SUPPORTING INFORMATION

DOI:

Title: A catalyst-free, one-pot multicomponent synthesis of spiro-benzimidazoquinazolinones via Knoevenagel-Michael-Imine pathway: A microwave assisted approach

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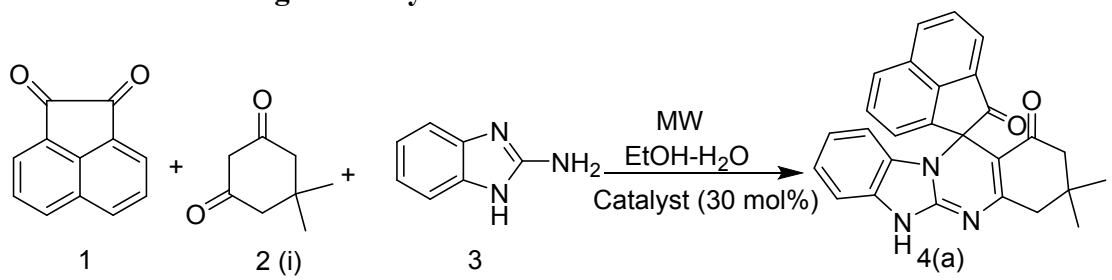
1. General Considerations:-

All chemicals were purchased from Sigma Aldrich and all solvents were analytically pure grade were used as received without any further purification. A CEM microwave synthesizer of (Model-Discover System-908010)voltage 180/264 and frequency 50/60Hz, operating by utilizing 700 W with maximum microwave power level of 300 W, was employed for the synthesis work Some of the derivatives of compound **5** were synthesized according to literature methods.[29]Analytical TLC were performed using 2.5X 5 cm plates coated with 0.25 mm thickness of silica gel 60F-254 Merck and visualization was accomplished with UV light, iodine and or $KMnO_4$ staining.^{1}HNMR ,^{13}CNMR and DEPT-135 spectra were obtained from Bruker's 500 spectrometer (at 500 MHz and 125 MHz respectively) and are reported in ppm (δ) with respect to tetramethylsilane (TMS, 0.00 ppm) and solvent (DMSO-d_6 = 39.43 ppm)as an internal standard. The abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, dd=double doublet, m=multiplet, br.s=broad singlet &br=broad signal. Melting points were recorded on Buchi M-565 melting point apparatus and are uncorrected. Mass spectra were recorded on LCMS MS spectrometer Advion, USA using Electron Spray Ionization (ESI) in Positive/Negative mode. IR data were recorded on Perkin Elmer FT-IR spectrometer using KBr pellets. All the computational analysis has been carried out using Gaussian 09 program suit.

2. Detailed results of Screening

2.1 *Table S1:* Screening of Catalyst

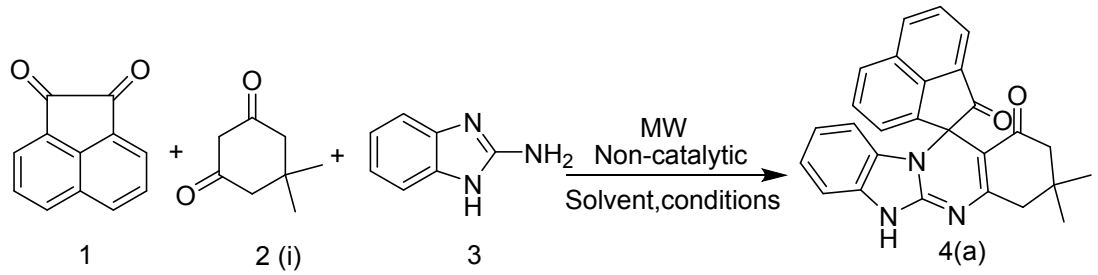


1 2 (i) 3 4(a)

S.No.	Catalyst	Conditions	Yield (%)[a]
1.	p-TSA	160 °C, 5 min	20
2.	$Yb(OTF)_3$	160 °C, 5 min	No reaction
3.	Et_3N	160 °C, 5min	48
4.	PEG	160 °C, 5 min	30

[a]*Isolated yield*

2.2 *Table S2:* Solvent effect

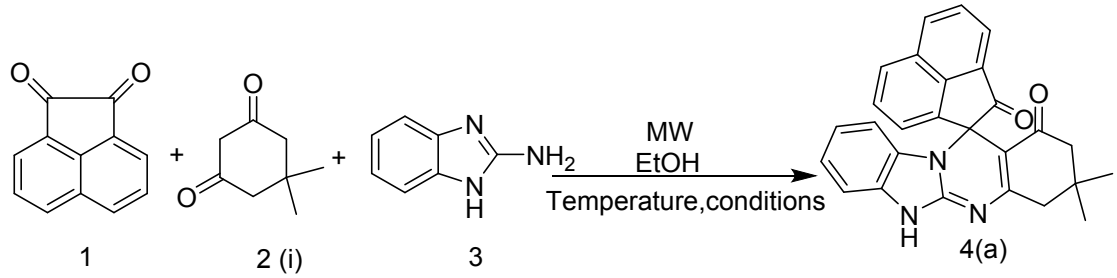


1 2 (i) 3 4(a)

S.No.	Solvent	Conditions	Yield (%)[a]
1	EtOH-H_2O	160°C, 5min	55
2	H_2O	160°C, 5min	65
3	Methanol	160°C, 5 min	47
4	**Ethanol**	**160°C, 5min**	**75**

[a]*Isolated yield*

2.3 ***Table S3:*** **Temperature effect**

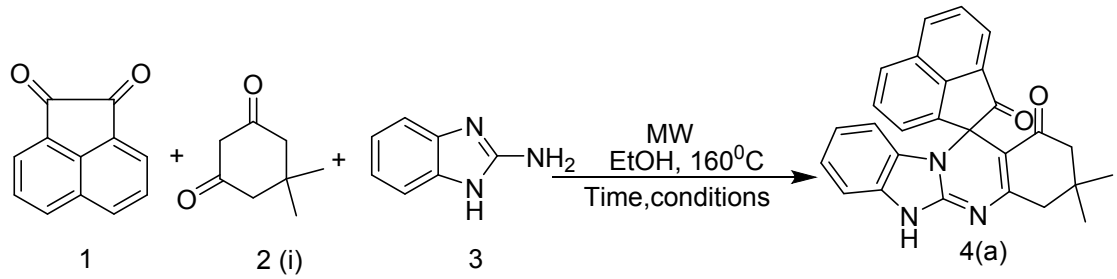


1 2 (i) 3 4(a)

S.No.	Temperature	Conditions	Yield (%)[a]
1	140 °C	5min	50
2	150 °C	5min	55
3	**160 °C**	5min	**75**
4	170 °C	5min	70
5	180 °C	5min	60

[a]*Isolated yield*

2.4 ***Table S4:*** **Time effect**

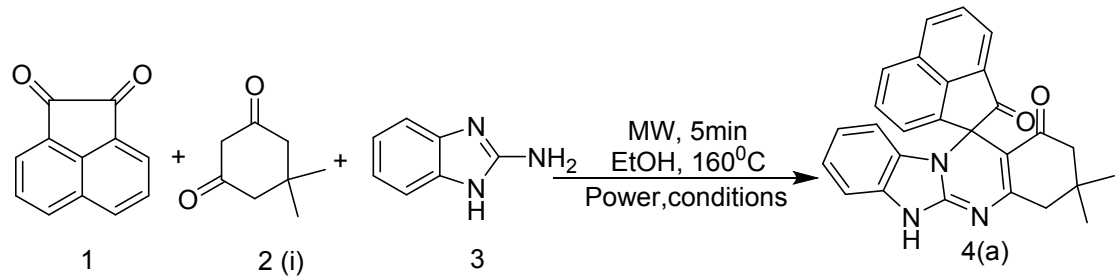


1 2 (i) 3 4(a)

S.No.	Time (min)	Yield (%)[a]
1	3	65
2	**5**	**75**
3	7	74
4	9	72
5	11	70
6	15	40

[a]*Isolated yield*

2.5 ***Table S5:*** **Power effect**

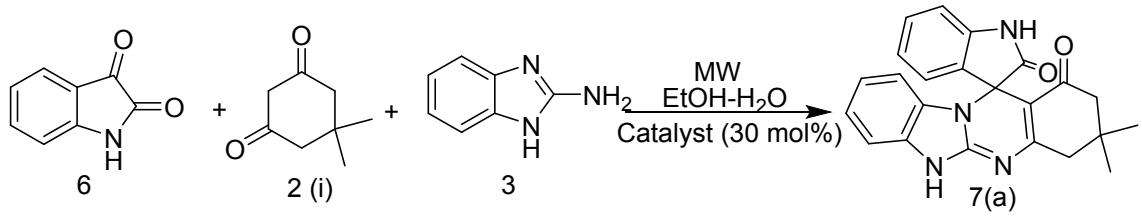


1 2 (i) 3 4(a)

S.No.	Power (watt)	Yield (%)[a]
1	120	10
2	150	54
3	**180**	**75**

4	240	75

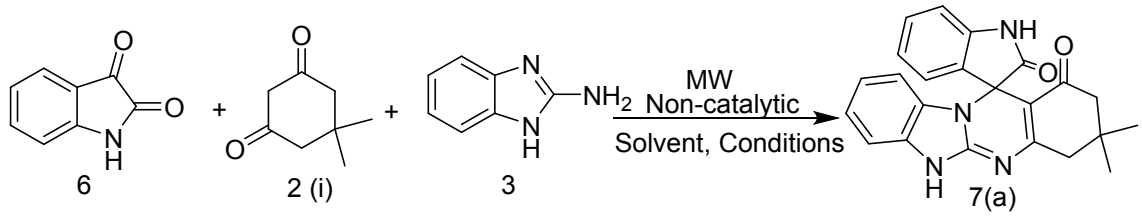
2.6 *Table S6:* Screening of Catalyst



S.No.	Catalyst	Conditions	Yield (%)[a]
1.	p-TSA	160 °C, 5 min	40
2.	$Yb(OTF)_3$	160 °C, 5 min	No reaction
3.	Et_3N	160 °C, 5min	10
4.	PEG	160 °C, 5 min	20

[a]*Isolated yield*

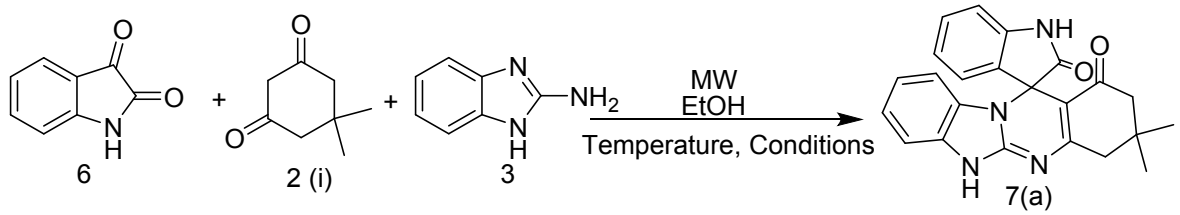
2.7 *Table S7:* Solvent effect



S.No.	Solvent	Conditions	Yield (%)[a]
1	EtOH-H_2O	160°C, 5min	20
2	H_2O	160°C, 5min	65
3	Methanol	160°C, 5 min	10
4	Ethanol	160°C, 5 min	75

[a]*Isolated yield*

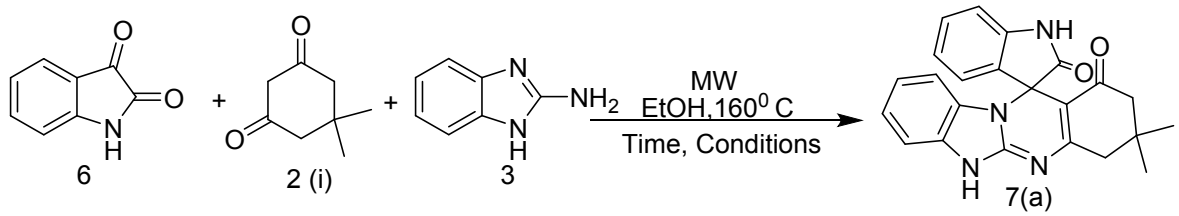
2.8 *Table S8:* Temperature effect



S.No.	Temperature	Conditions	Yield (%)[a]
1	140 °C	5min	50
2	160 °C	5 min	75
3	180 °C	5 min	70

[a]*Isolated yield*

2.9 *Table S9:* Time effect

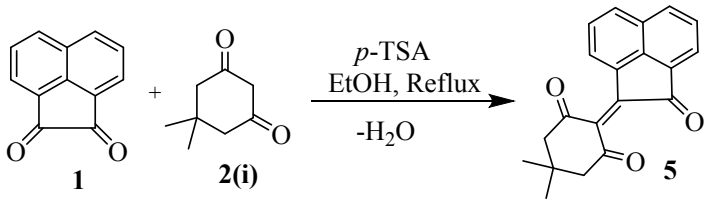


S.No.	Time (min)	Yield (%)[a]
1	3	65
2	**5**	**75**
3	7	30

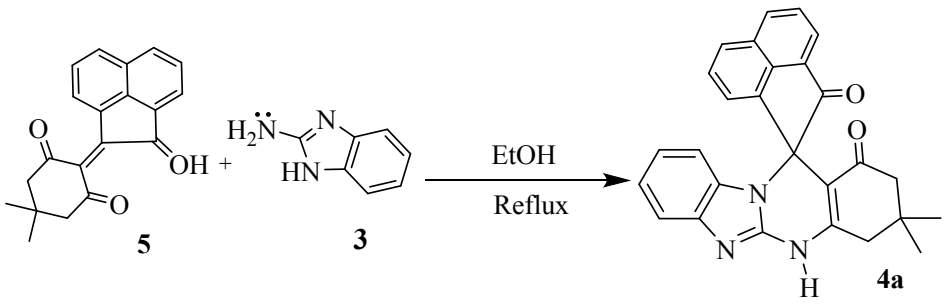
[a]*Isolated yield*

3. Control experiment:

We designed control experiments to isolate intermediate **5**, by the Knoevenagel condensation reaction of compound **1** and **2(i)** as shown in scheme A. For this reaction, was carried out using *p*-TSA as catalyst under ethanol reflux and after 1 hr a new non-polar spot appeared on TLC. We then isolated and characterised that spot as intermediate **5**, by HRMS and carried out its subsequent reaction with compound **3** under standard condition**.** Futher**,** progress of the reaction was then monitored on TLC and product spot first appeared after 2 hrs and then its intensity goes on increasing and intermediate spot diminishes with time and after 12 hrs no intermediate left on TLC and product spot gets intensified as shown in Table **1** of manuscript.



Scheme ***S1***: Control Experiment for synthesis of intermediate **5**

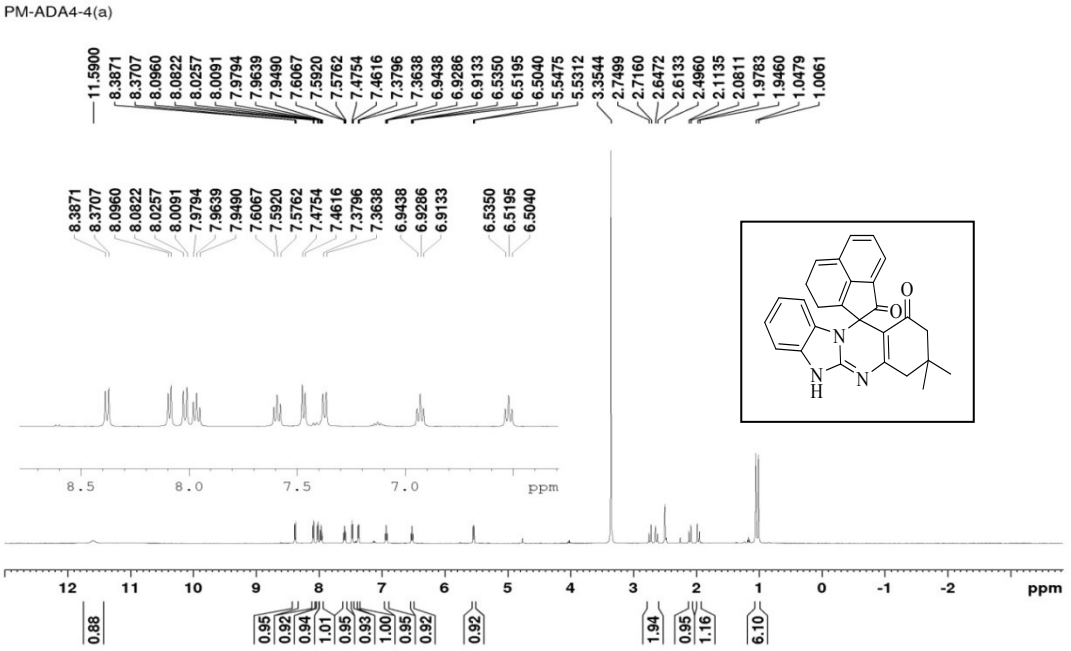


Scheme ***S2***: Control Experiment for synthesis of product **4a**

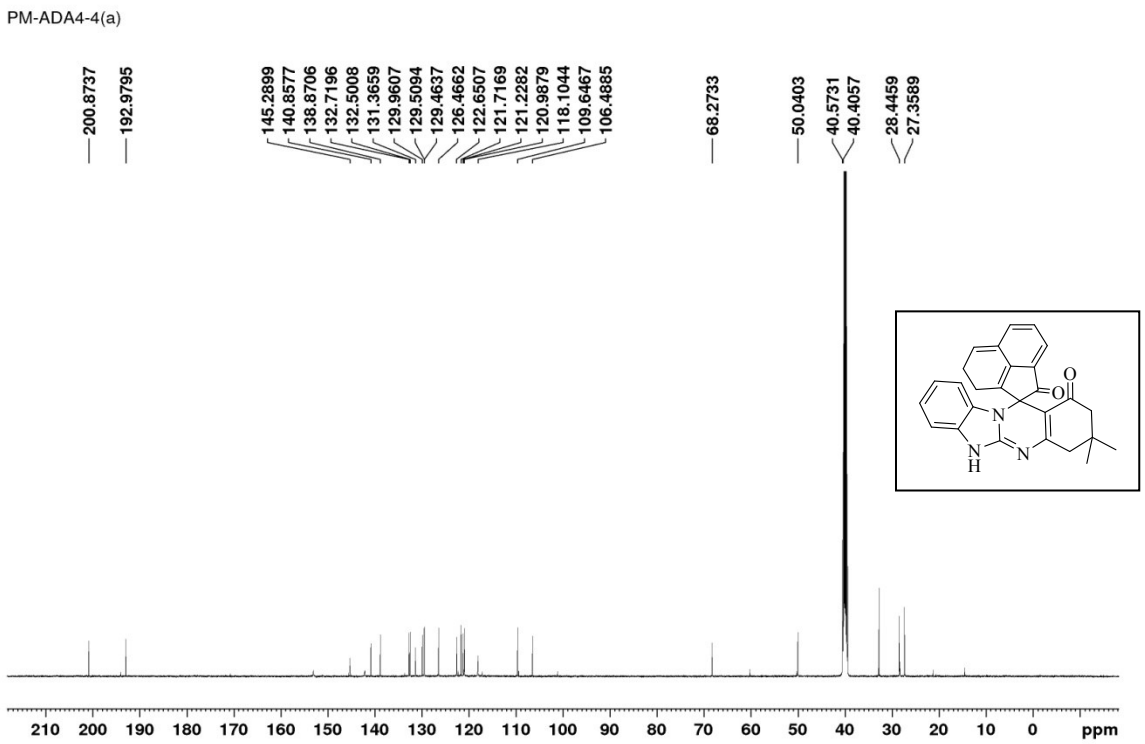
4. Crystal data parameters for compounds 4a

Compound	**4a**	**6a**
Formula	$C_{27}H_{21}N_3O_2$	$C_{23}H_{20}N_4O_2$
Formula weight	419.47	384.43
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
Temperature (K)	100(2)	100(2)
a (Å)	9.0977(4)	9.2047(4)
b (Å)	11.2713(5)	14.1206(7)
c (Å)	11.4682(5)	16.6580(8)
α (º)	118.8560(11)	75.9437(14)
β (º)	92.1720(13)	74.4957(14)
γ (º)	91.3380(12)	87.8667(15)
Volume (Å^3)	1028.06(8)	2022.99(17)
Z	2	2
2θ range for data collection (°)	5.88 to 50.49	4.41 to 56.786
Reflections collected/unique	15709 / 3708	31479 / 10157
R_{int} / R_{sigma}	0.0339 / 0.0415	0.0747/0.1121
Data/restraints/parameters	3708 / 0 / 295	10157/0/527
Goodness-of-fit on F^2	1.055	0.967
Final *R* indices [$I>2\sigma(I)$][a]	R_1 = 0.0400,wR_2 = 0.0955	R_1 = 0.0660,wR_2 = 0.1478
R indices (all data)[a]	R_1 = 0.0508,wR_2 = 0.1012	R_1 = 0.1303,wR_2 = 0.1647
Largest residuals (e.Å^{-3})	0.22 and -0.27	0.33 and -0.39

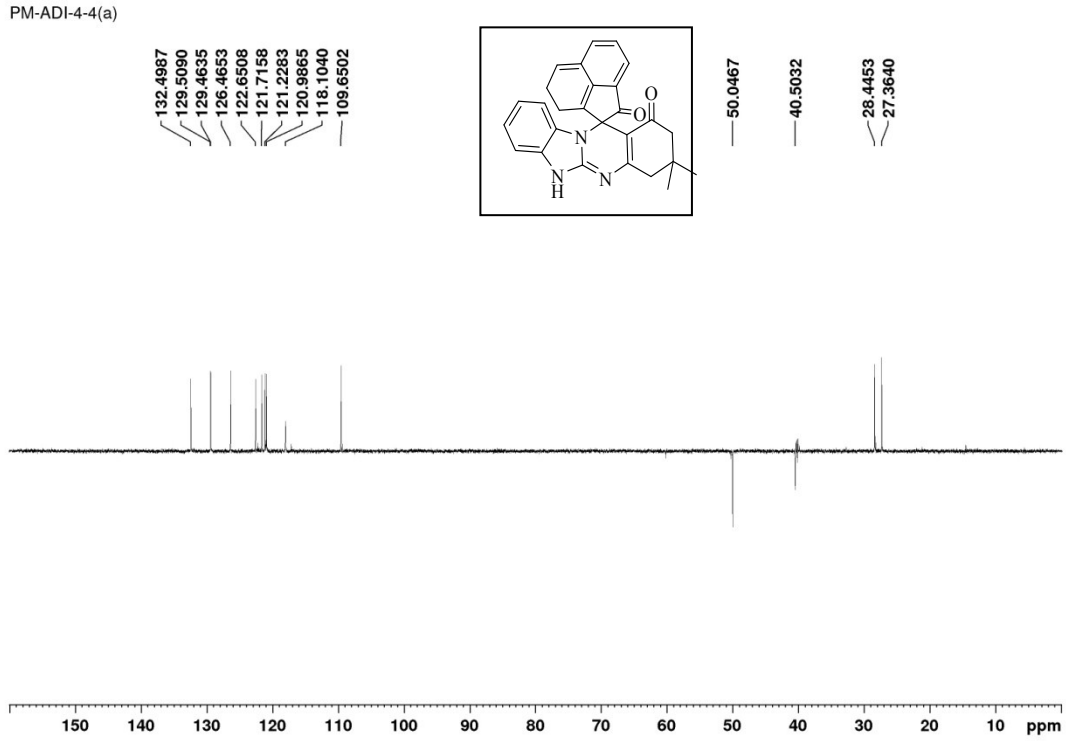
6. Copies of 1H, 13C, DEPT and HRMS spectra for compounds 4(a -c)



