Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Exploration of aminomethylene linkage in carbazole based donor-pi-acceptor molecules for AIE properties and hydrazine sensing

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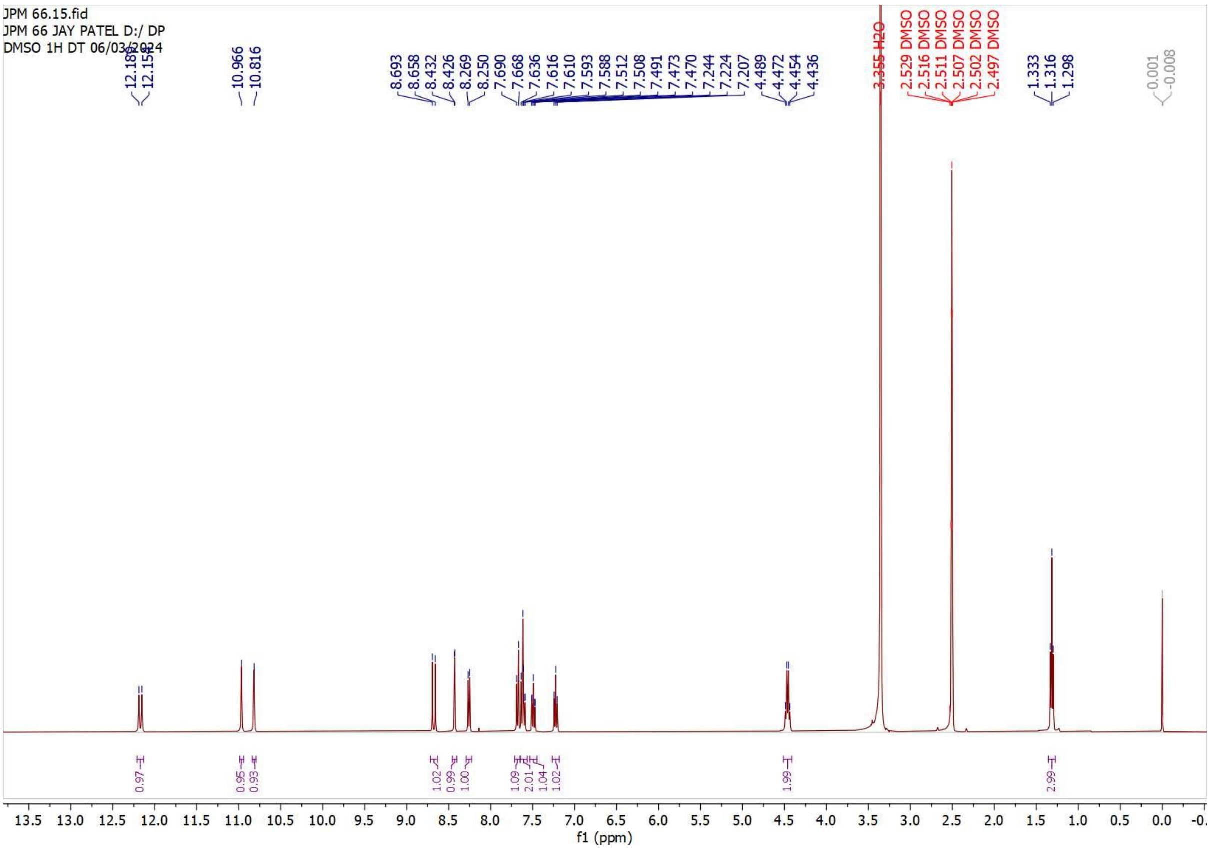
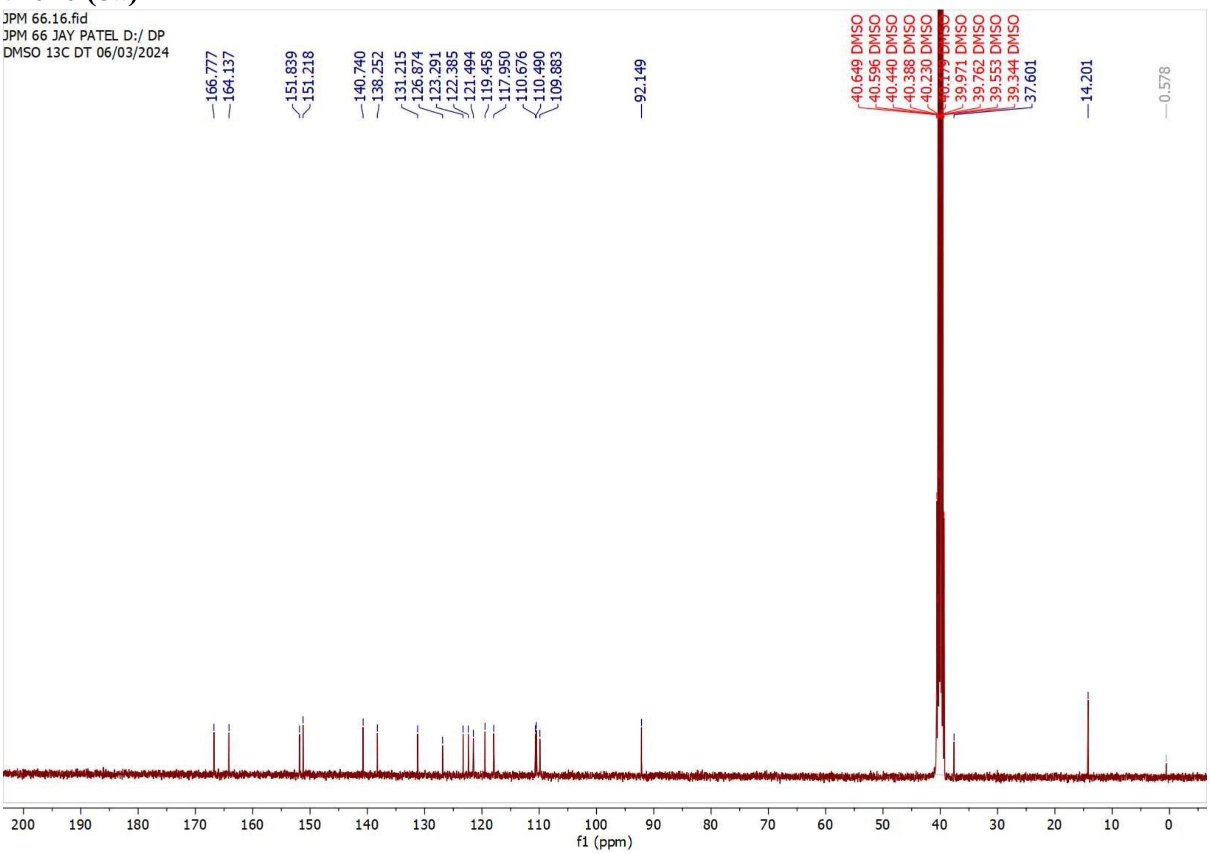
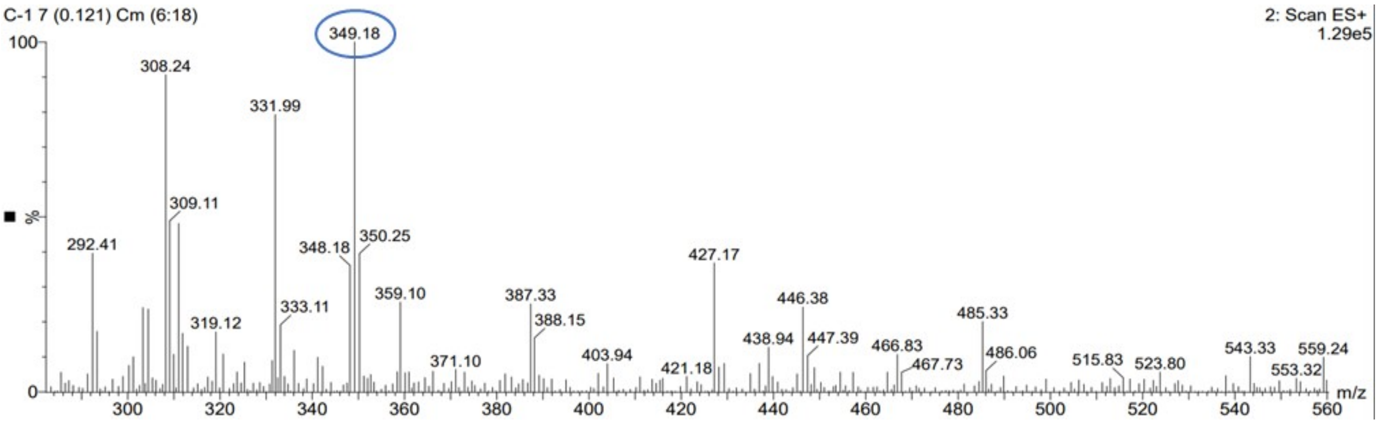
[1]H-NMR of 5-(((9-ethyl-9H-carbazol-3-yl)amino)methylene)pyrimidine-2,4,6(1H,3H,5H)-trione **(8a)**



