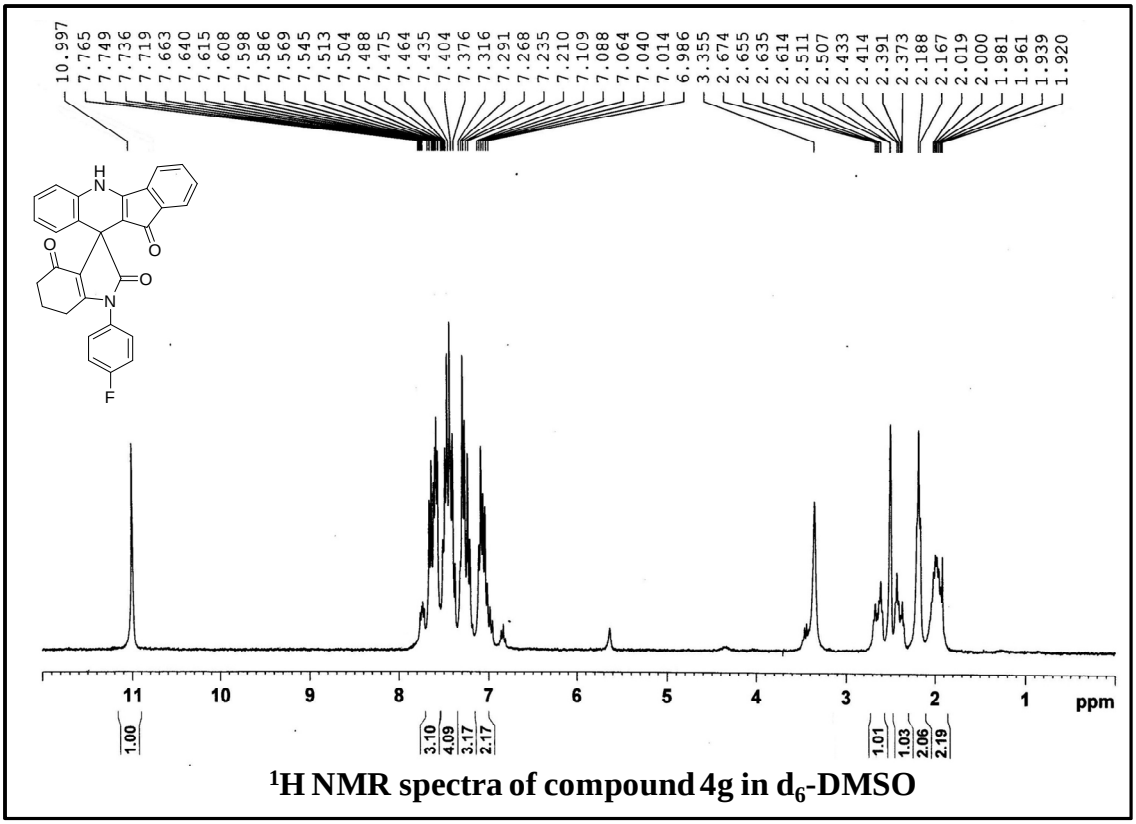
^{13}C NMR spectra of compound 4e in d_6-DMSO



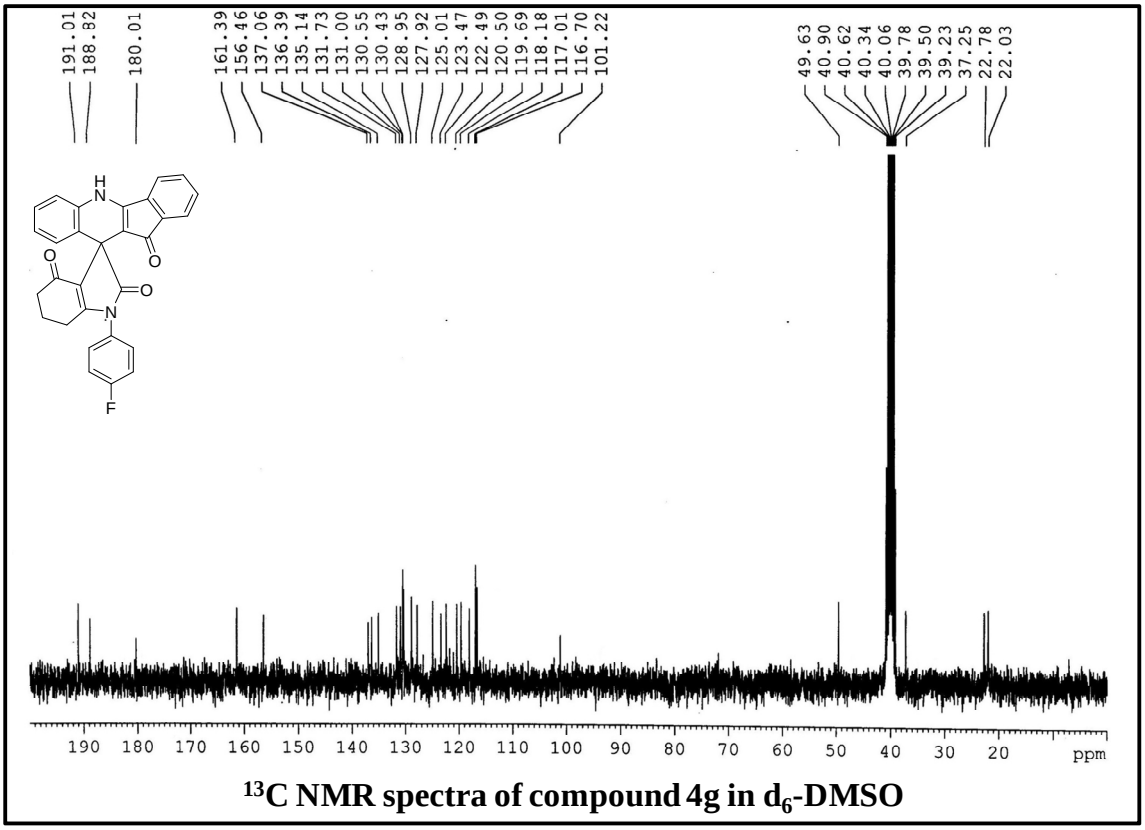
^{1}H NMR spectra of compound 4f in d_6-DMSO



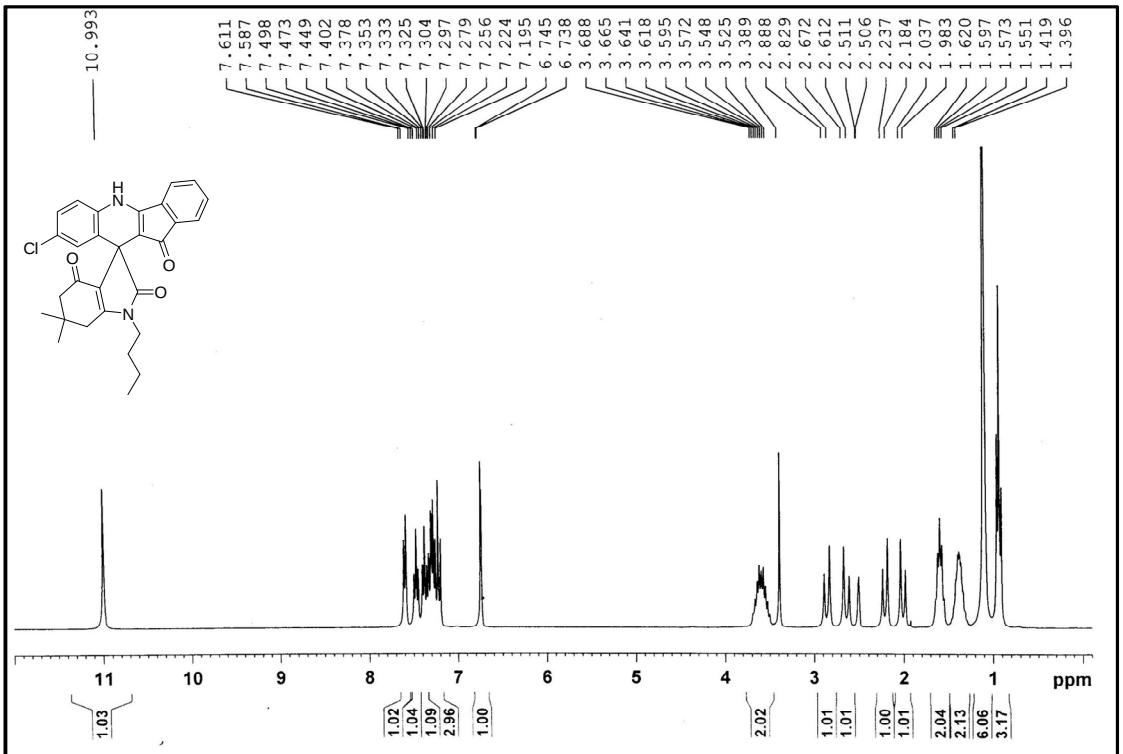
^{13}C NMR spectra of compound 4f in d_6-DMSO



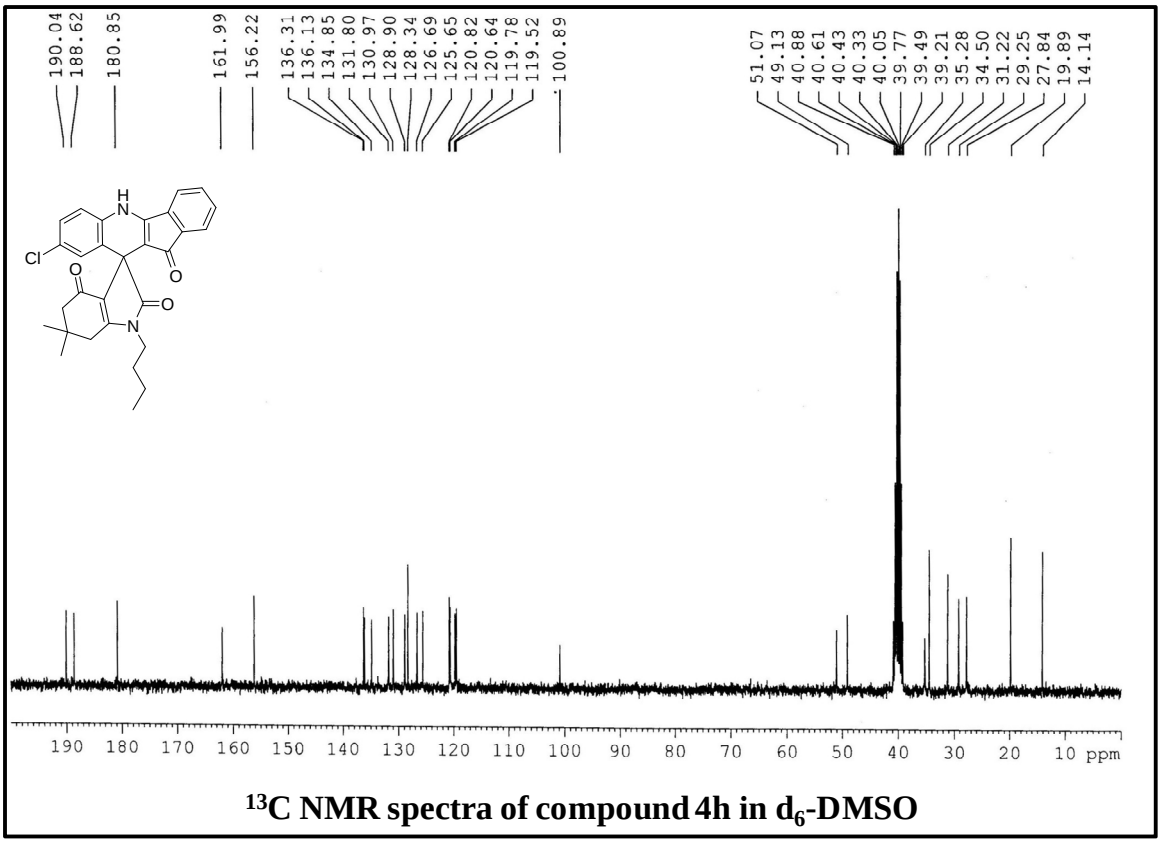
^{1}H NMR spectra of compound 4g in d_6-DMSO



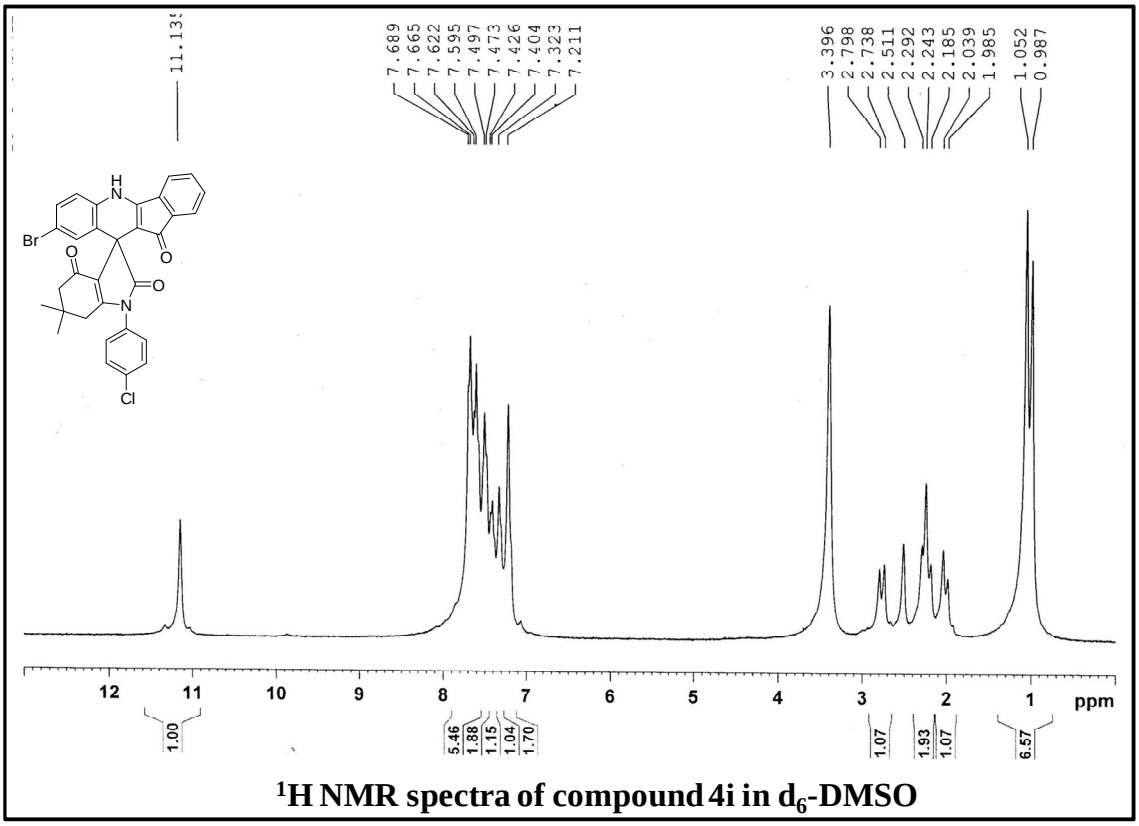
^{13}C NMR spectra of compound 4g in d_6-DMSO



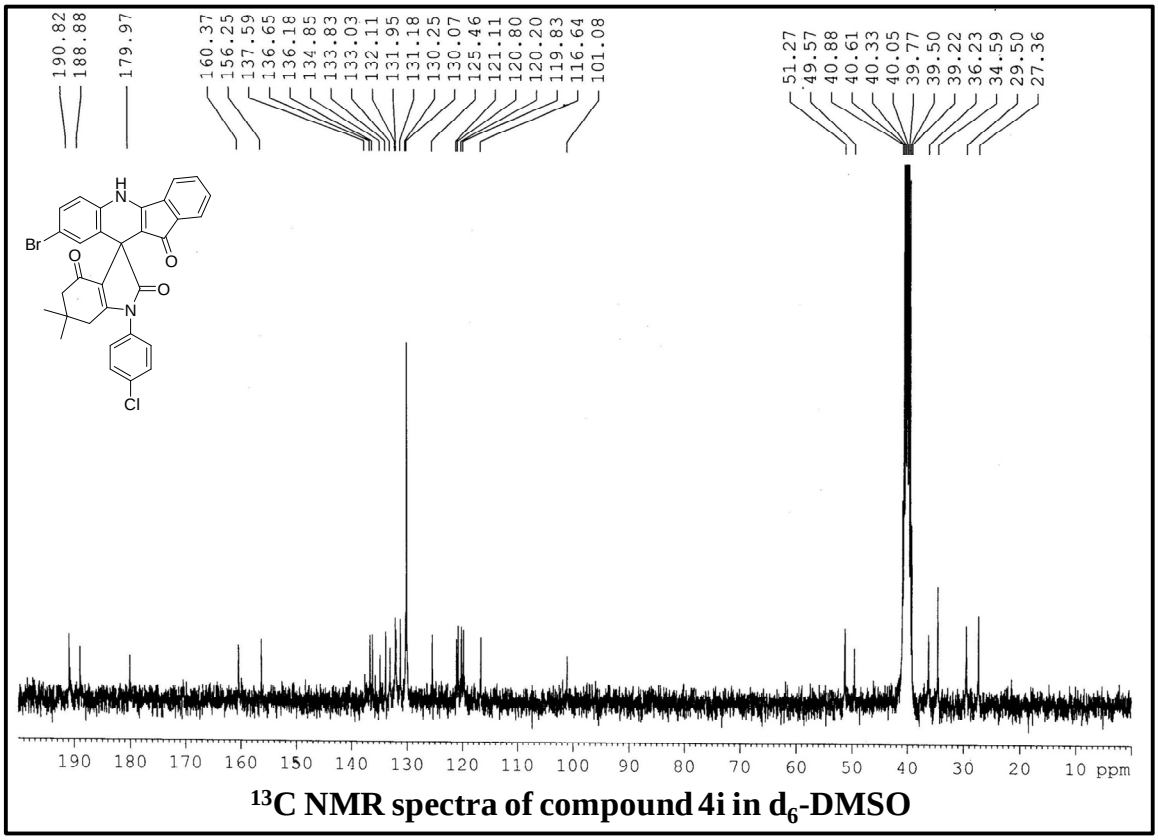
^{1}H NMR spectra of compound 4h in d_6-DMSO



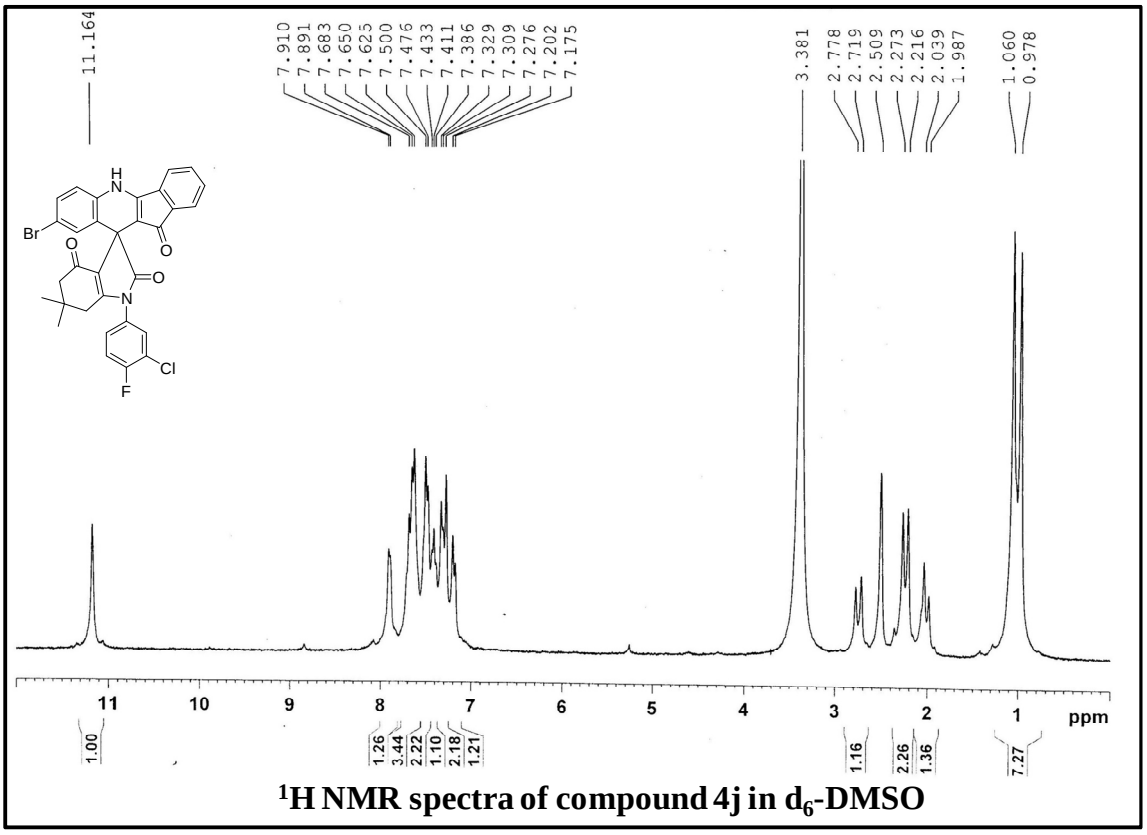
^{13}C NMR spectra of compound 4h in d_6-DMSO



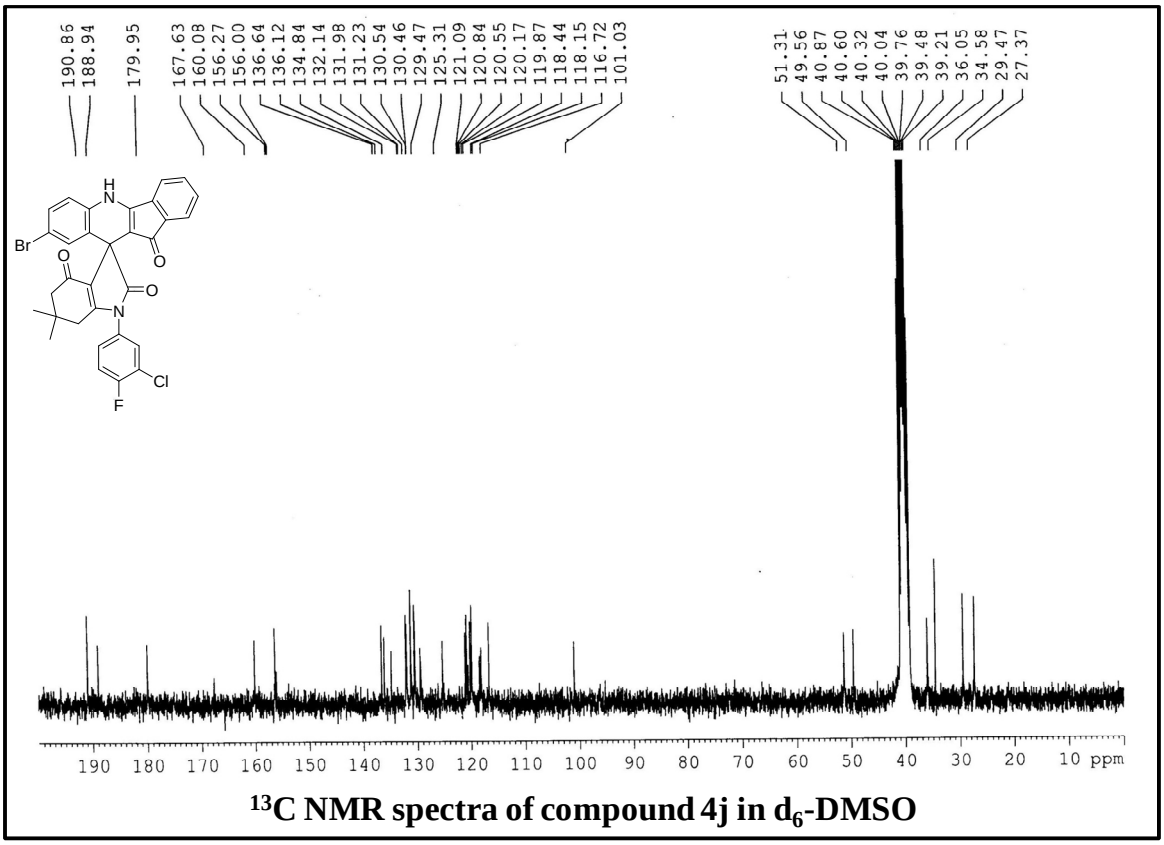
^{1}H NMR spectra of compound 4i in d_6-DMSO