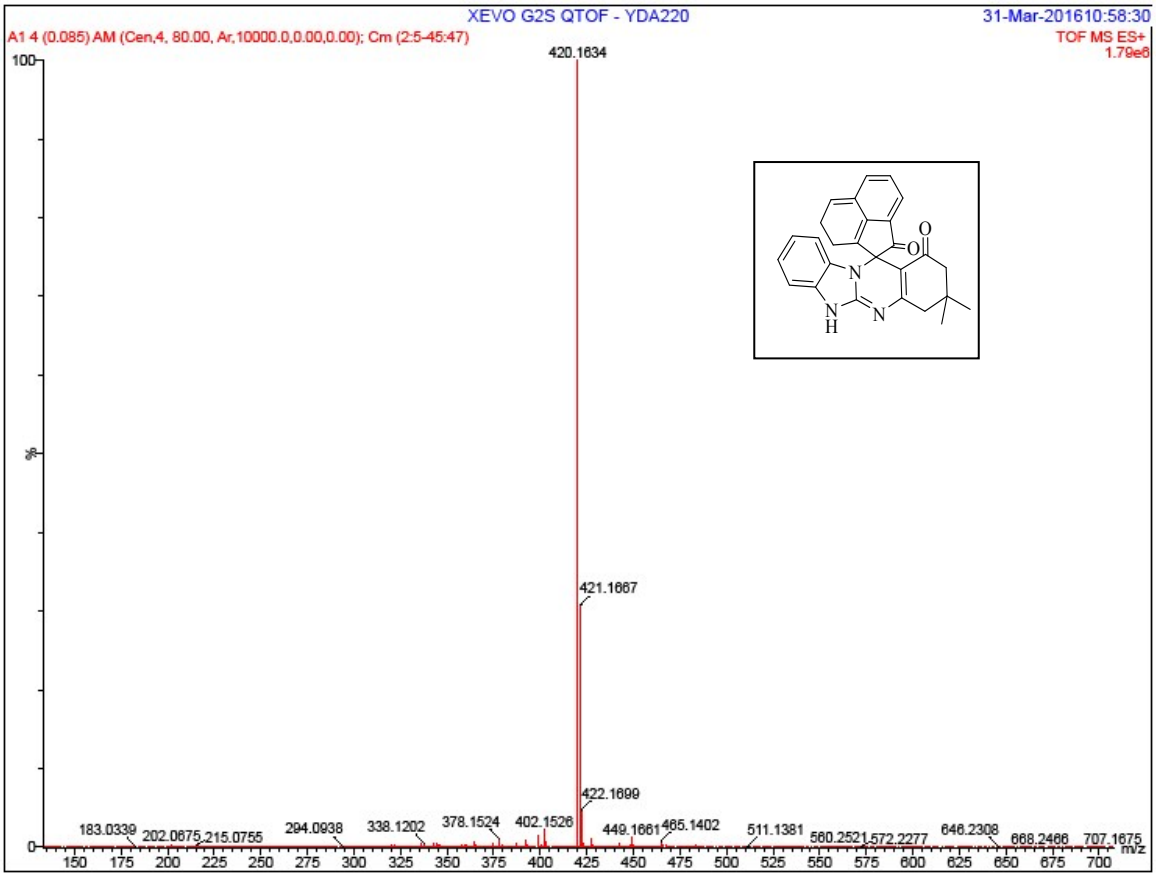
^{1}H NMR spectrum of compound 4a



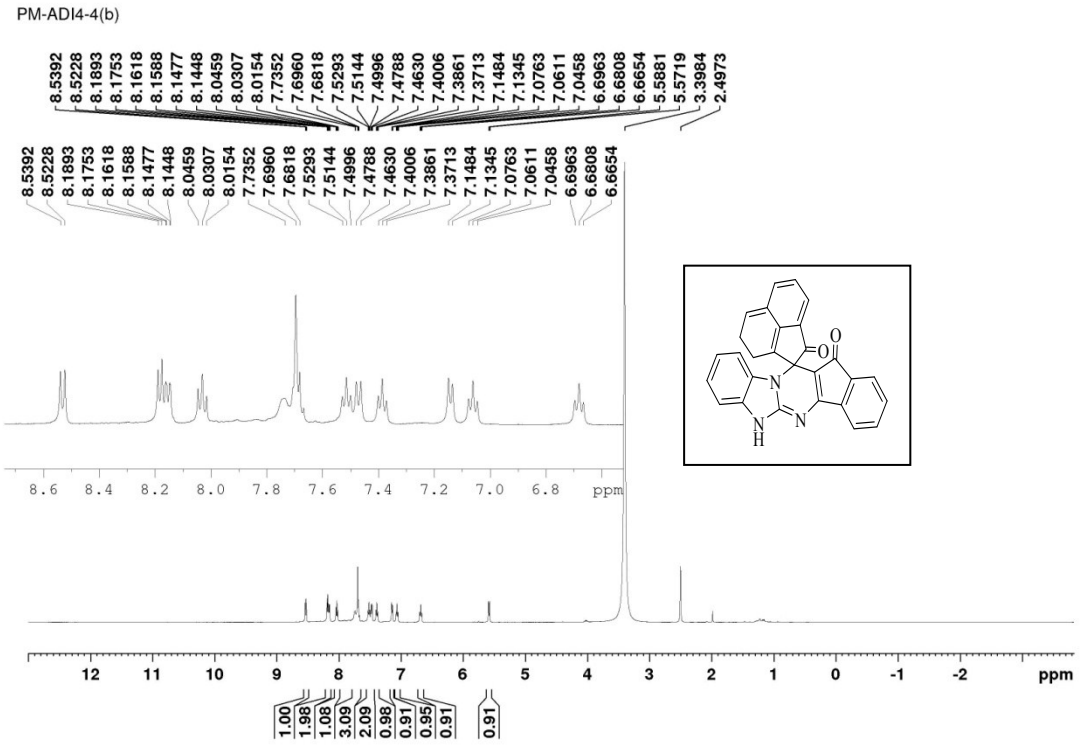
^{13}C NMR spectrum of compound 4a



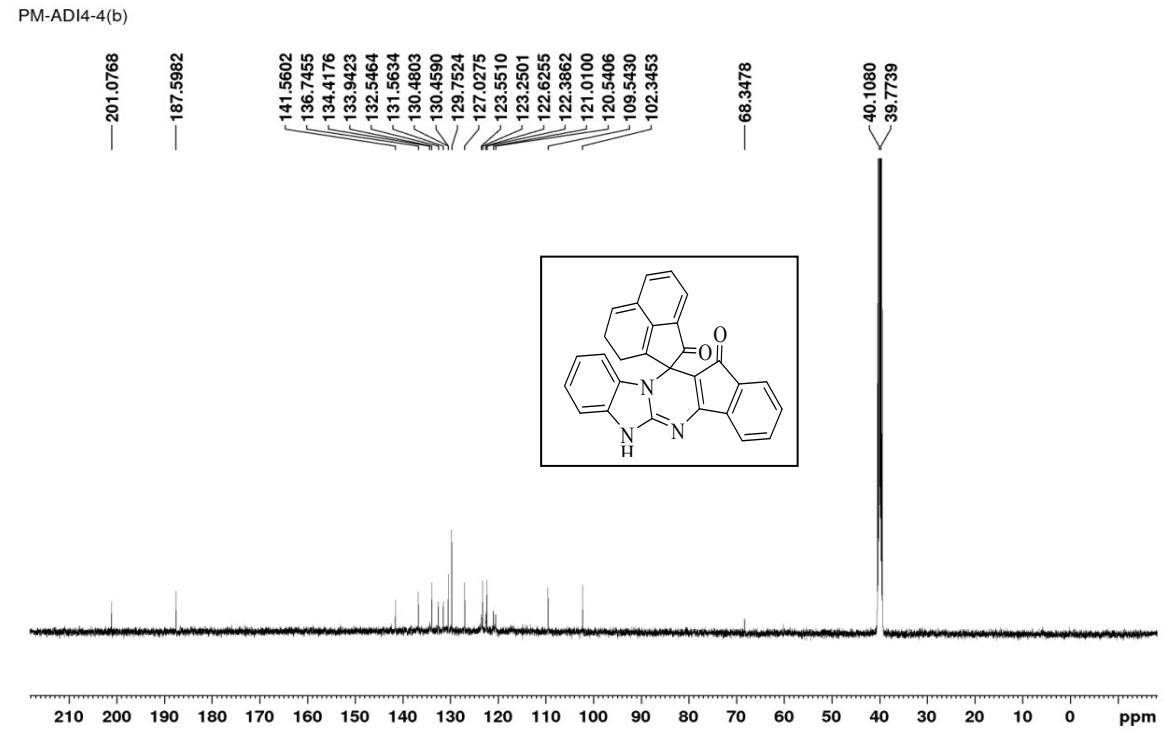
DEPT-135spectrum of compound 4a



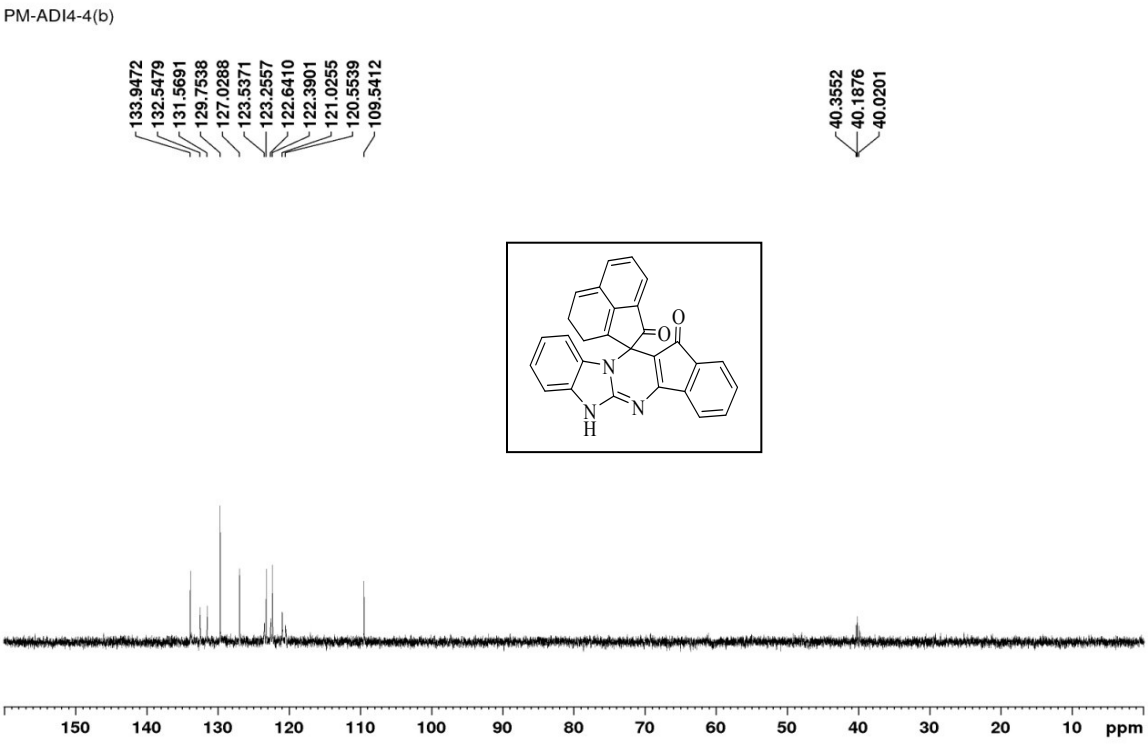
HRMSspectrum of compound 4a



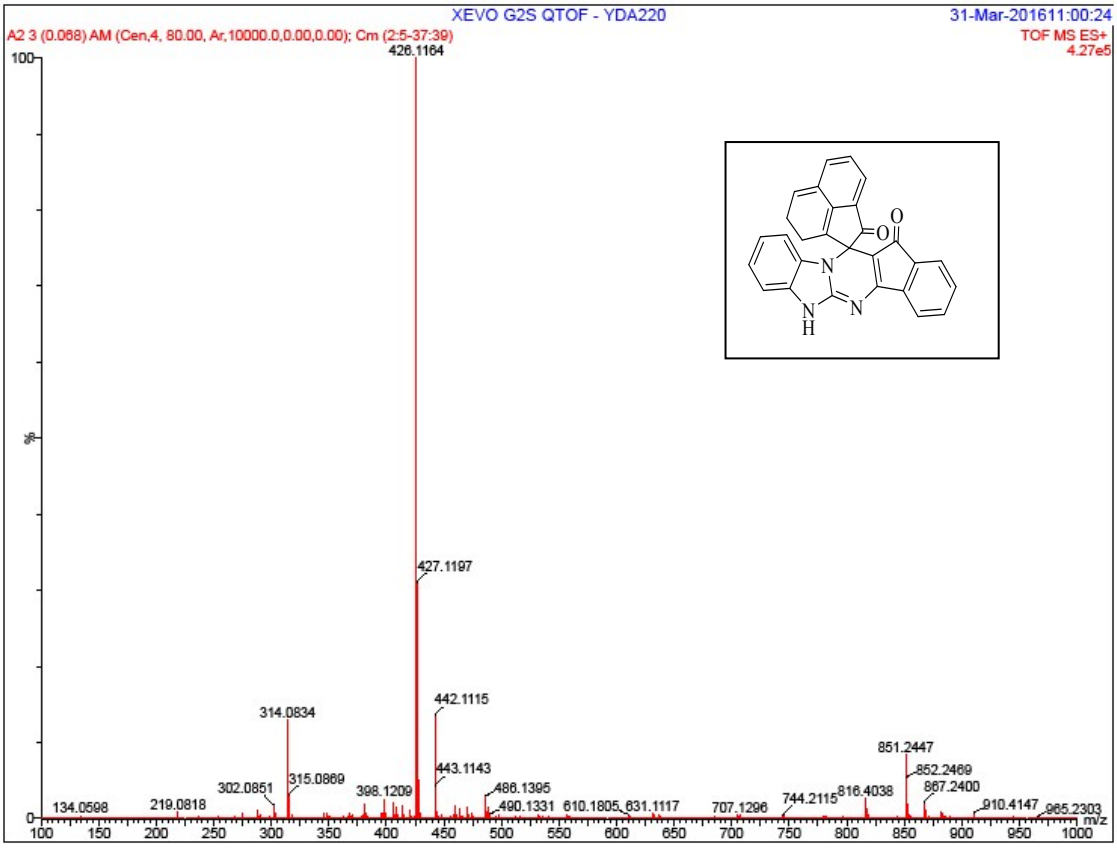
[1]H NMR spectrum of compound 4b



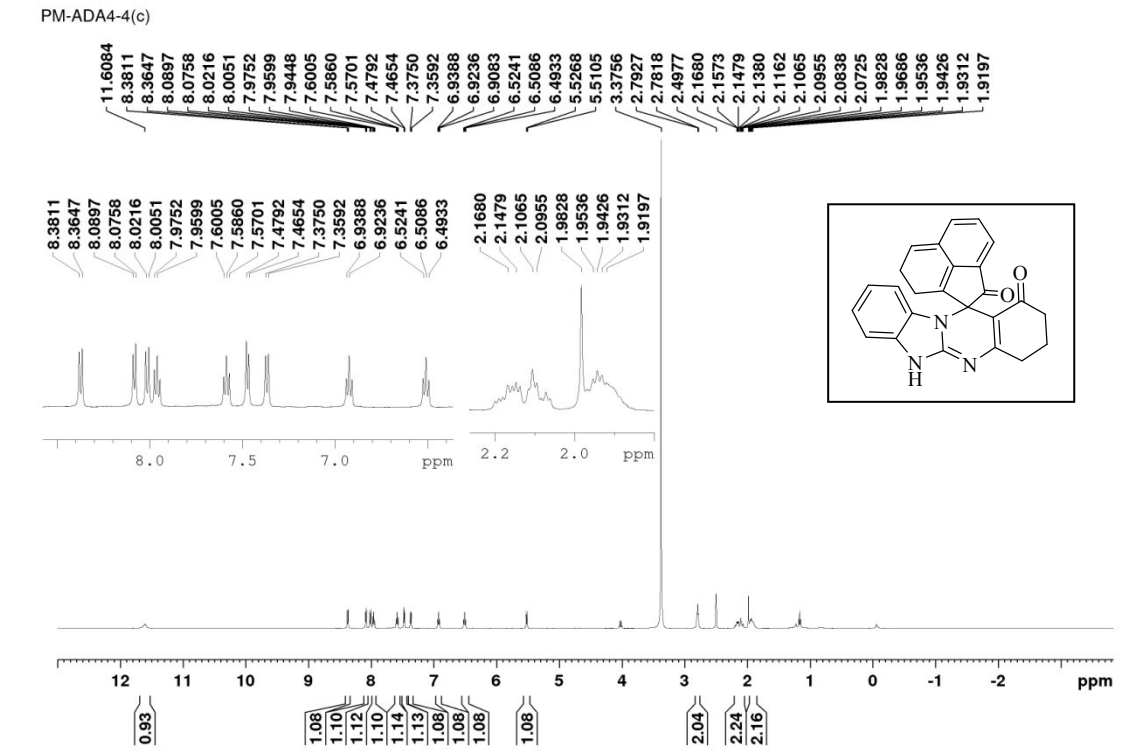
[13]C NMR spectrum of compound 4b



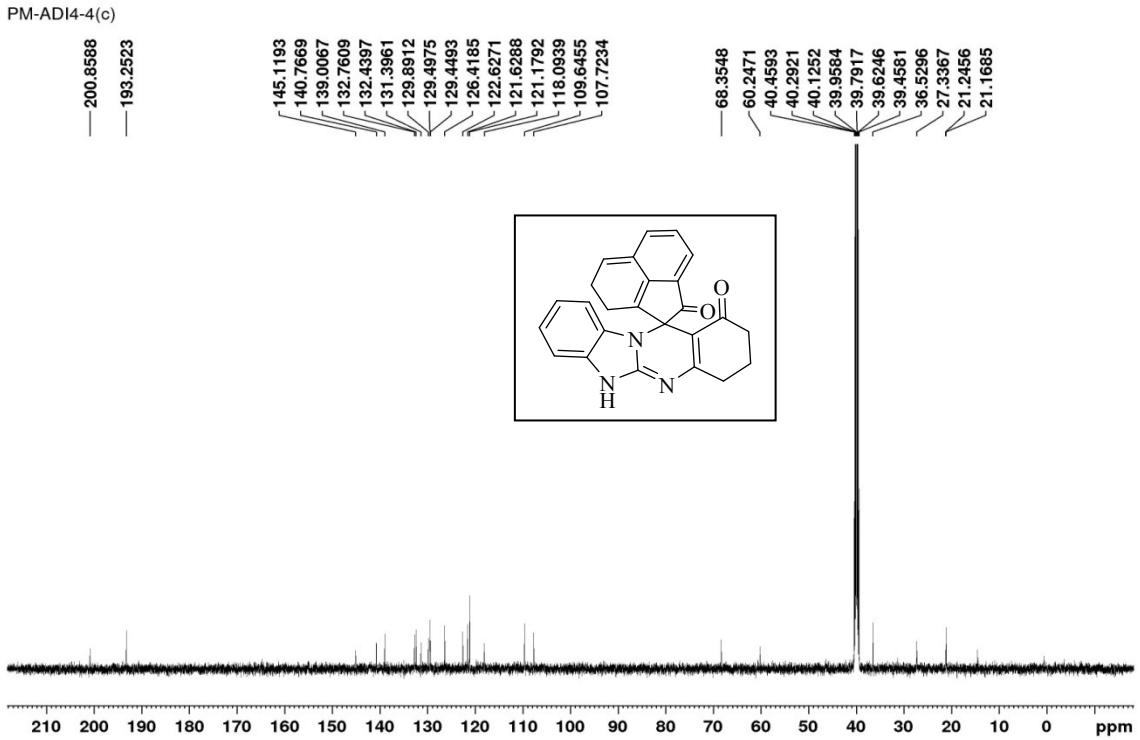
DEPT-135spectrum of compound 4b



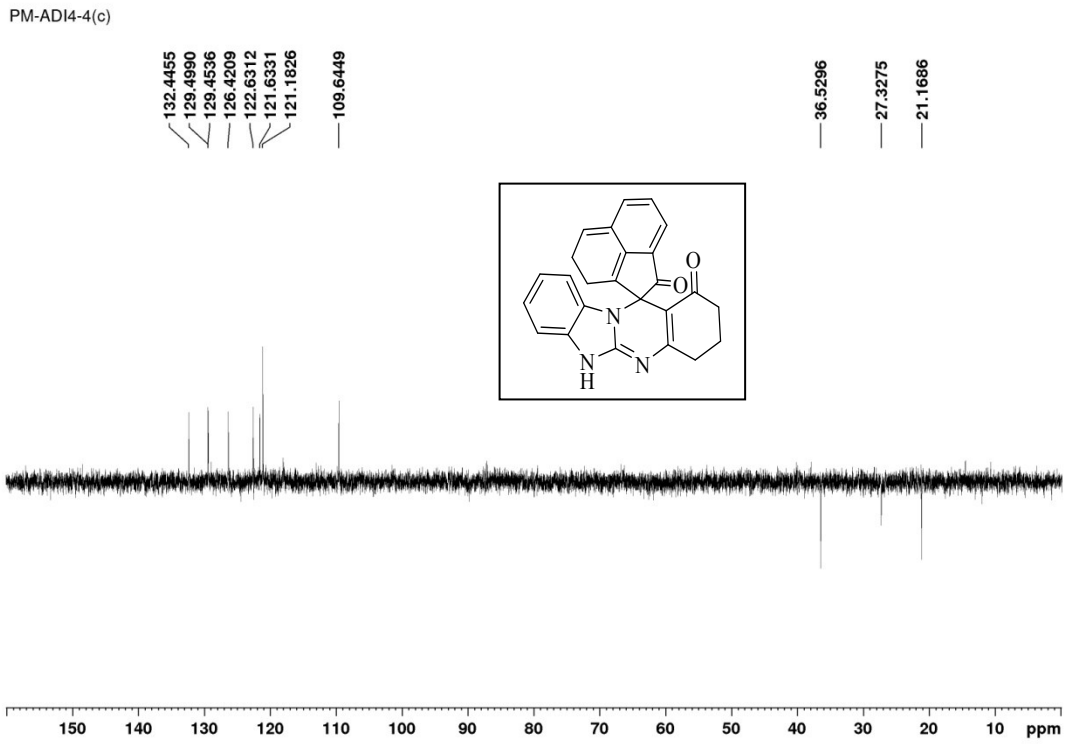
HRMSspectrum of compound 4b



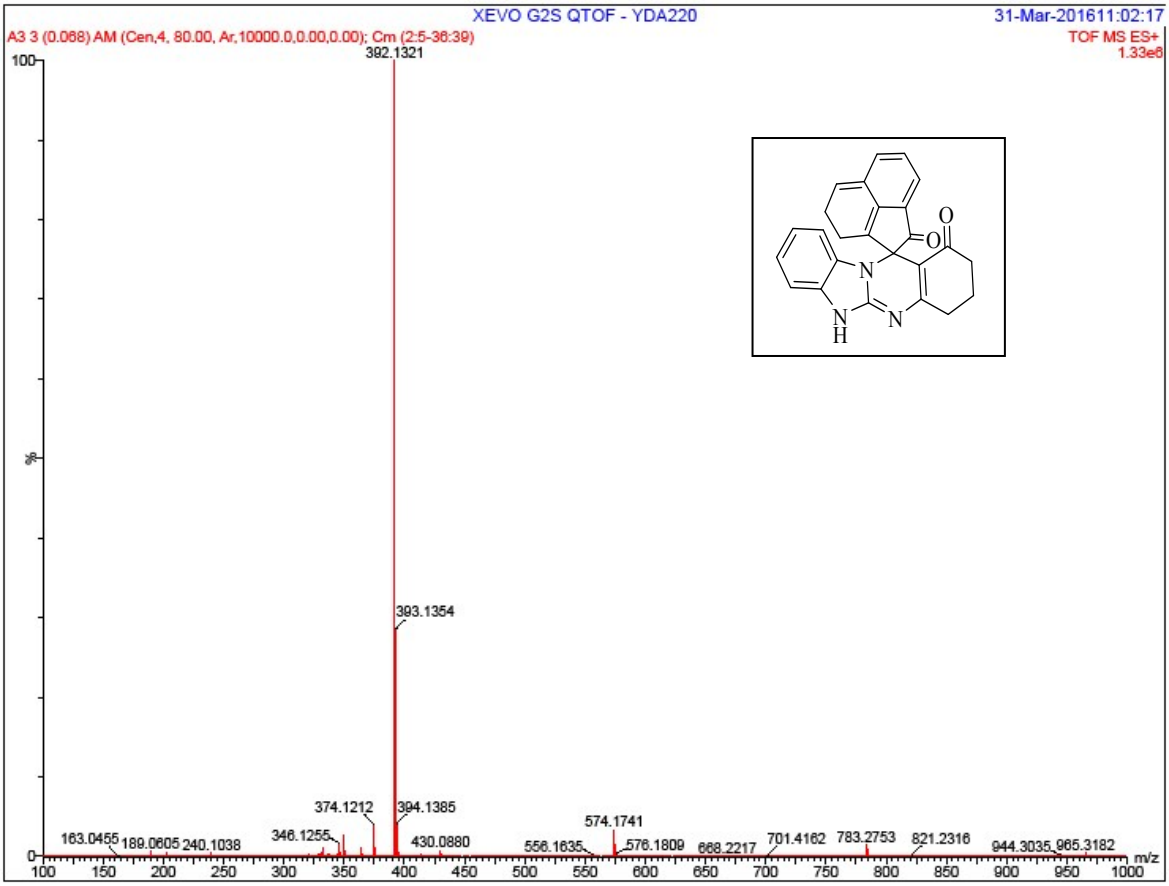
1H NMRspectrum of compound 4c