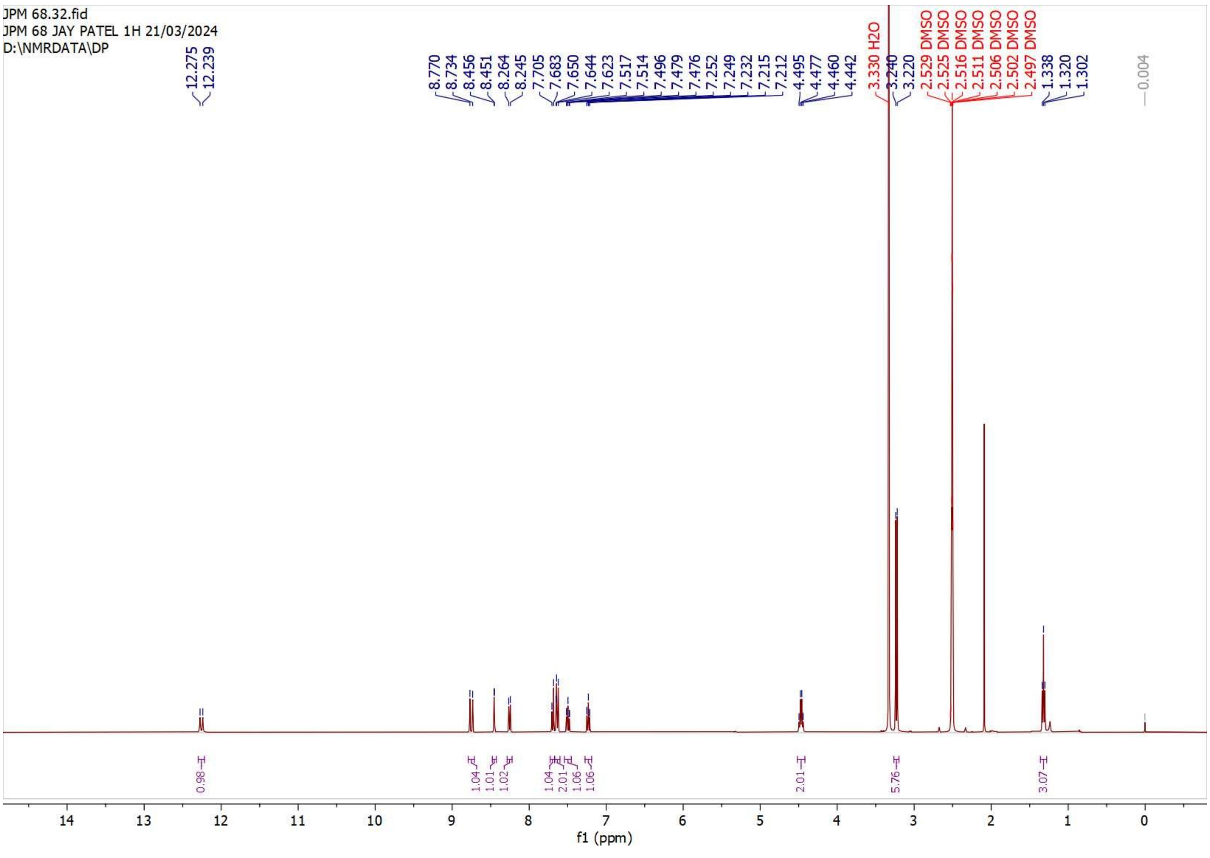
[13]C-NMR of 5-(((9-ethyl-9H-carbazol-3-yl)amino)methylene)pyrimidine-2,4,6(1H,3H,5H)-trione **(8a)**



Mass of 5-(((9-ethyl-9H-carbazol-3-yl)amino)methylene)pyrimidine-2,4,6(1H,3H,5H)-trione **(8a)**



¹H-NMR of 5-(((9-ethyl-9H-carbazol-3-yl)amino)methylene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione **(8b)**