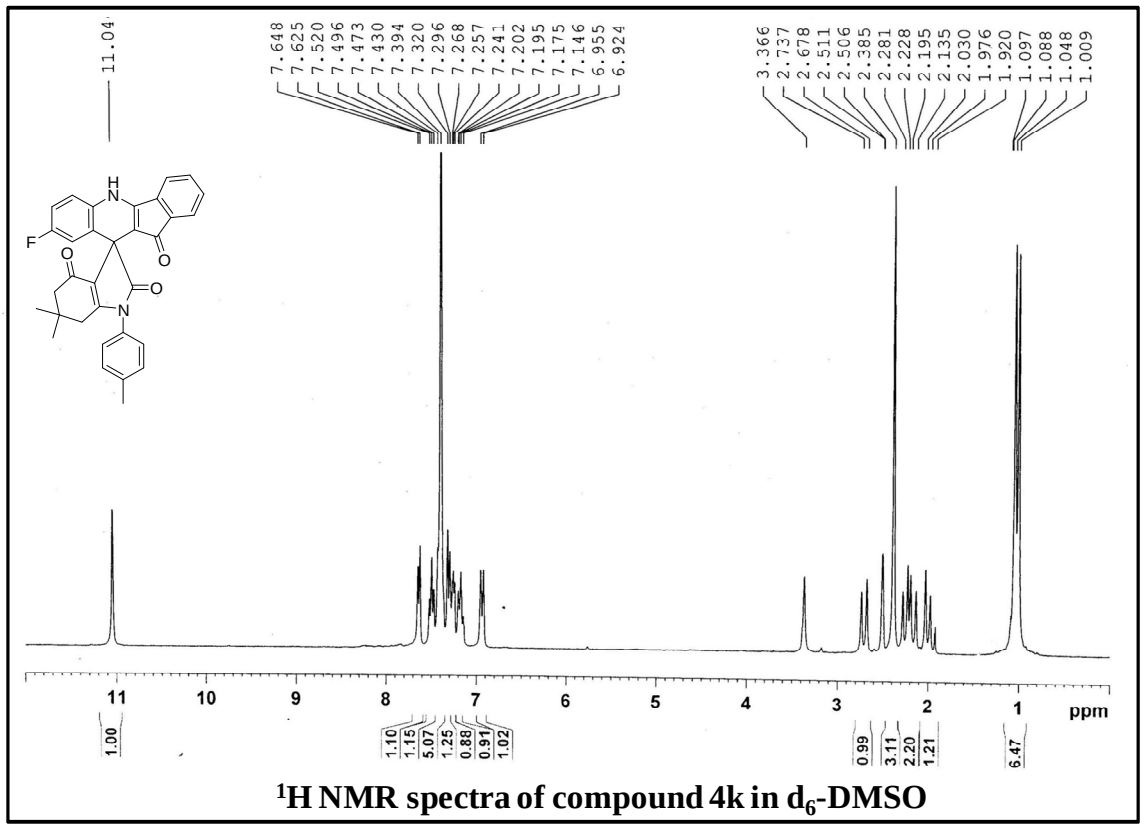
^{13}C NMR spectra of compound 4i in d_6-DMSO



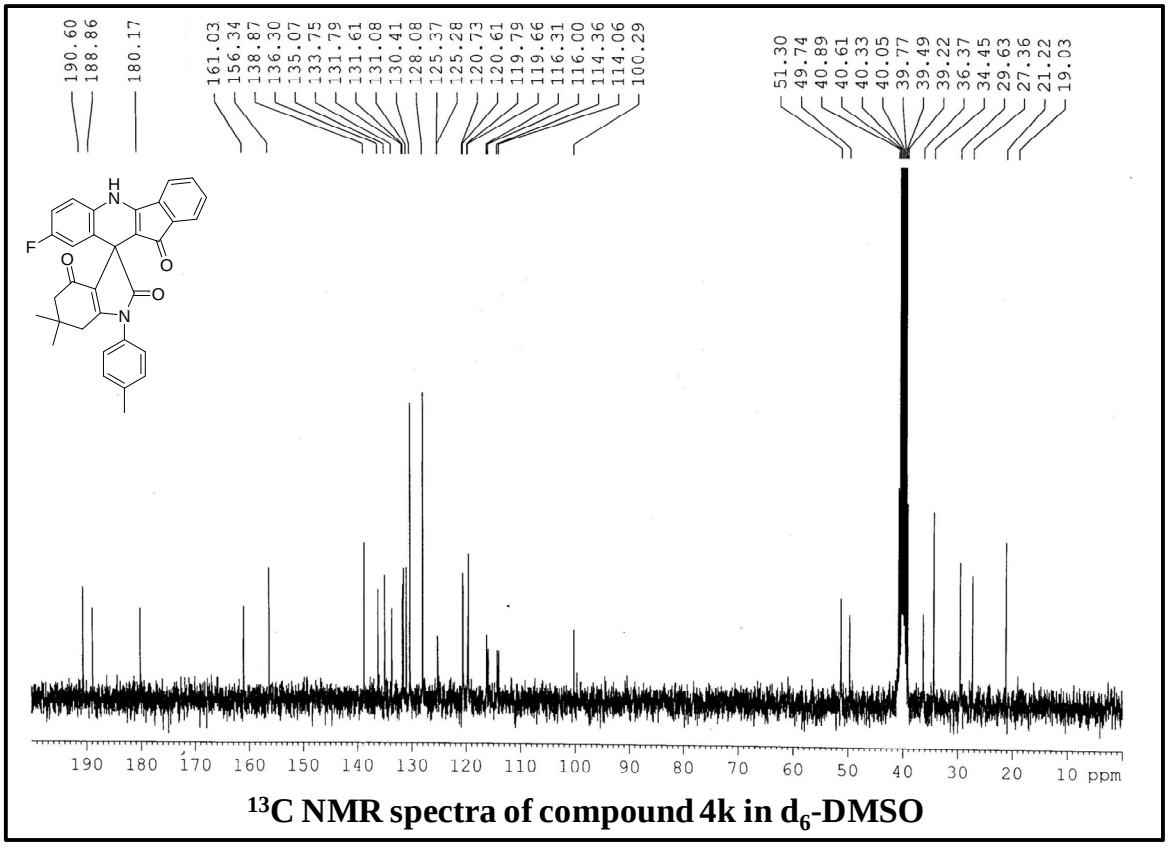
^{1}H NMR spectra of compound 4j in d_6-DMSO



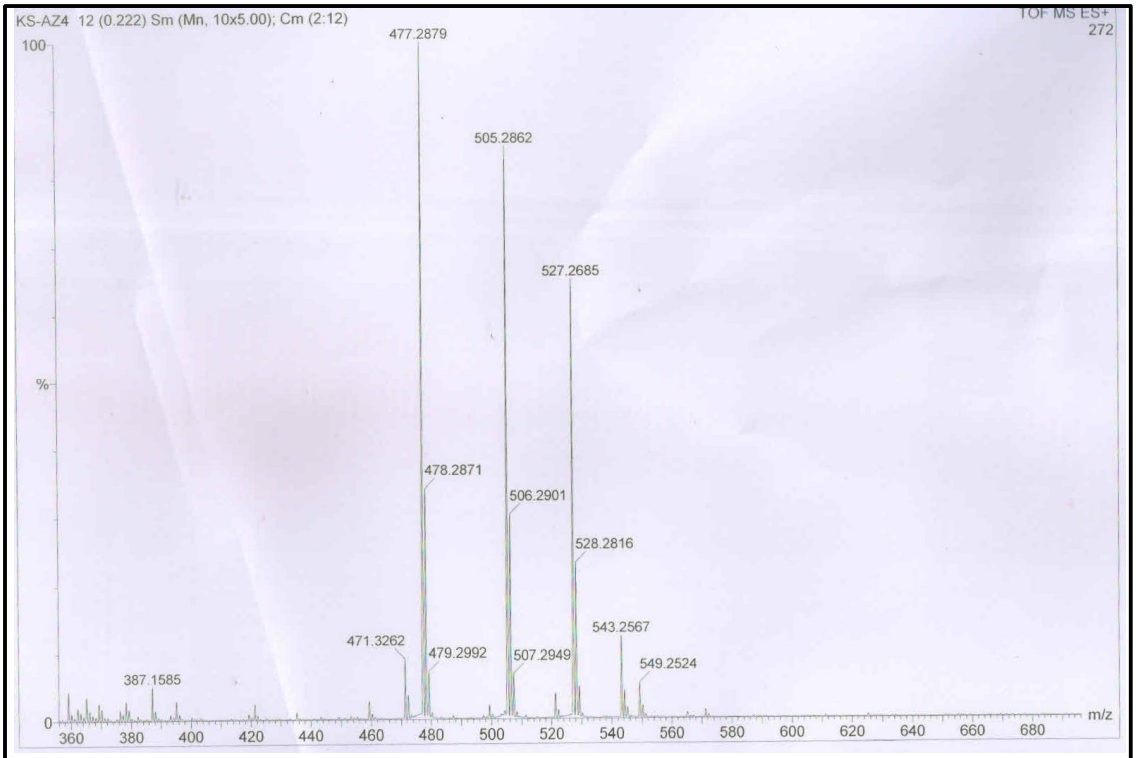
^{13}C NMR spectra of compound 4j in d_6-DMSO



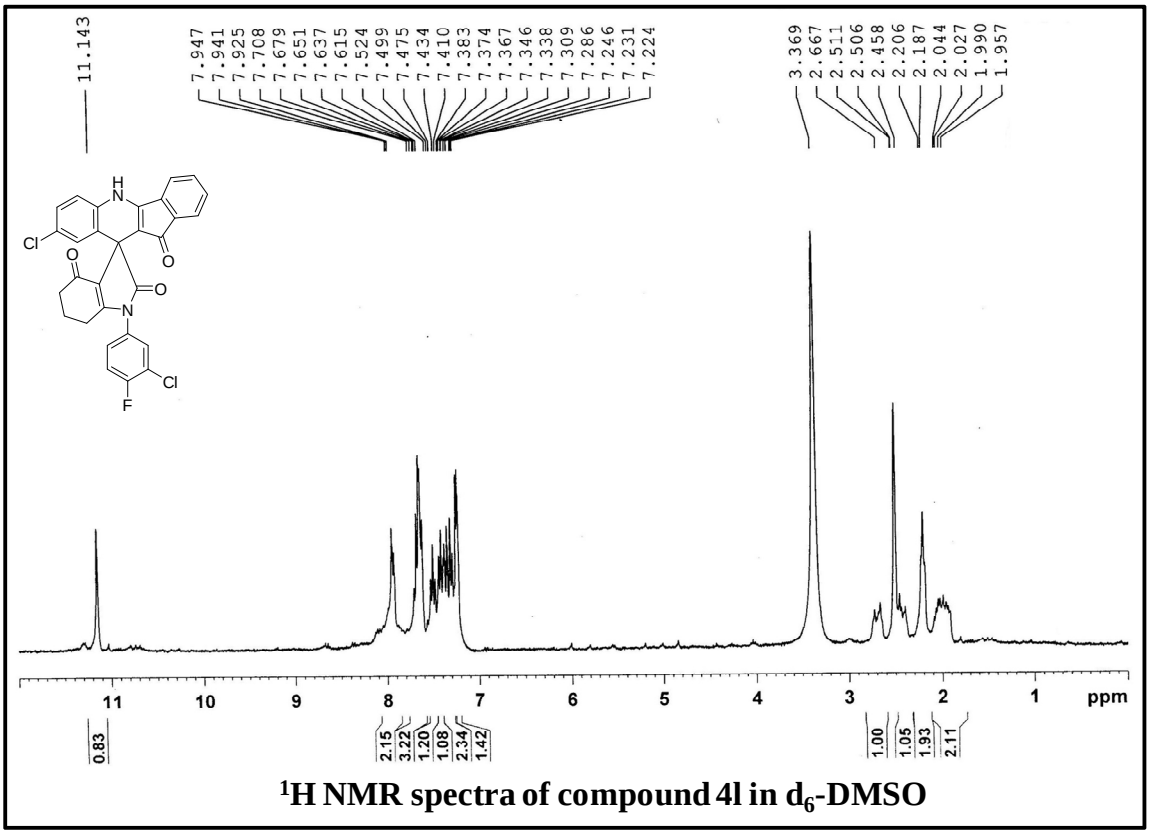
^{1}H NMR spectra of compound 4k in d_6-DMSO



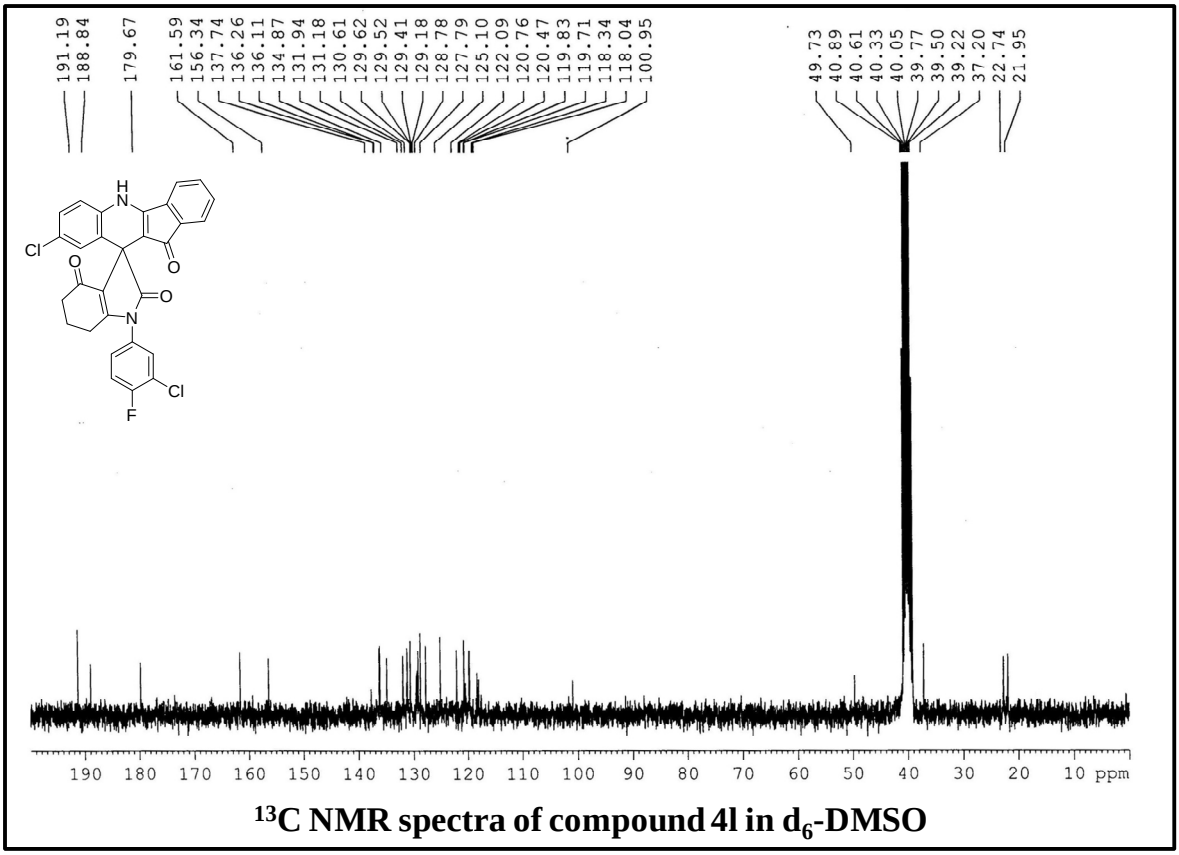
^{13}C NMR spectra of compound 4k in d_6-DMSO



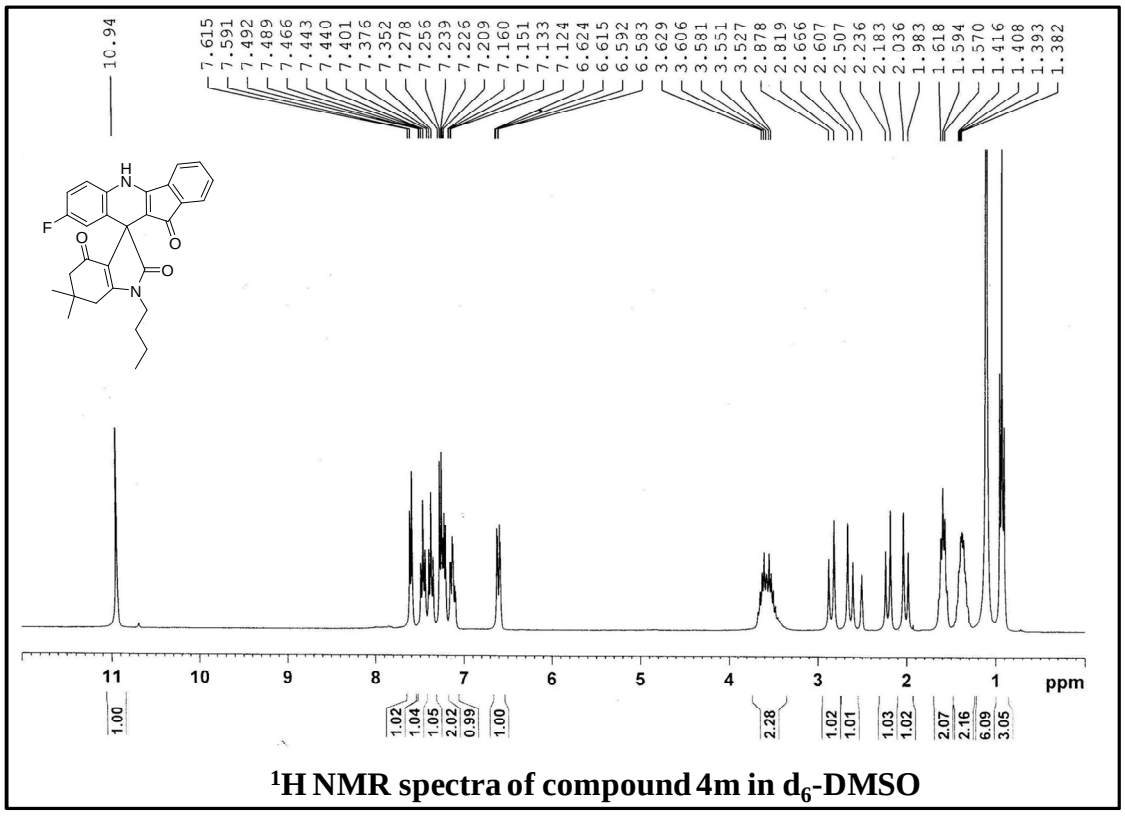
HR-ESI-MS of compound 4k



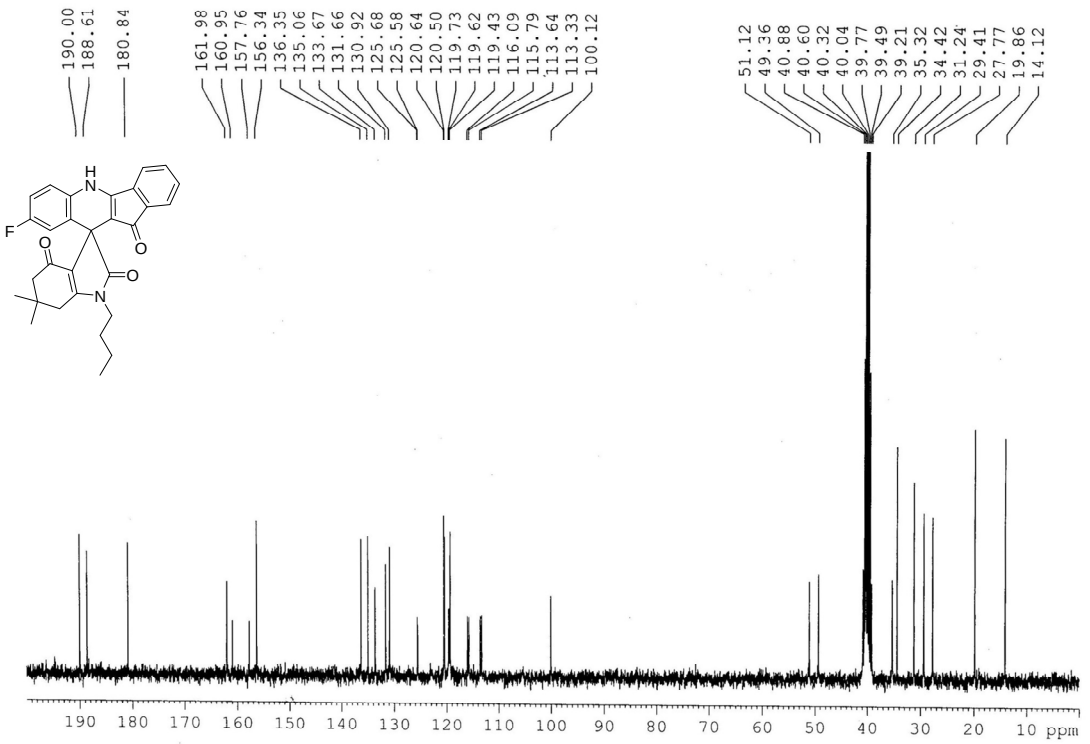
^{1}H NMR spectra of compound 4l in d_6-DMSO



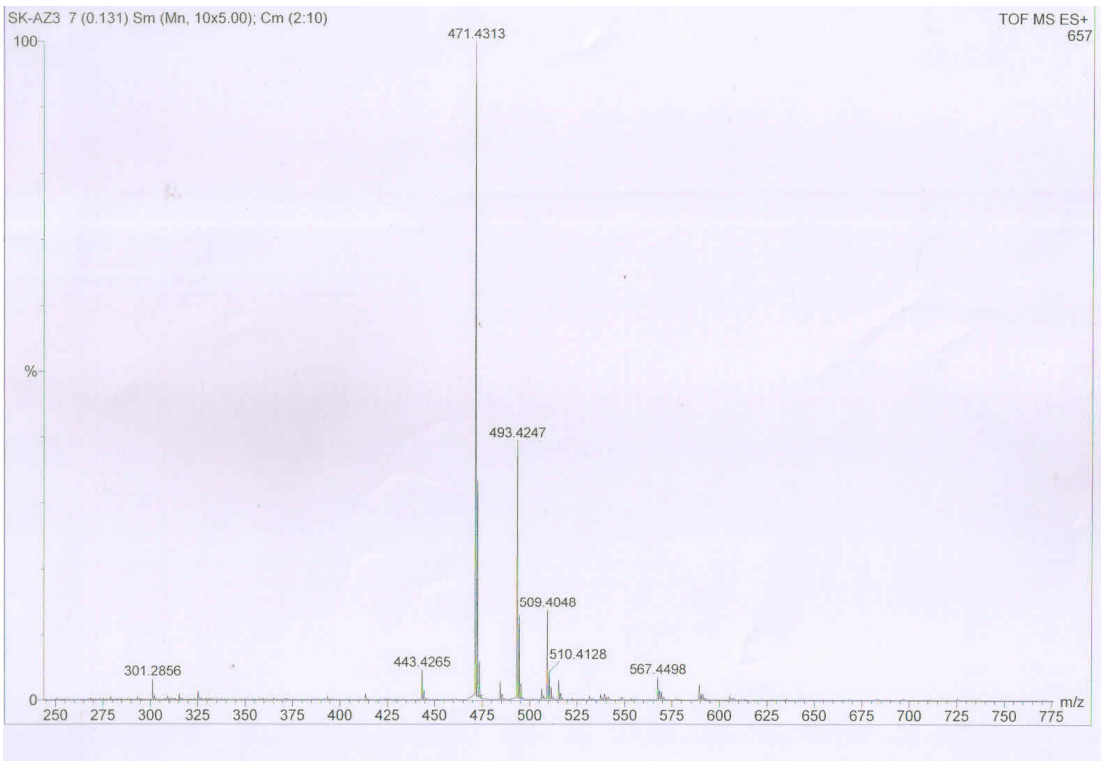
^{13}C NMR spectra of compound 4l in d_6-DMSO



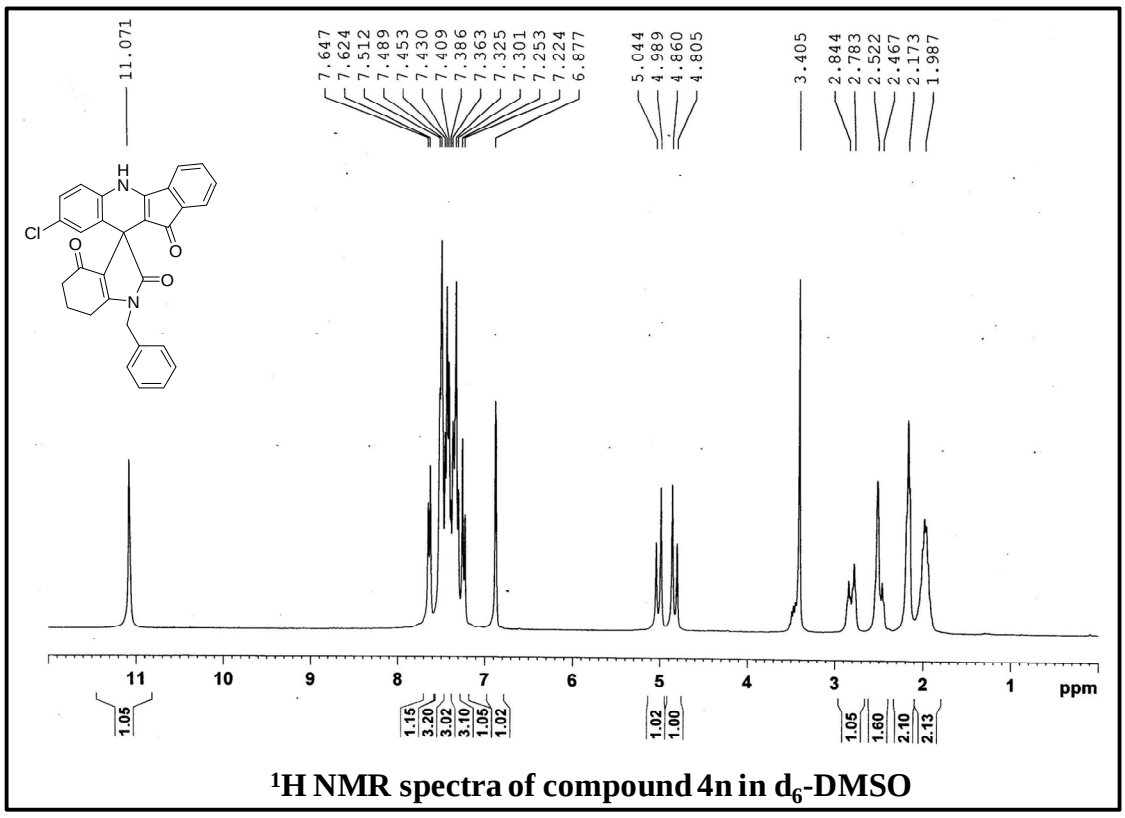
^{1}H NMR spectra of compound 4m in d_6-DMSO