13C NMRspectrum of compound 4c

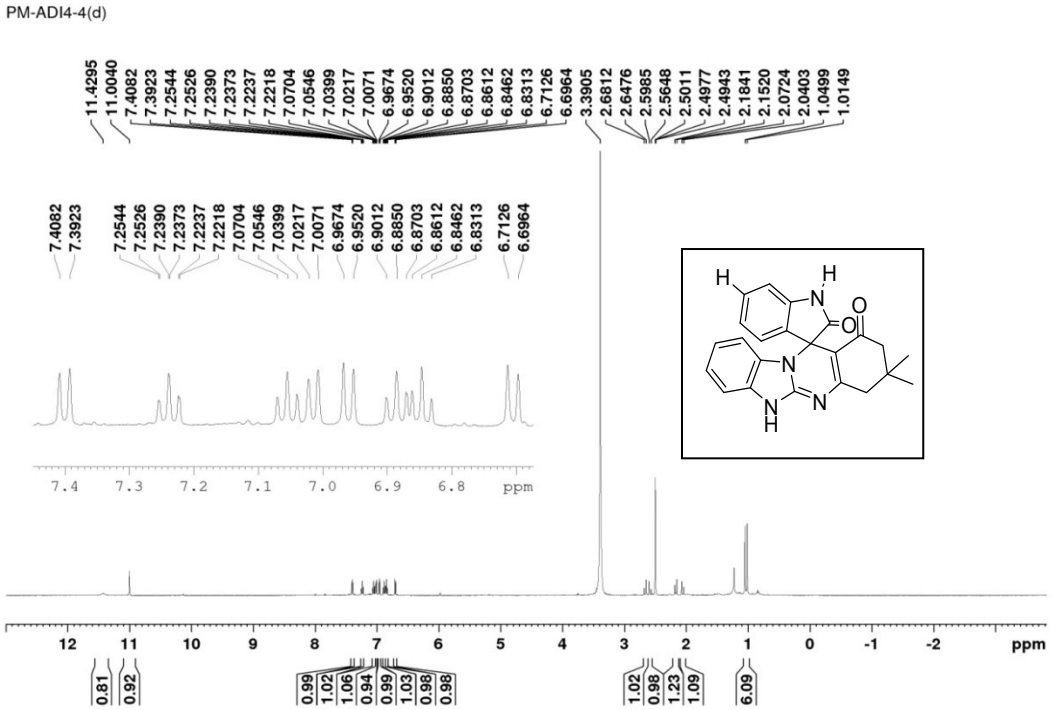


DEPT-135 NMRspectrum of compound 4c



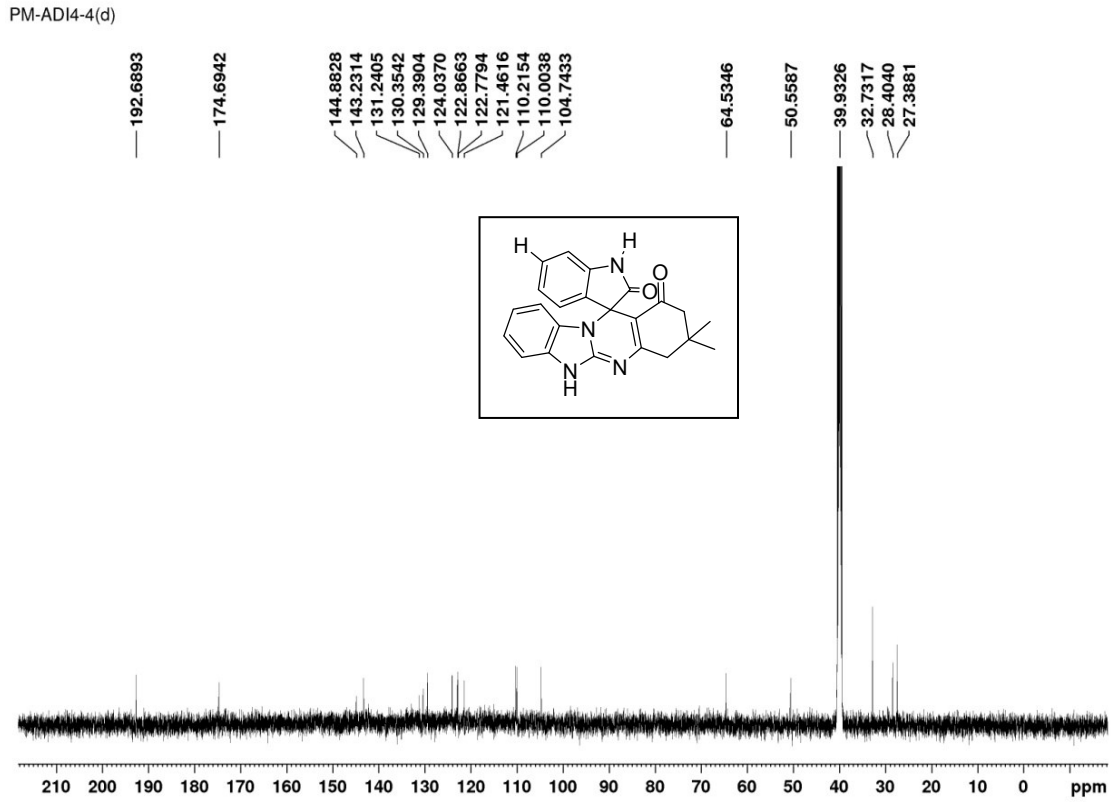
HRMS spectrum of compound 4c

7. Copies of1H, 13C, DEPT and HRMS spectra for compounds 7(a -n)

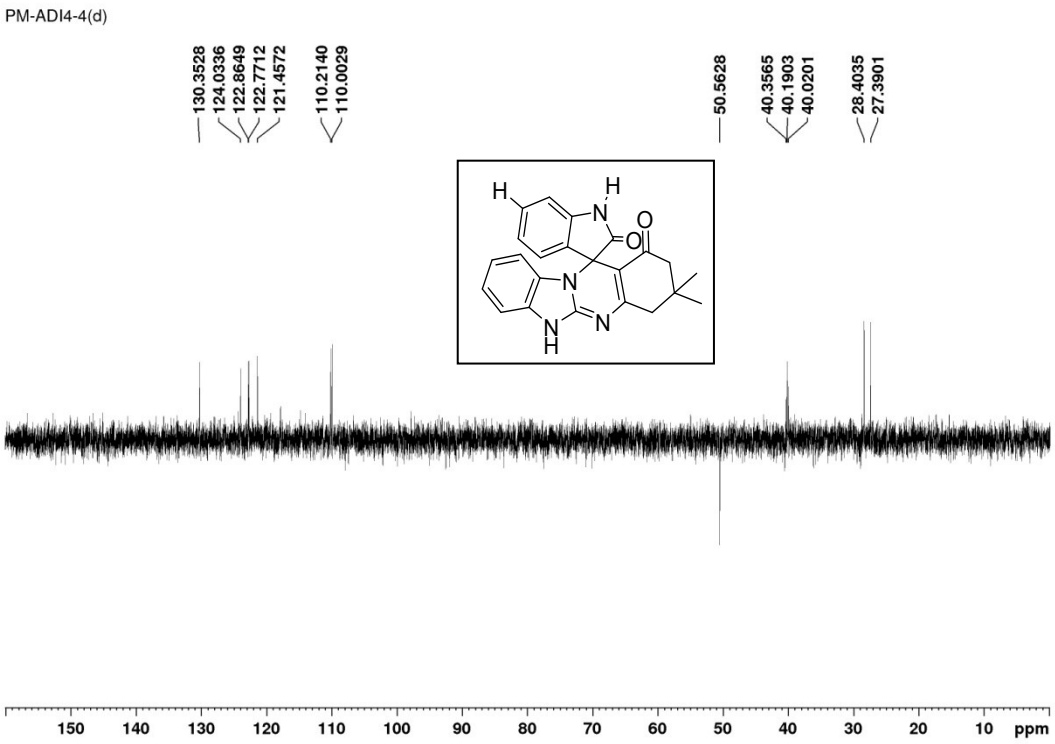


1

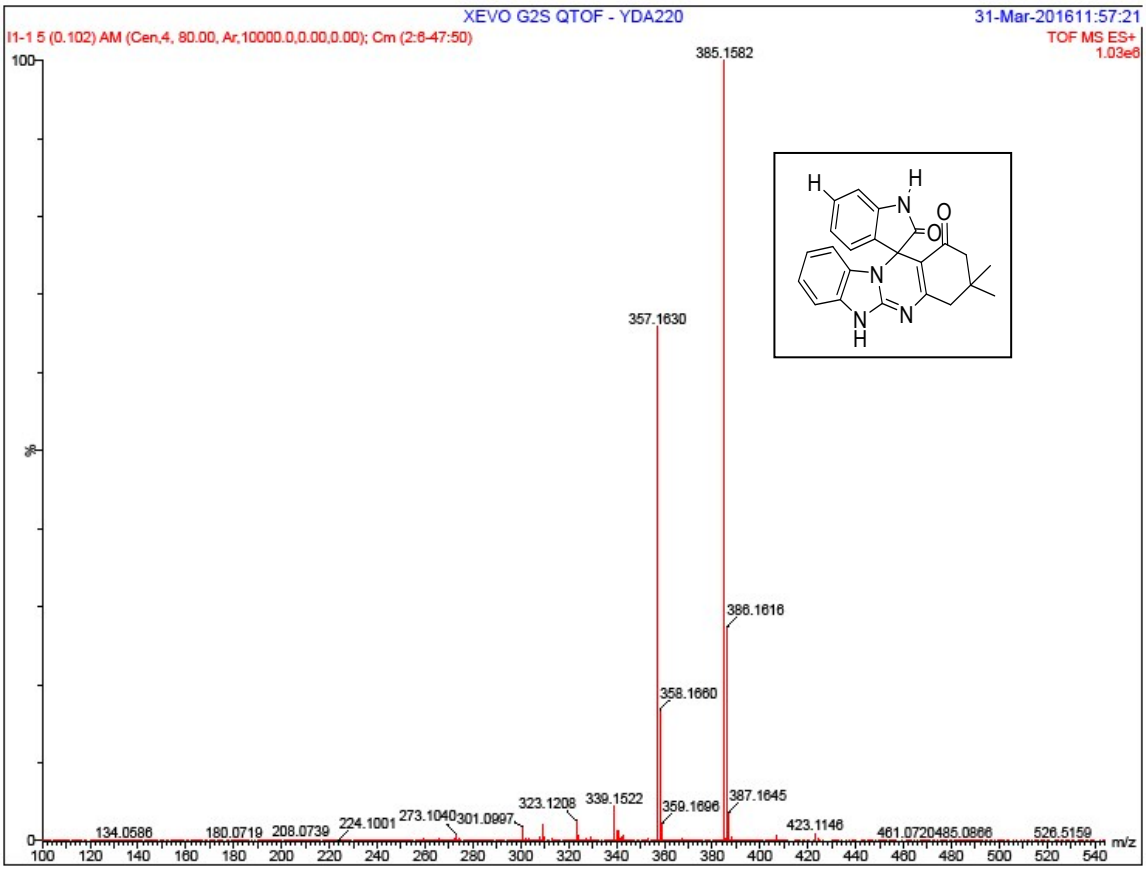
H NMRspectrum of compound 7a



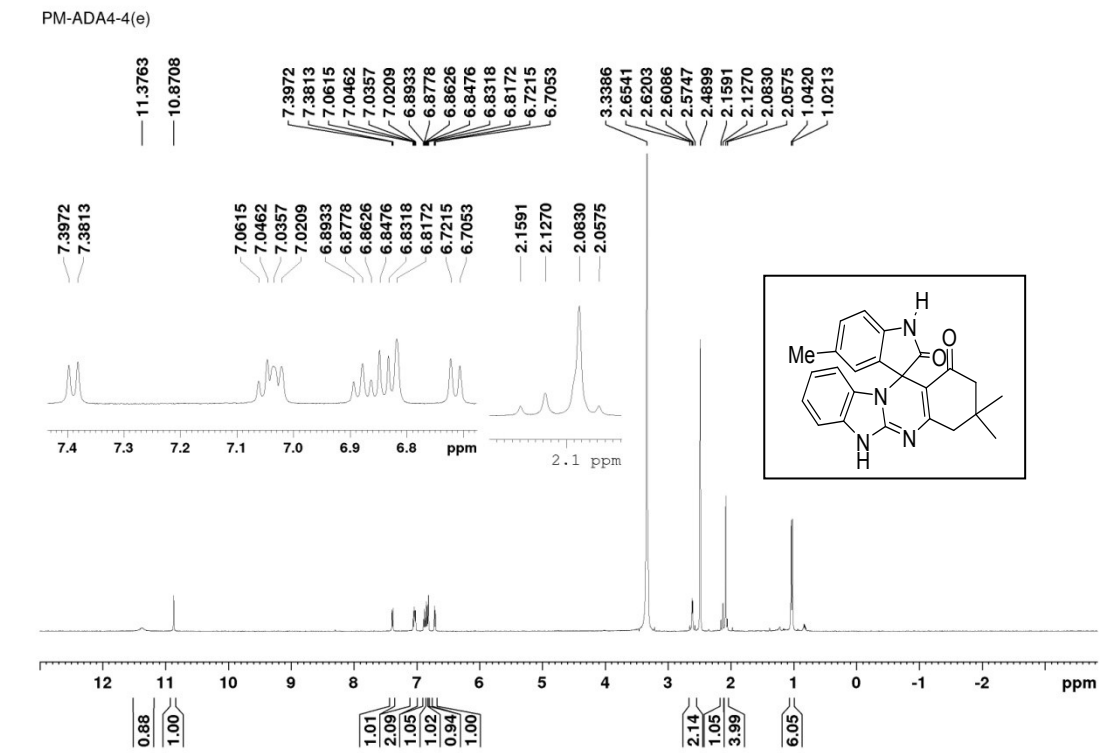
13C NMRspectrum of compound 7a



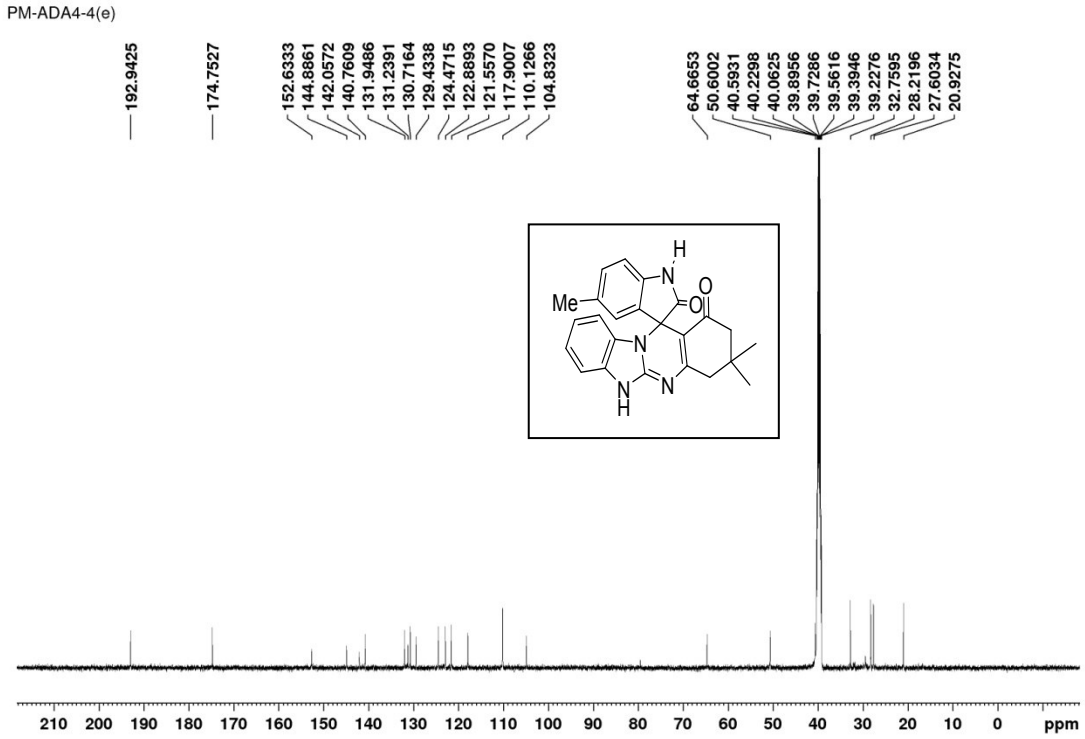
DEPT-135 NMRspectrum of compound 7a



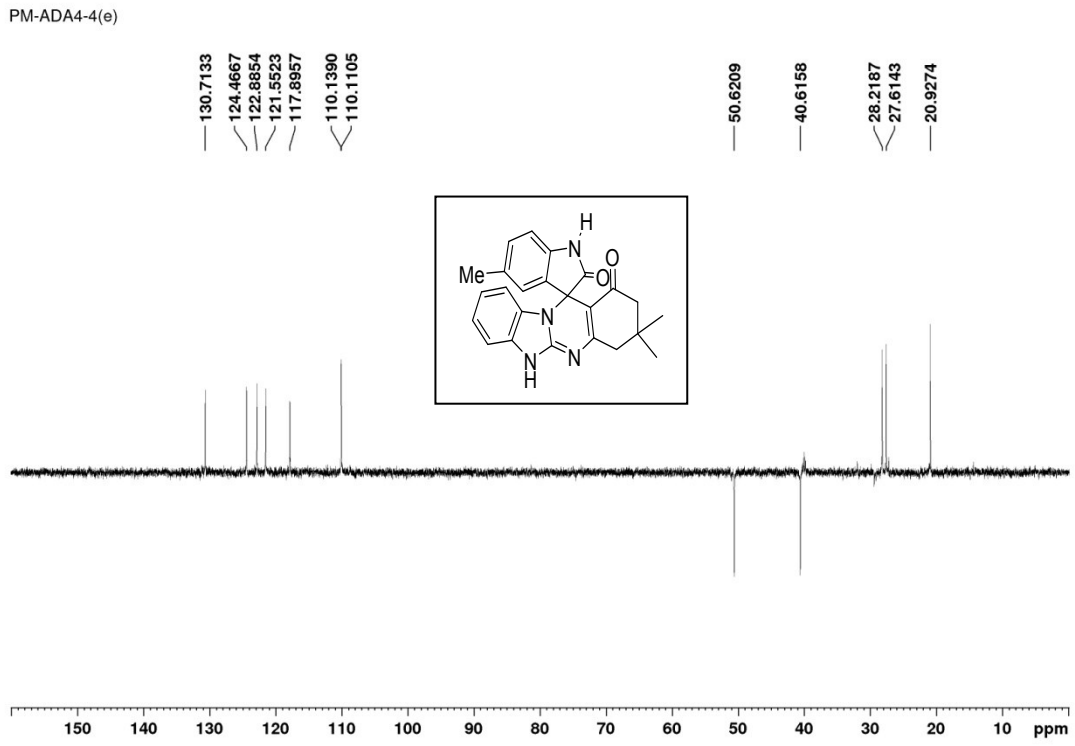
HRMS spectrum of compound 7a



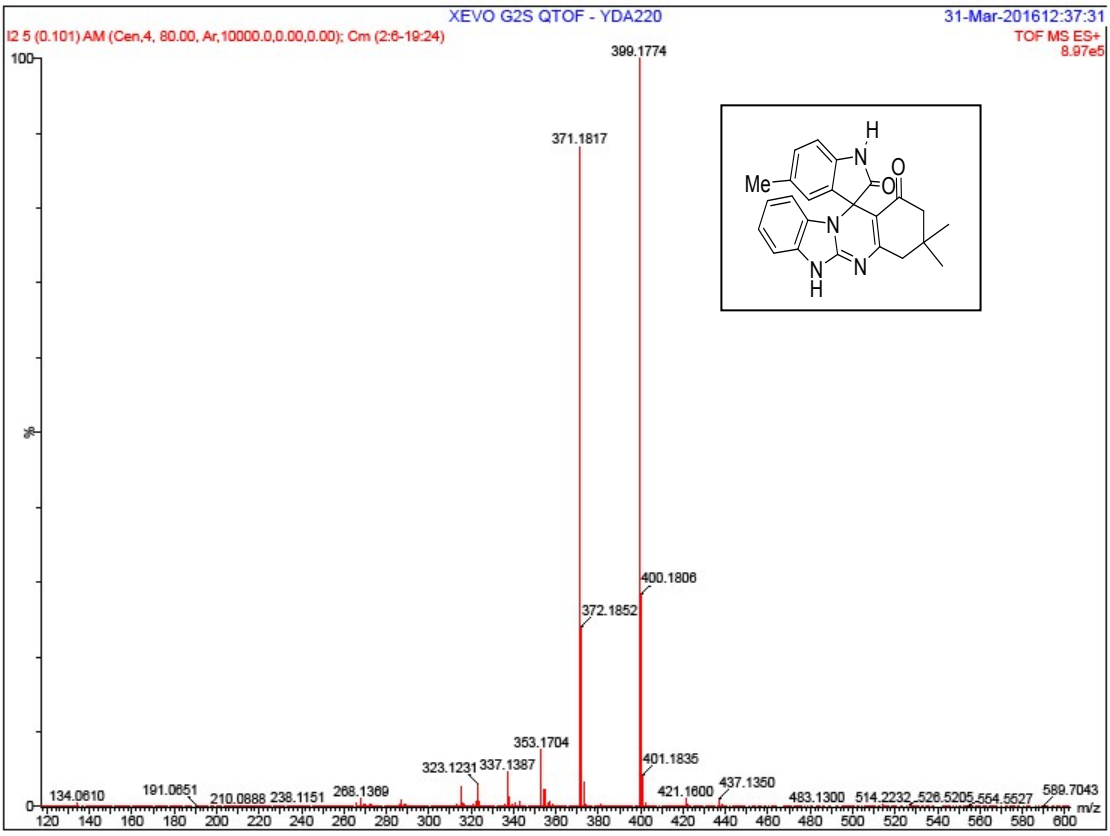
1H NMR spectrum of compound 7b