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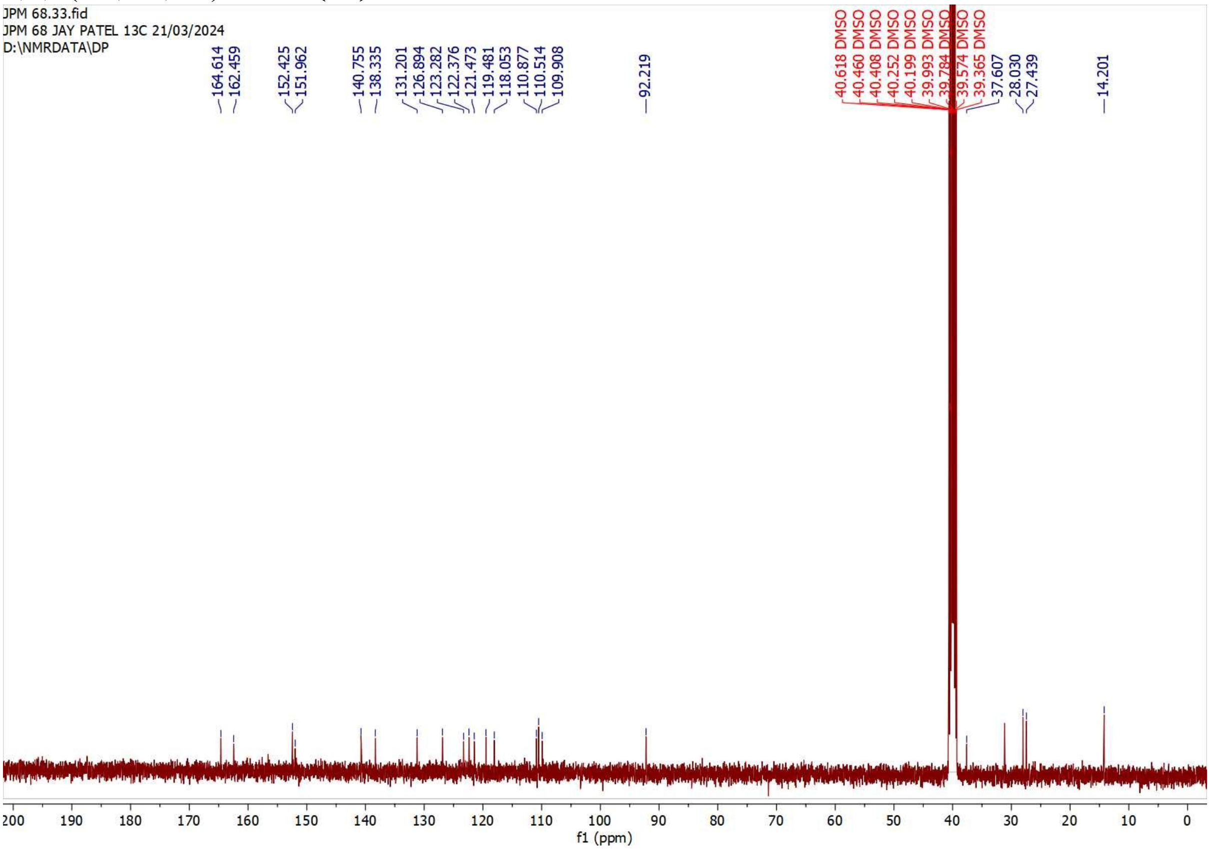

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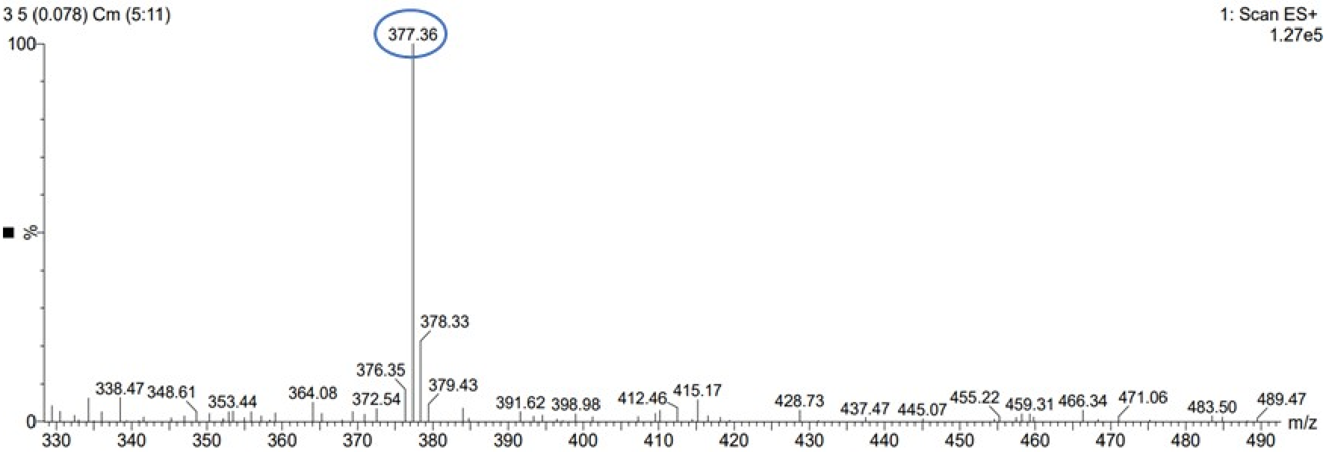
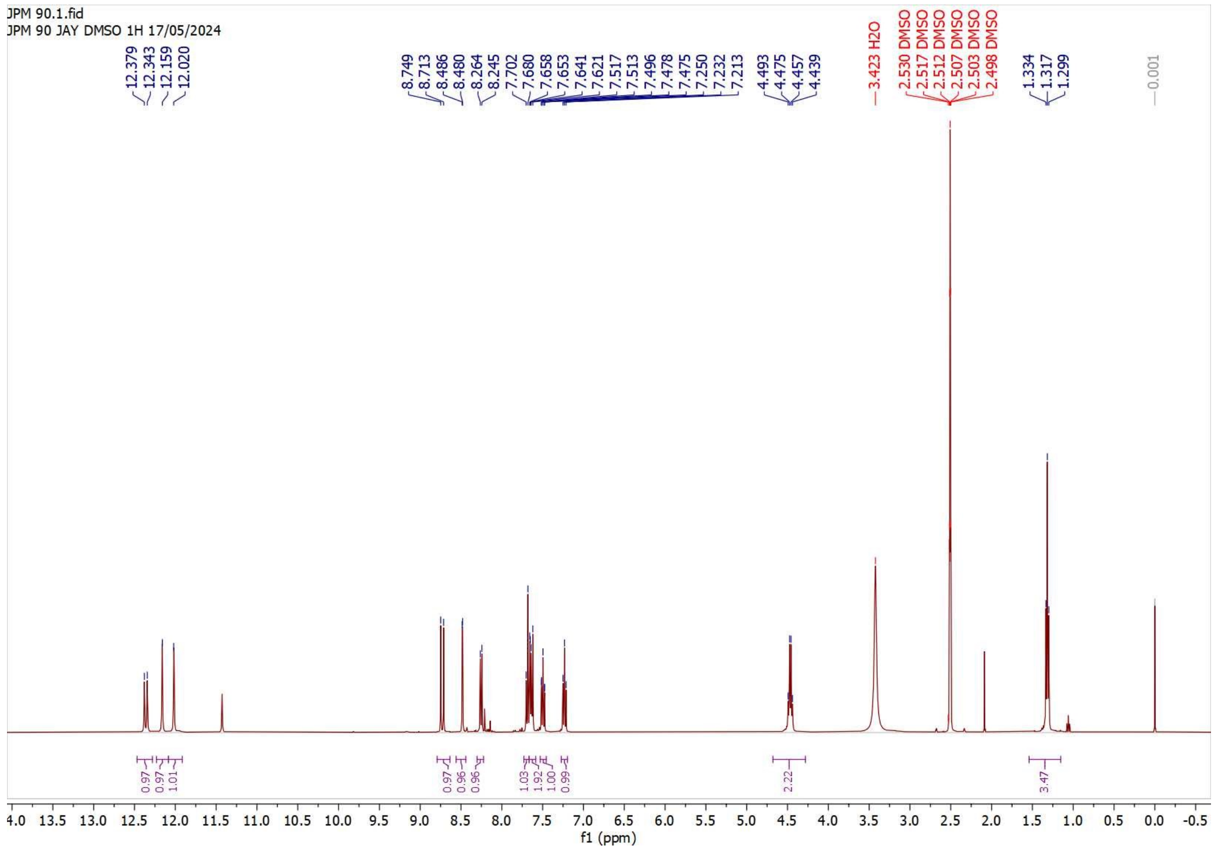