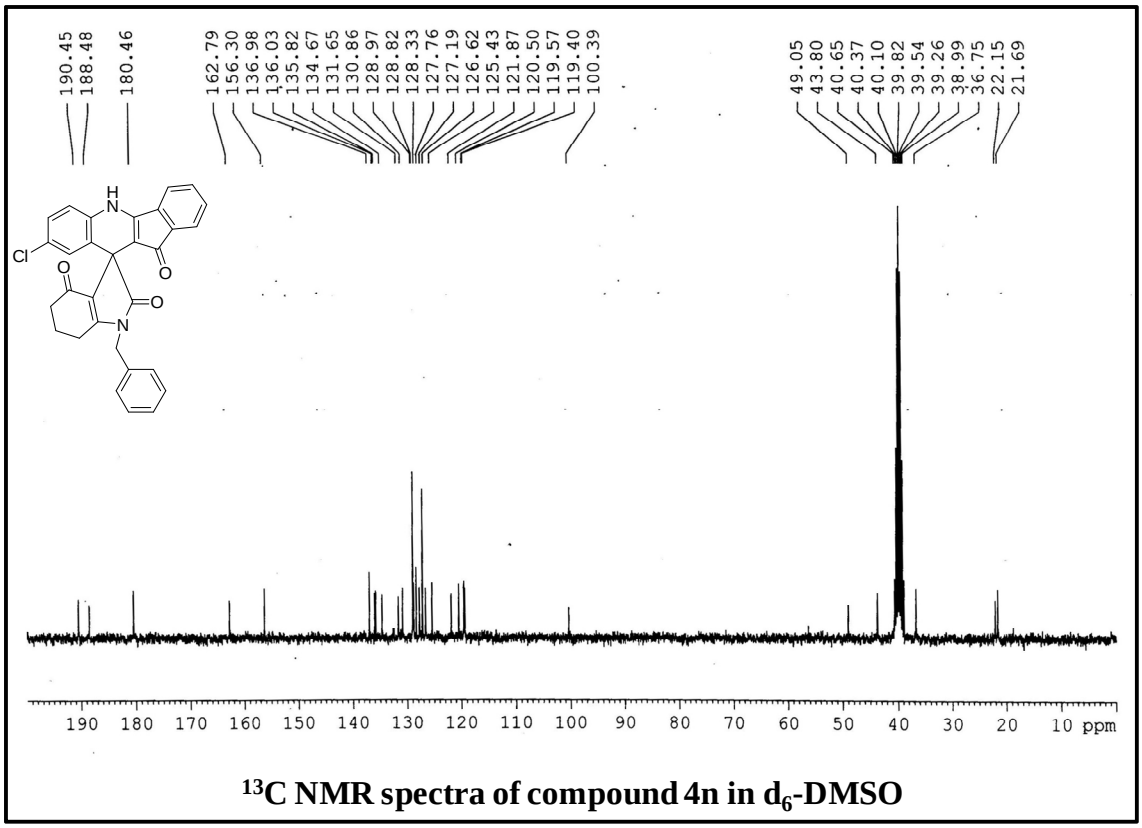
^{13}C NMR spectra of compound 4m in d_6-DMSO



HR-ESI-MS of compound 4m

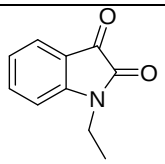
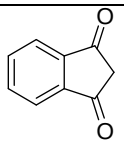
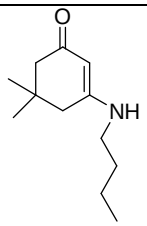
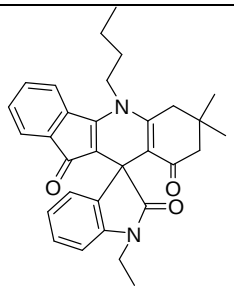
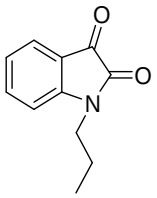
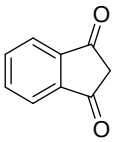
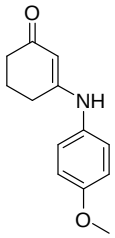
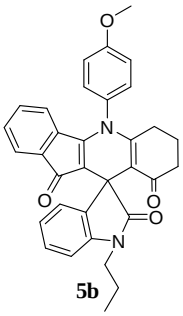
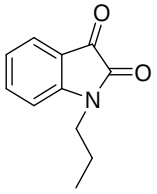
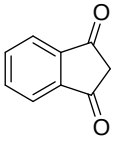
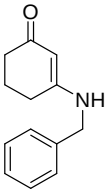
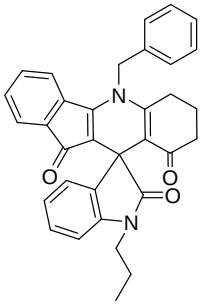
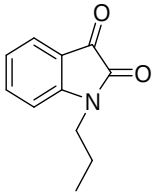
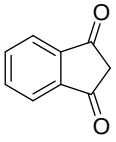
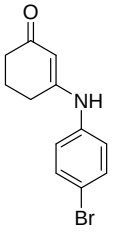
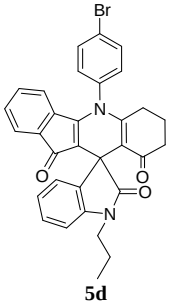


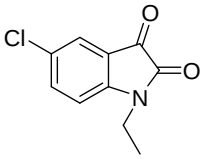
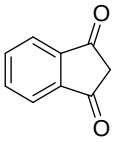
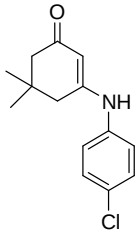
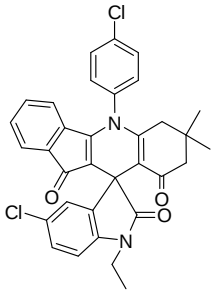
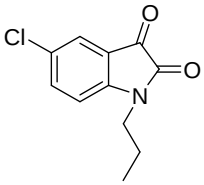
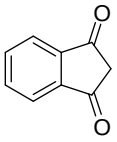
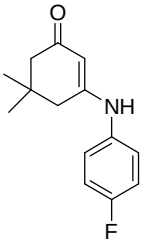
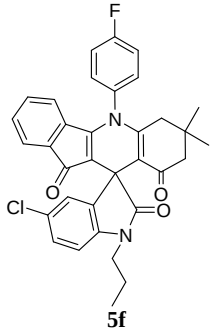
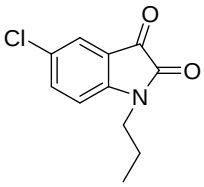
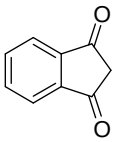
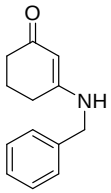
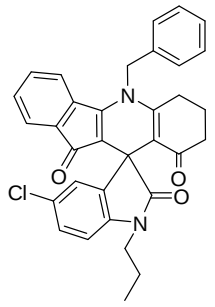
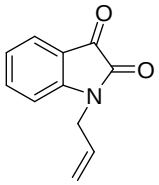
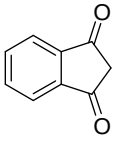
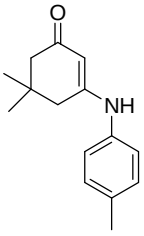
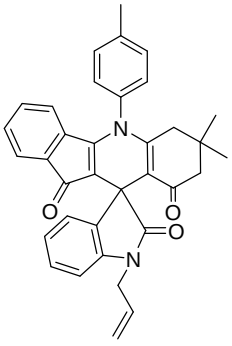
^{1}H NMR spectra of compound 4n in d_6-DMSO

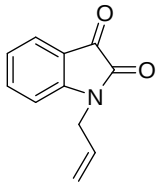
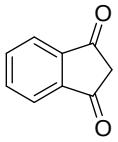
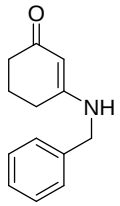
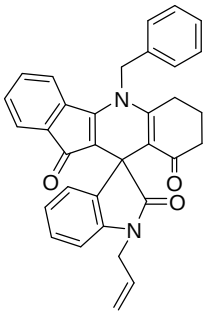
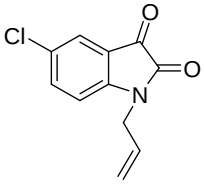
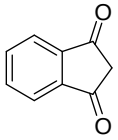
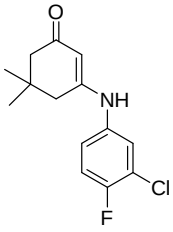
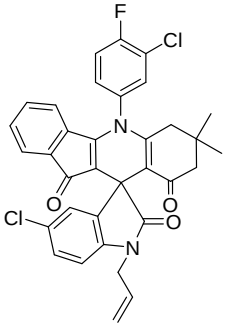
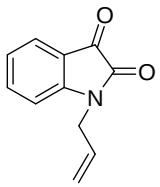
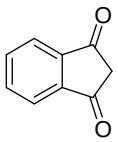
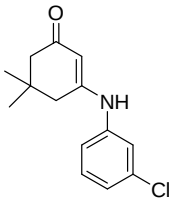
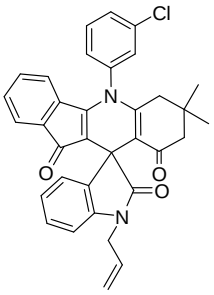
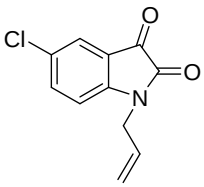
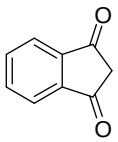
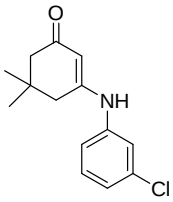
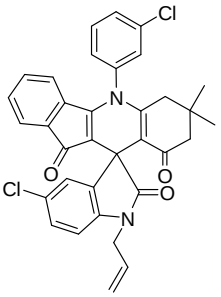


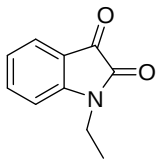
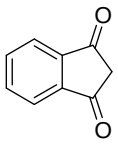
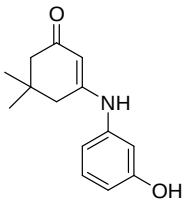
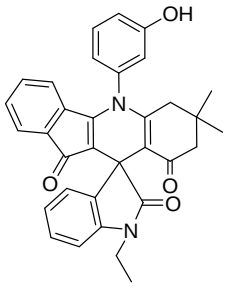
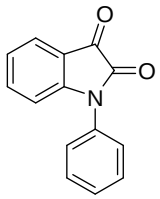
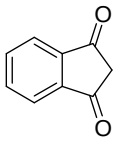
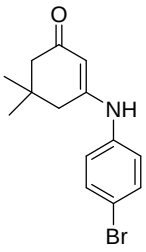
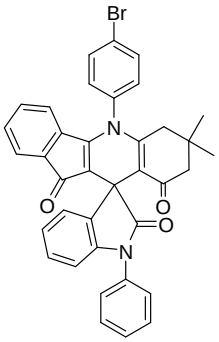
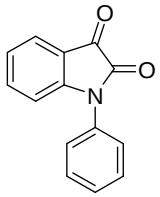
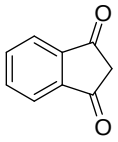
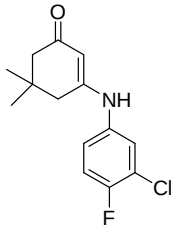
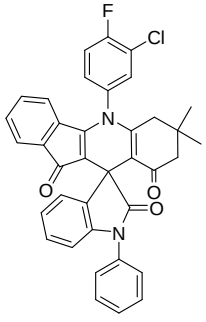
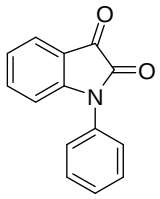
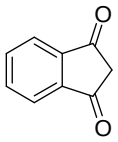
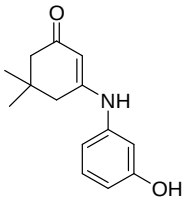
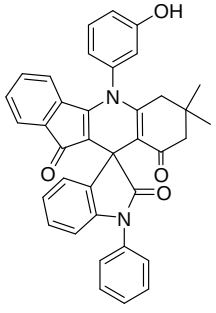
^{13}C NMR spectra of compound 4n in d_6-DMSO

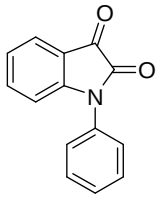
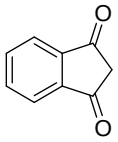
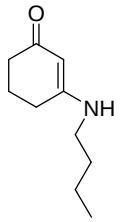
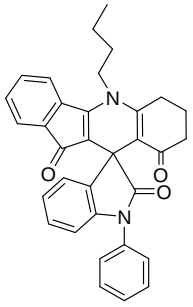
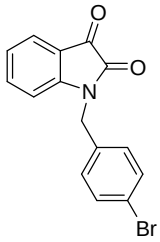
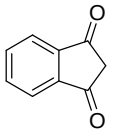
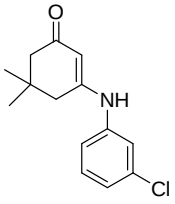
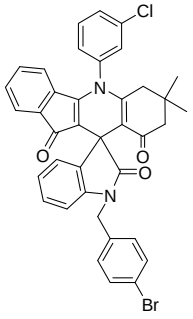
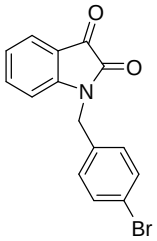
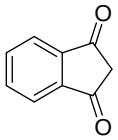
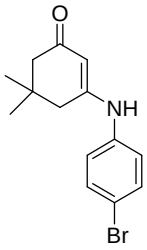
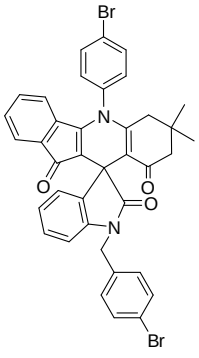
Table S2: Synthesis of indenoquinoline-spirooxindoles **5a**–**s** through a three-component reaction

Entry	1	2	3	Product (5)	Yield[a] (%)	Melting Point (ºC)
1				 **5a**	87	200-202
2				 **5b**	80	302-304
3				 **5c**	77	200-202
4				 **5d**	78	308-310

5				 **5e**	79	174-176
6				 **5f**	80	262-264
7				 **5g**	84	204-206
8				 **5h**	82	260-262

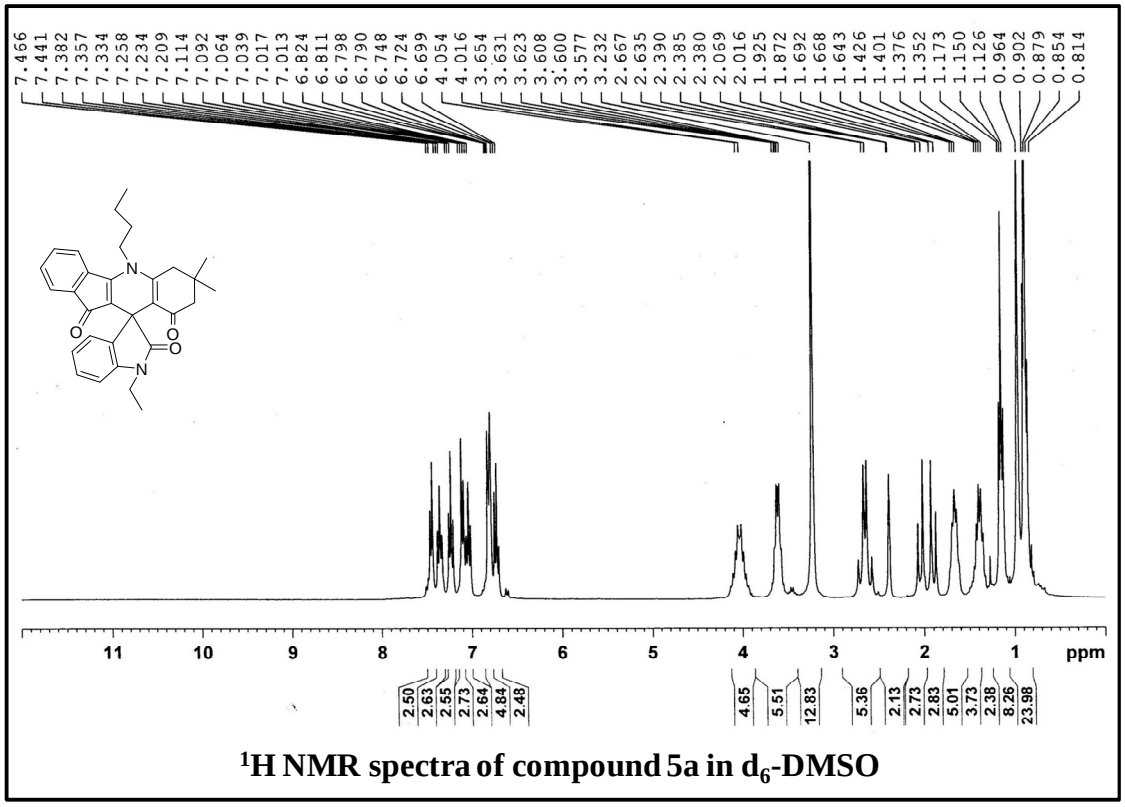
9				 **5i**	79	212-214
10				 **5j**	82	306-308
11				 **5k**	75	242-244
12				 **5l**	73	>300

13				 **5m**	76	>300
14				 **5n**	80	162-164
15				 **5o**	78	186-188
16				 **5p**	76	>300

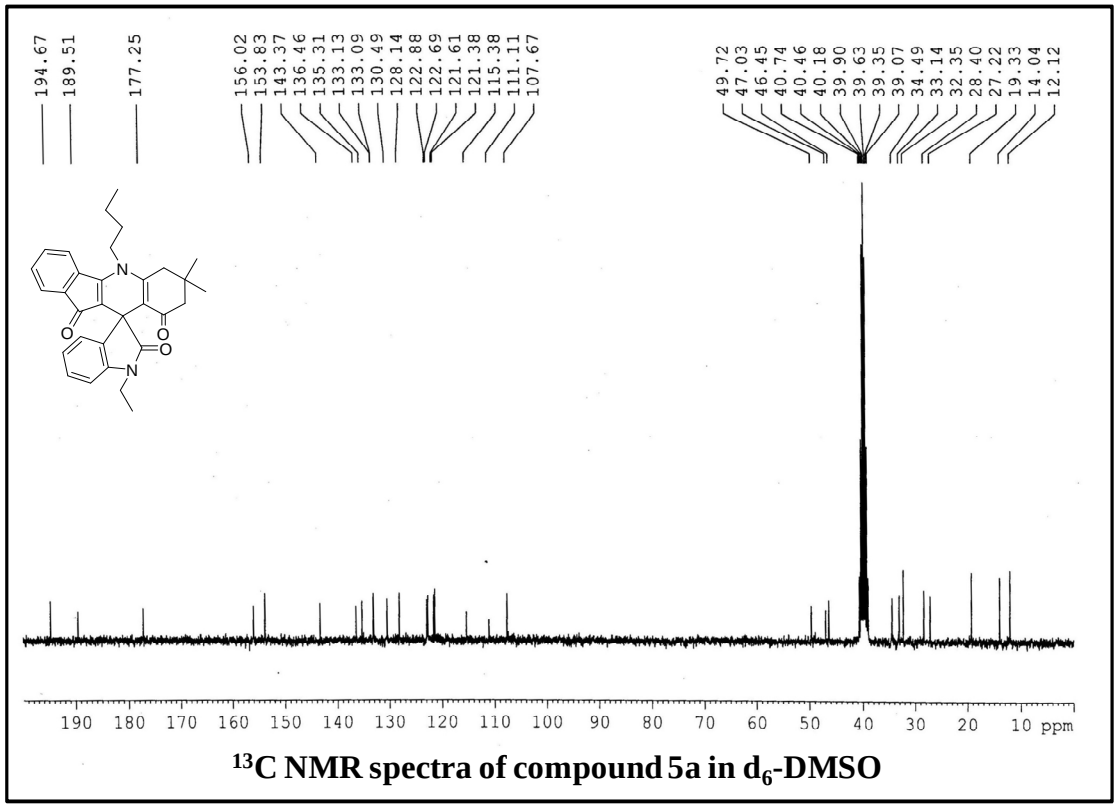
17				 **5q**	79	210-212
18				 **5r**	83	170-172
19				 **5s**	85	>300

[a]Isolated Yields(%)

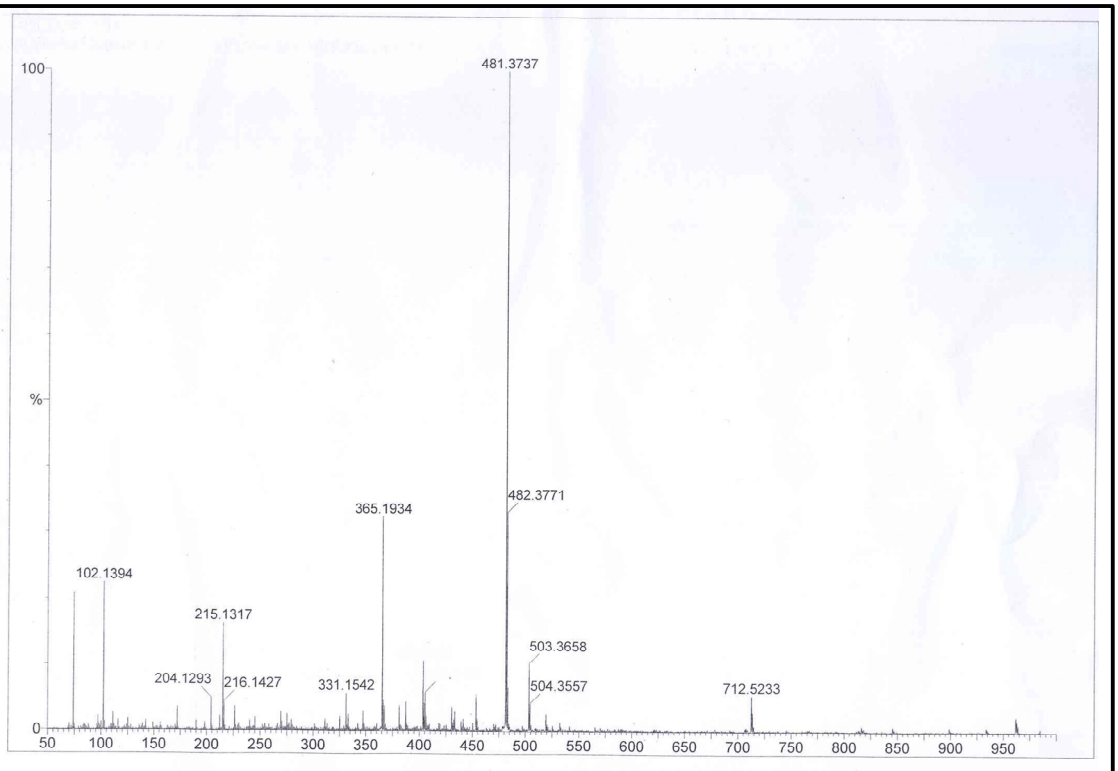
Spectral Data of 5a-s:



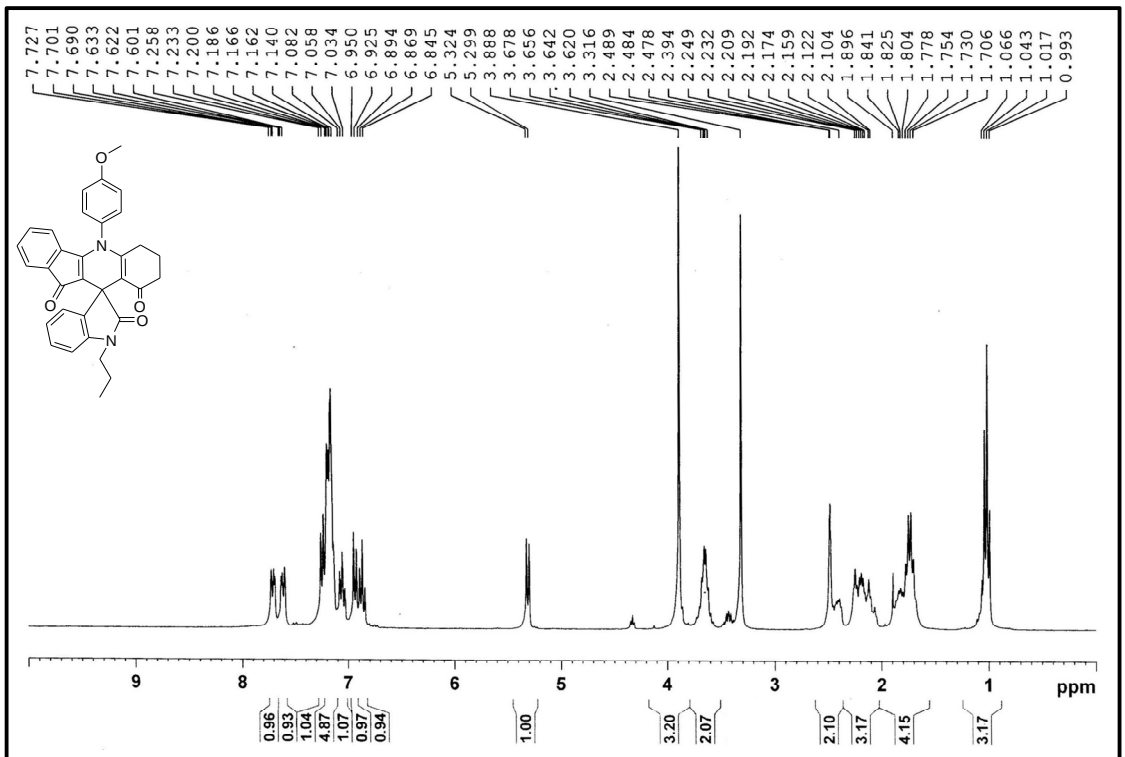
^{1}H NMR spectra of compound 5a in d_6-DMSO