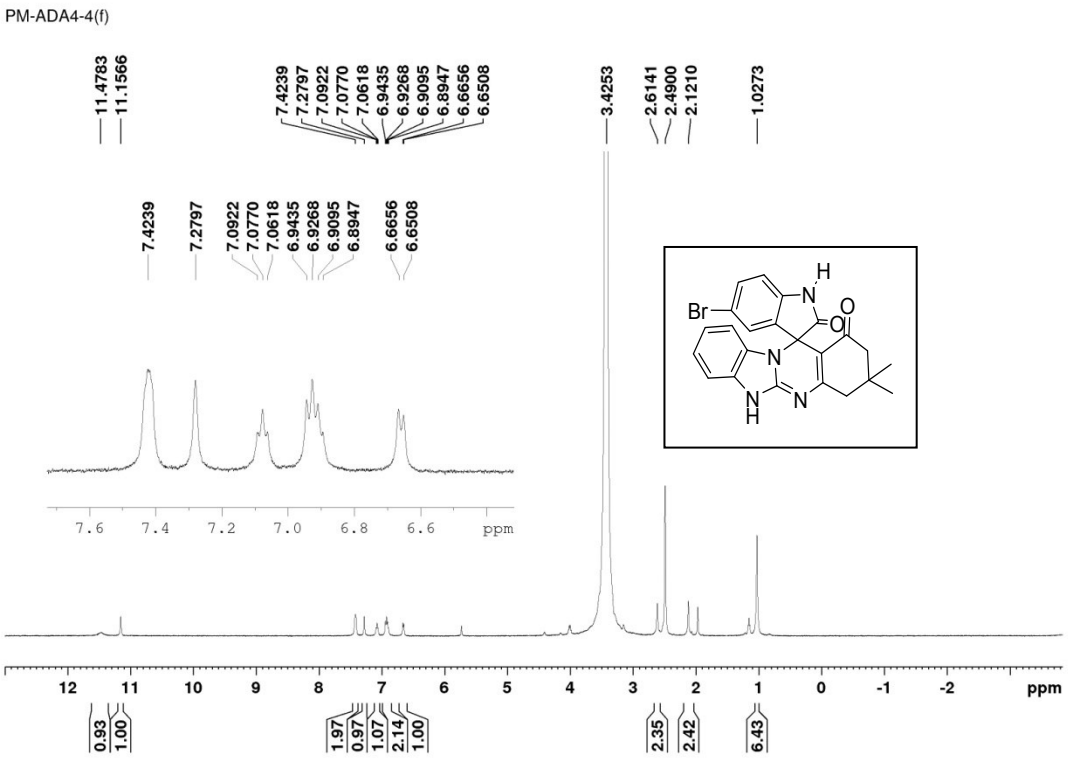
13C NMRspectrum of compound 7b



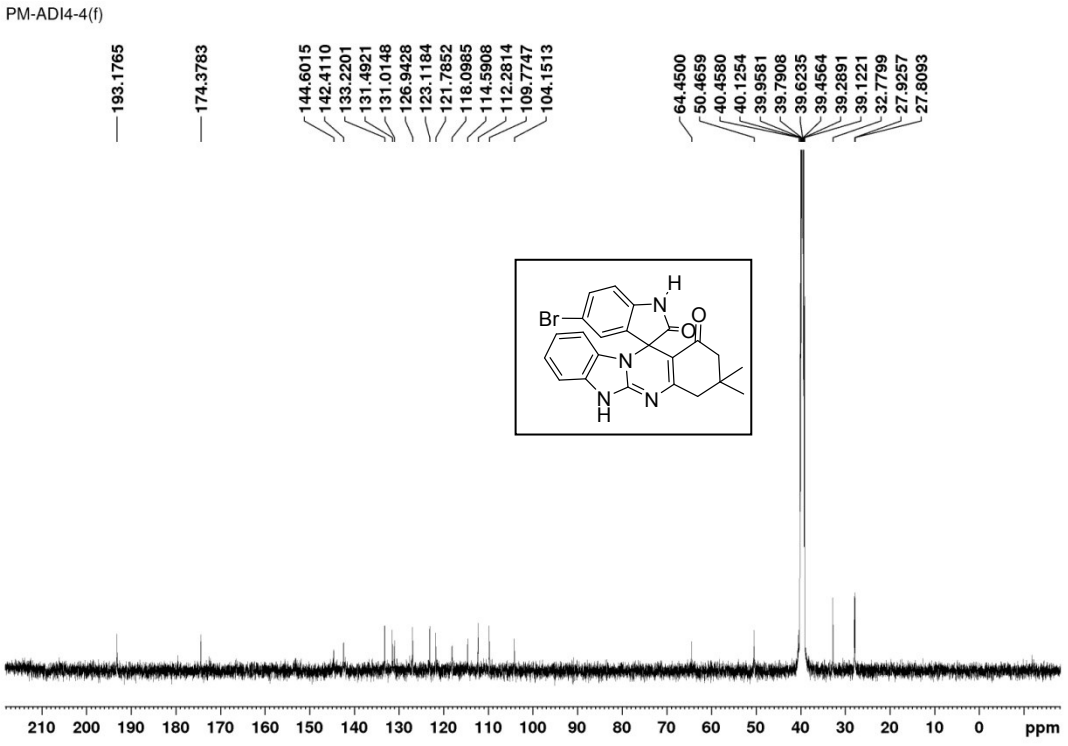
DEPT-135 NMRspectrum of compound 7b



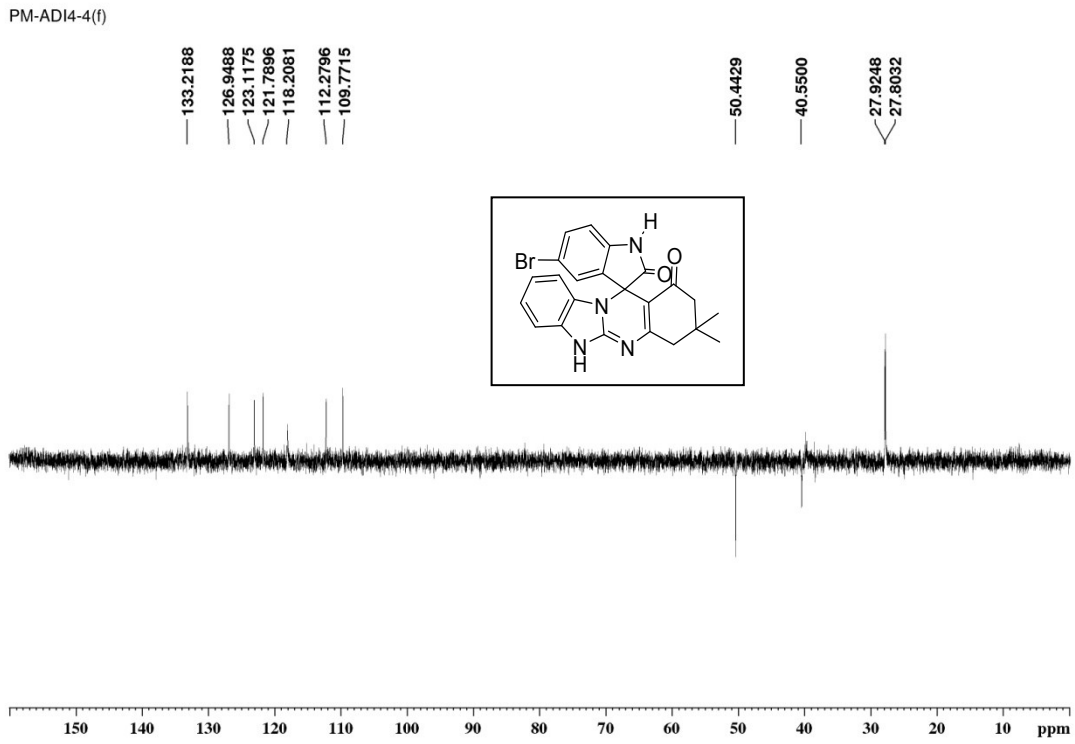
HRMS spectrum of compound 7b



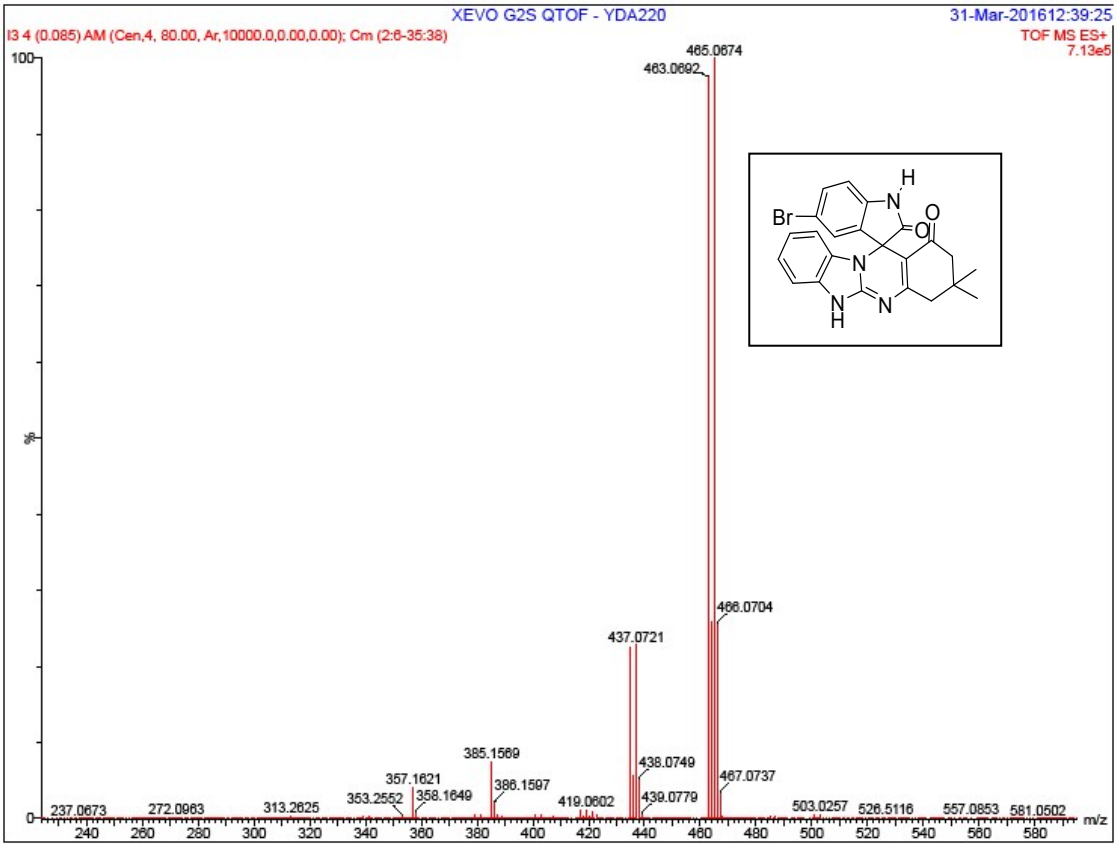
1H NMR spectrum of compound 7c



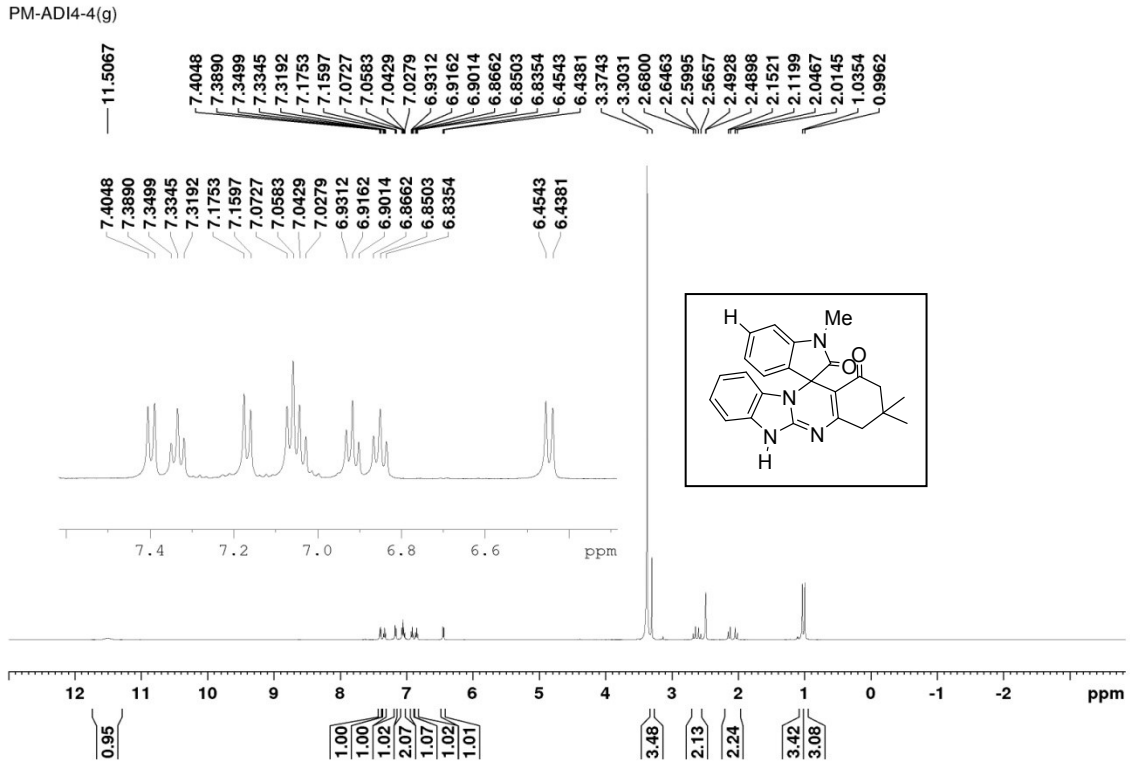
13C NMR spectrum of compound 7c



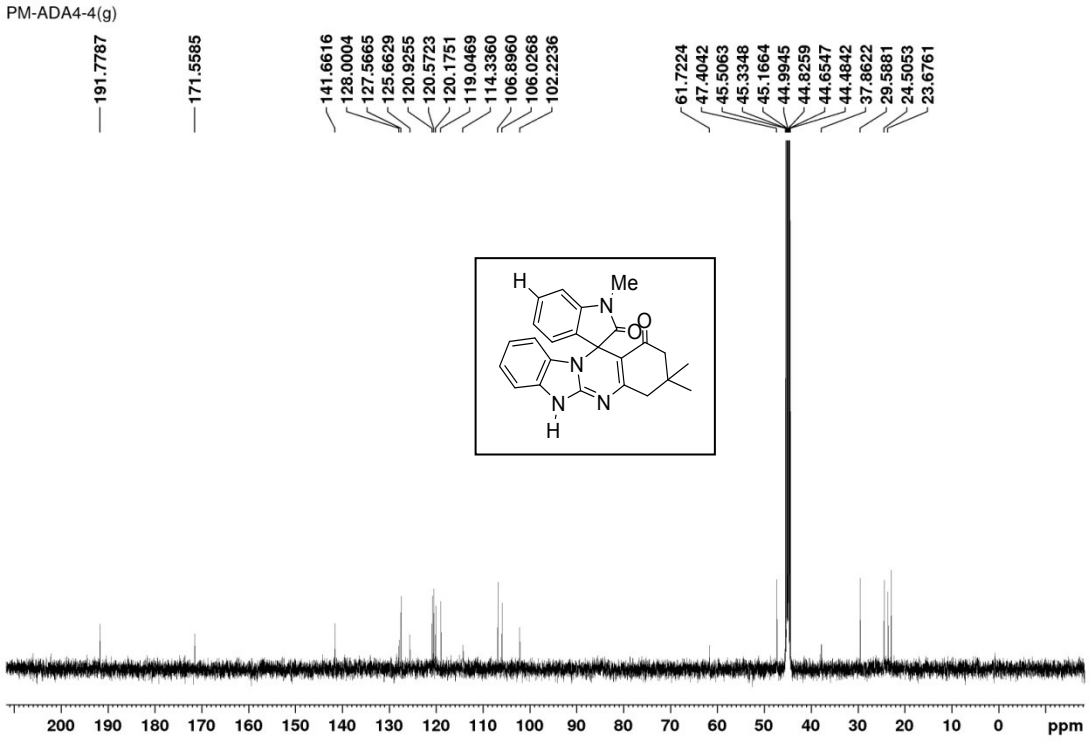
DEPT-135 NMR spectrum of compound 7c



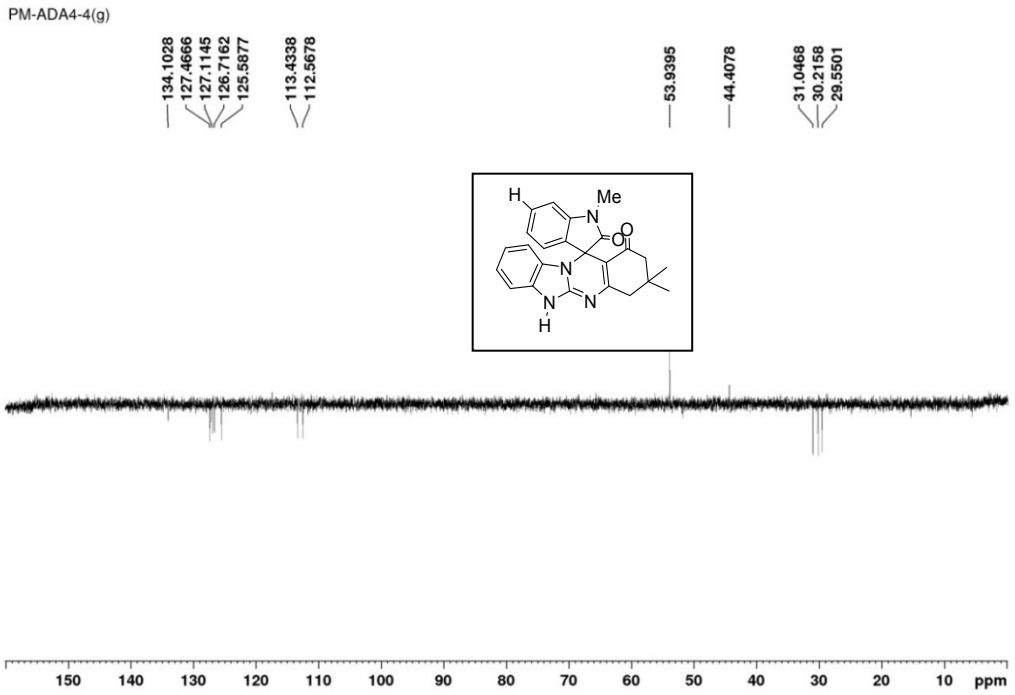
HRMS spectrum of compound 7c



1H NMR spectrum of compound 7d

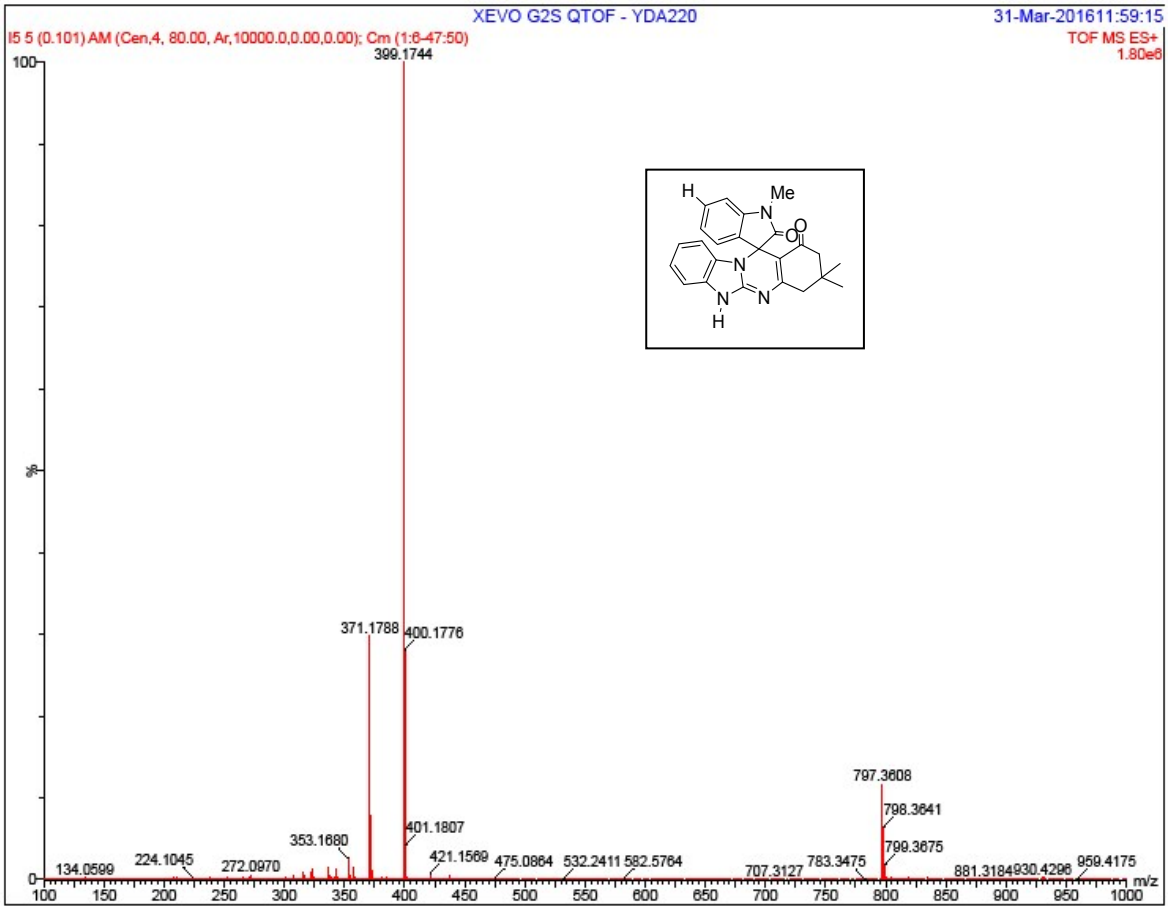


13C NMR spectrum of compound 7d

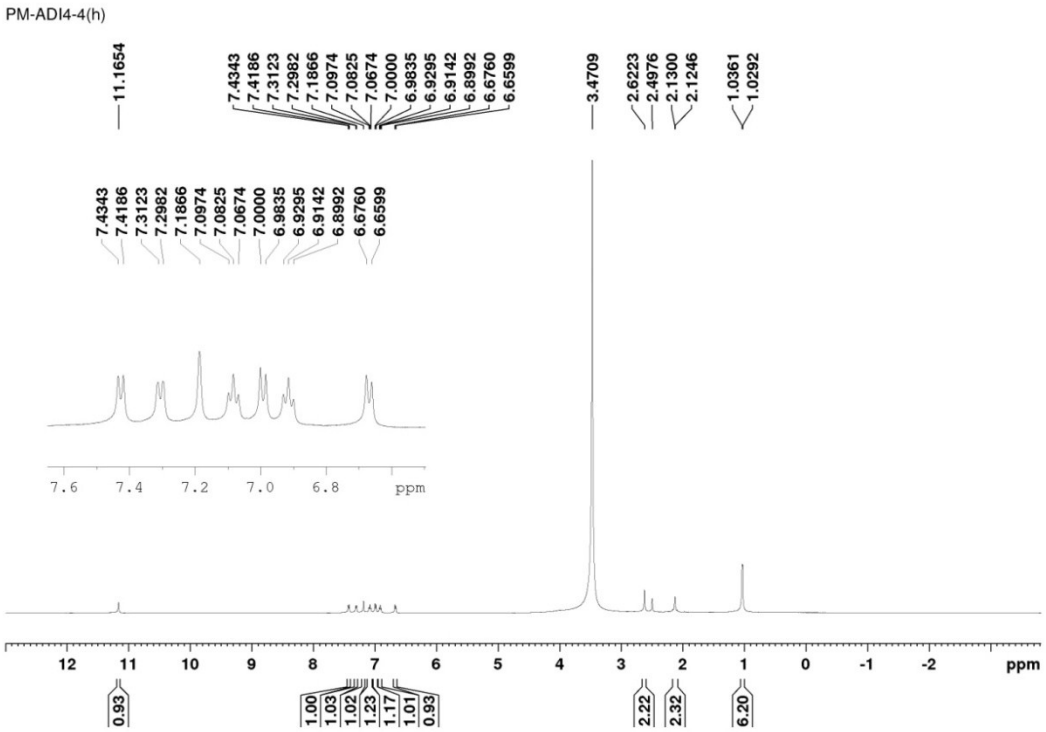


D