^{1}H-NMR of 5-(((9-ethyl-9H-carbazol-3-yl)amino)methylene)-2-thioxodihydropyrimidine-4,6(1H,5H)-dione **(8c)**



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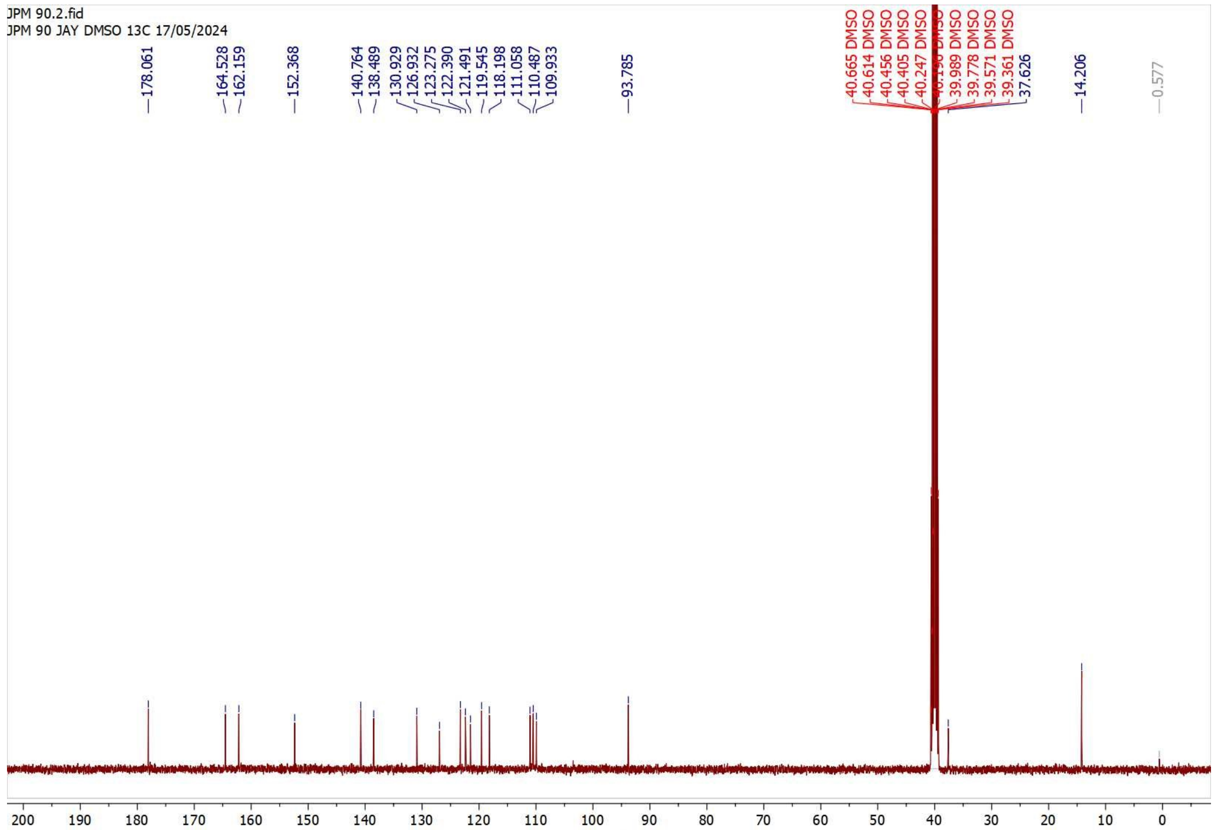