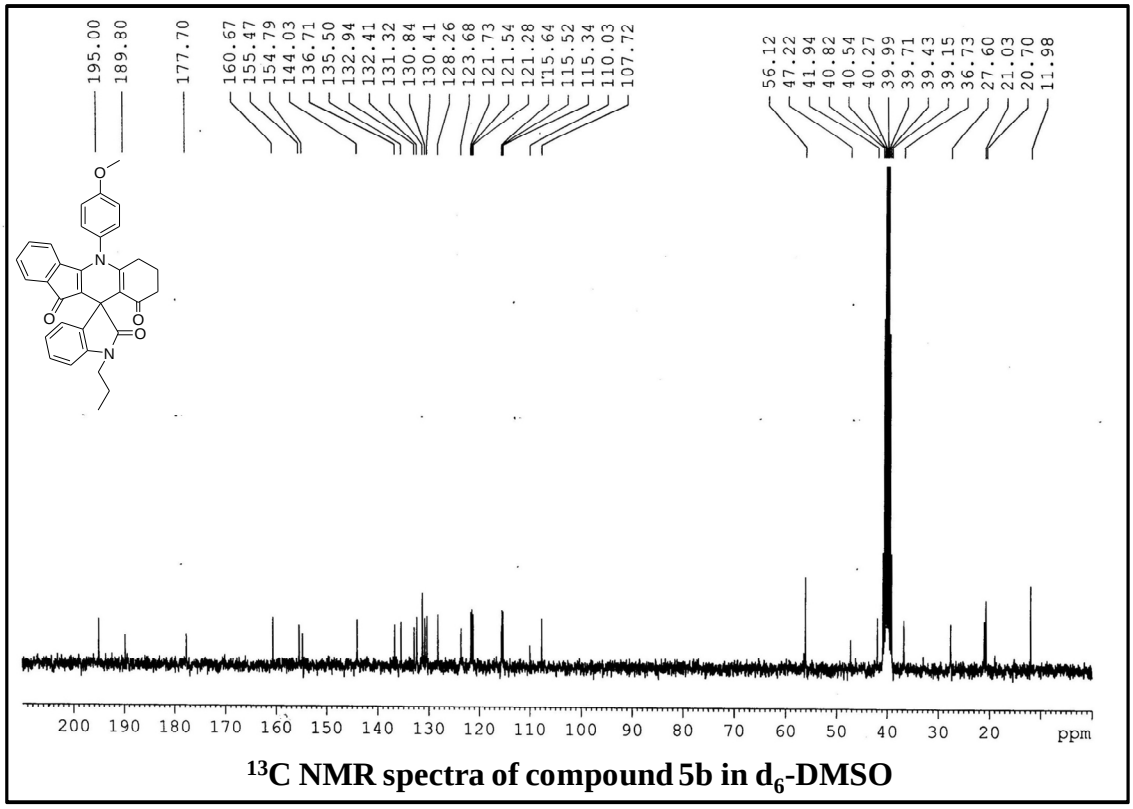
^{13}C NMR spectra of compound 5a in d_6-DMSO



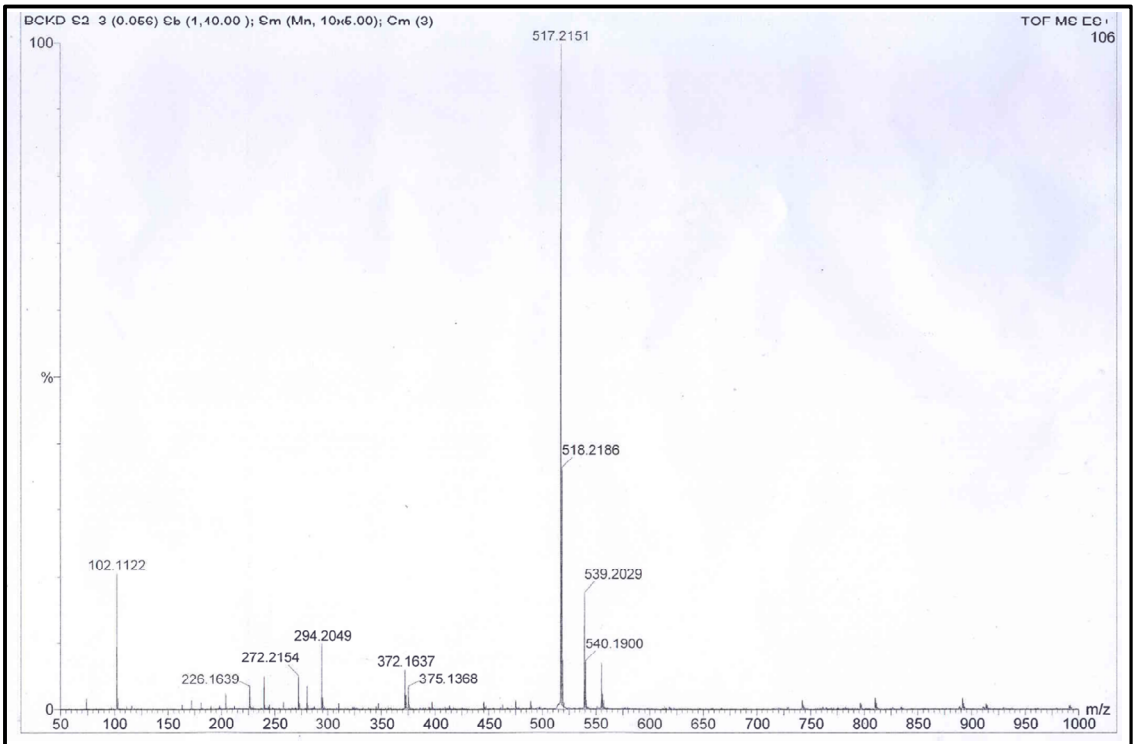
HR-ESI-MS of compound 5a



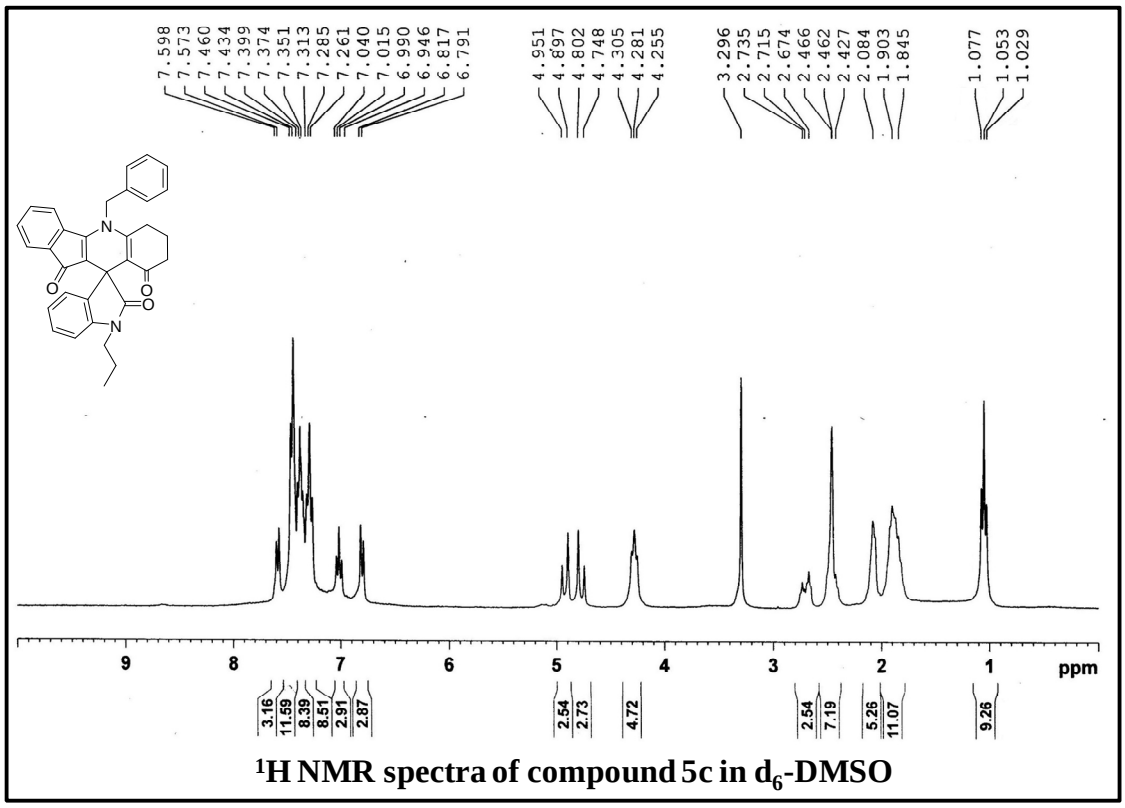
^{1}H NMR spectra of compound 5b in d_6-DMSO



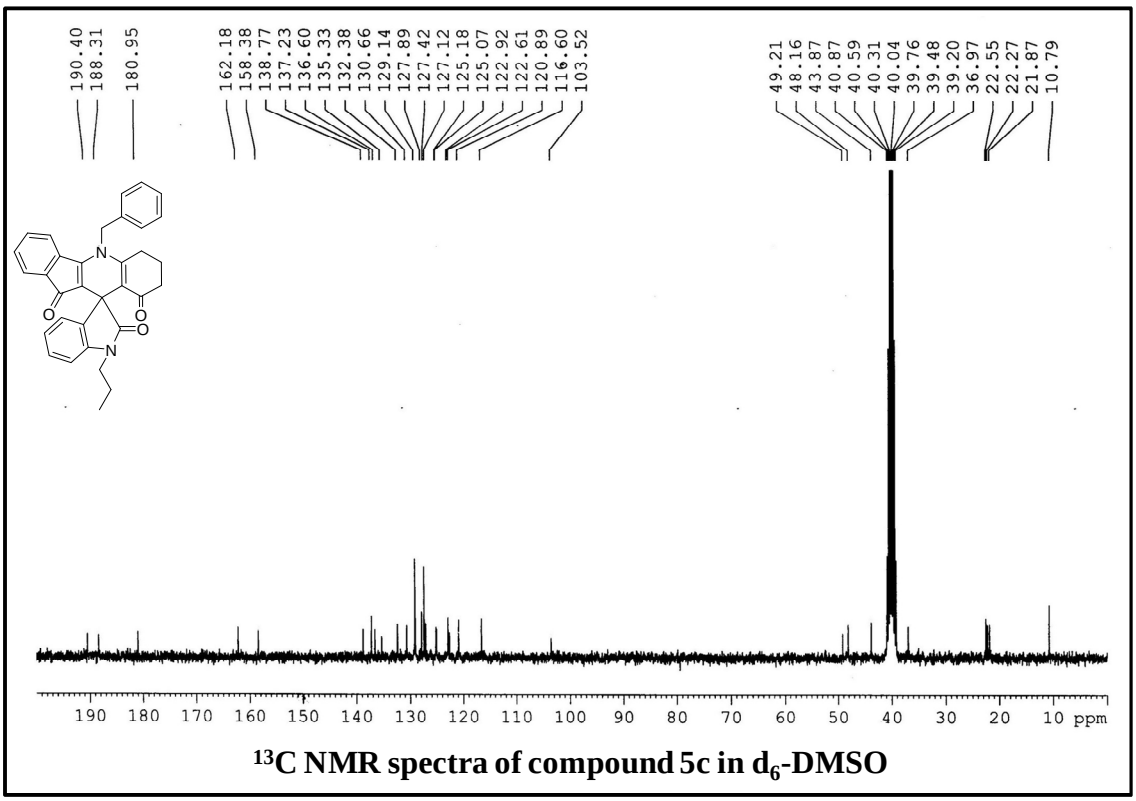
^{13}C NMR spectra of compound 5b in d_6-DMSO



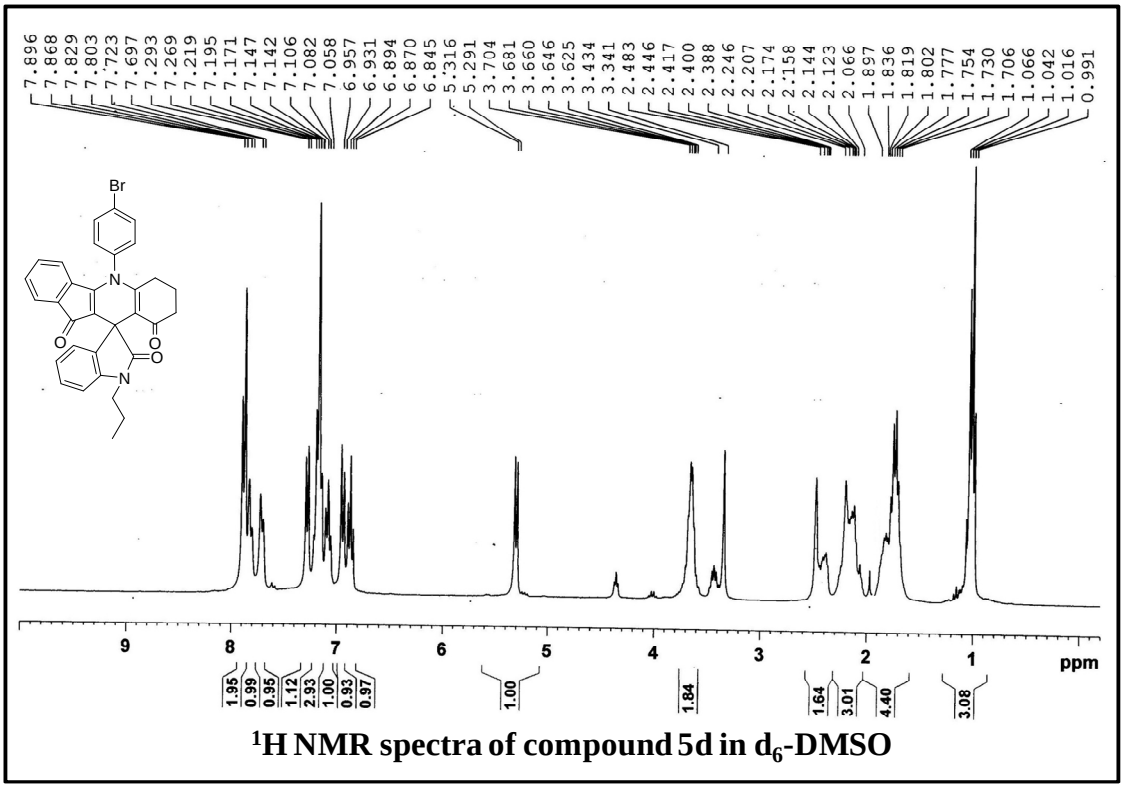
HR-ESI-MS of compound 5b



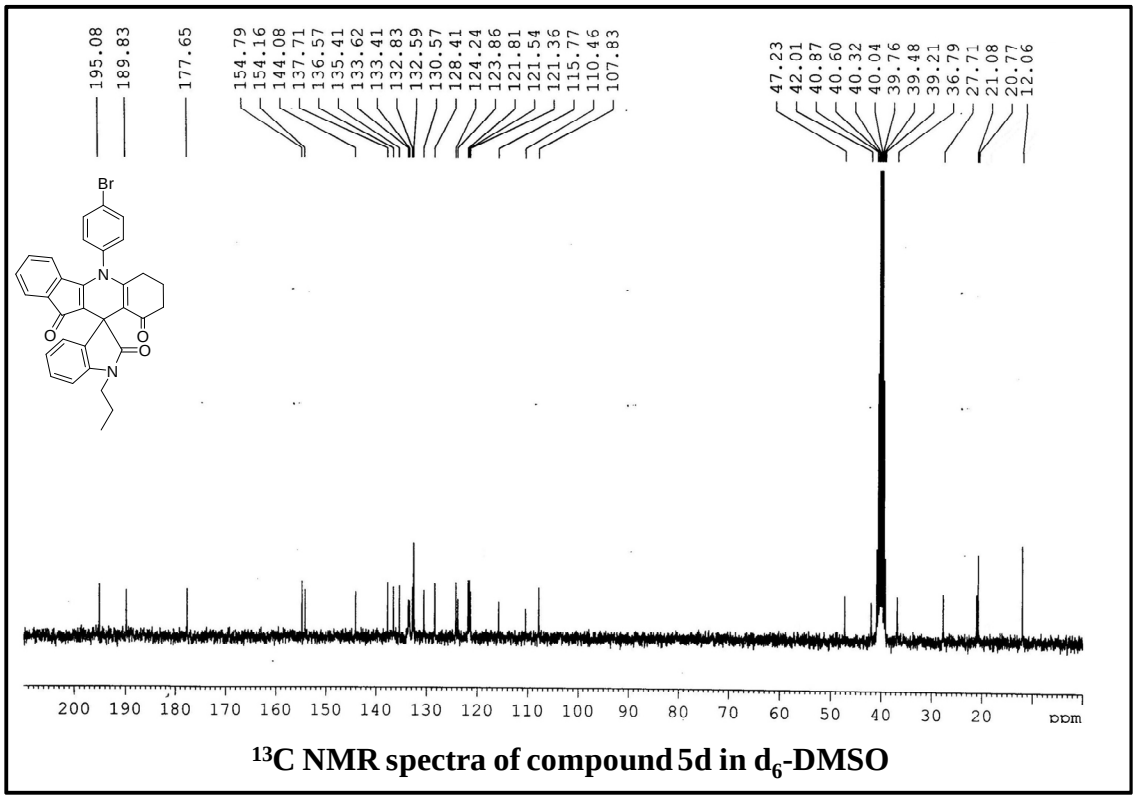
^{1}H NMR spectra of compound 5c in d_6-DMSO



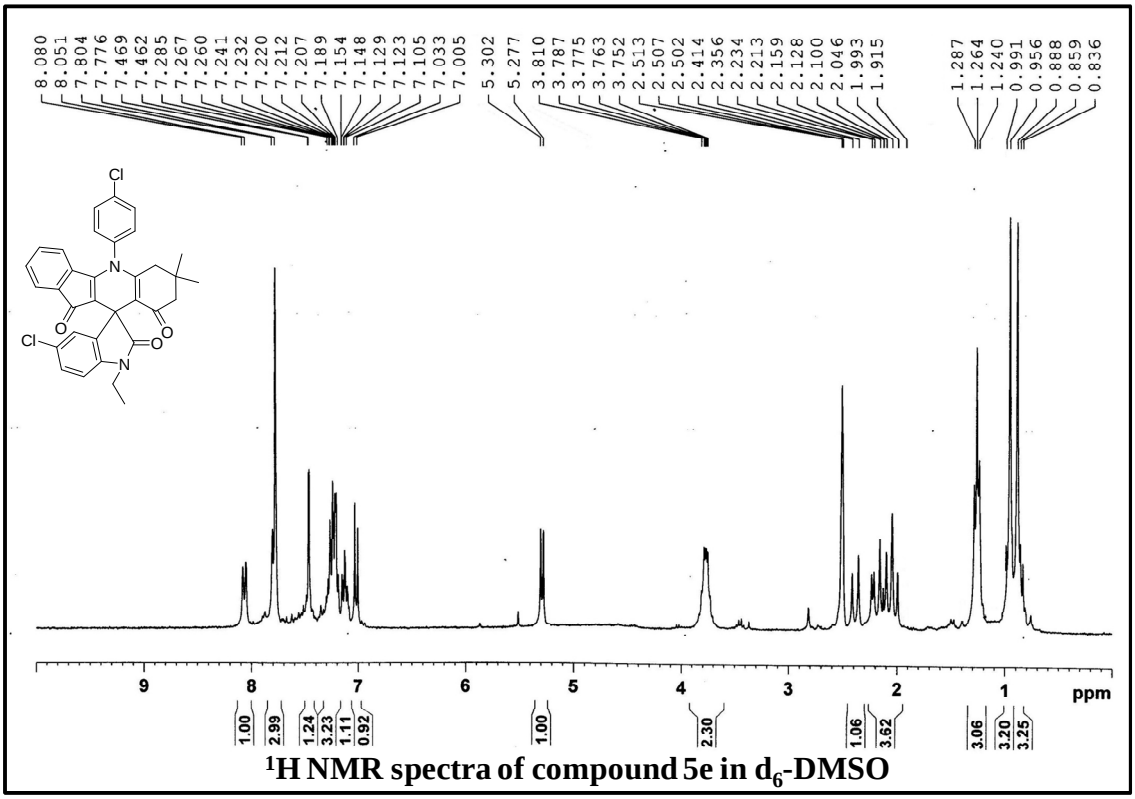
^{13}C NMR spectra of compound 5c in d_6-DMSO



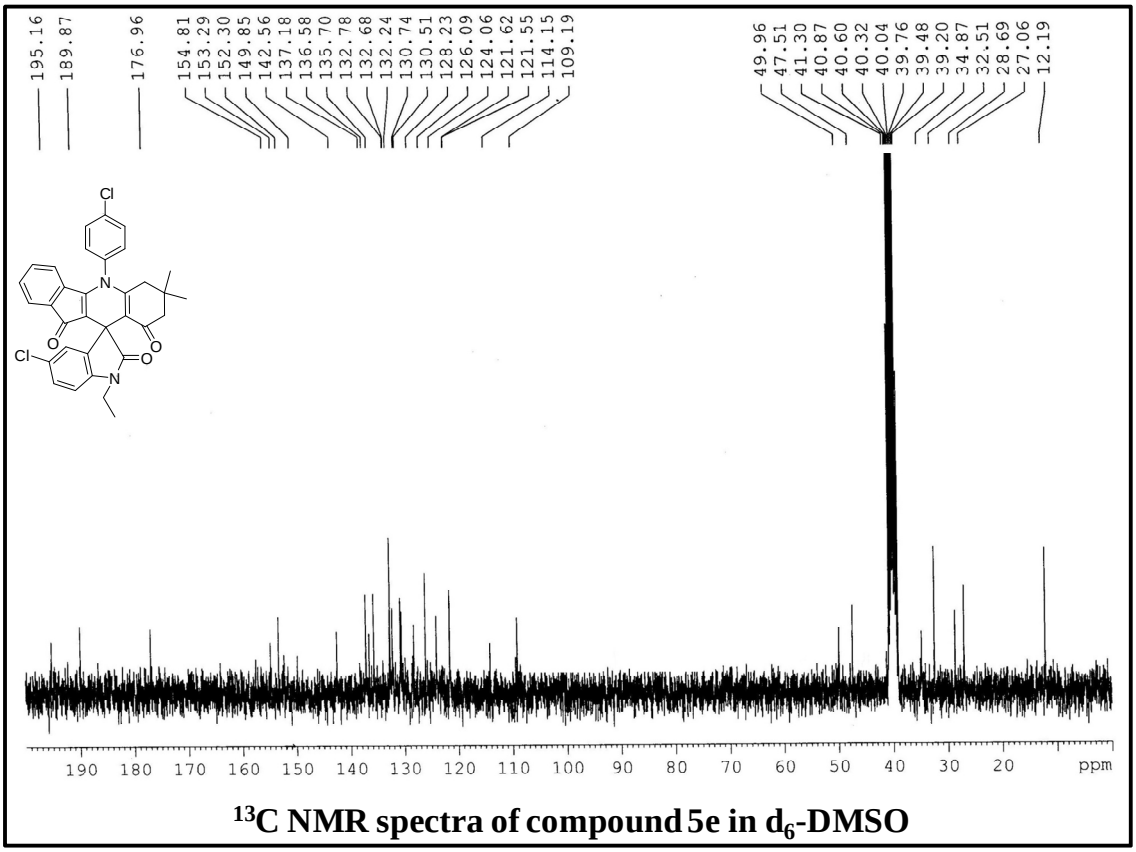
^{1}H NMR spectra of compound 5d in d_6-DMSO