EPT-135 NMR spectrum of compound 7d

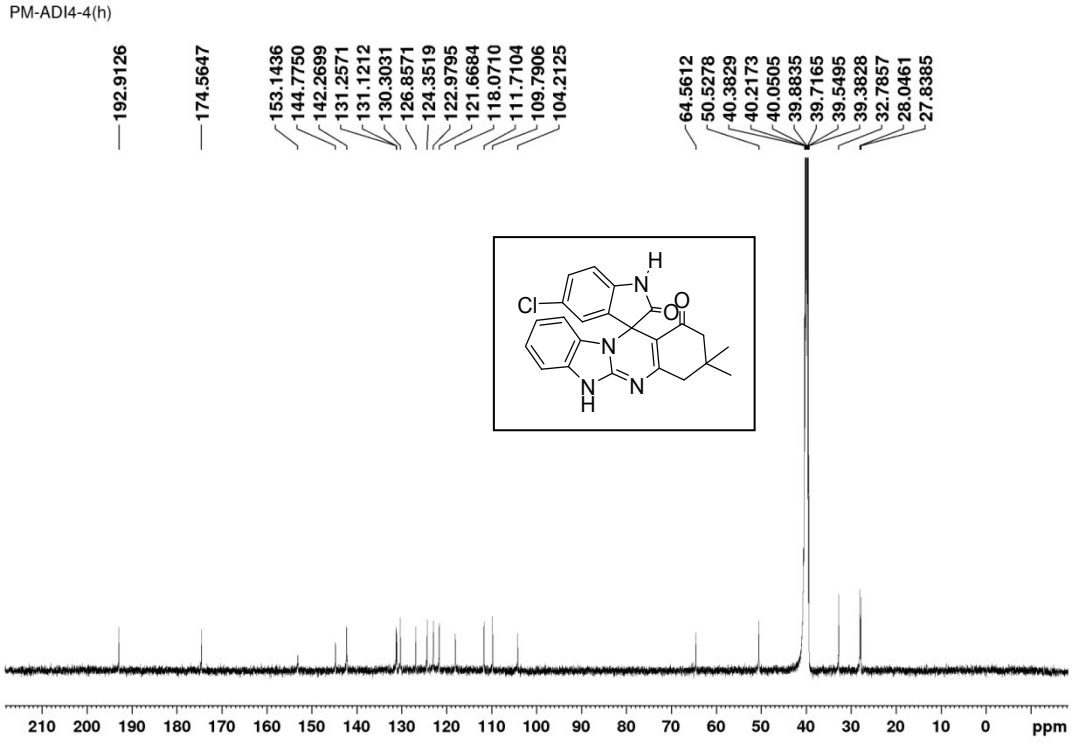


HRMS spectrum of compound 7d

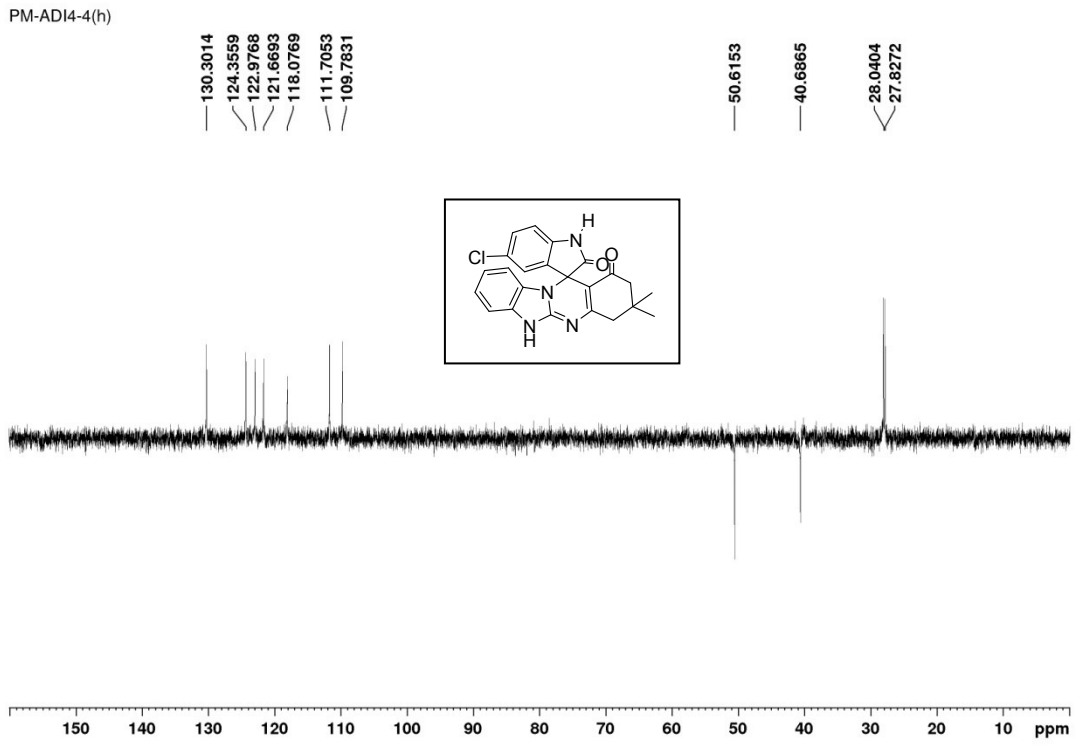


1

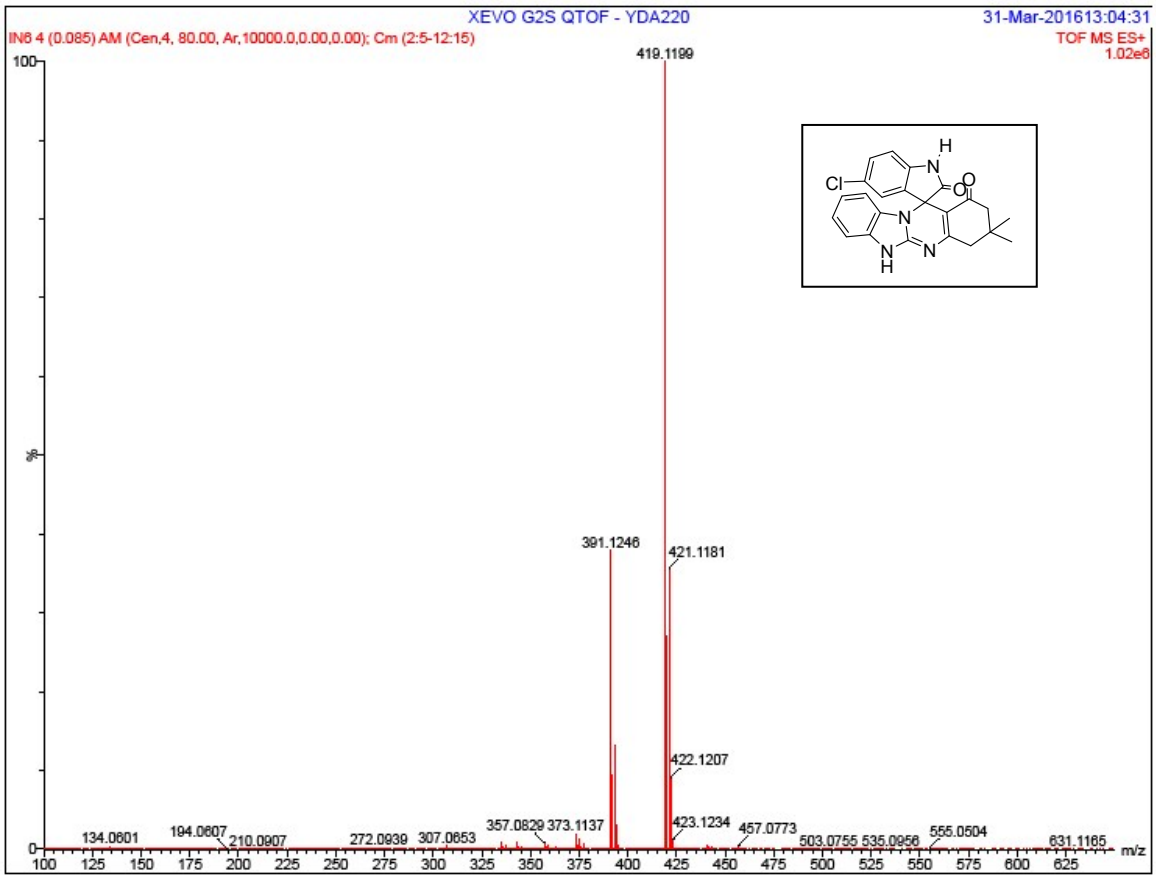
H NMRspectrum of compound 7e



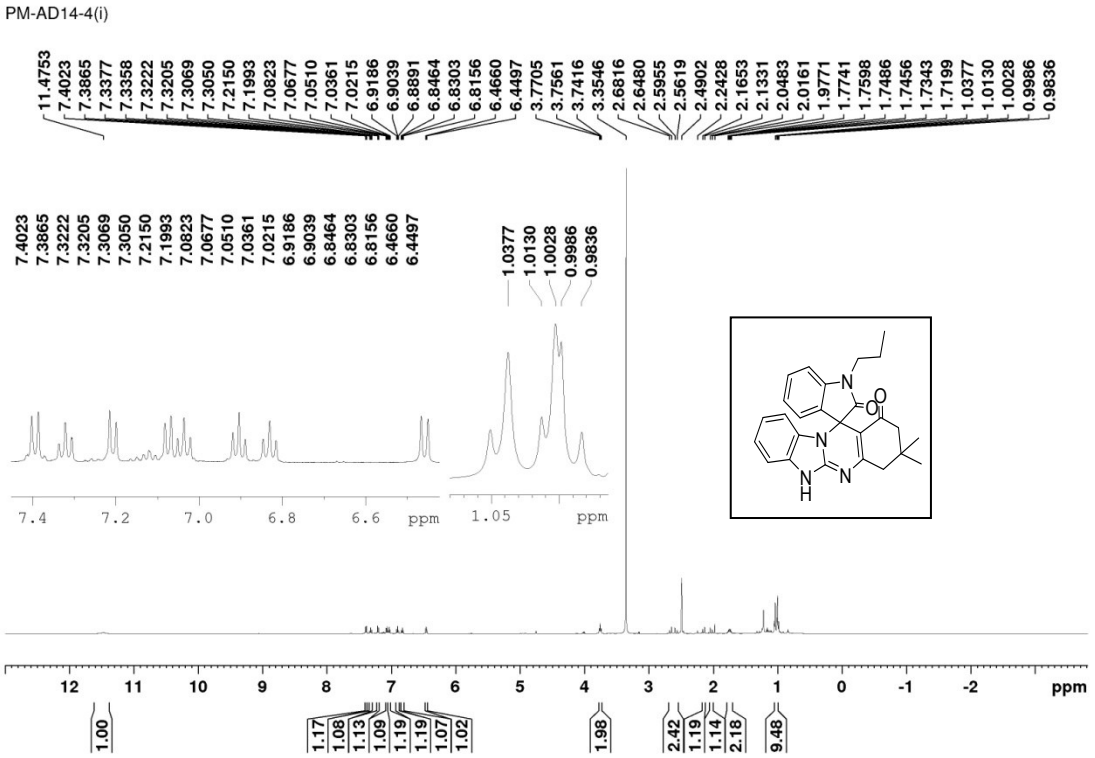
13 C NMRspectrum of compound 7e



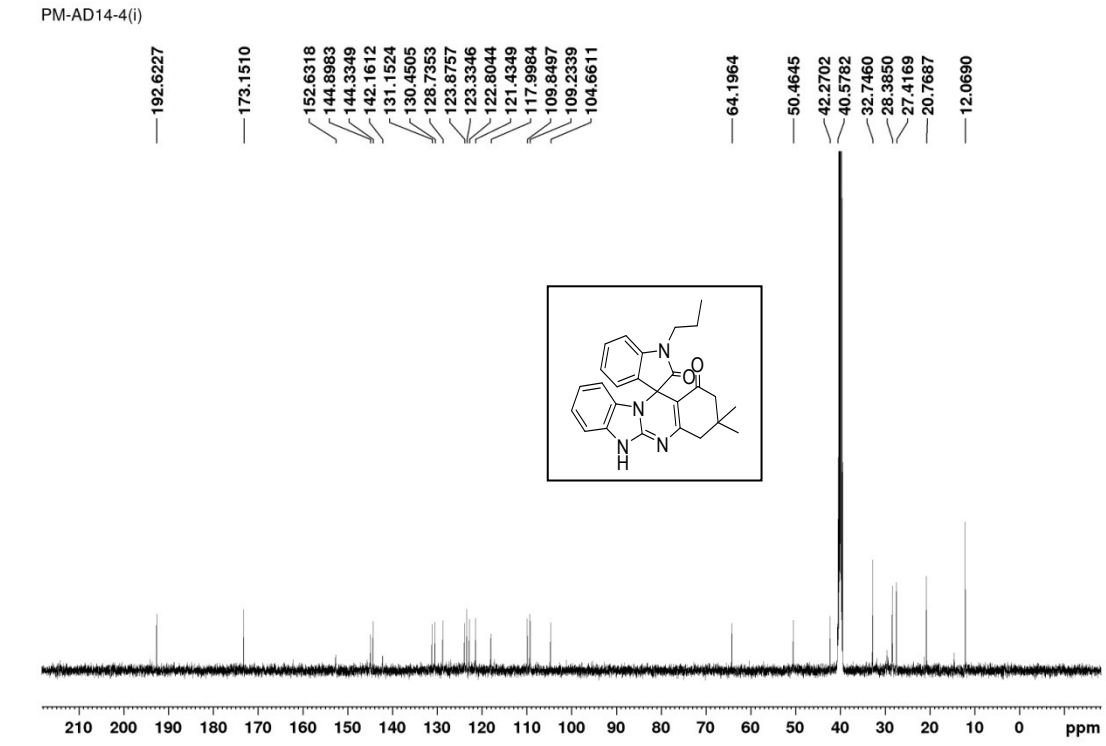
DEPT-135 NMRspectrum of compound 7e



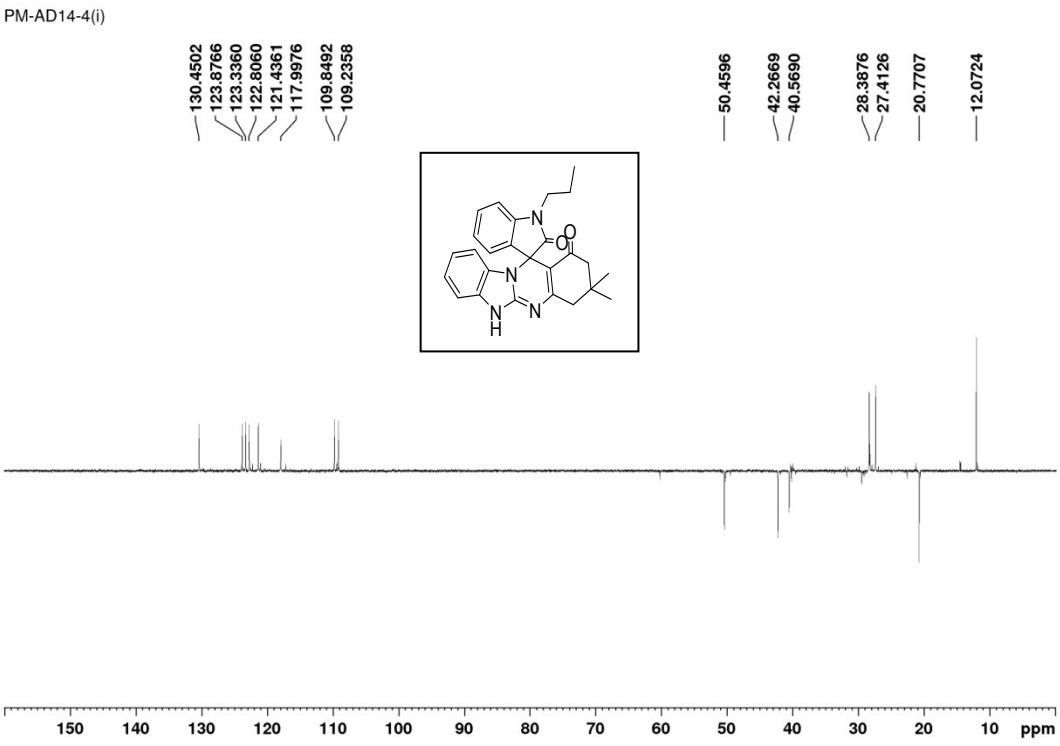
HRMS spectrum of compound 7e



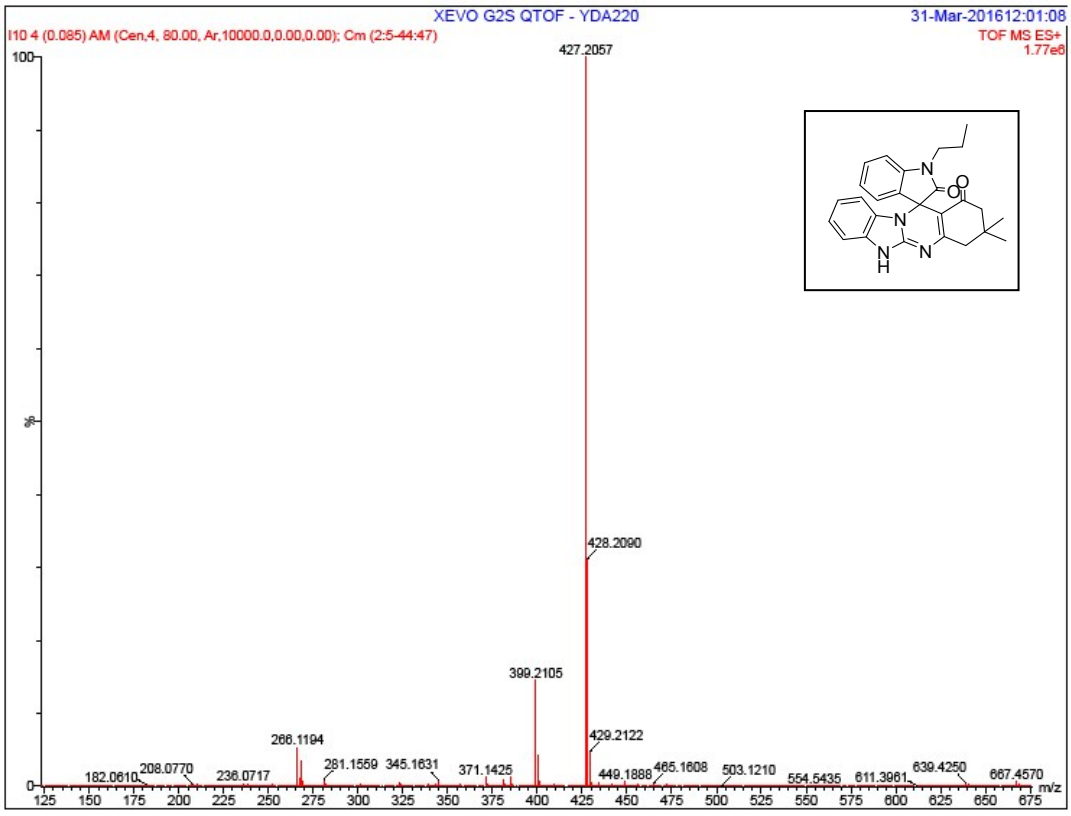
1H NMRspectrum of compound 7f



13C NMRspectrum of compound 7f

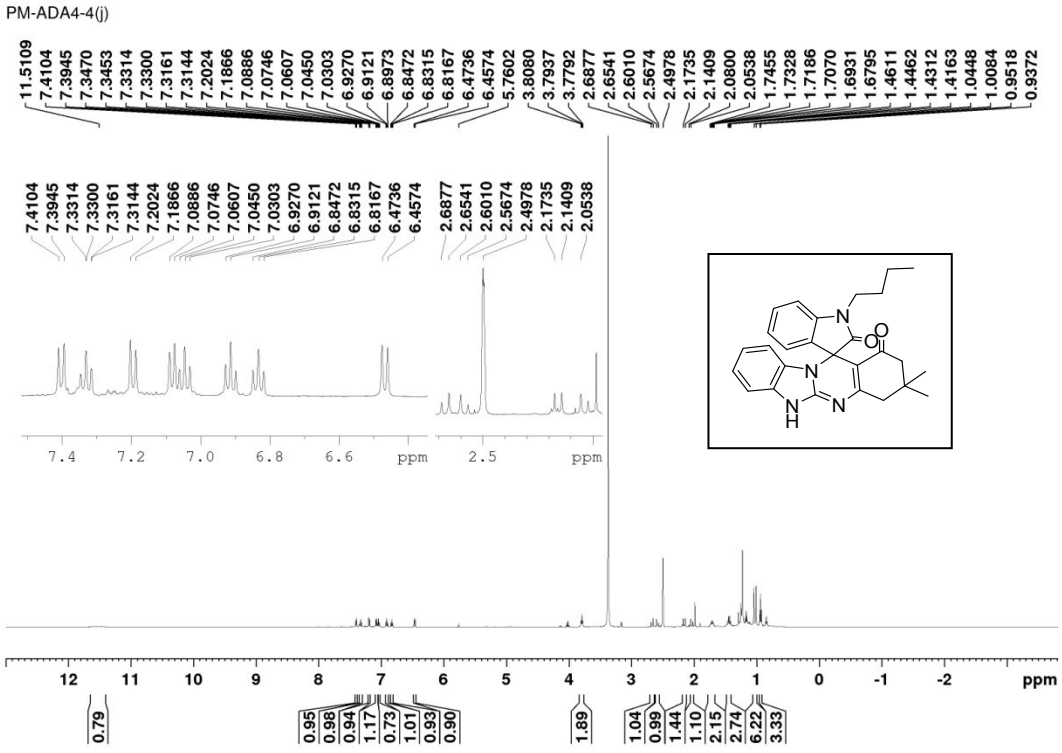


DEPT-135 NMRspectrum of compound 7f

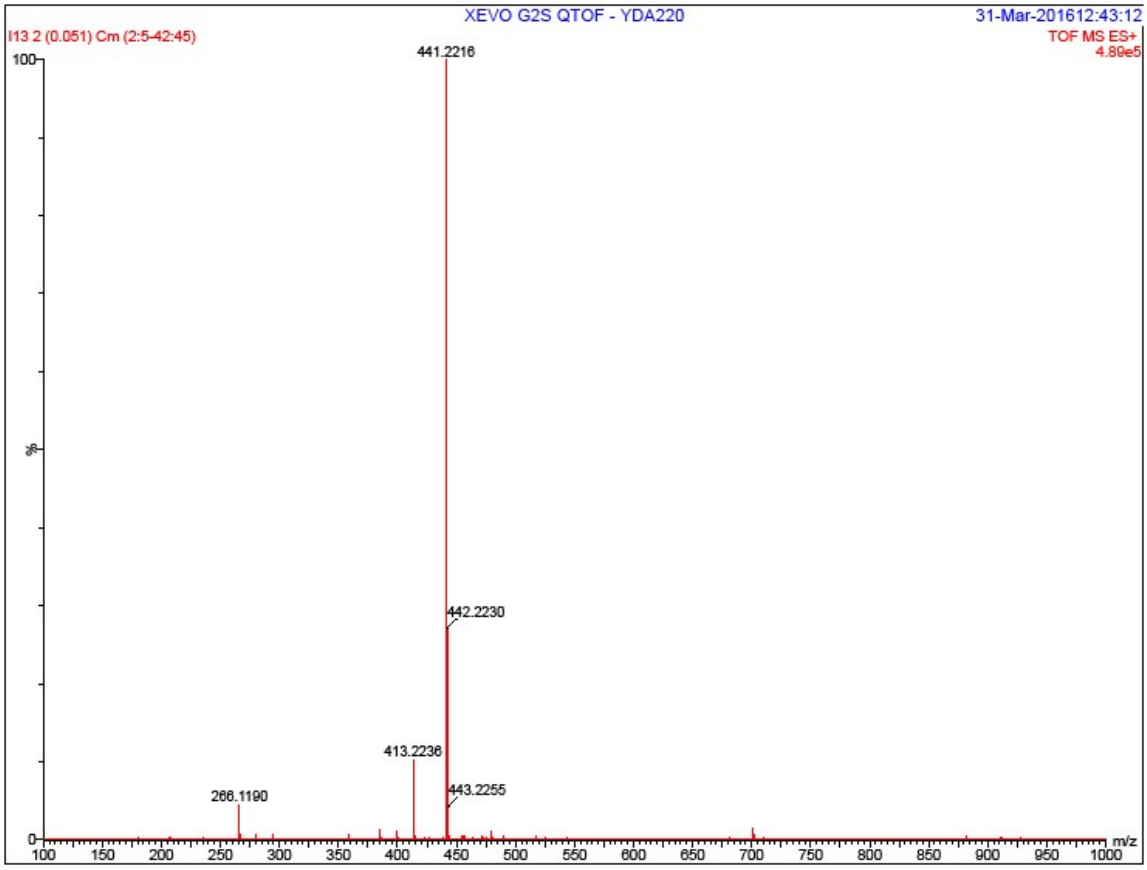


M