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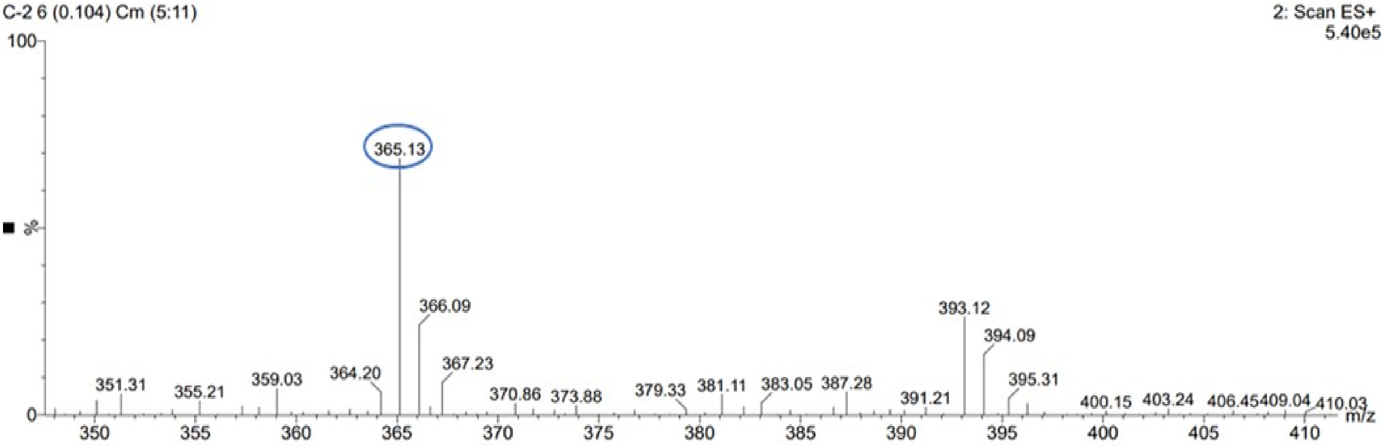
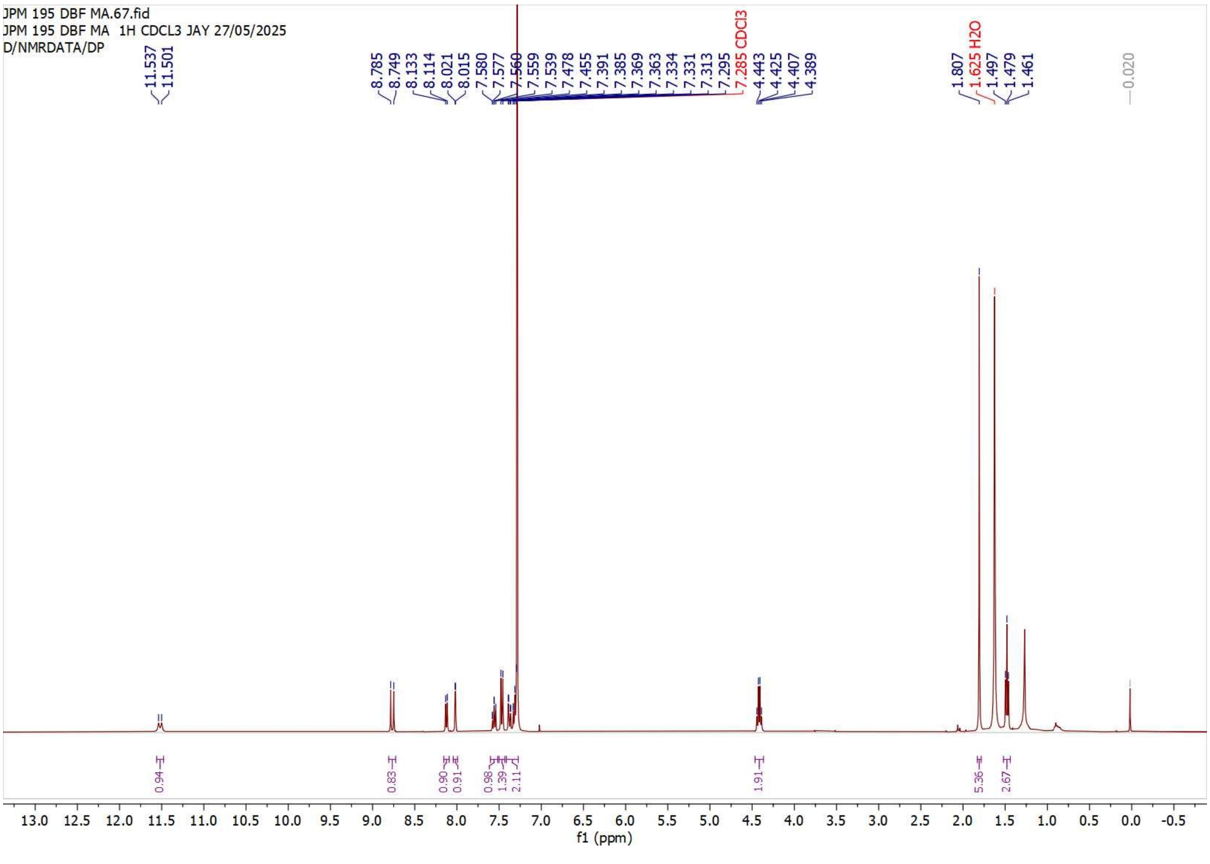


^{1}H-NMR of 5-(((9-ethyl-9H-carbazol-3-yl)amino)methylene)-2,2-dimethyl-1,3-dioxane-4,6-dione **(8d)**



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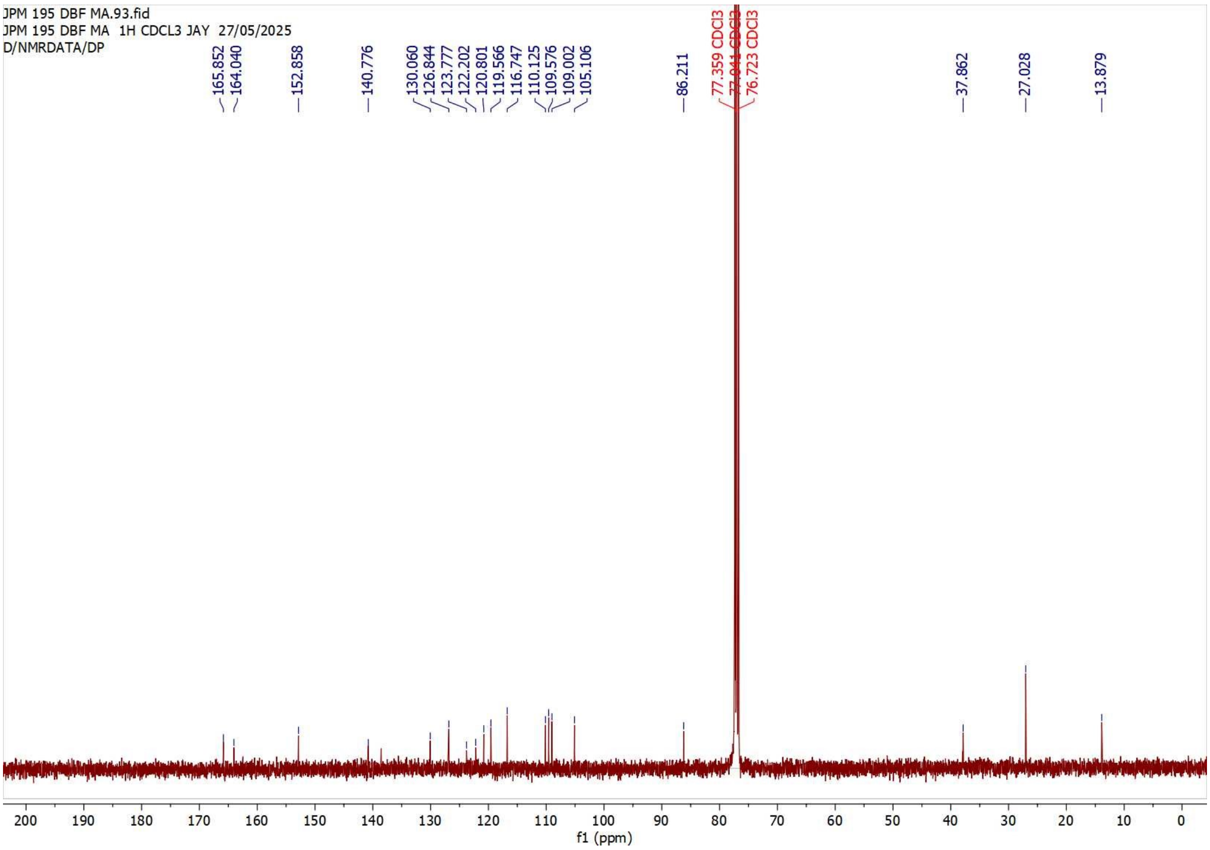