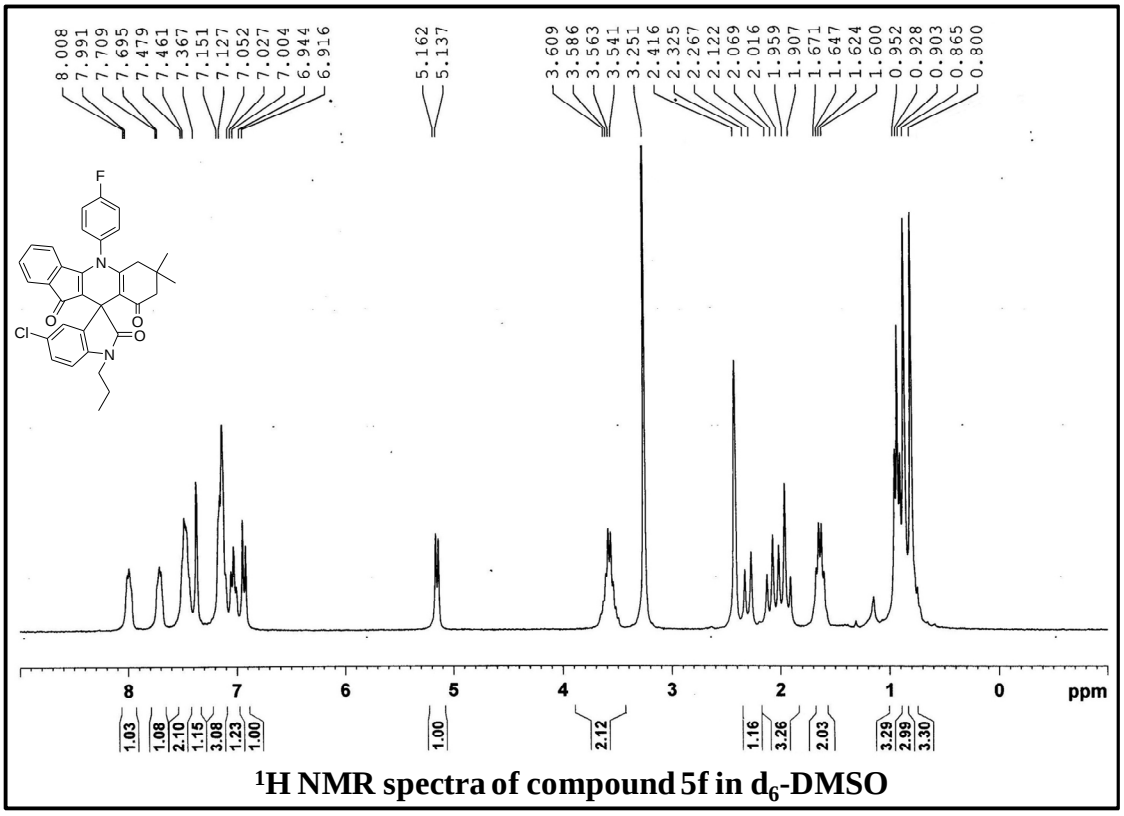
^{13}C NMR spectra of compound 5d in d_6-DMSO



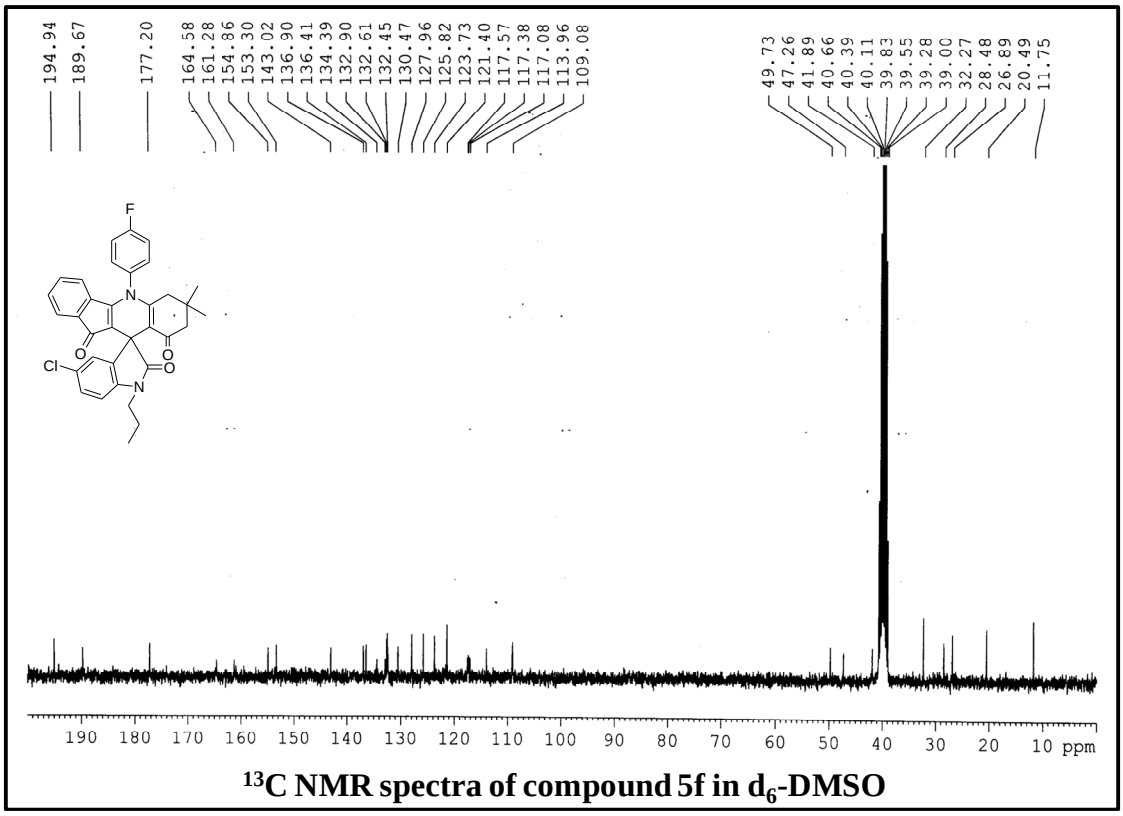
^{1}H NMR spectra of compound 5e in d_6-DMSO



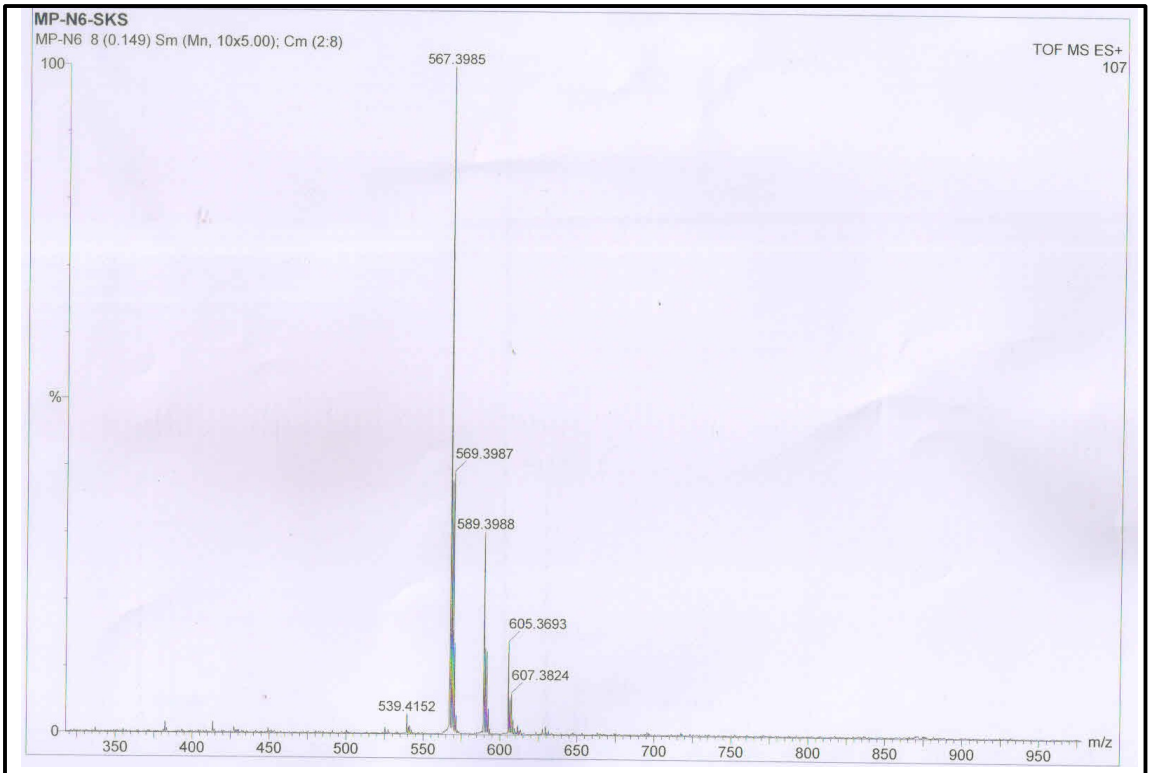
^{13}C NMR spectra of compound 5e in d_6-DMSO



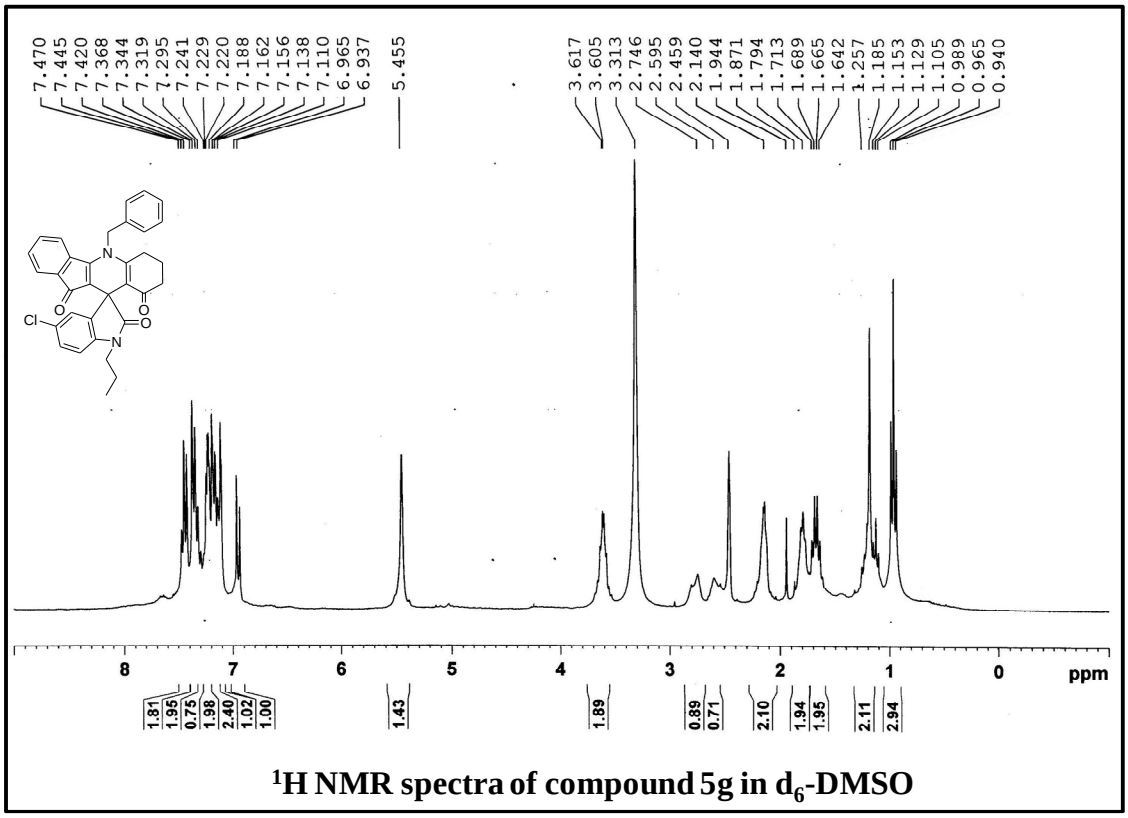
^{1}H NMR spectra of compound 5f in d_6-DMSO



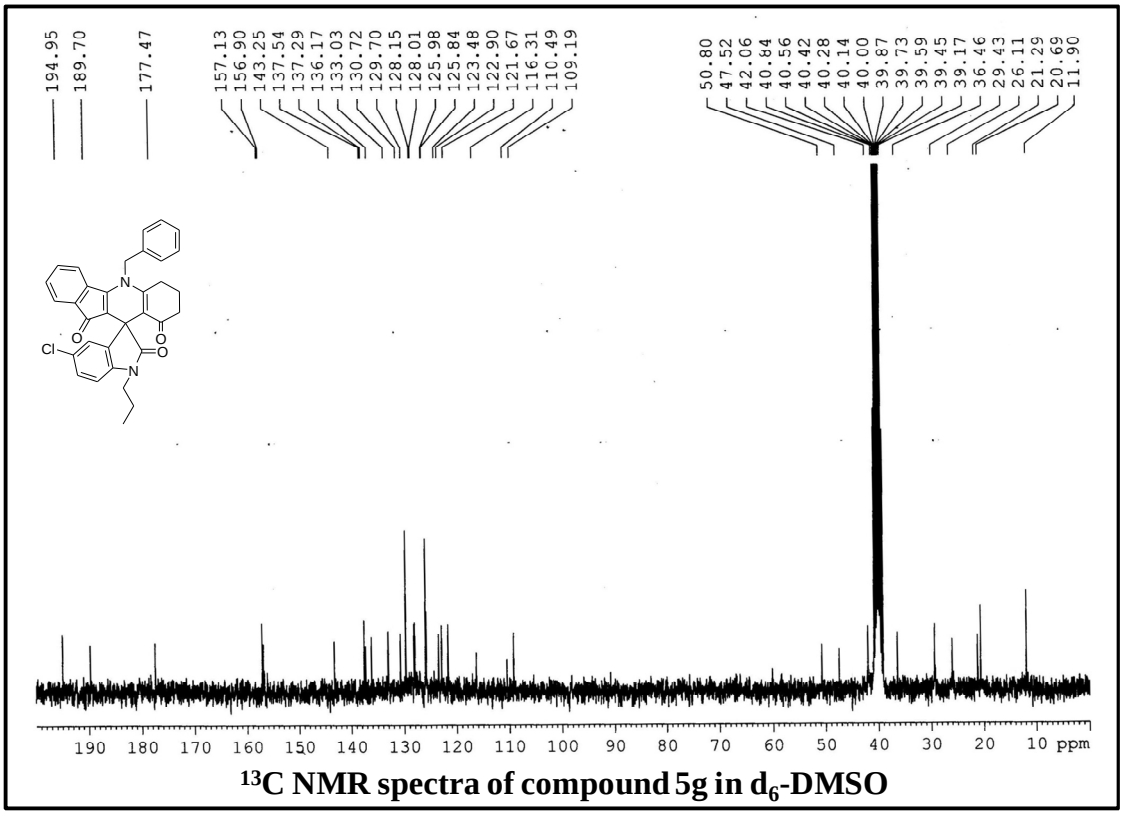
^{13}C NMR spectra of compound 5f in d_6-DMSO



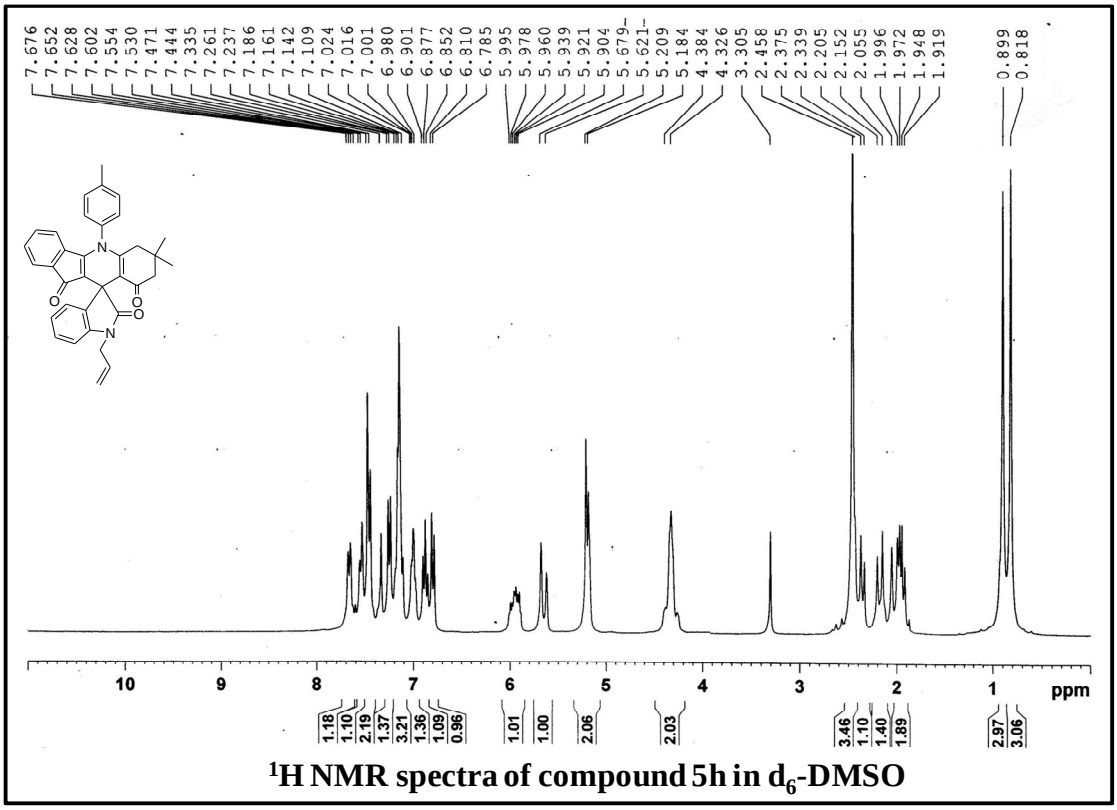
HR-ESI-MS of compound 5f



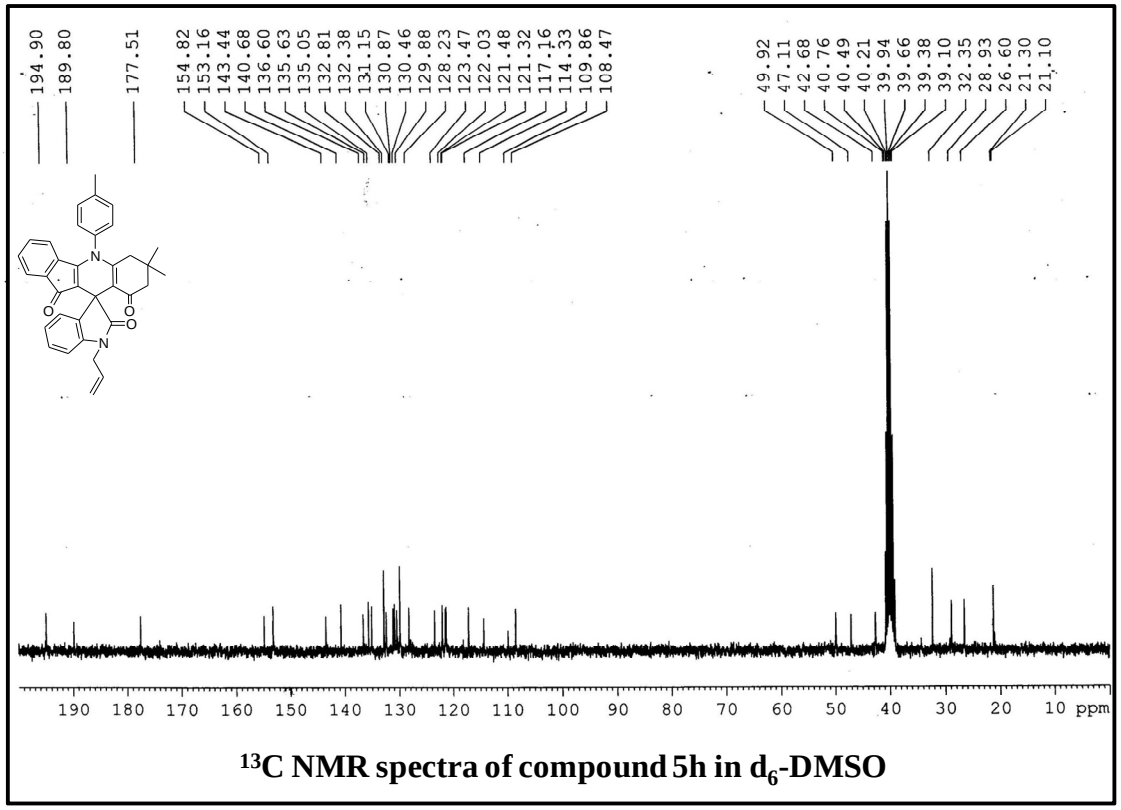
^{1}H NMR spectra of compound 5g in d_6-DMSO



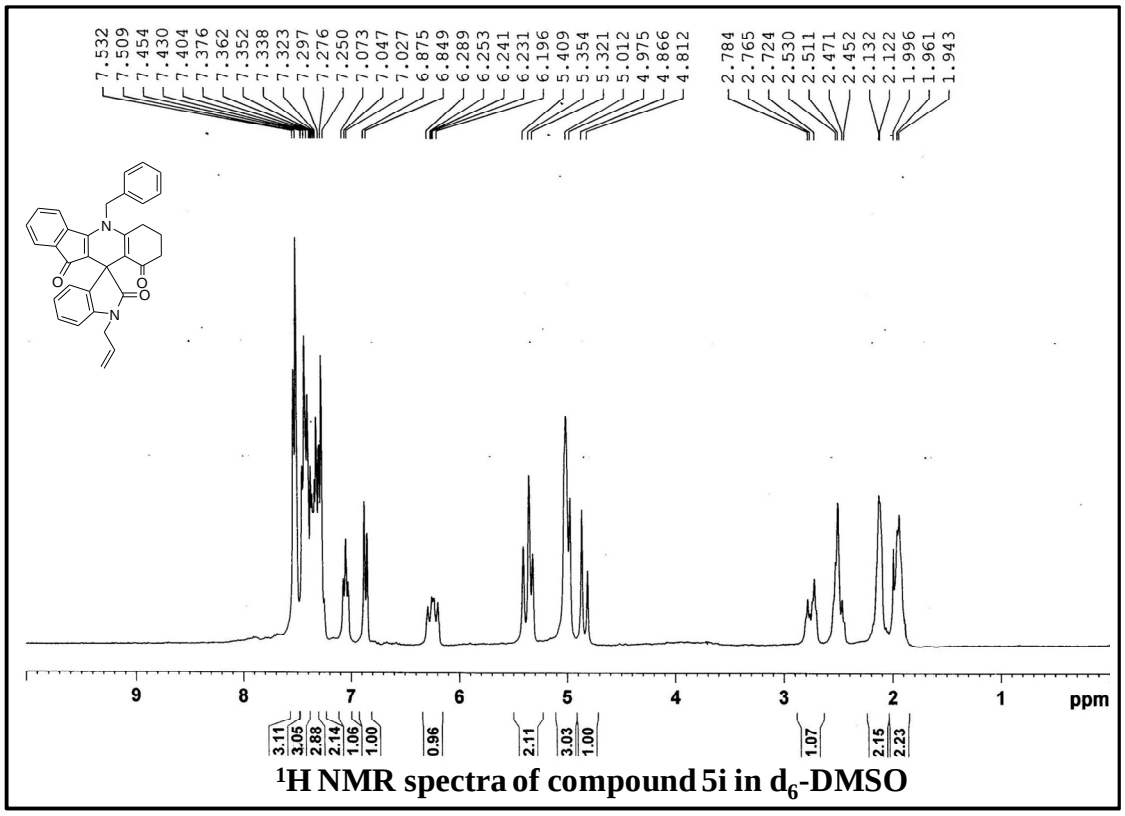
^{13}C NMR spectra of compound 5g in d_6-DMSO



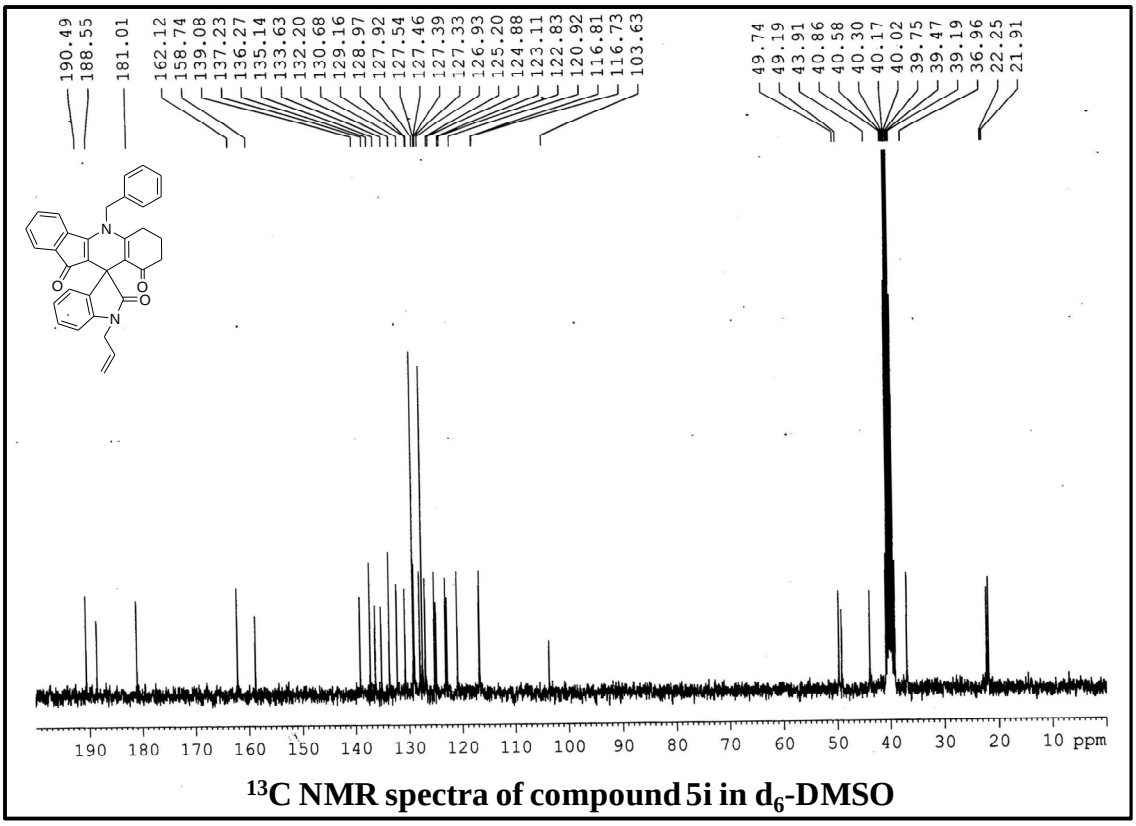
^{1}H NMR spectra of compound 5h in d_6-DMSO