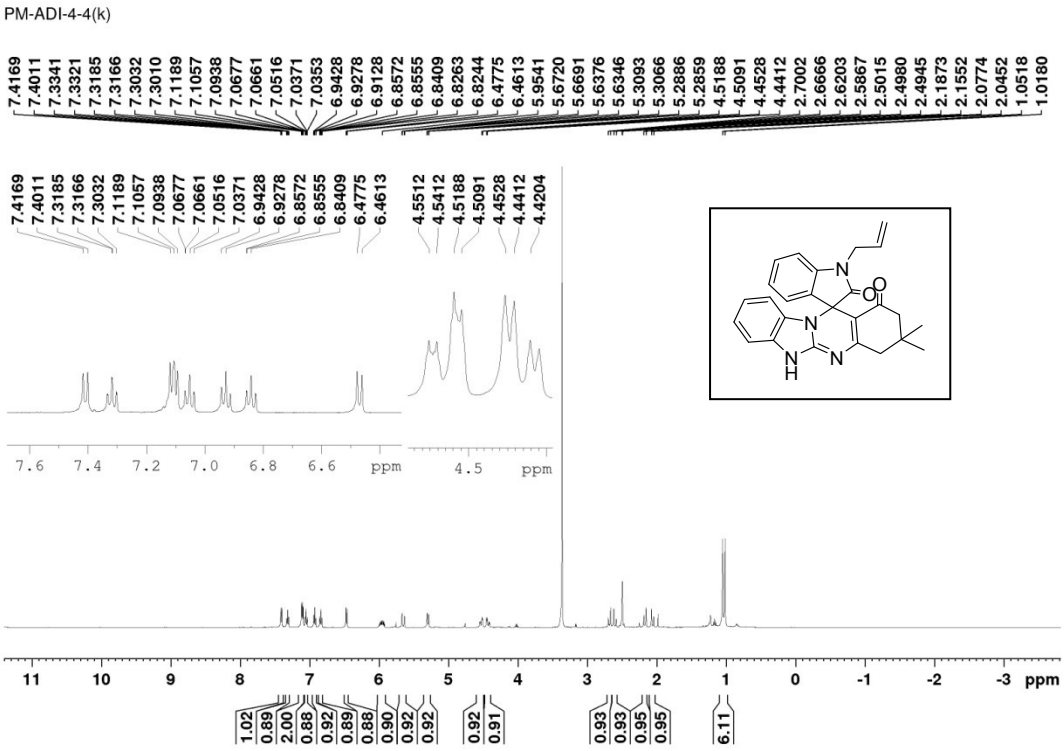
assspectrum of compound 7f



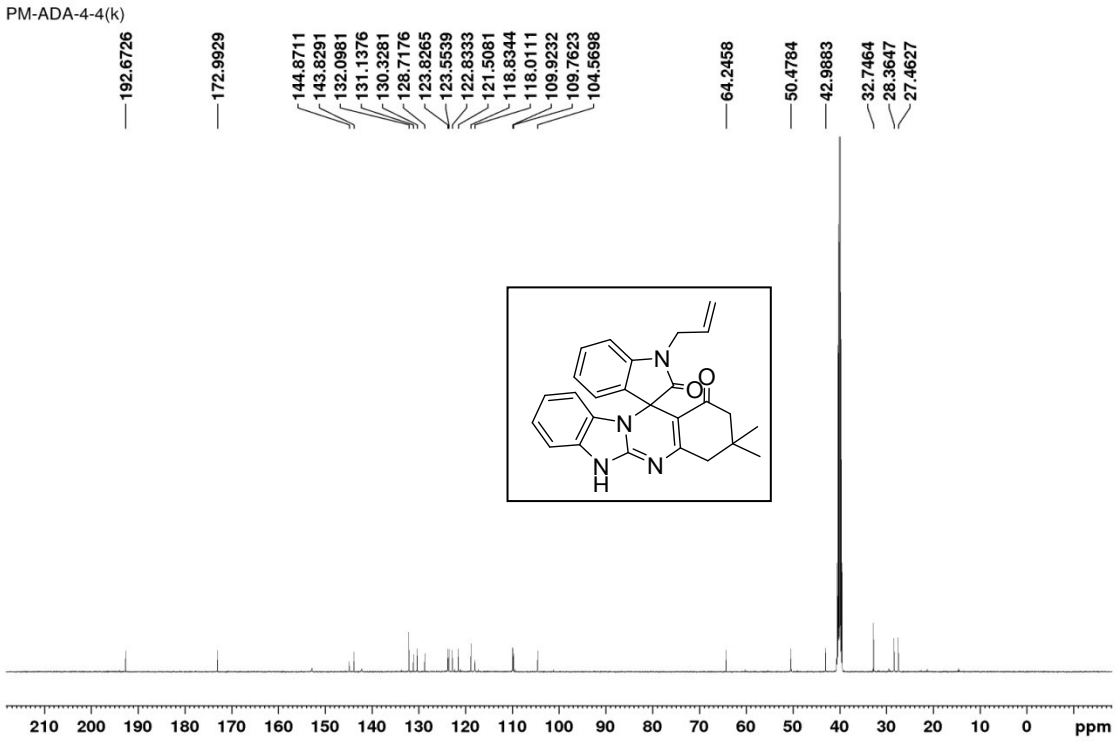
1H NMRspectrum of compound 7g



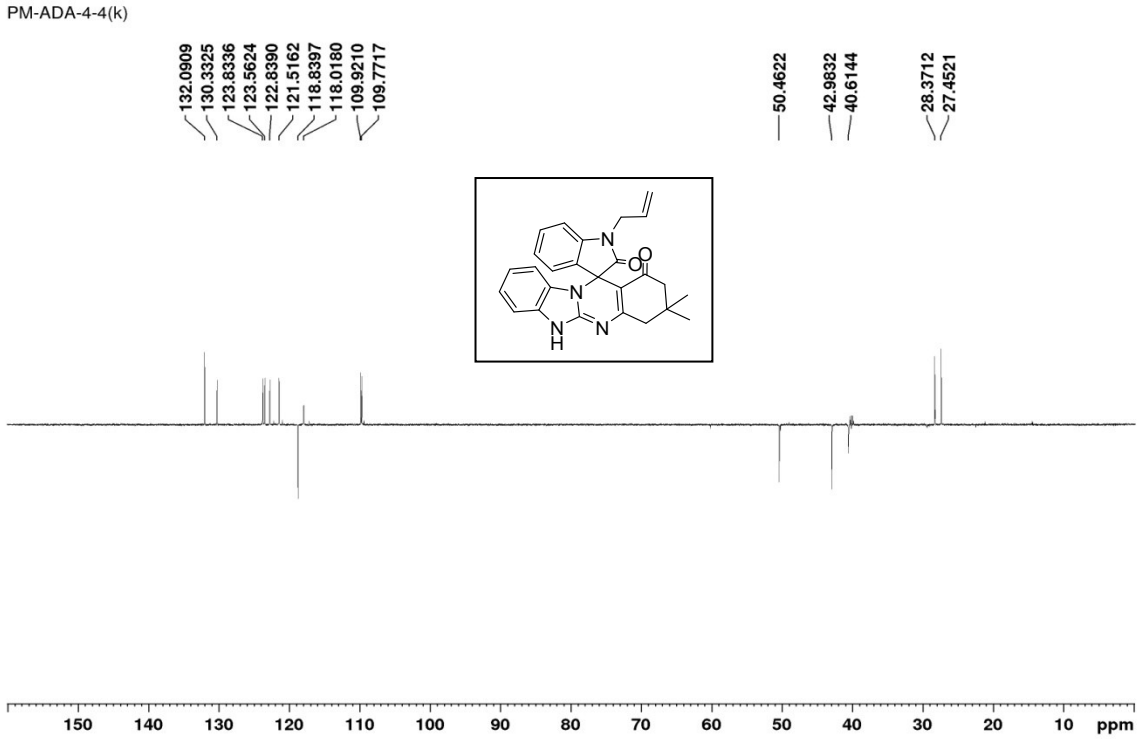
HRMS spectrum of compound 7g



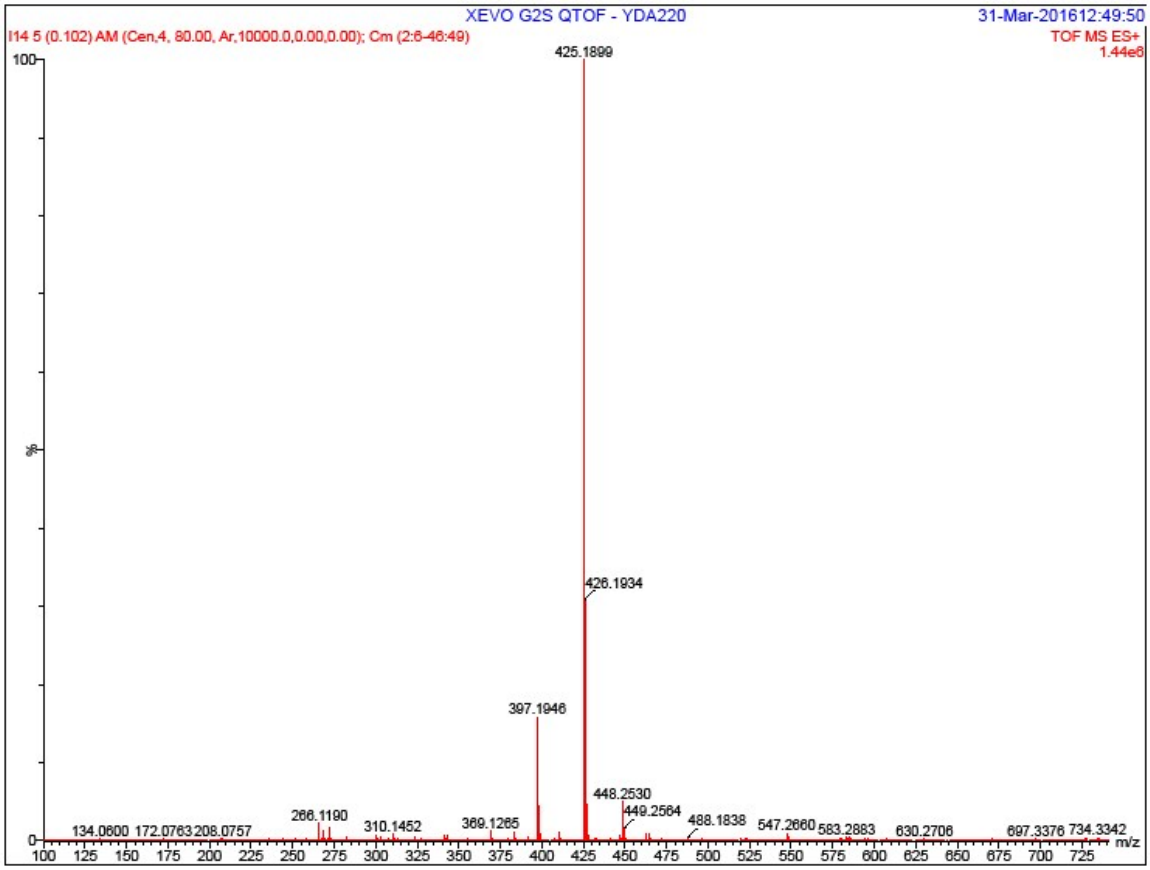
1H NMRspectrum of compound 7h



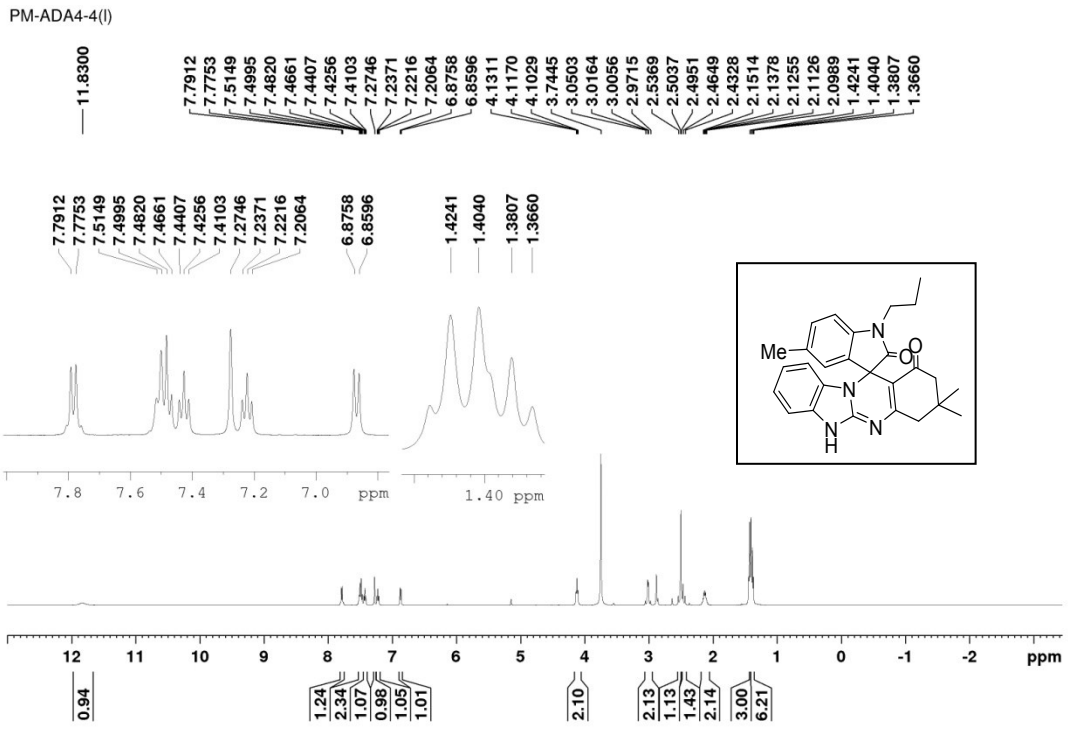
13C NMRspectrum of compound 7h



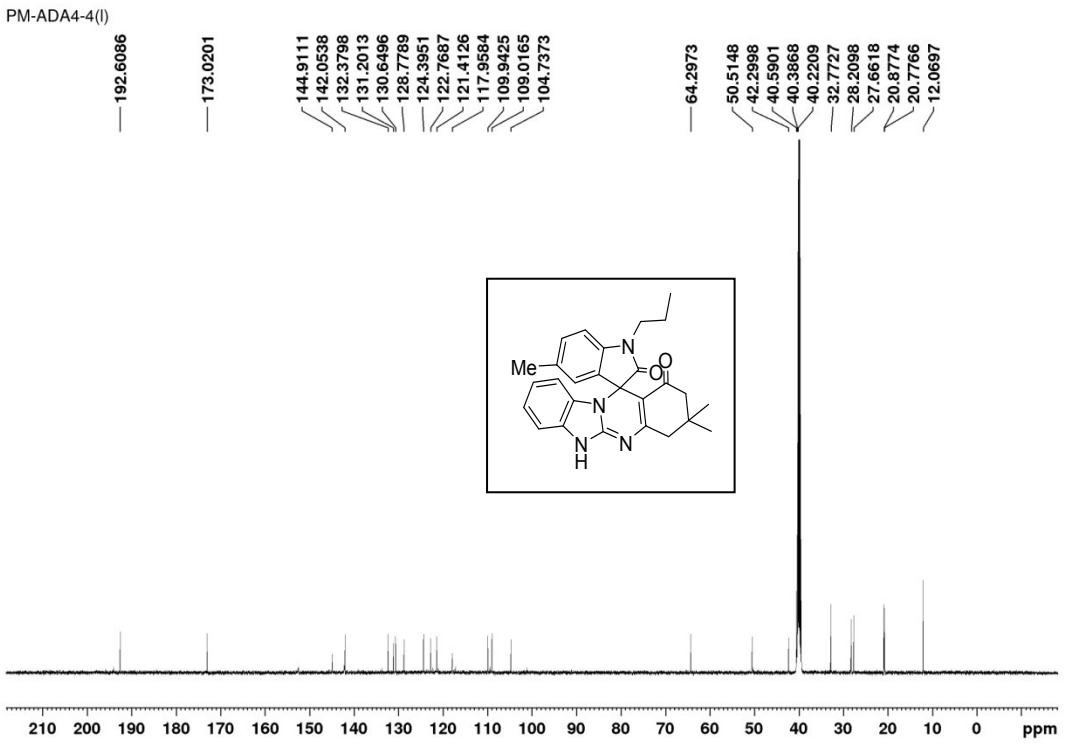
DEPT-135 NMR spectrum of compound 7h



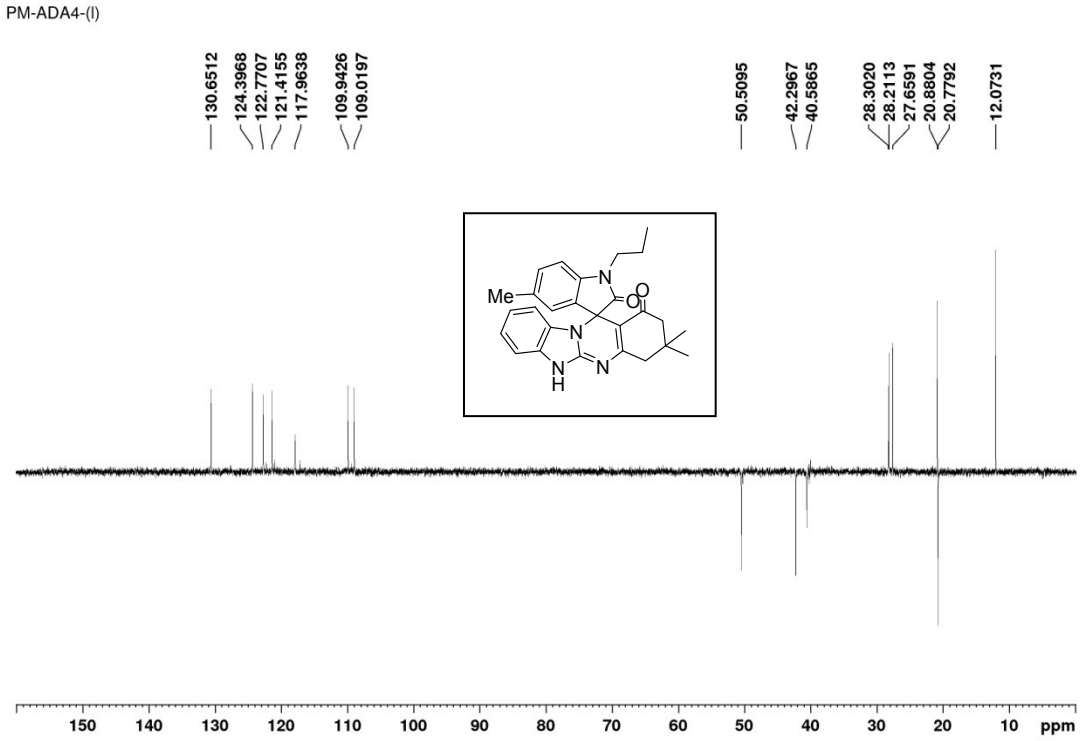
HRMS spectrum of compound 7h



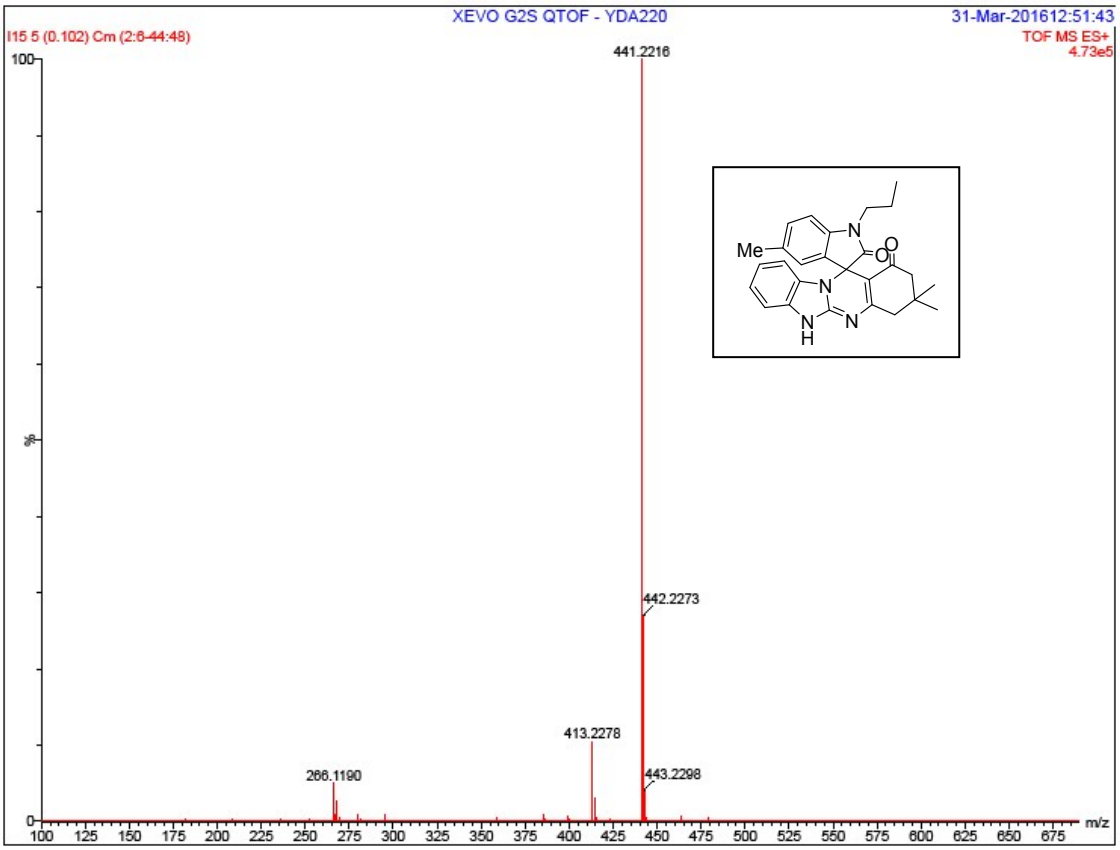
1H NMRspectrum of compound 7i



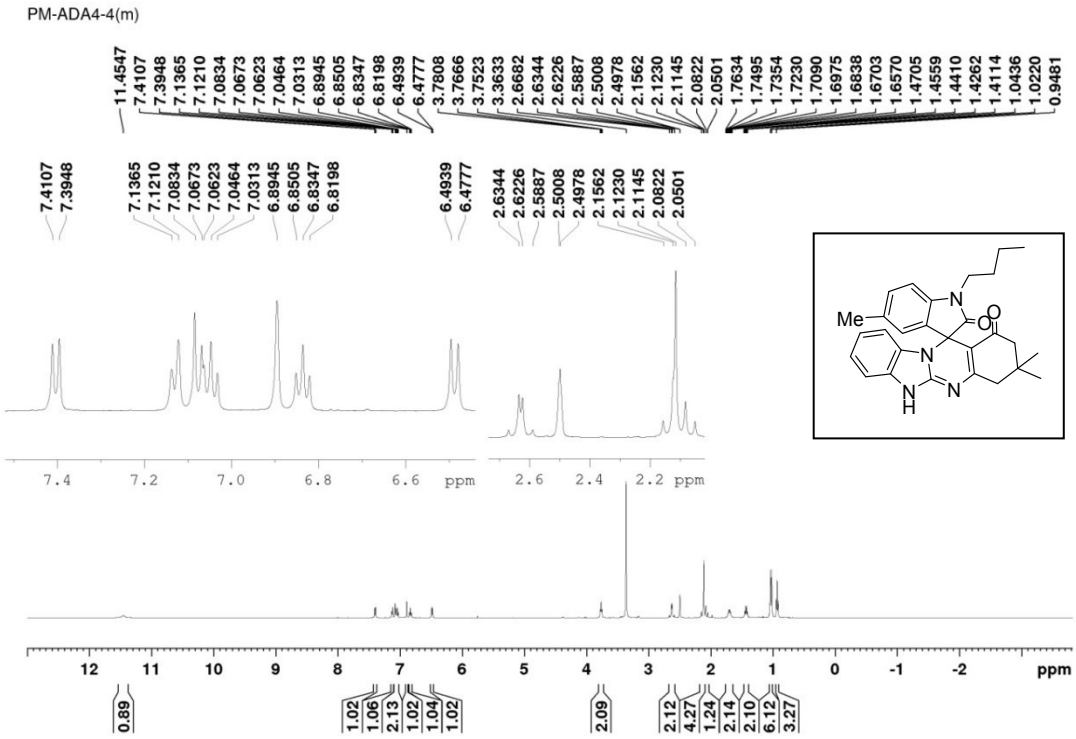
13C NMR spectrum of compound 7i