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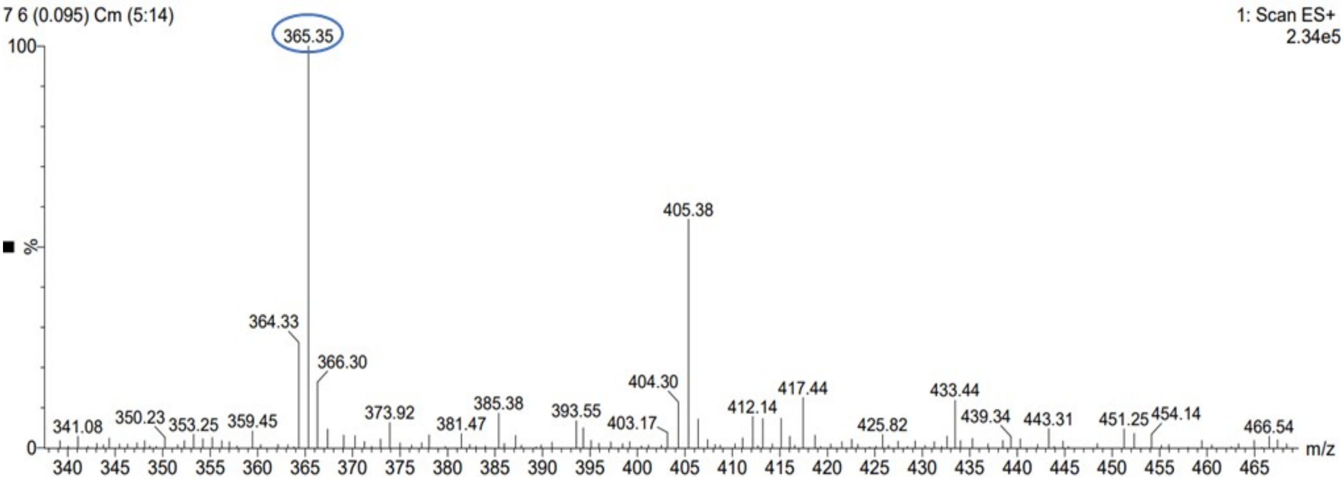
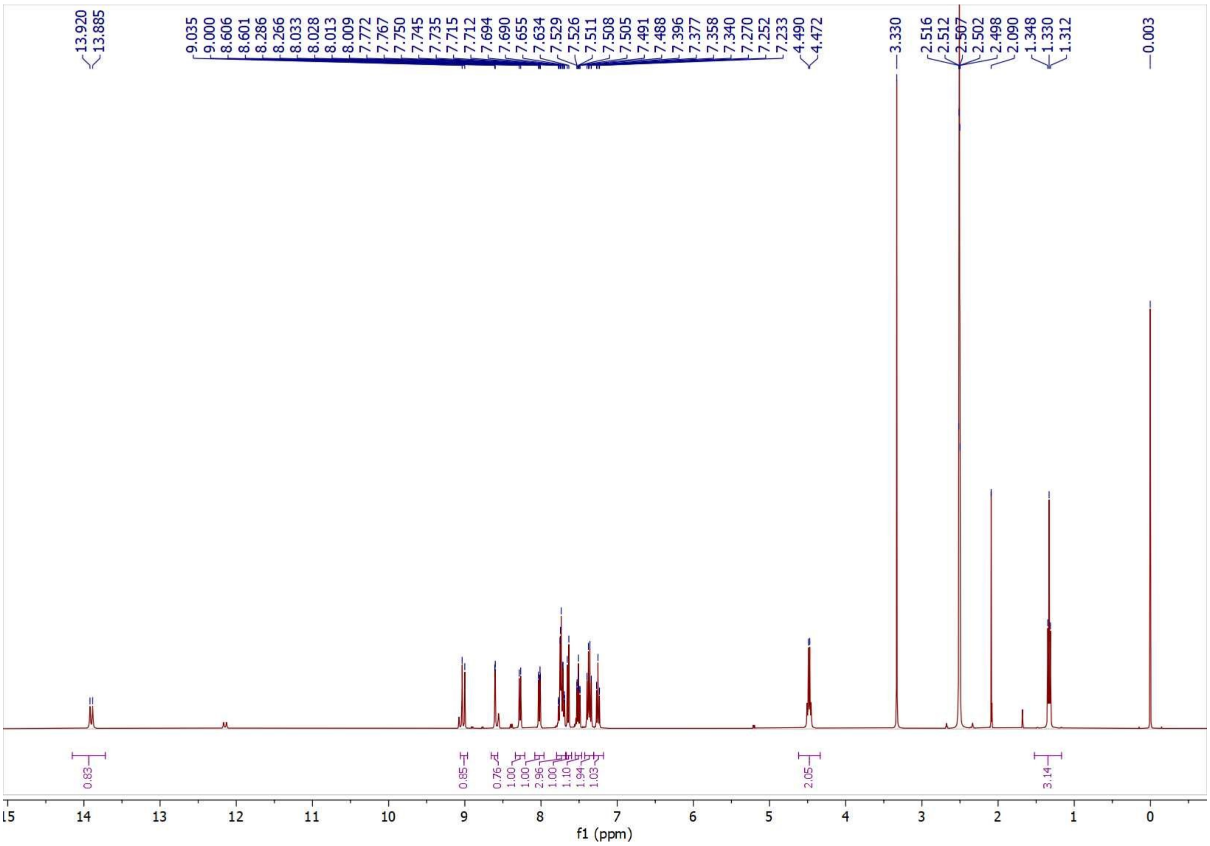
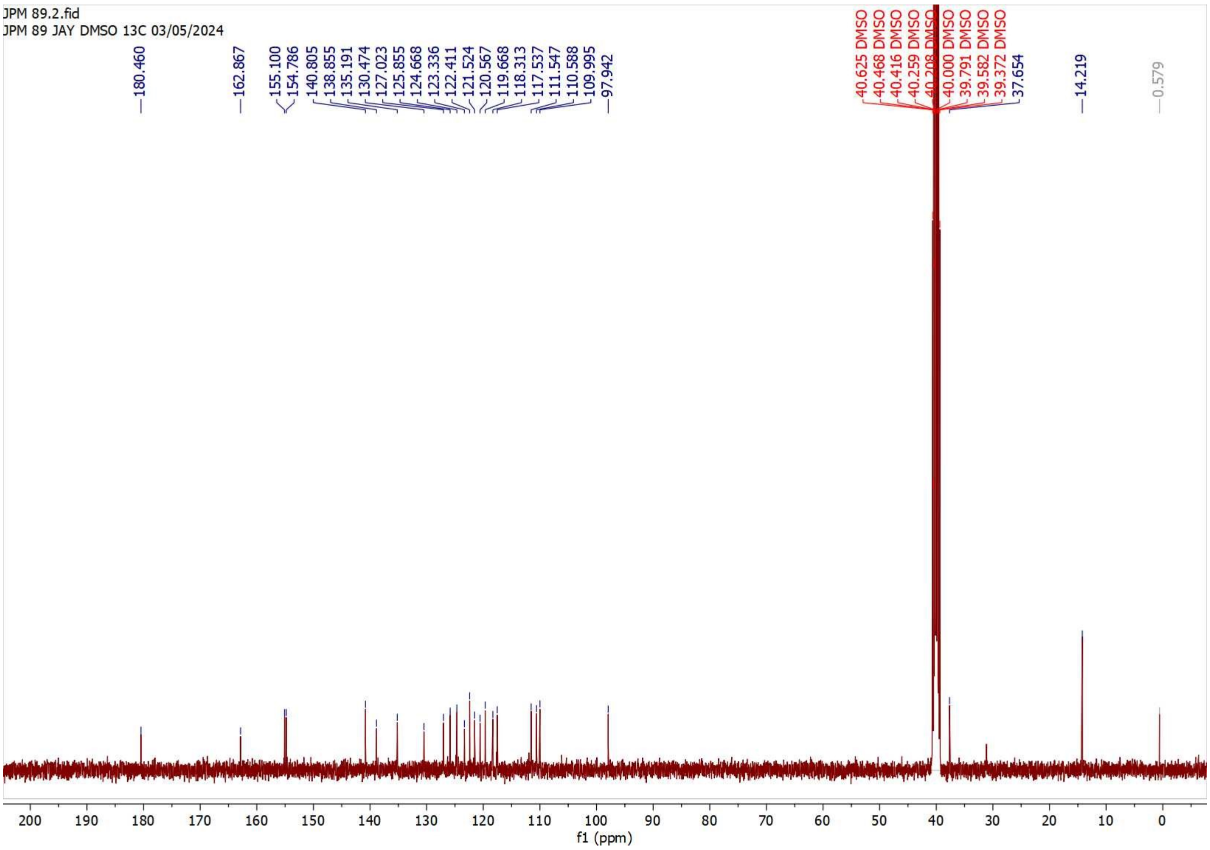