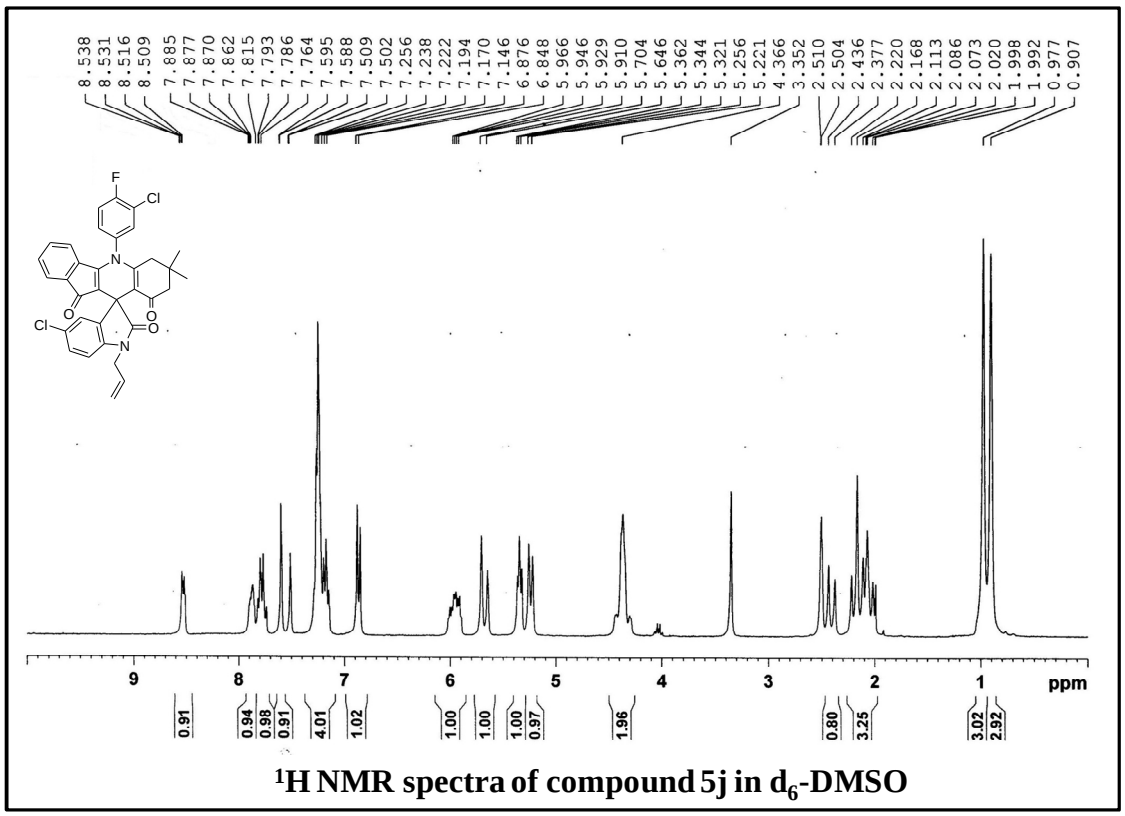
^{13}C NMR spectra of compound 5h in d_6-DMSO



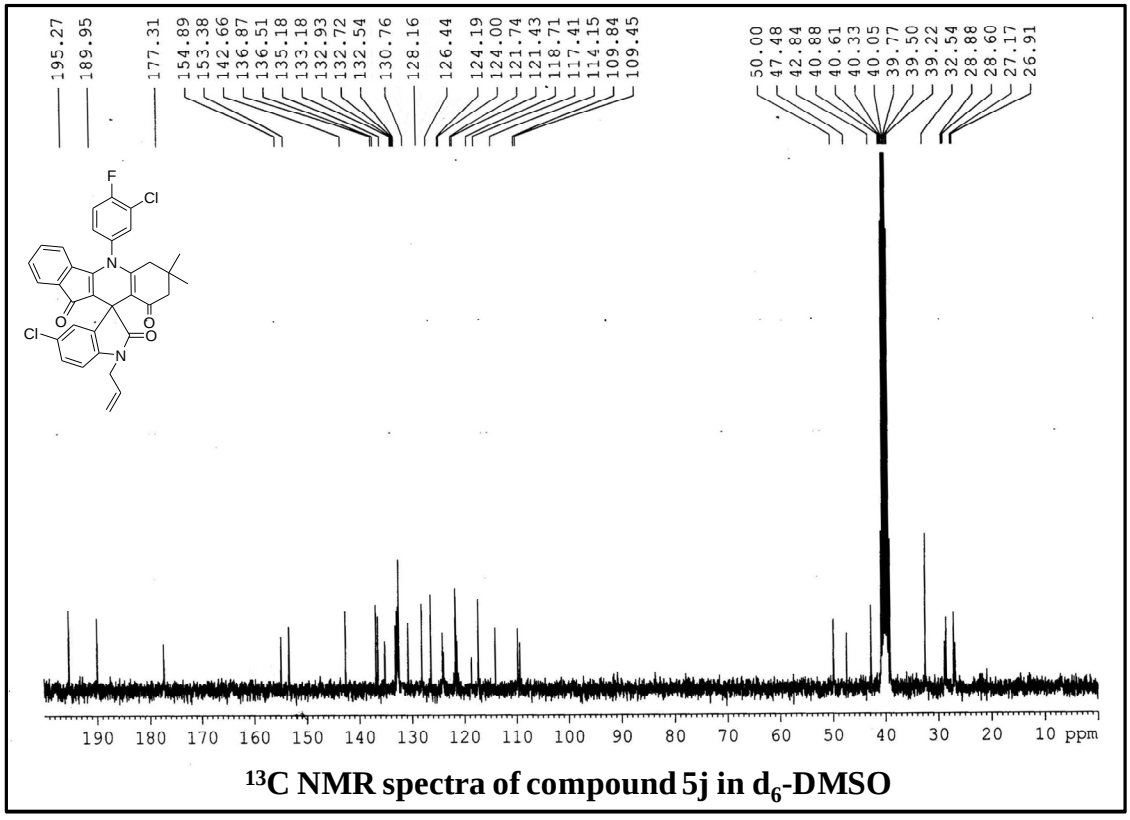
^{1}H NMR spectra of compound 5i in d_6-DMSO



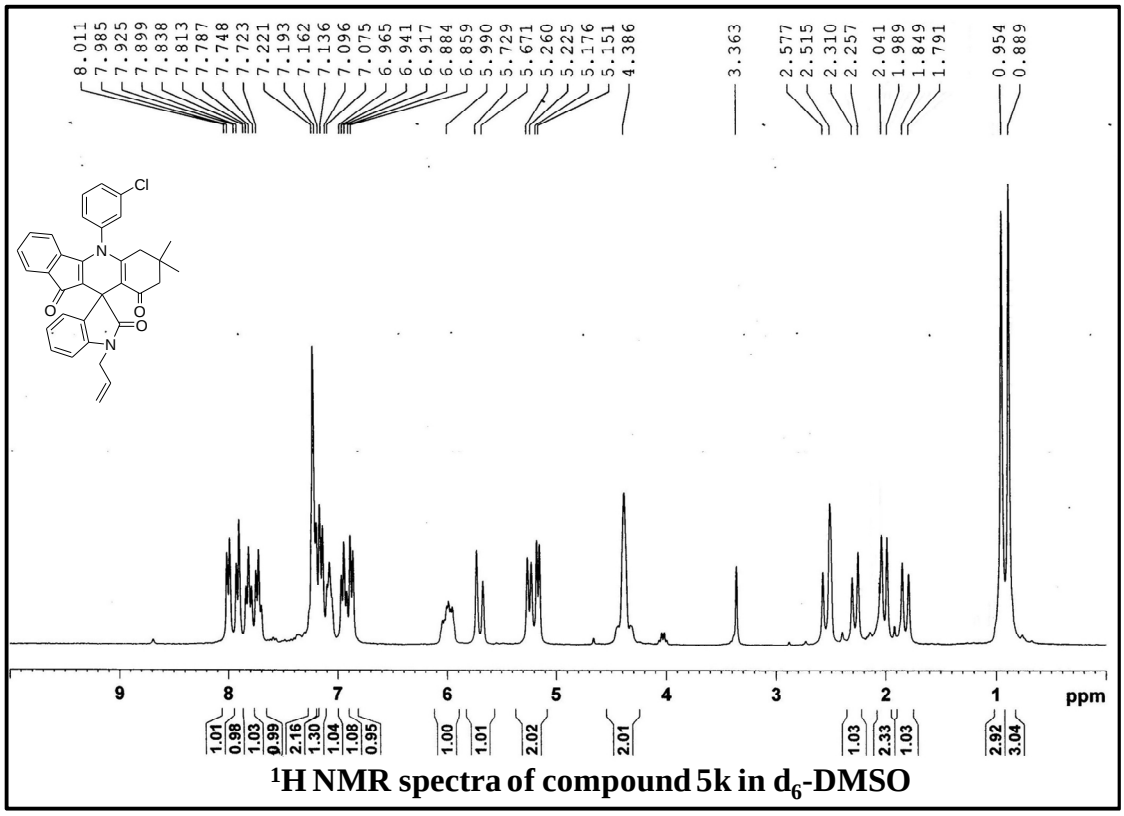
^{13}C NMR spectra of compound 5i in d_6-DMSO



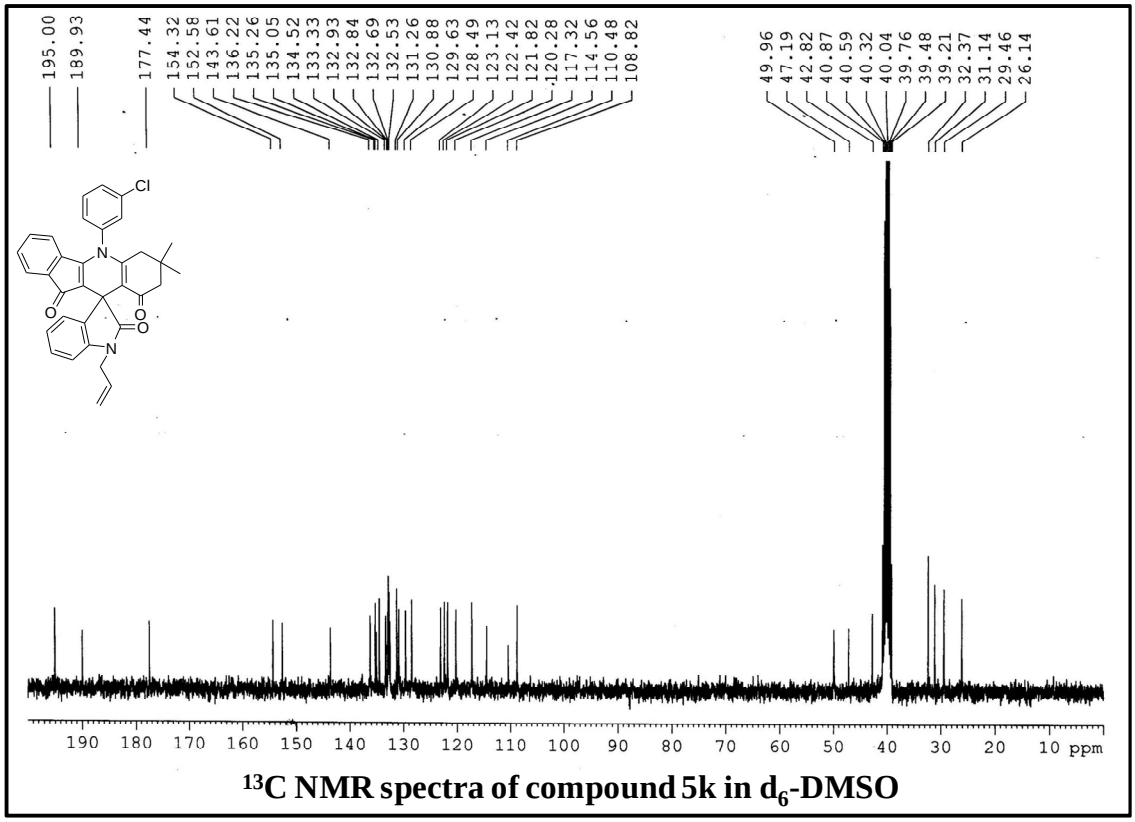
^{1}H NMR spectra of compound 5j in d_6-DMSO



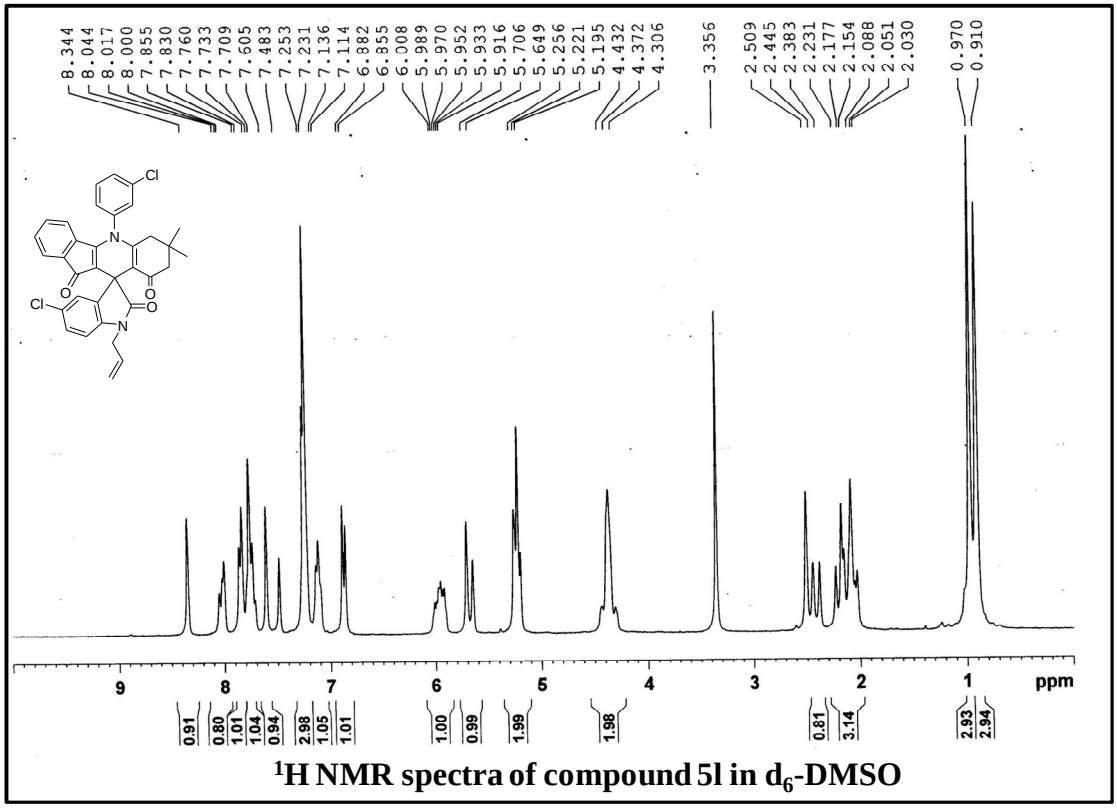
^{13}C NMR spectra of compound 5j in d_6-DMSO



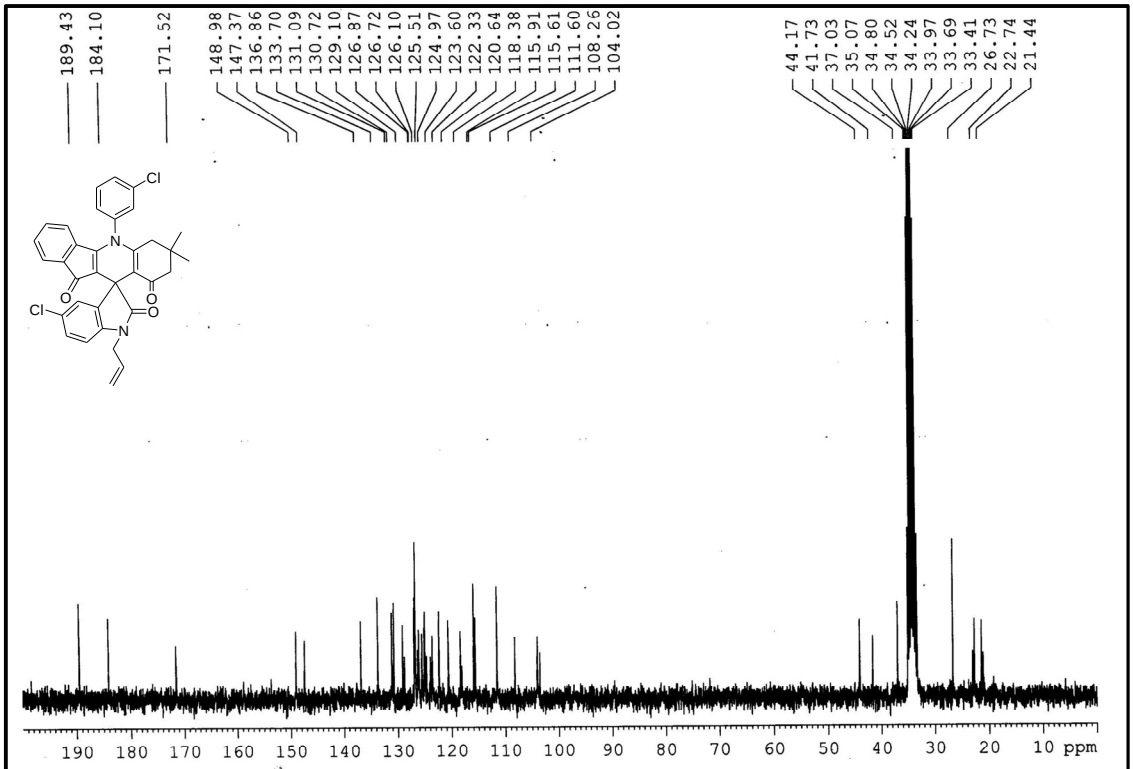
^{1}H NMR spectra of compound 5k in d_6-DMSO



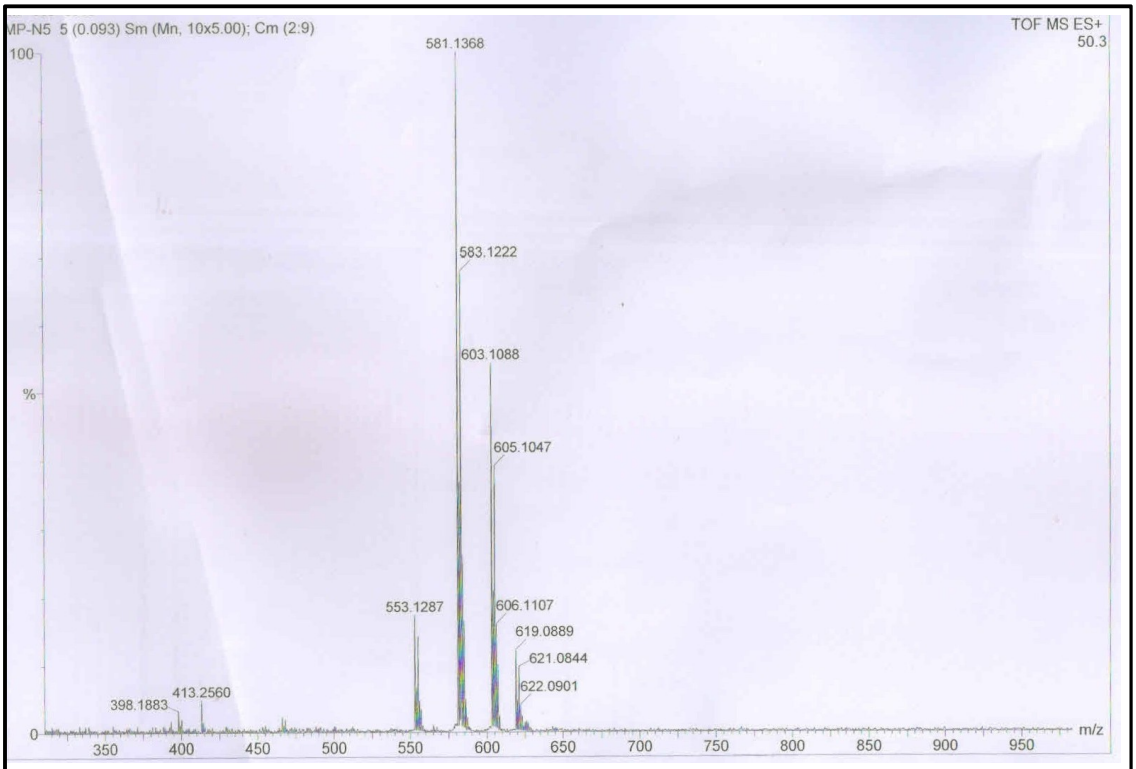
^{13}C NMR spectra of compound 5k in d_6-DMSO



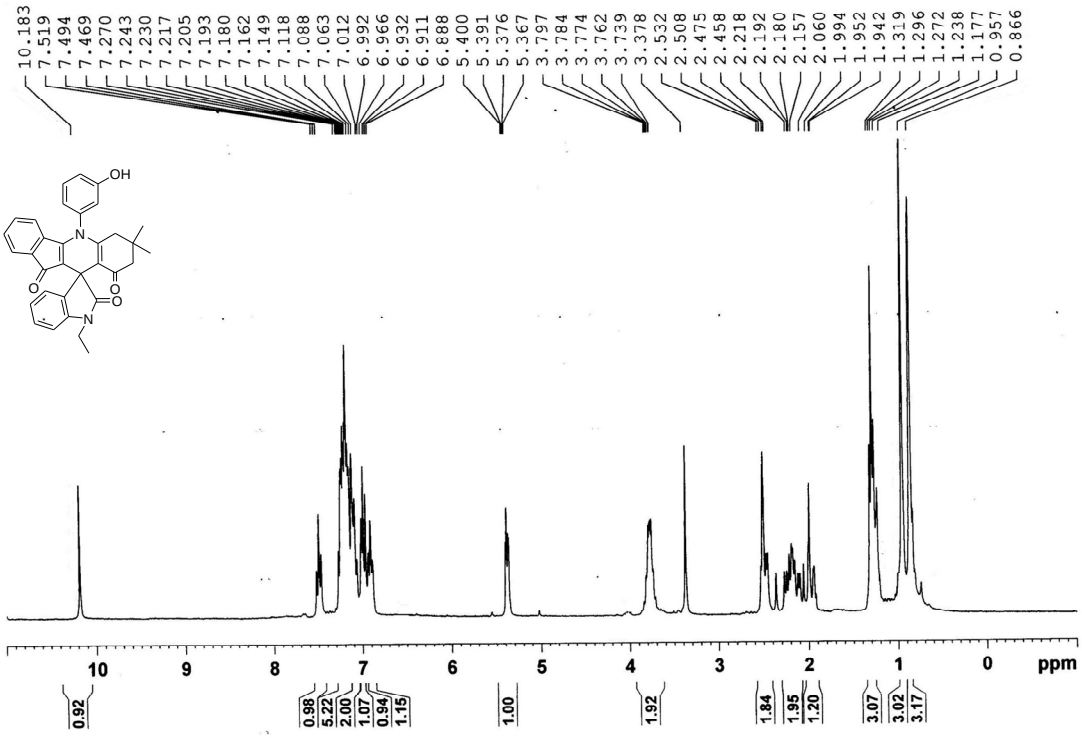
^{1}H NMR spectra of compound 5l in d_6-DMSO



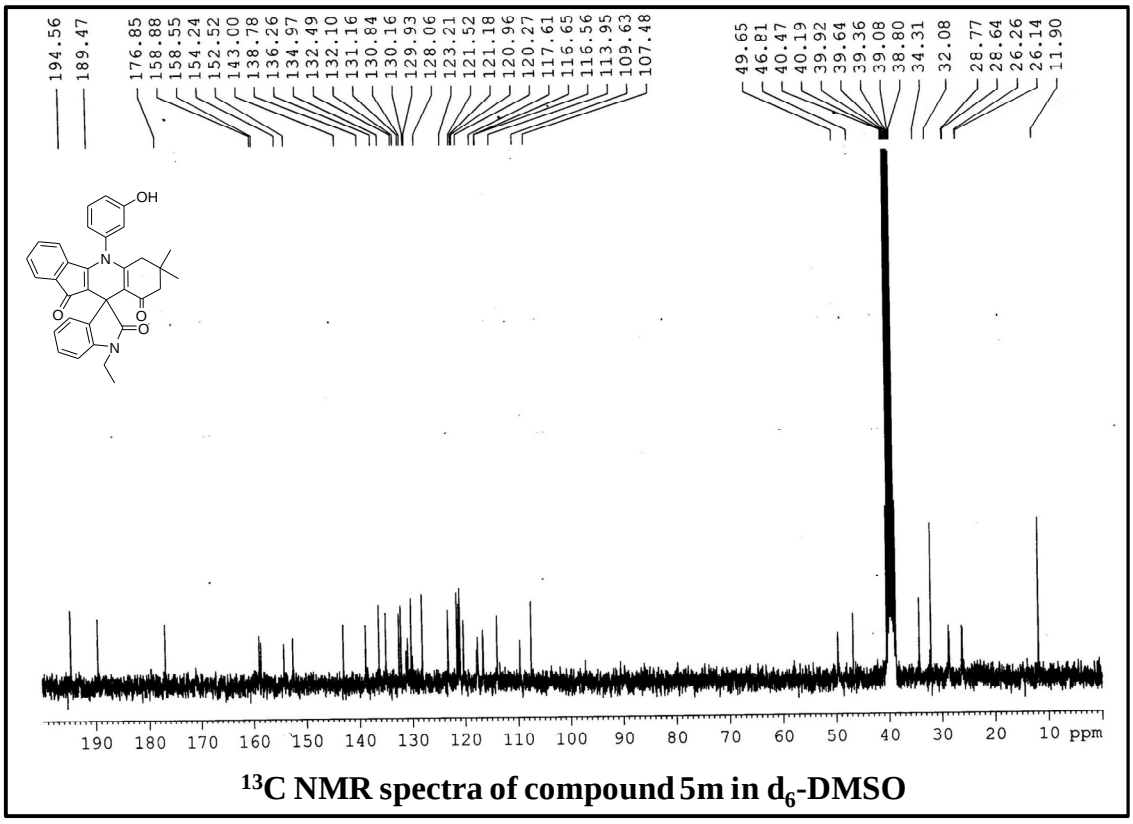
^{13}C NMR spectra of compound 5l in d_6-DMSO