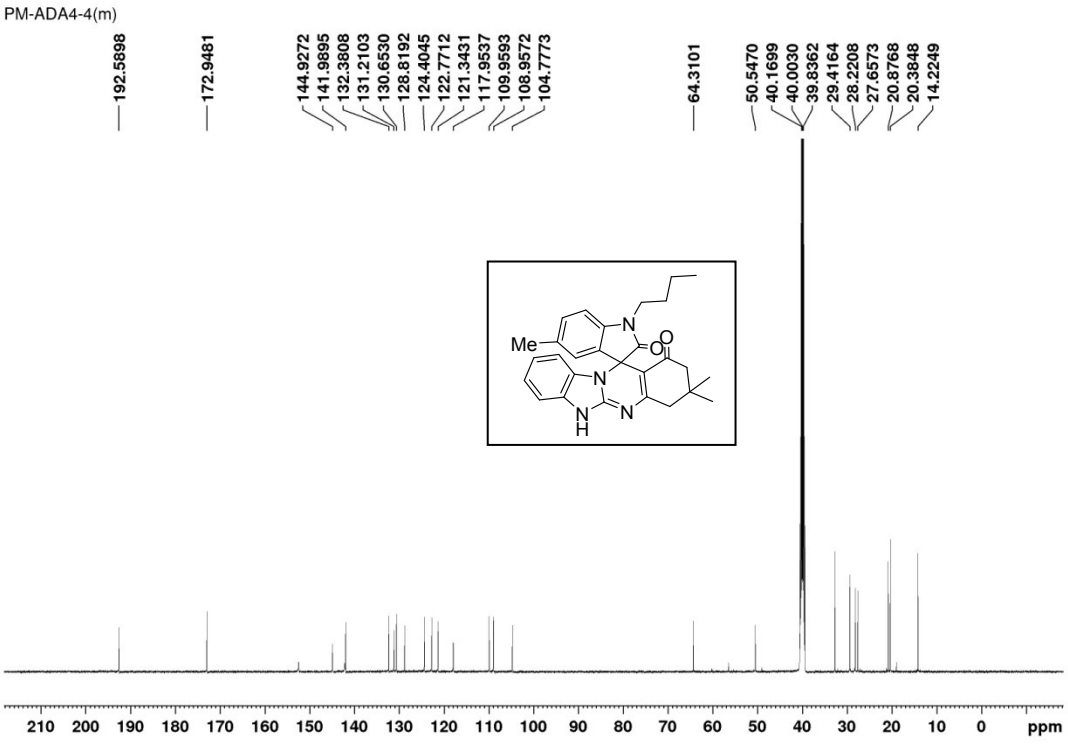
DEPT-135 NMR spectrum of compound 7i



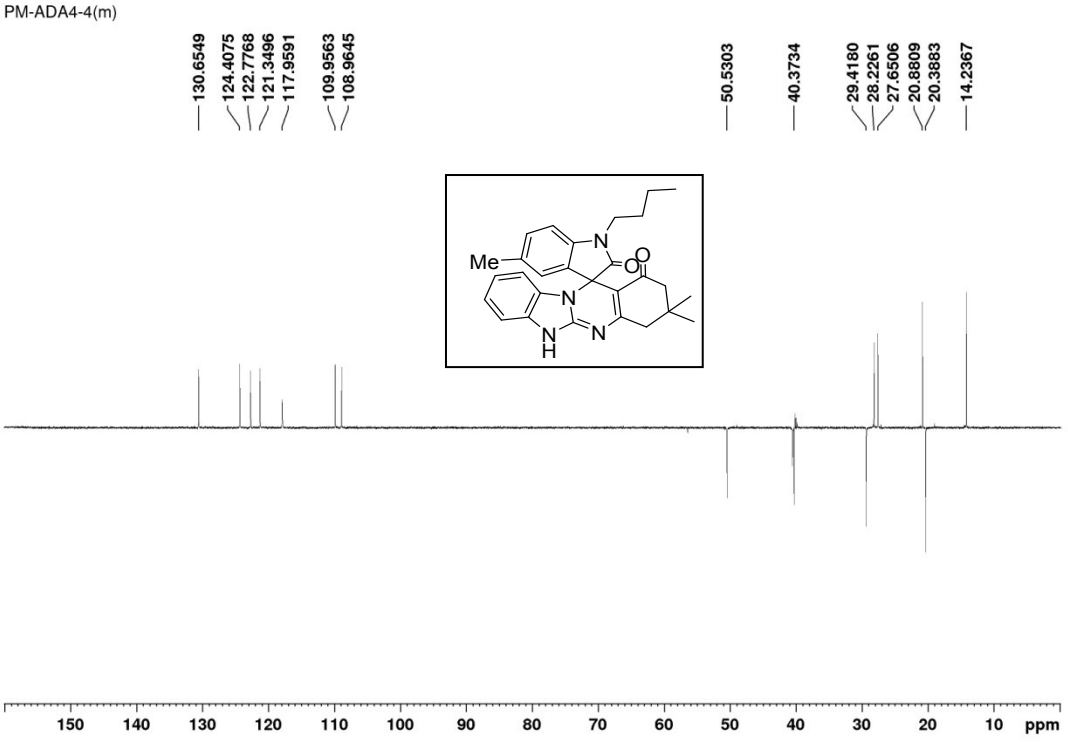
HRMS spectrum of compound 7i



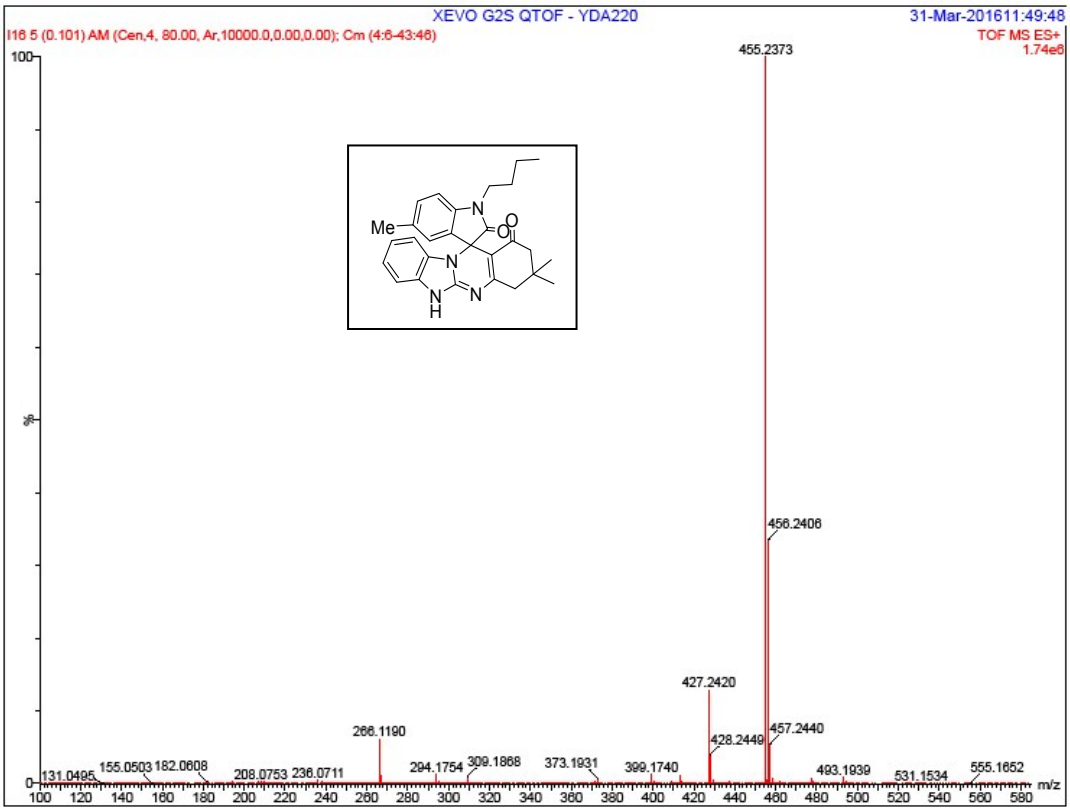
1H NMRspectrum of compound 7j



13C NMRspectrum of compound 7j

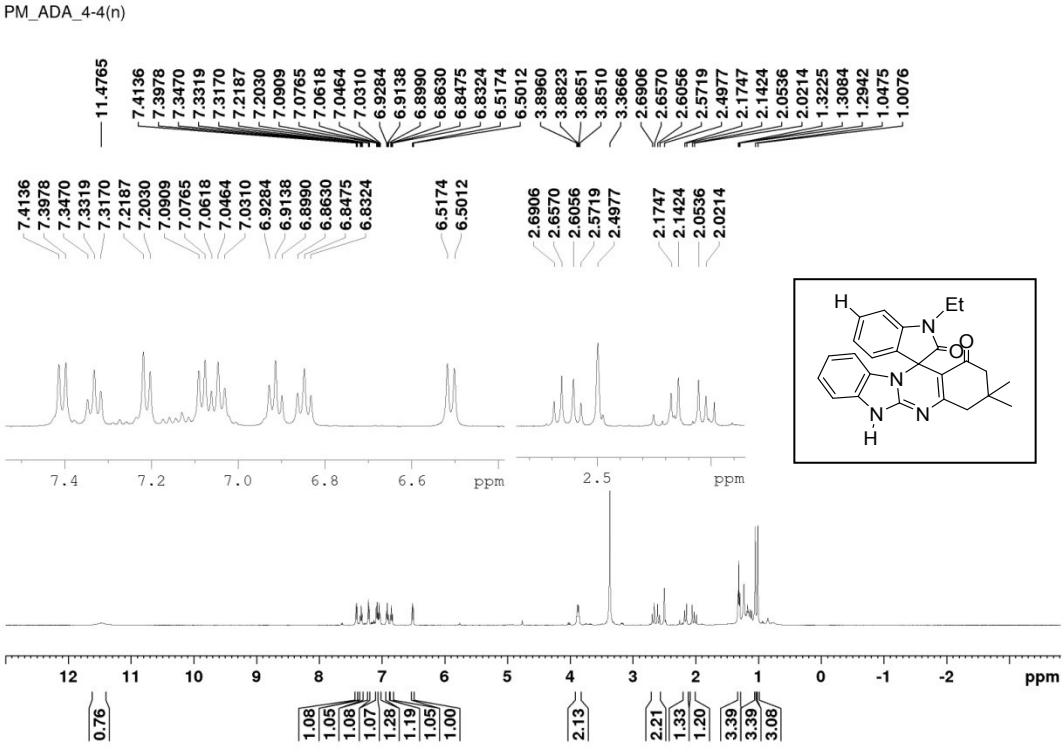


DEPT-135 NMR spectrum of compound 7j

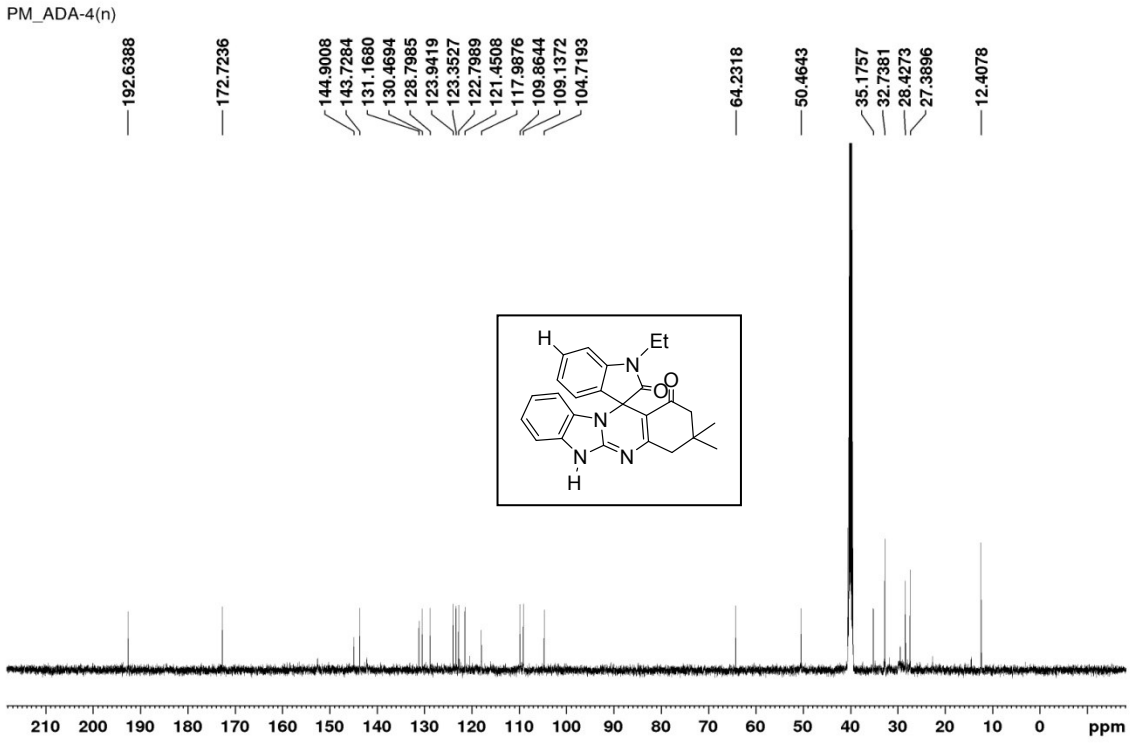


H

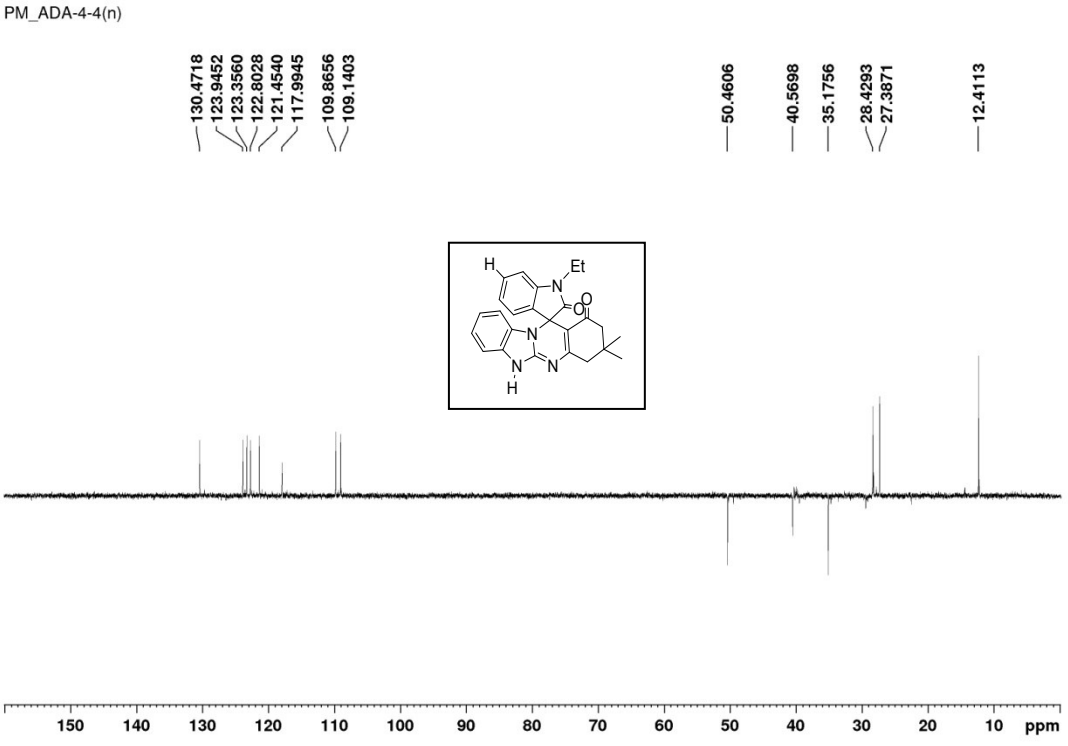
RMS spectrum of compound 7j



1H NMRspectrum of compound 7k



13C NMRspectrum of compound 7k



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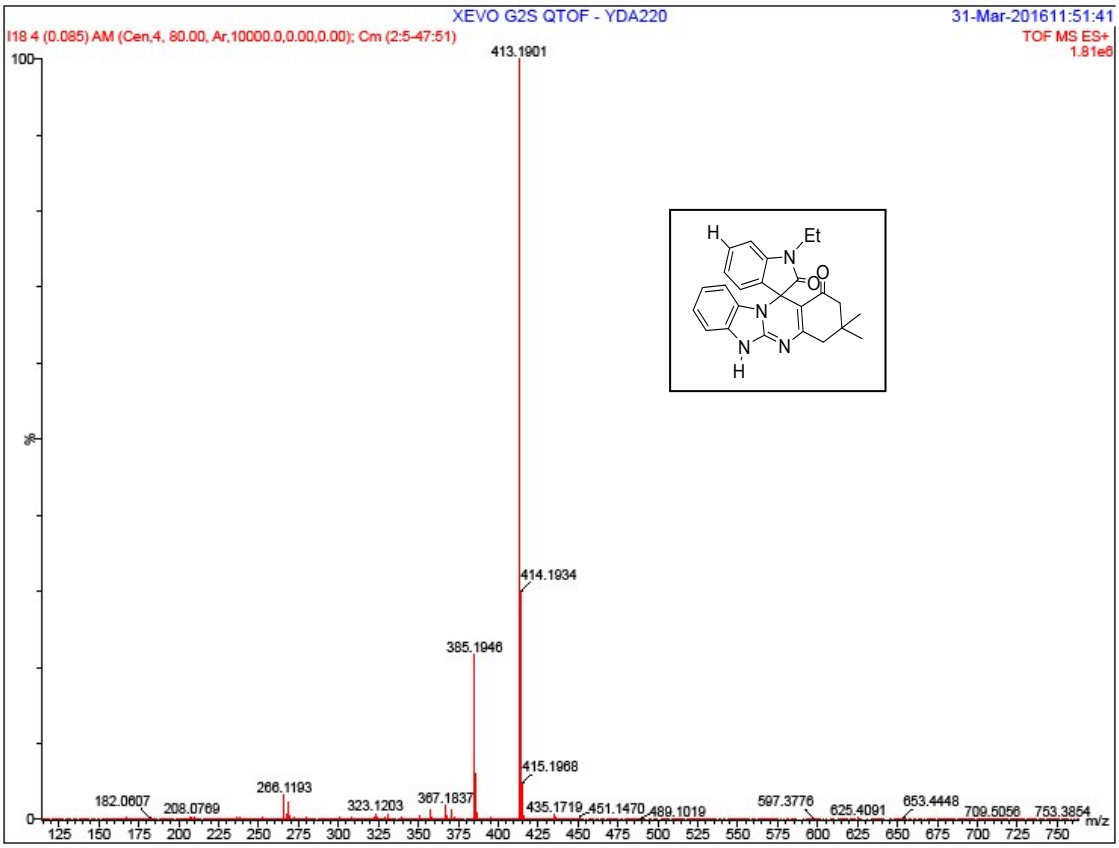
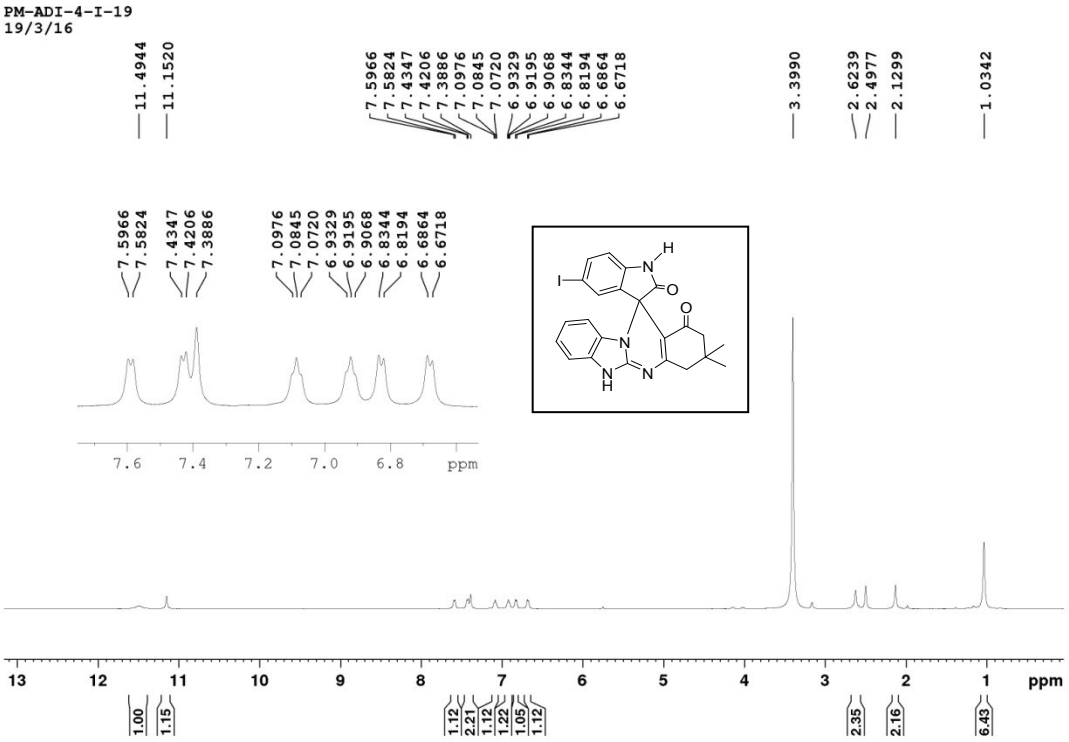
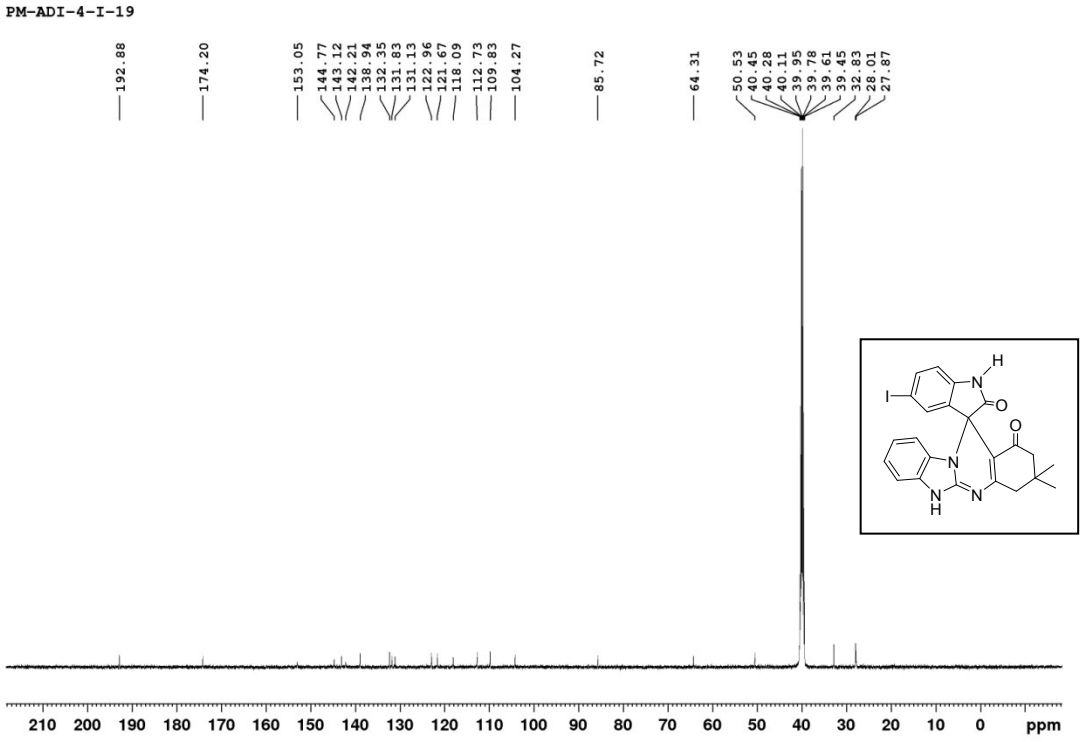