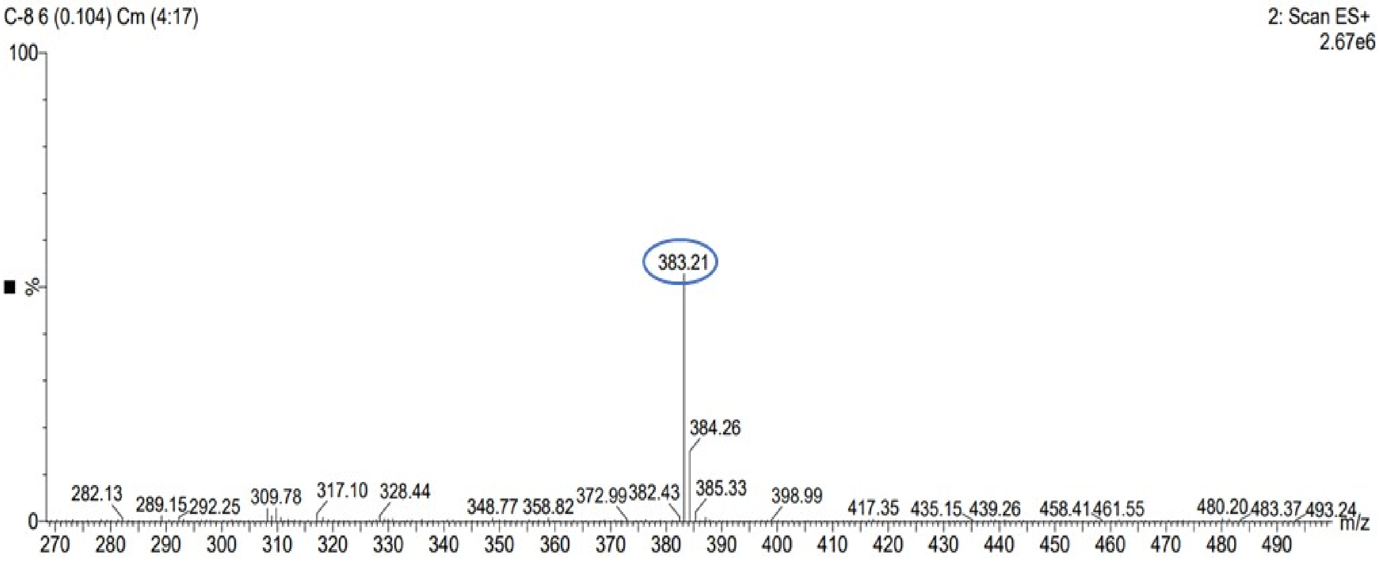
^{1}H-NMR of (Z)-3-(((9-ethyl-9H-carbazol-3-yl)amino)methylene)chromane-2,4-dione **(8e)**