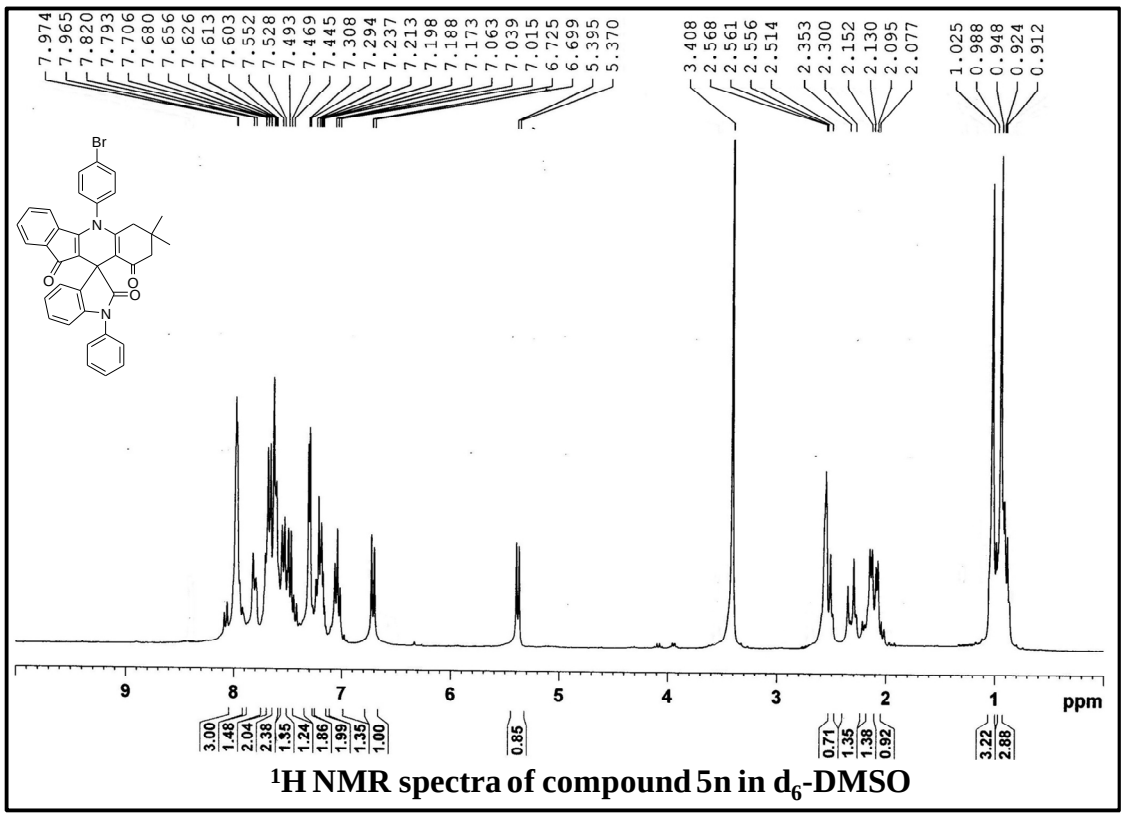
HR-ESI-MS of compound 5l



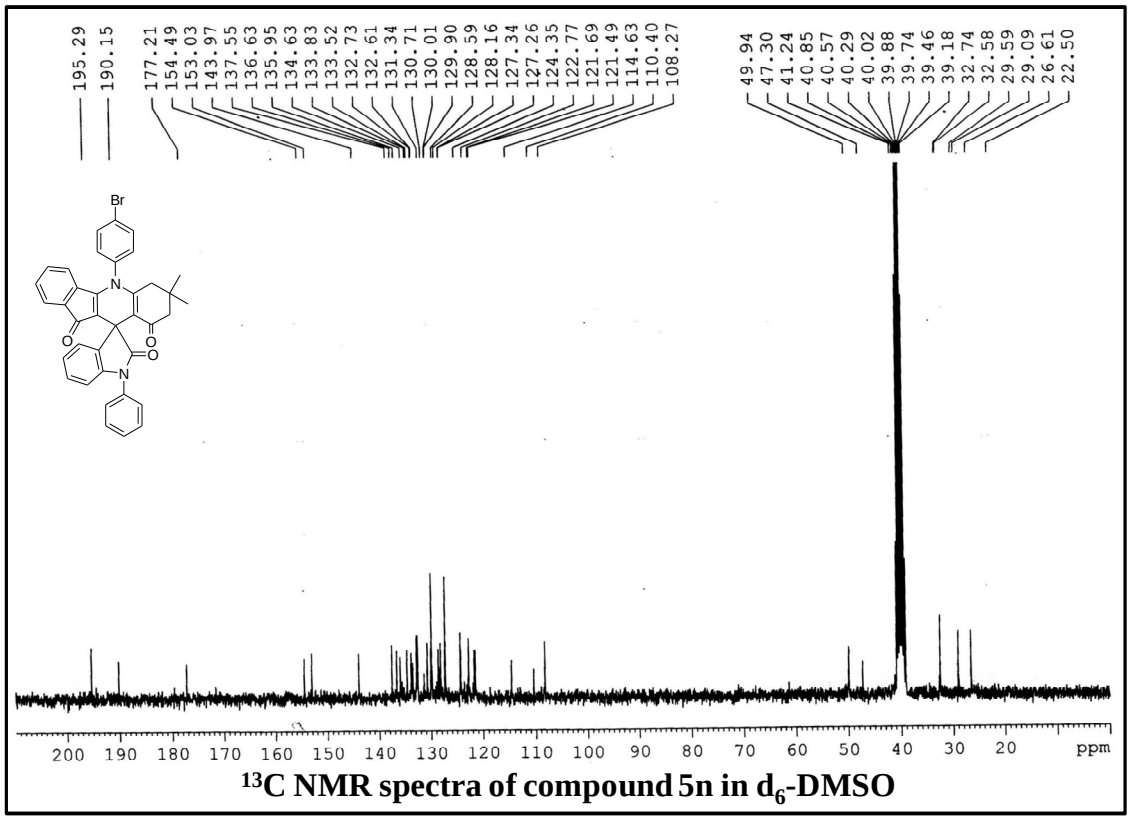
^{1}H NMR spectra of compound 5m in d_6-DMSO



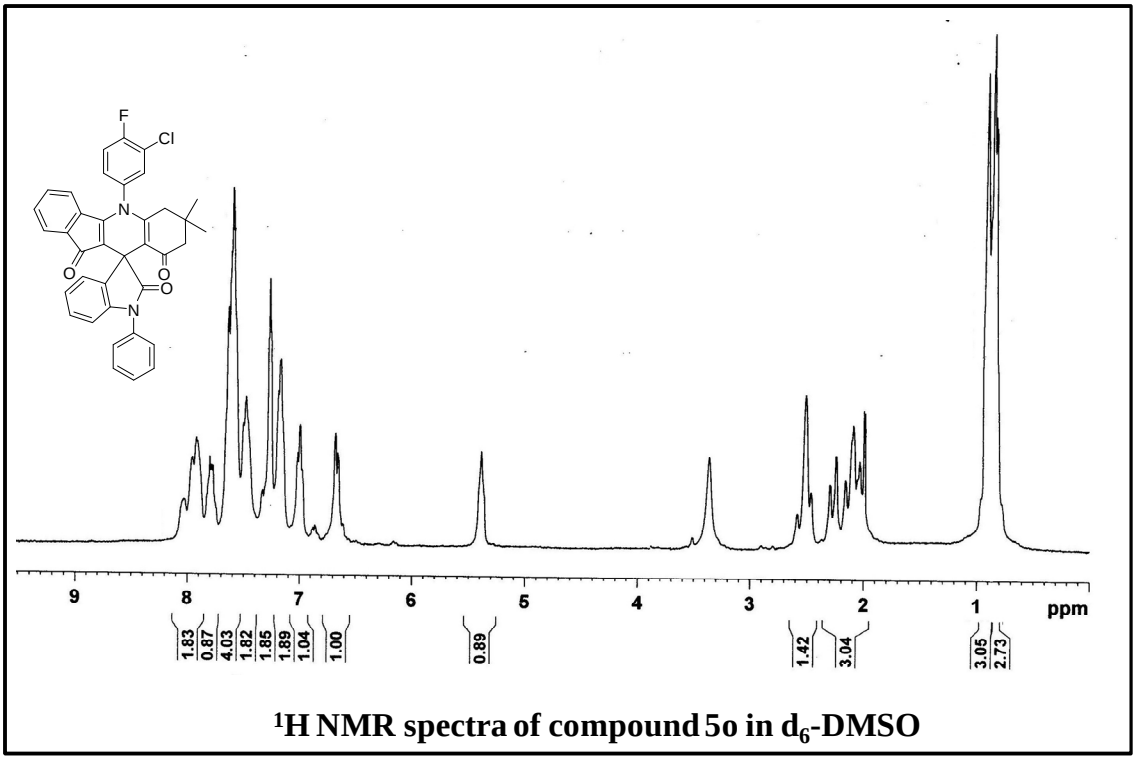
^{13}C NMR spectra of compound 5m in d_6-DMSO



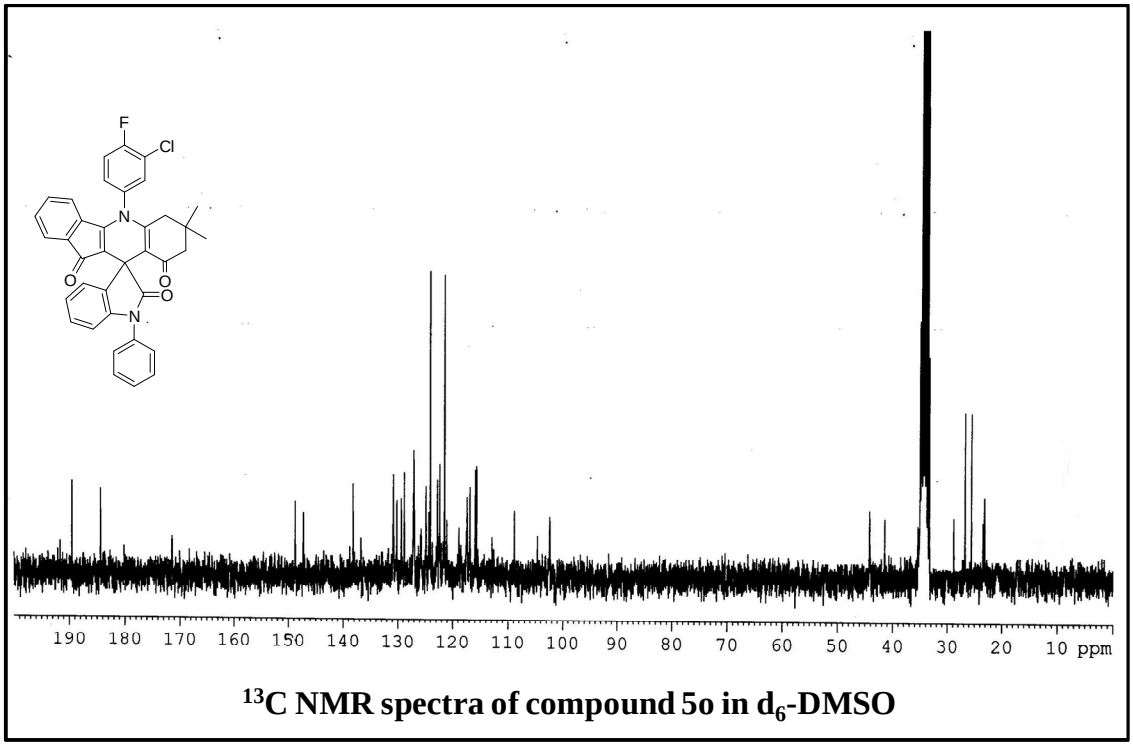
^{1}H NMR spectra of compound 5n in d_6-DMSO



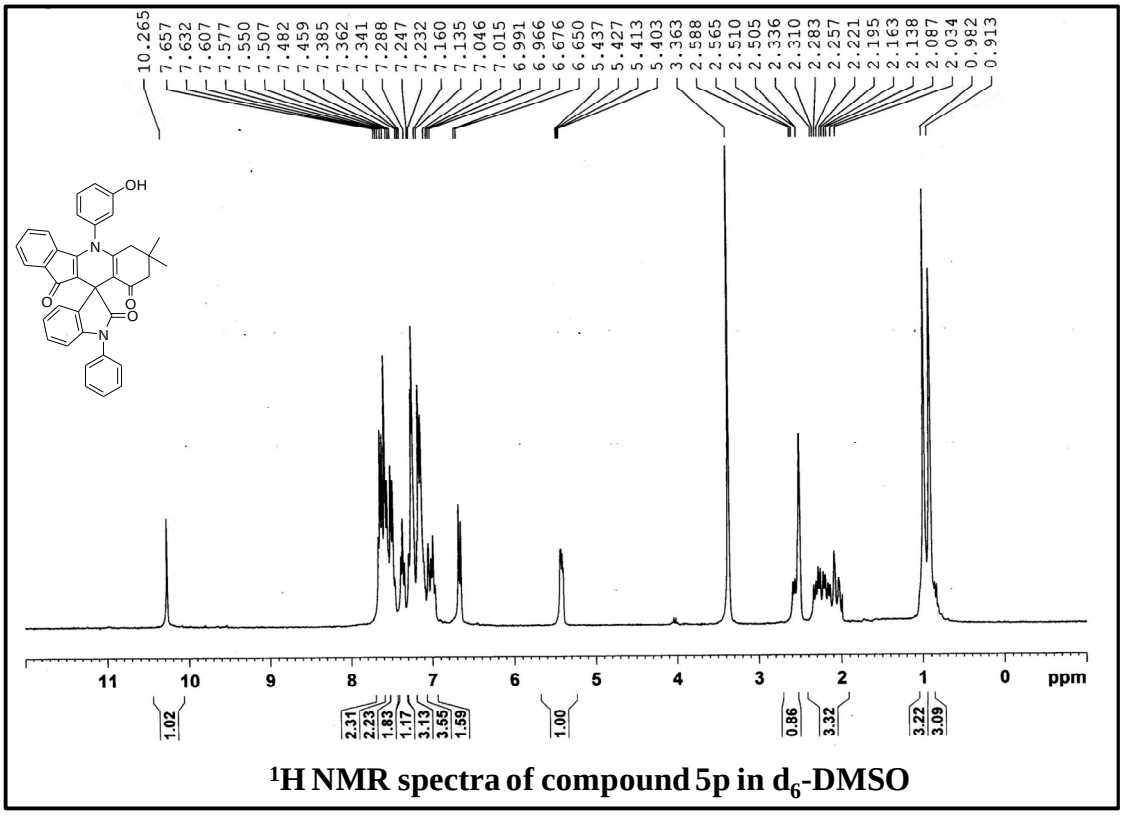
^{13}C NMR spectra of compound 5n in d_6-DMSO



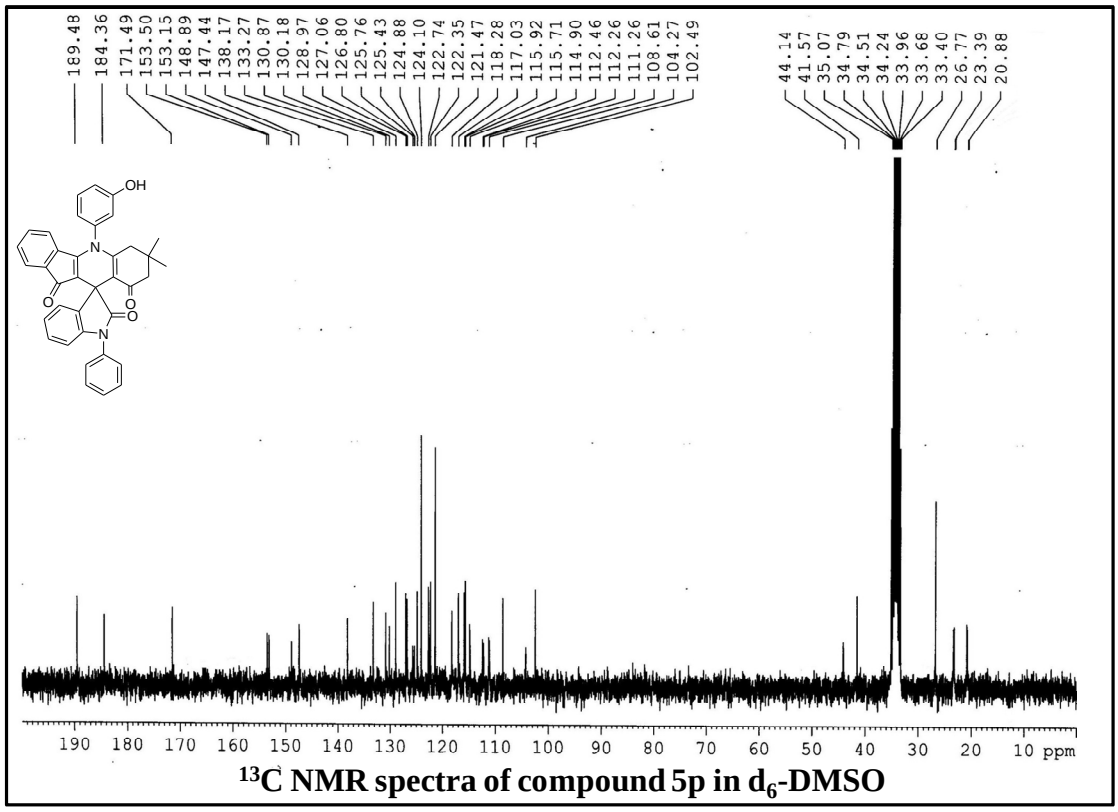
^{1}H NMR spectra of compound 5o in d_6-DMSO



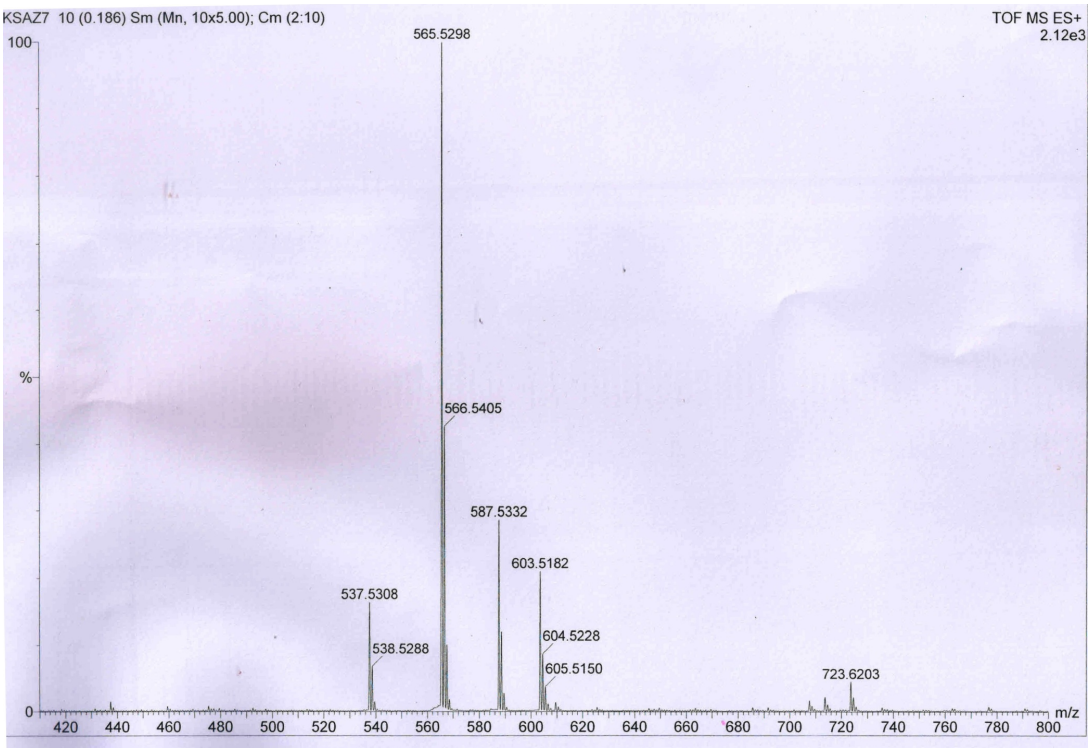
^{13}C NMR spectra of compound 5o in d_6-DMSO



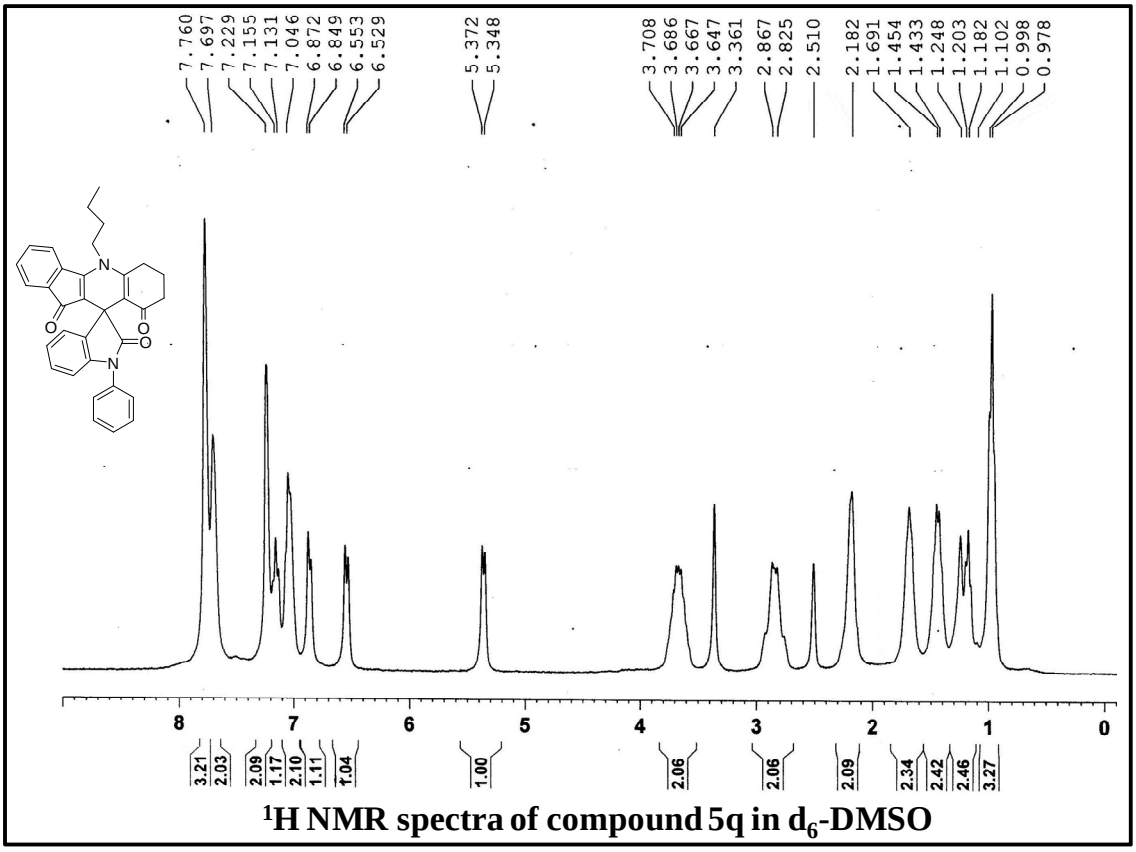
^{1}H NMR spectra of compound 5p in d_6-DMSO