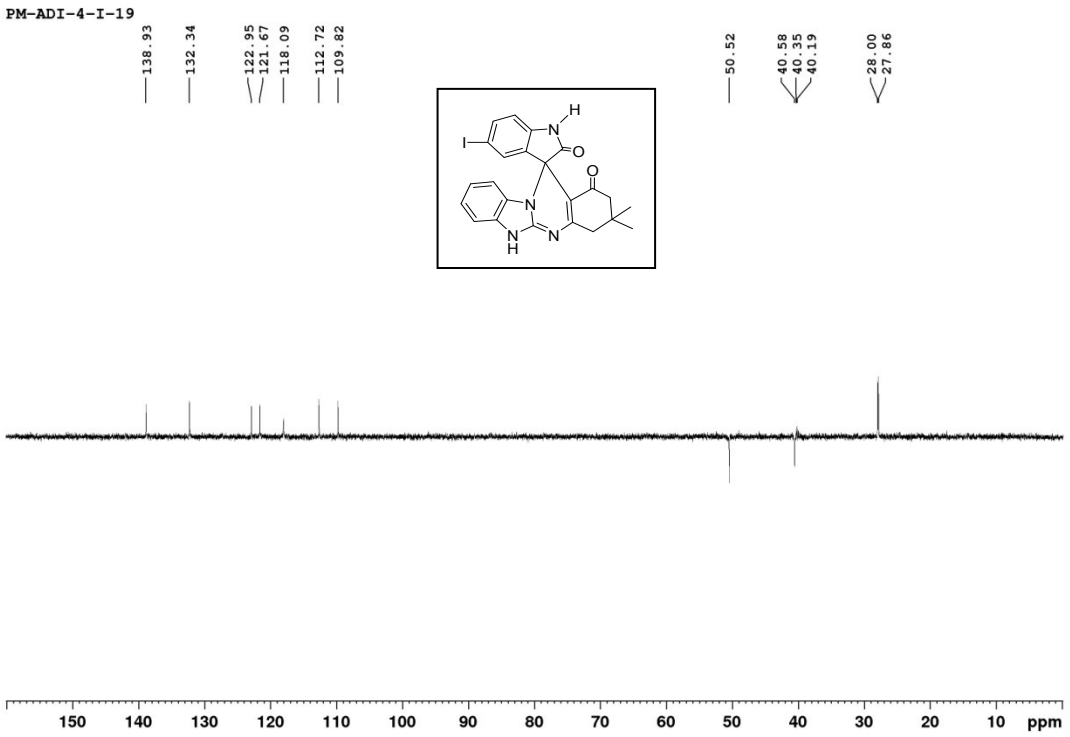
HRMS spectrum of compound 7k



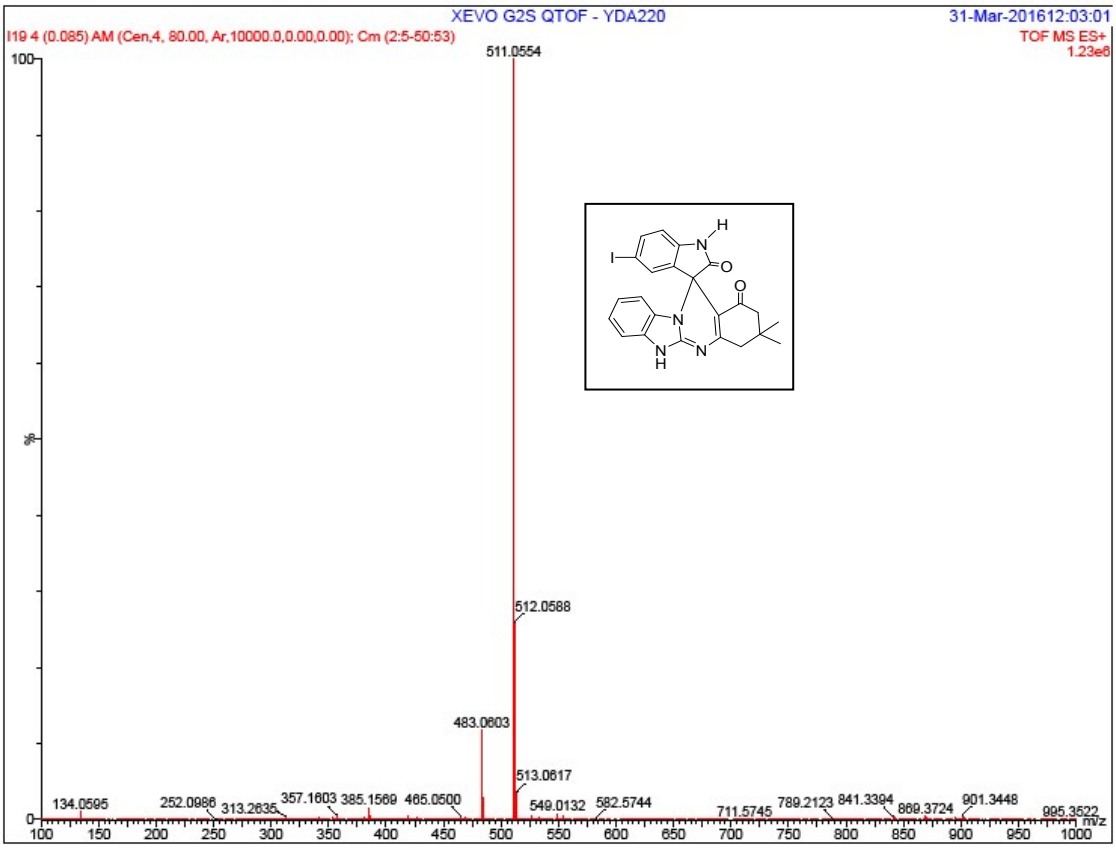
1H NMRspectrum of compound 7l



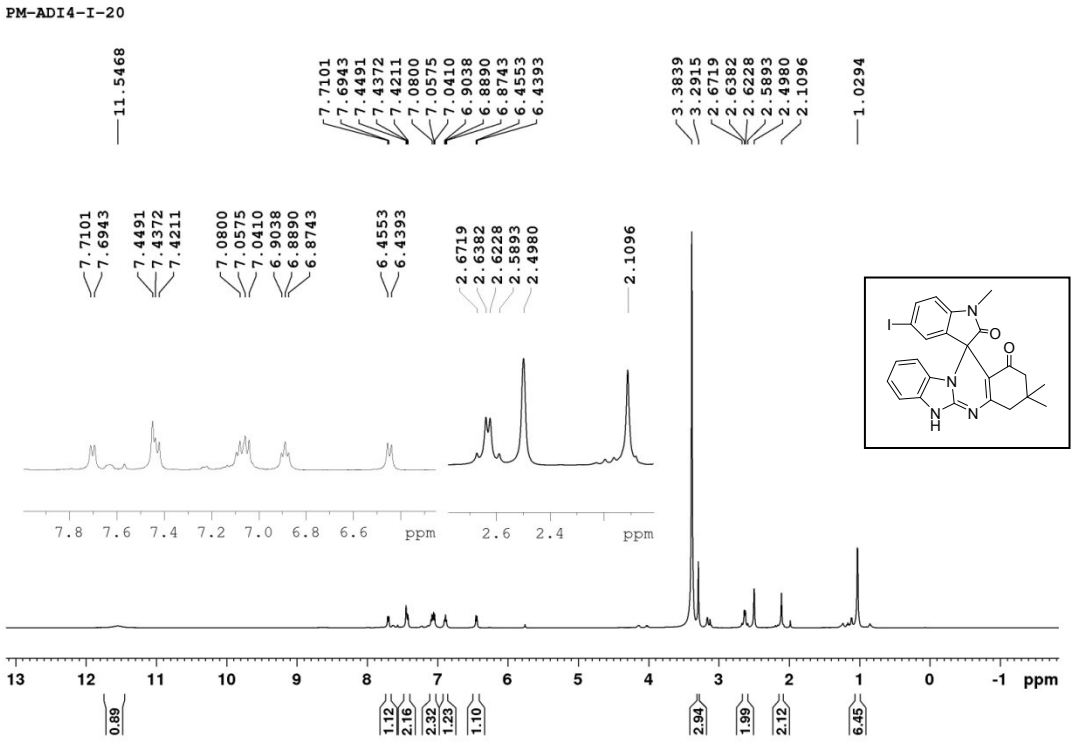
13C NMRspectrum of compound 7l



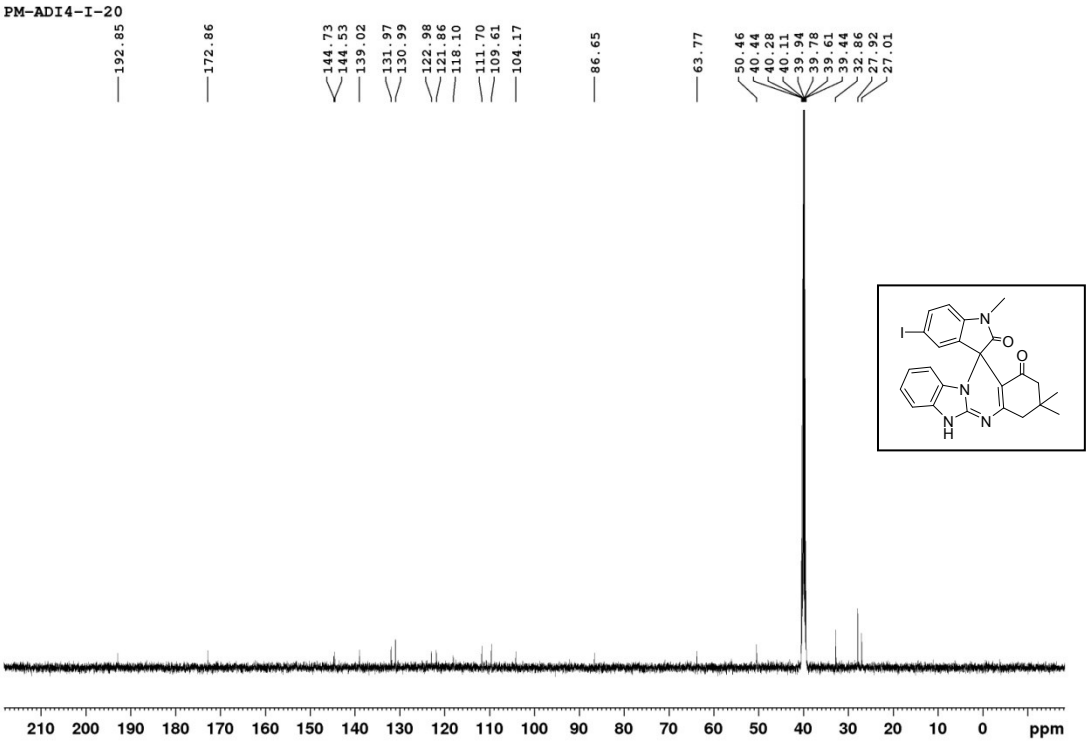
DEPT-135 NMRspectrum of compound 7l



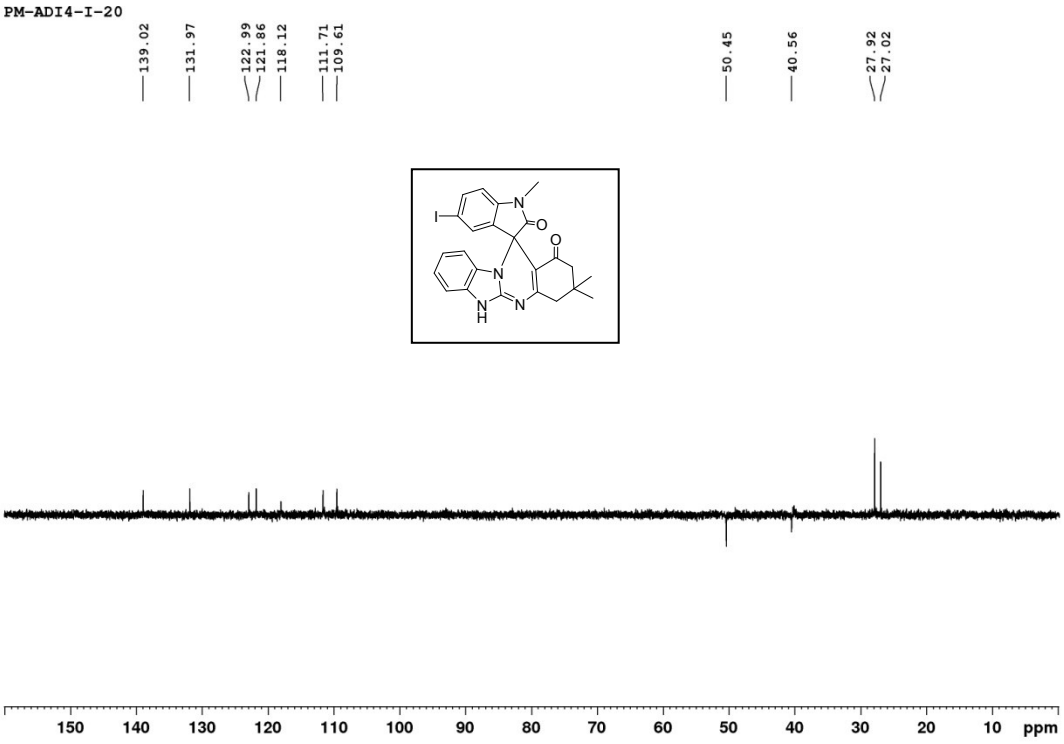
HRMS spectrum of compound 7l



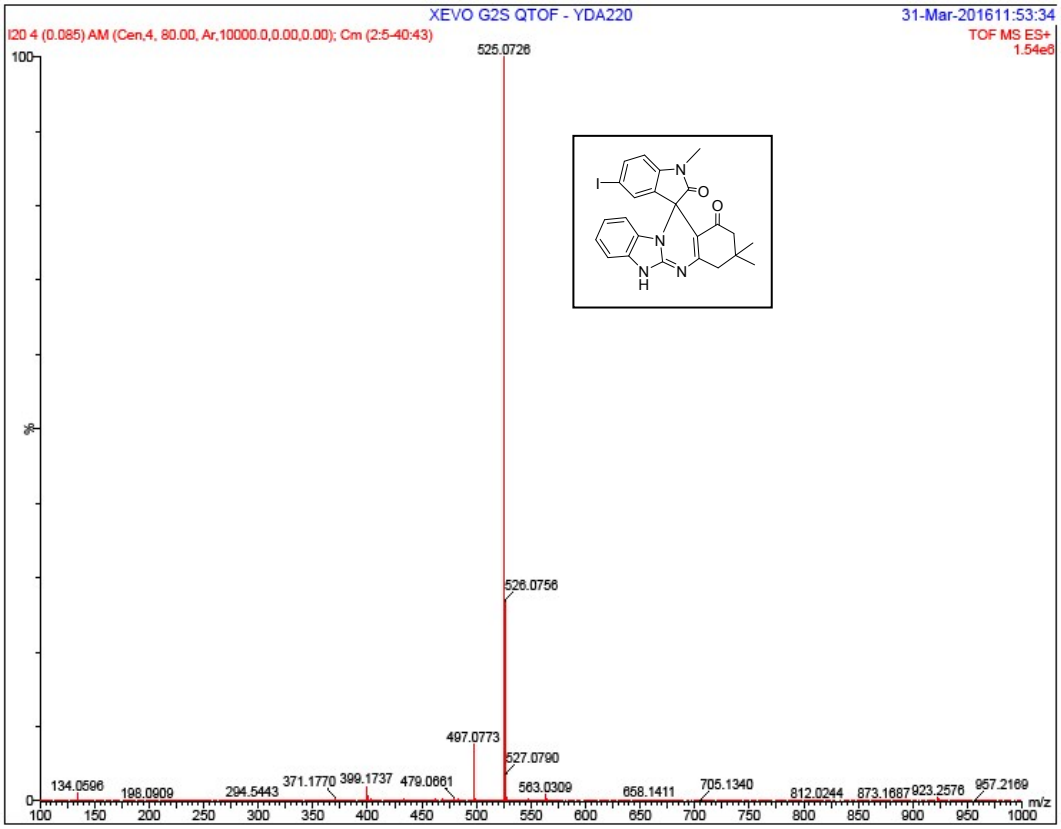
1H NMRspectrum of compound 7m



13C NMRspectrum of compound 7m

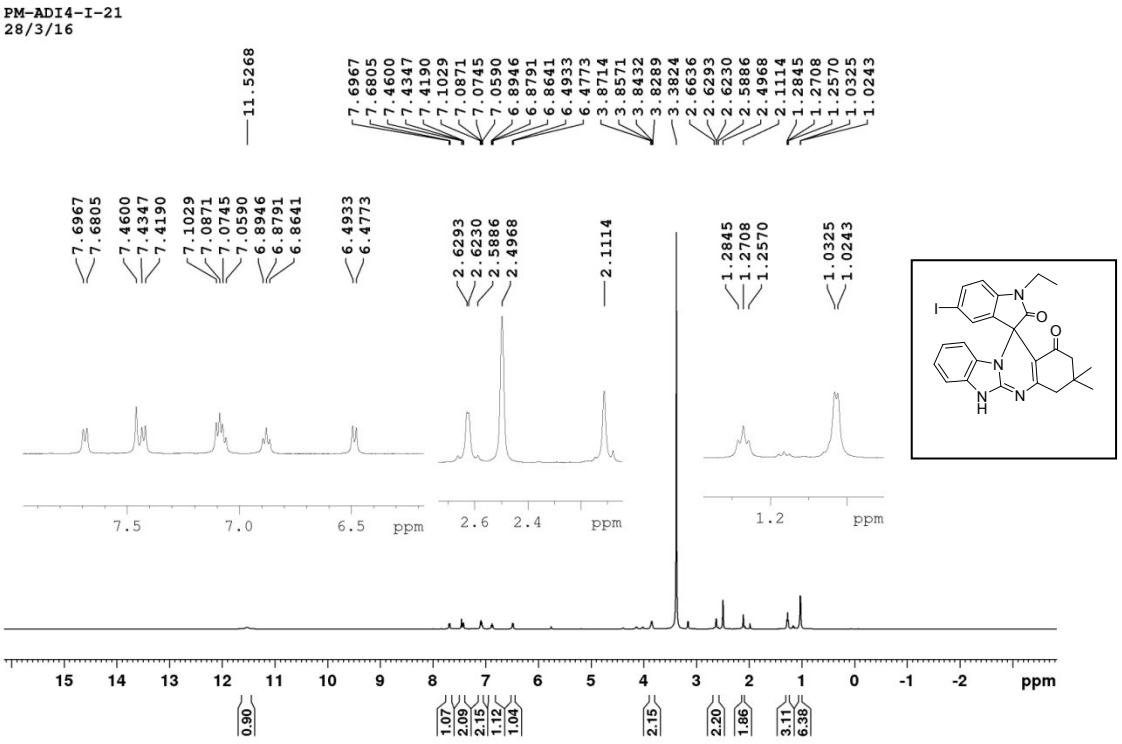


DEPT-135 NMRspectrum of compound 7m

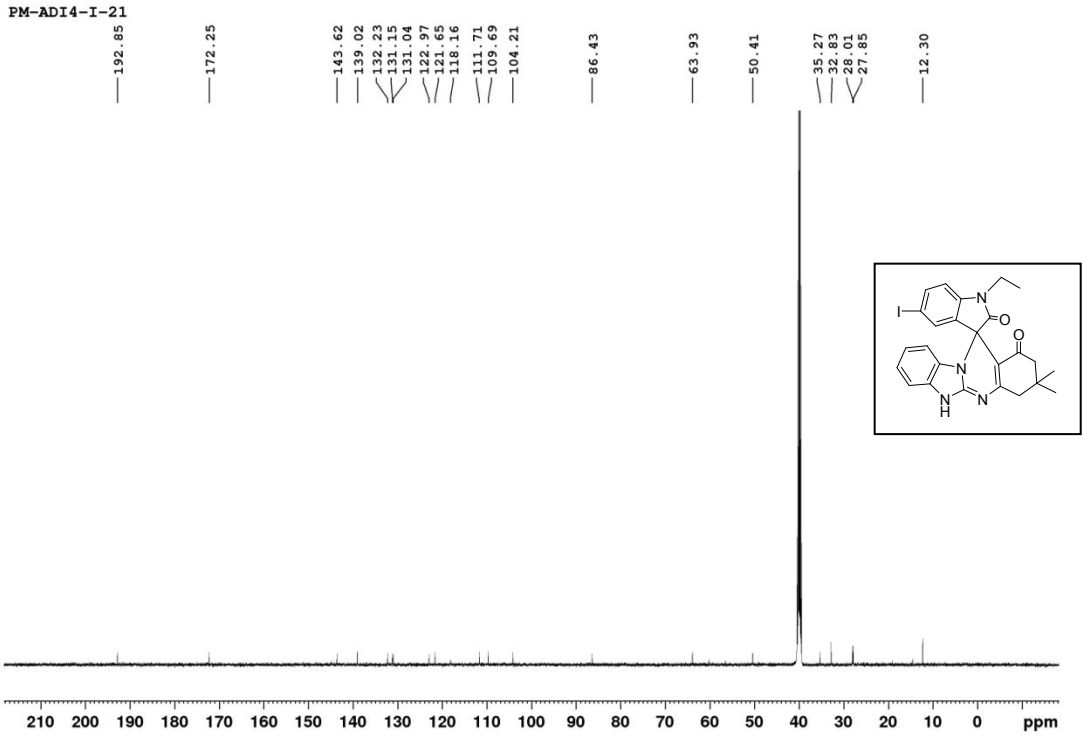


HR

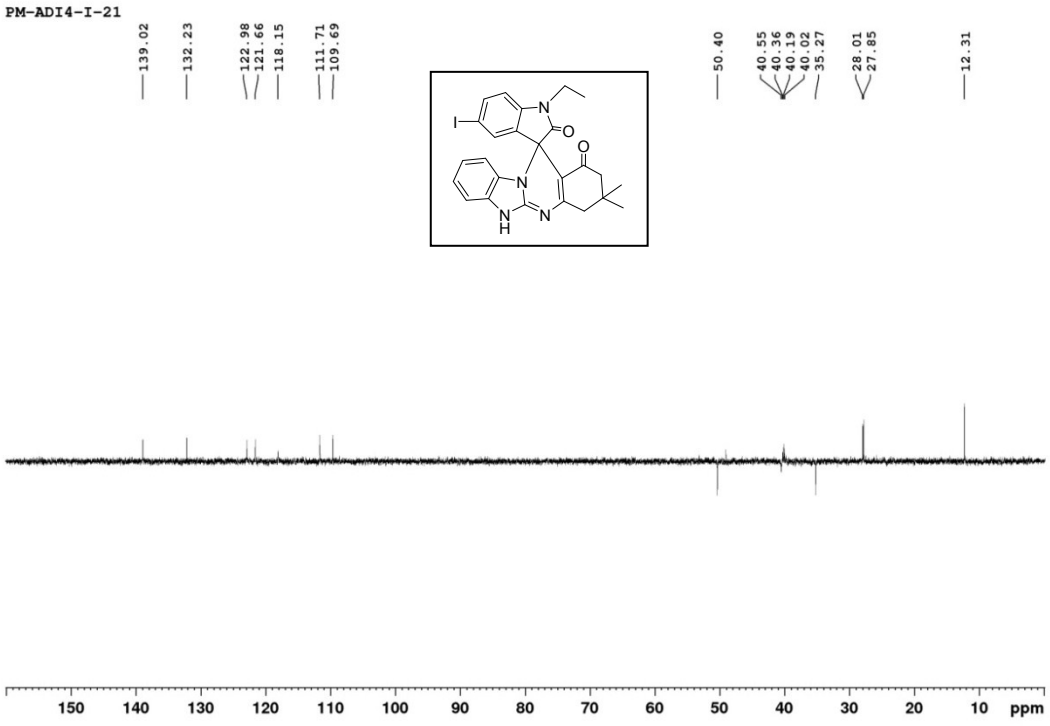
MS spectrum of compound 7m



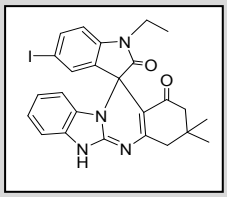
1H NMRspectrum of compound 7n



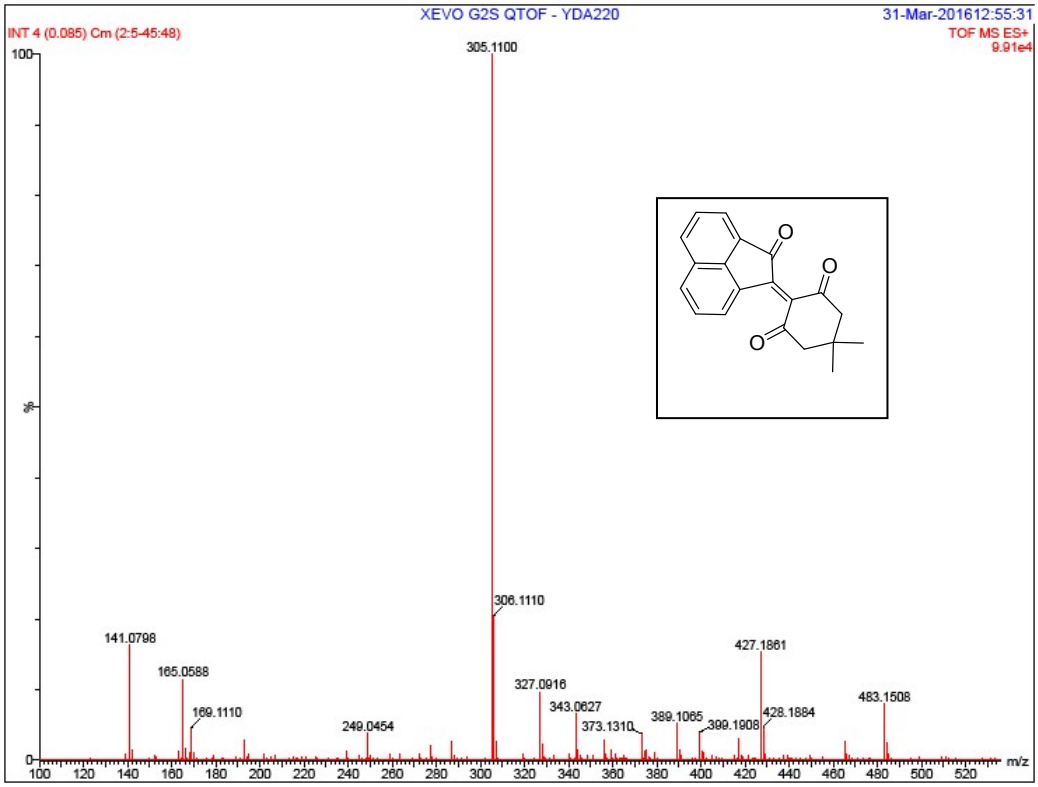
13C NMRspectrum of compound 7n



DEPT-135 NMRspectrum of compound 7n



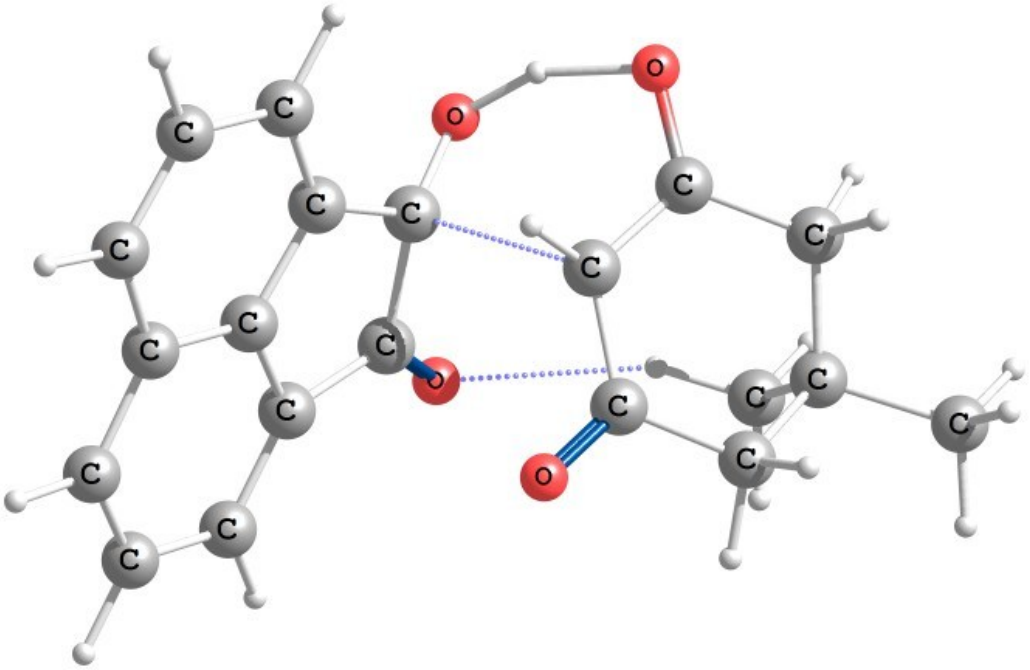
HRMS spectrum of compound 7n



HRMS spectrum of compound 5

8. Optimized Transition States

T.S.-I



T.S.-III