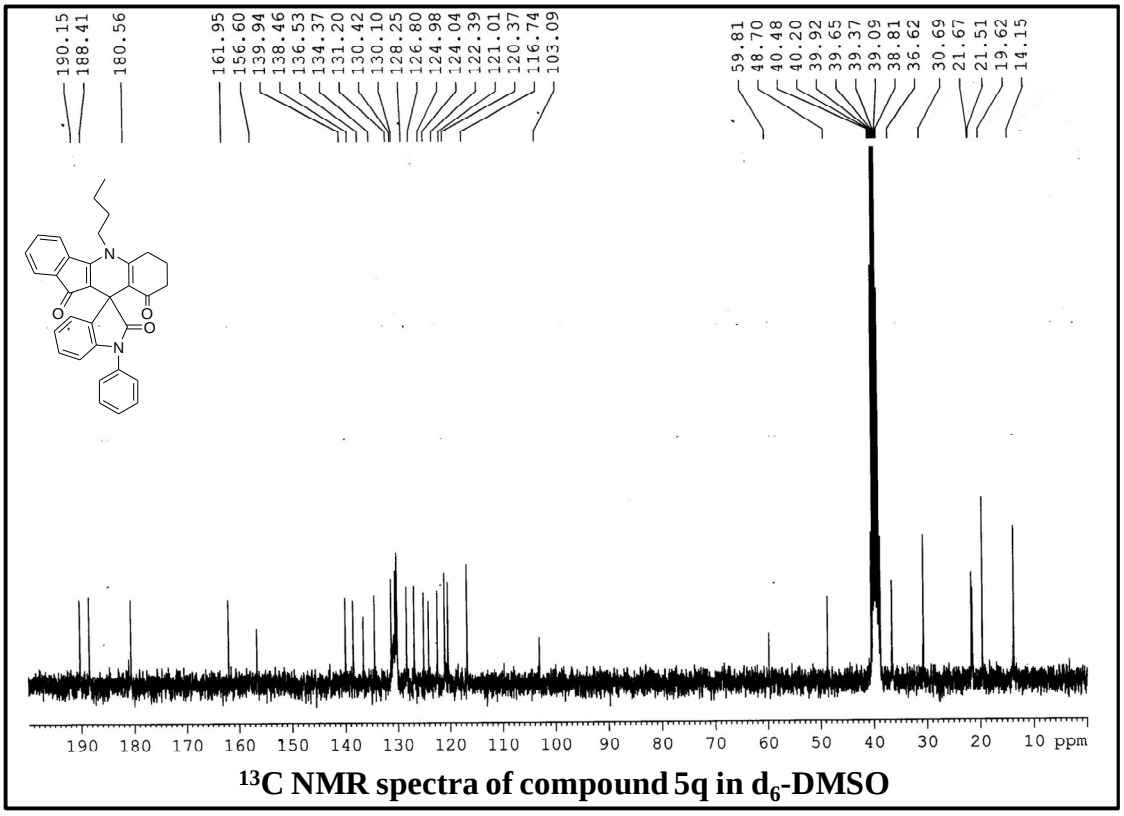
^{13}C NMR spectra of compound 5p in d_6-DMSO



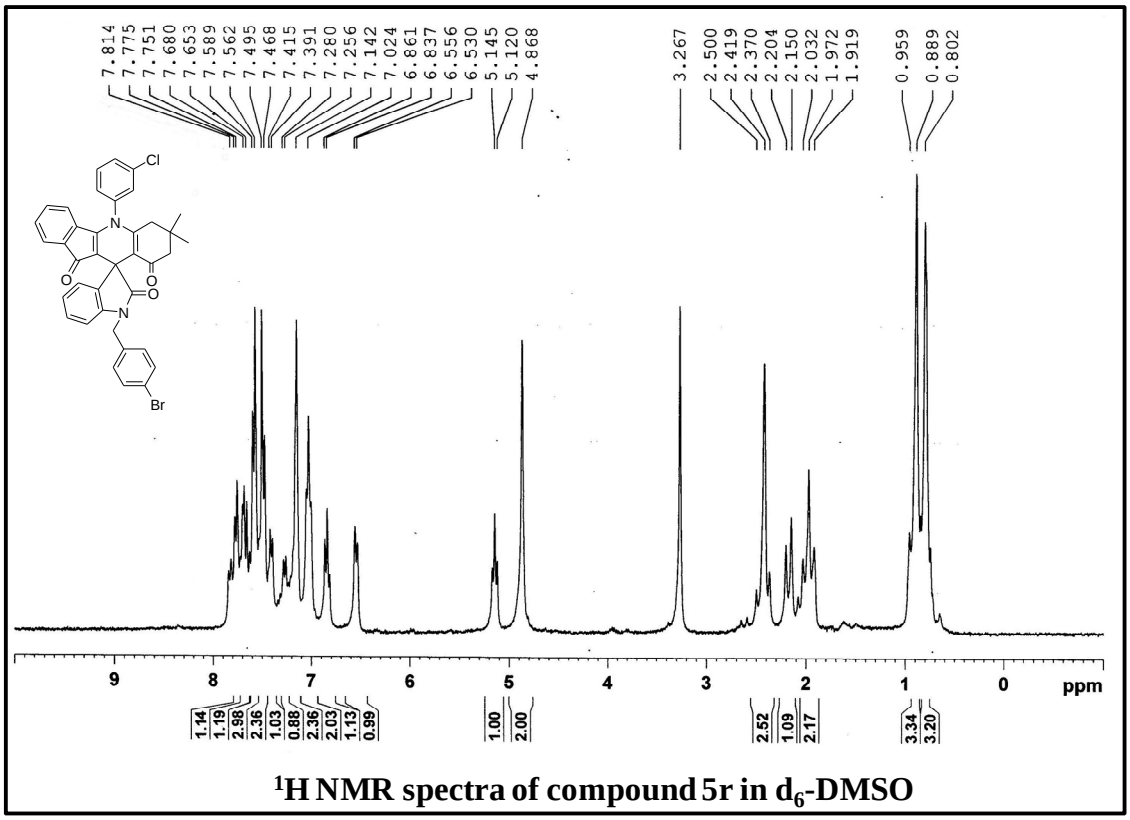
HR-ESI-MS of compound 5p



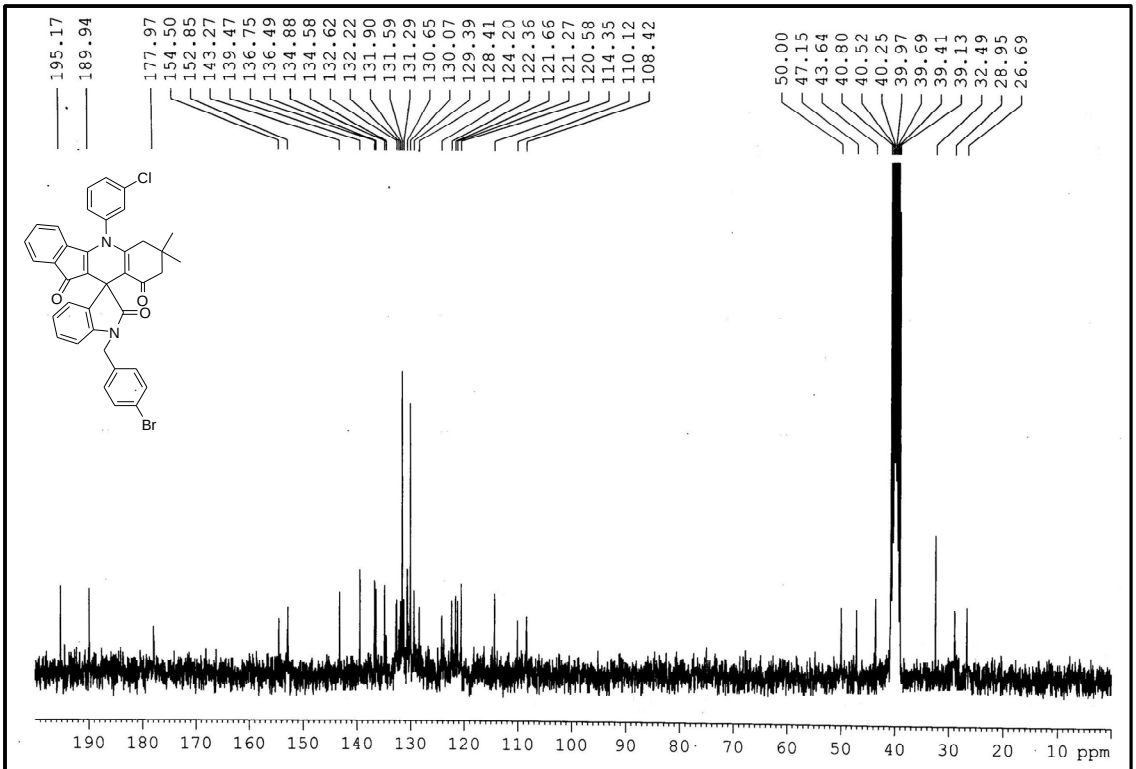
^{1}H NMR spectra of compound 5q in d_6-DMSO



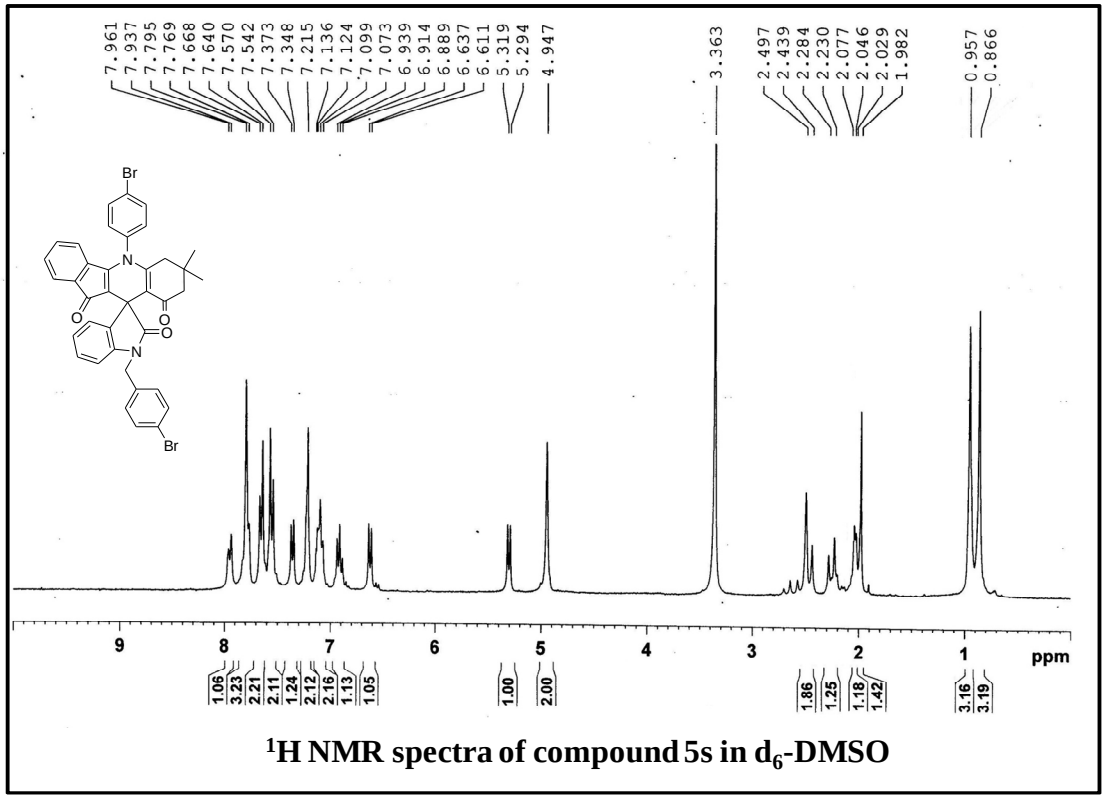
^{13}C NMR spectra of compound 5q in d_6-DMSO



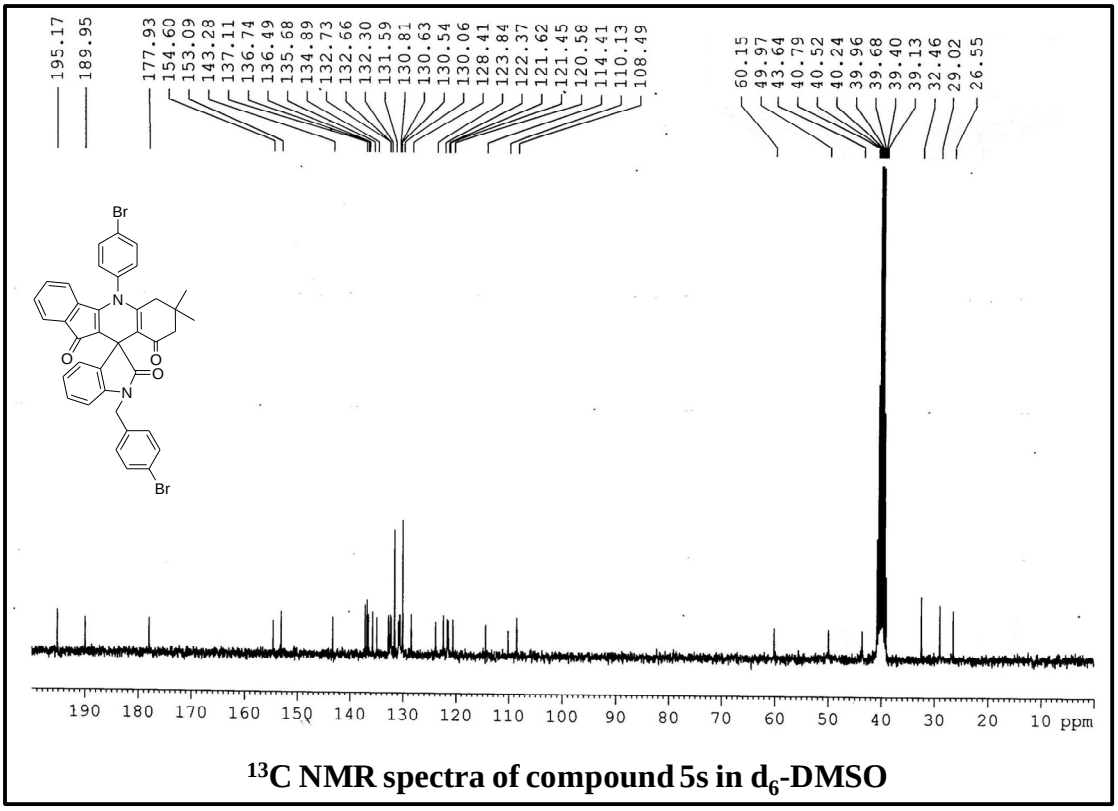
^{1}H NMR spectra of compound 5r in d_6-DMSO



^{13}C NMR spectra of compound 5r in d_6-DMSO



^{1}H NMR spectra of compound 5s in d_6-DMSO



^{13}C NMR spectra of compound 5s in d_6-DMSO

Preparation of the Catalyst:

Preparation of Fe_3O_4 nano particle:[2] $FeCl_3 \cdot 6H_2O$ (8.1 g) and urea (5.4 g) were stirred in 300 mL double distilled water at 85 to 90 °C for 2 h. The resultant brown colored reaction mixture was cooled to room temperature and $FeSO_4 \cdot 7H_2O$ (4.2 g) was added into it. The pH of the resultant solution was maintained at 10 by addition of 0.1 M NaOH solution. The molar ratio of Fe(III) to Fe(II) in the above system was nearly 2.0. The obtained hydroxides were kept under ultrasonication in the sealed flask at room temperature for 30 min. After ageing for 5 h, the obtained black powder of Fe_3O_4 nano particles was washed several times with distilled water, and dried under vacuum.

Preparation of Fe_3O_4-SO_3H catalyst:[2] In a two neck round bottom flask, one neck was equipped with a dropping funnel and other neck is fixed with water vacuum to suck HCl gas generated during the reaction. Magnetite, Fe_3O_4 nano particles (3.0 g) was then poured into round bottom flask and neat chlorosulfonic acid was added (1.0 mL) drop by drop over a period of 10 min at room temperature. HCl gas generated immediately from the reaction was removed by suction. After complete addition of chlorosulfonic acid, the mixture was stirred vigorously for 30 min and solid brown magnetic sulfonic acid, Nanocat-Fe-SO_3H (3.45 g) was collected.

Reusability Test:

XRD: Crystalline phase characterization of synthesized iron oxide nanoparticles, calcined at 500°C was carried out by XRD study. The diffraction peaks of the XRD pattern of Fe_3O_4 and freshly prepared Fe_3O_4-SO_3H MNPs and 5 times reused Fe_3O_4-SO_3H MNPs (Fig. S1A, B and C respectively) at (220), (311), (400), (422) and (440) lattice planes are observed at 2θ = 32.9°, 35.36°, 44.9°, 53.7° and 62.35° respectively. The peaks in the XRD patterns represent Bragg reflections of face centered cubic (FCC) iron oxide. Similar pattern of peaks is also obtained in Fe_3O_4-SO_3H NPs XRD spectra (Fig. S1B), with slight differentiation, may be due to the coating of sulfonic acid groups on the surface of the Fe_3O_4 nano-particles. No characteristics changes in the peaks are observed after 5 times reuse of the Nanocat- Fe_3O_4-SO_3H (Fig. S1C) which suggests that the structure of the catalyst remain unchanged after the reusability test. [2]

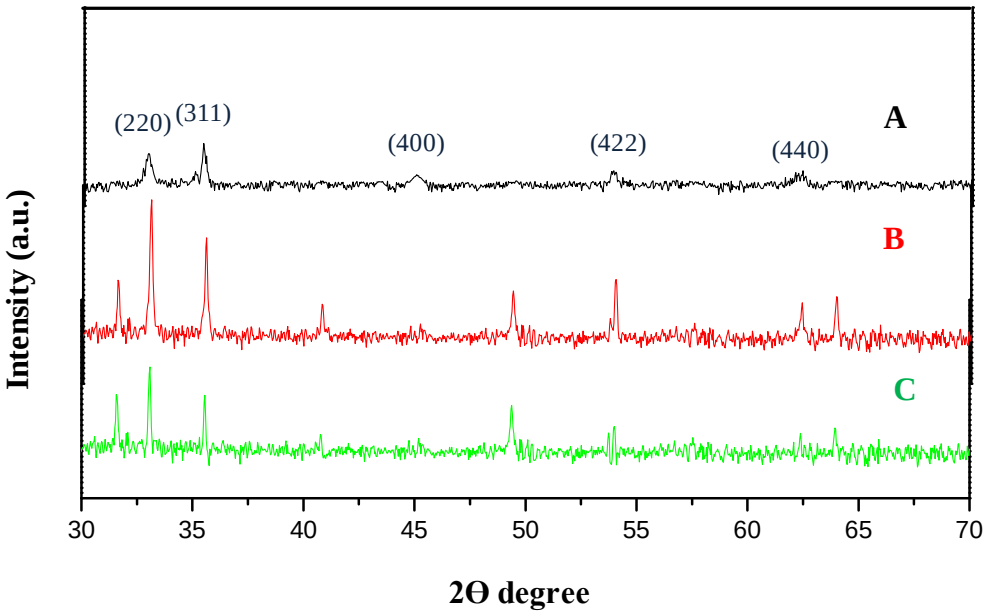


Fig. S1 XRD spectra of (A) Fe_3O_4, (B) freshly prepared Fe_3O_4-SO_3H MNPs and (C) 5 times reused Fe_3O_4-SO_3H MNPs

Infrared spectra: The infrared spectra of Fe_3O_4 and Nanocat-Fe_3O_4-SO_3H are depicted in Figure S2a. The band observed at 539 cm^{-1}, confirms the structure of Fe-O group, while for nanocat-Fe_3O_4-SO_3H, the characteristics peaks from the -SO_3H group of chlorosulfonic acid were observed at 3367 cm^{-1} (O-H stretching). Also detectable are the bands at 1629 and between 1211 and 968 cm-1 corresponding to S=O and S-O stretching which clearly indicates the presence of -SO3H group over magnetite surface. The infrared spectra of reused catalyst after five runs is depicted in Figure S2b. It is important to note that all corresponding peaks are intact without any change in characteristics. It indicates that structure of catalyst doesn't change even after 5 cycles.[2]

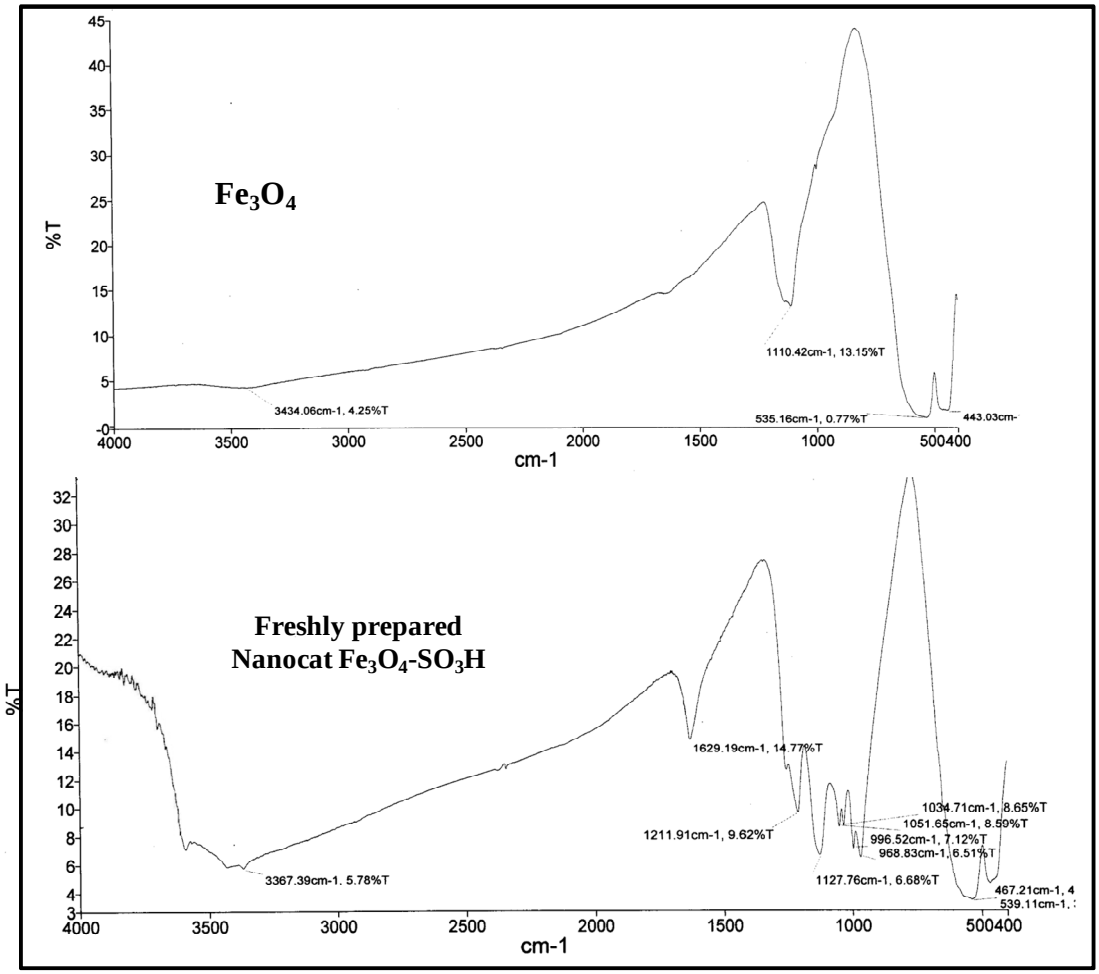


Fig. S2a FT infrared spectrum of Fe_3O_4 and Nanocat- Fe_3O_4-SO_3H

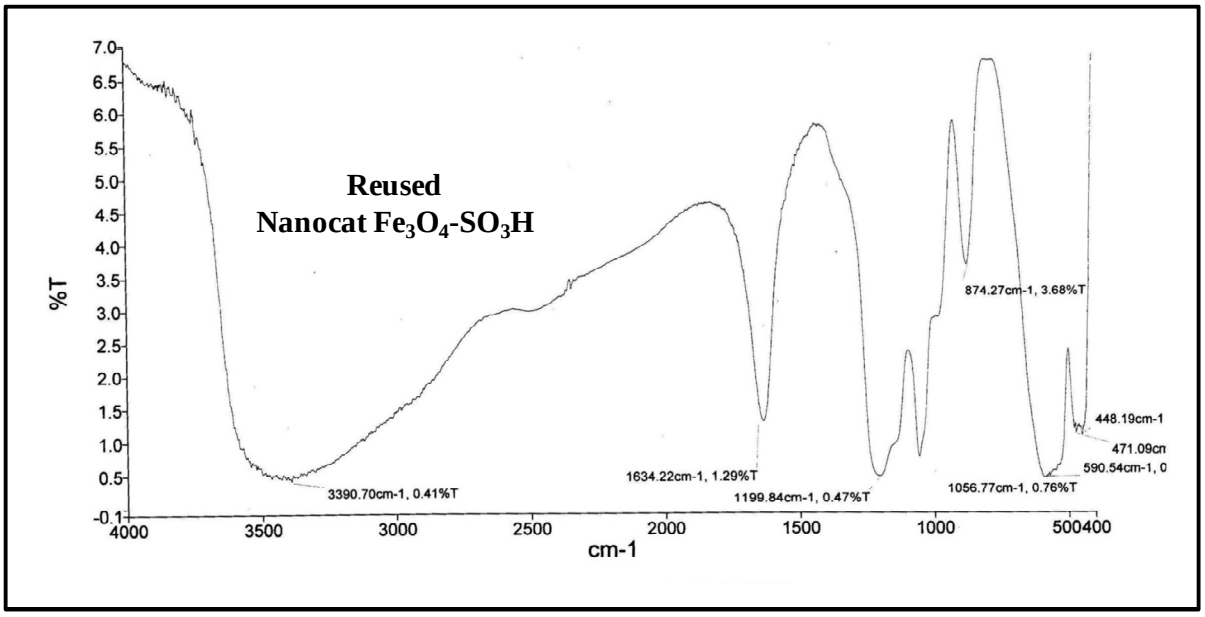


Fig. S2b FT infrared spectrum of 5 times reused Nanocat- Fe_3O_4-SO_3H

References

2 (a) C. G. Piscopo, S. Bühler, G. Sartori and R. Maggi, *Catal. Sci. Technol.*, 2012, **2**, 2449–2452; (b) M. B. Gawande, A. K. Rathi, I. D. Nogueira, R. S. Varma and P. S. Branco, *Green Chem.*, 2013, **15**, 1895.