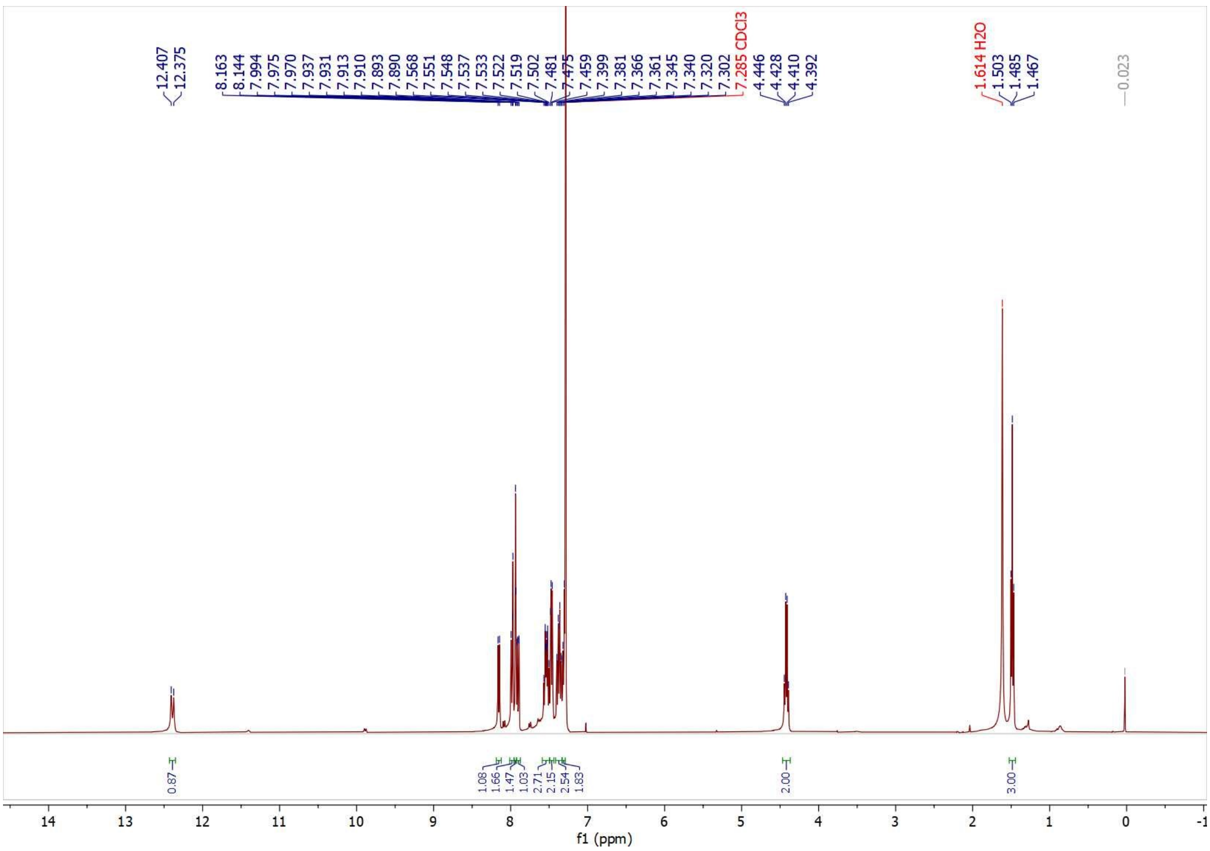
^{13}C-NMR of (Z)-3-(((9-ethyl-9H-carbazol-3-yl)amino)methylene)chromane-2,4-dione **(8e)**



Mass of (Z)-3-(((9-ethyl-9H-carbazol-3-yl)amino)methylene)chromane-2,4-dione **(8e)**



[1]**H-NMR** (Z)-2-(benzo[d]thiazol-2-yl)-3-((9-ethyl-9H-carbazol-3-yl)amino)acrylonitrile **(8f)**



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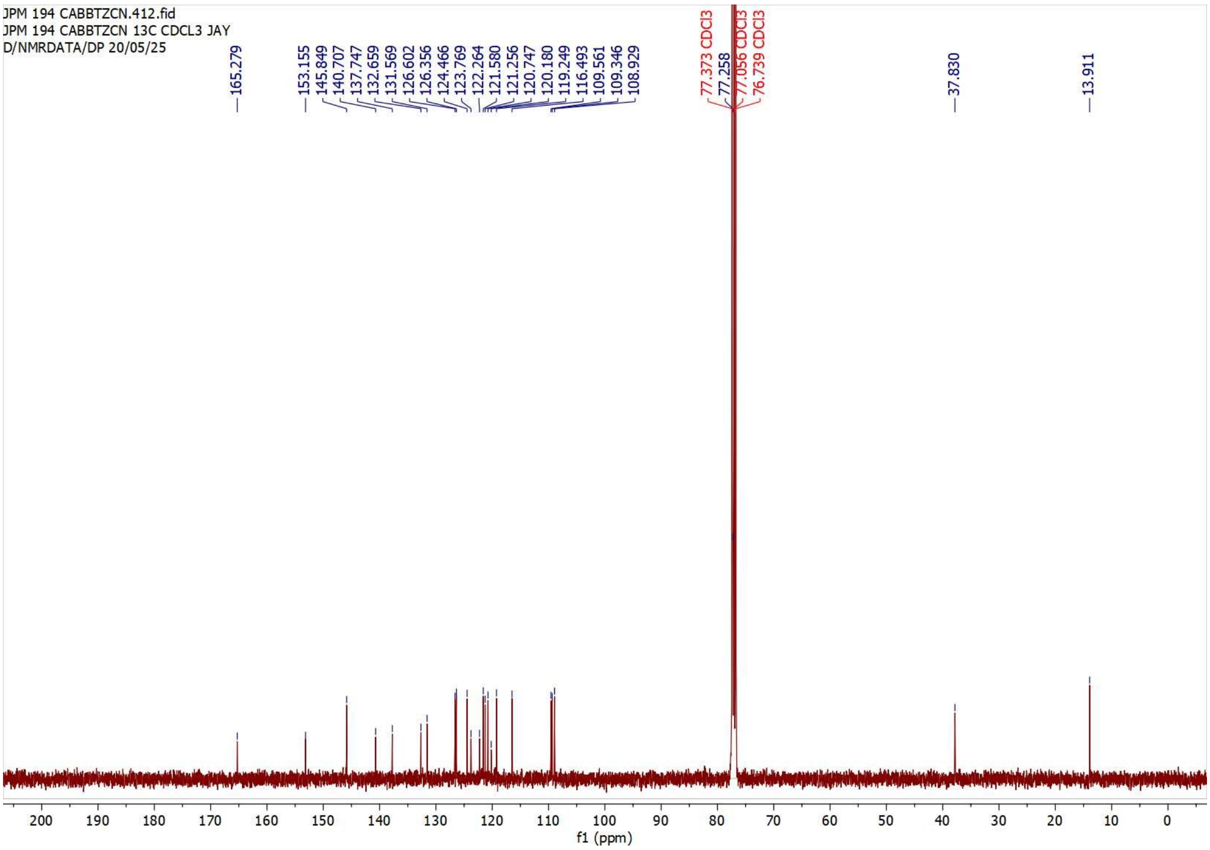

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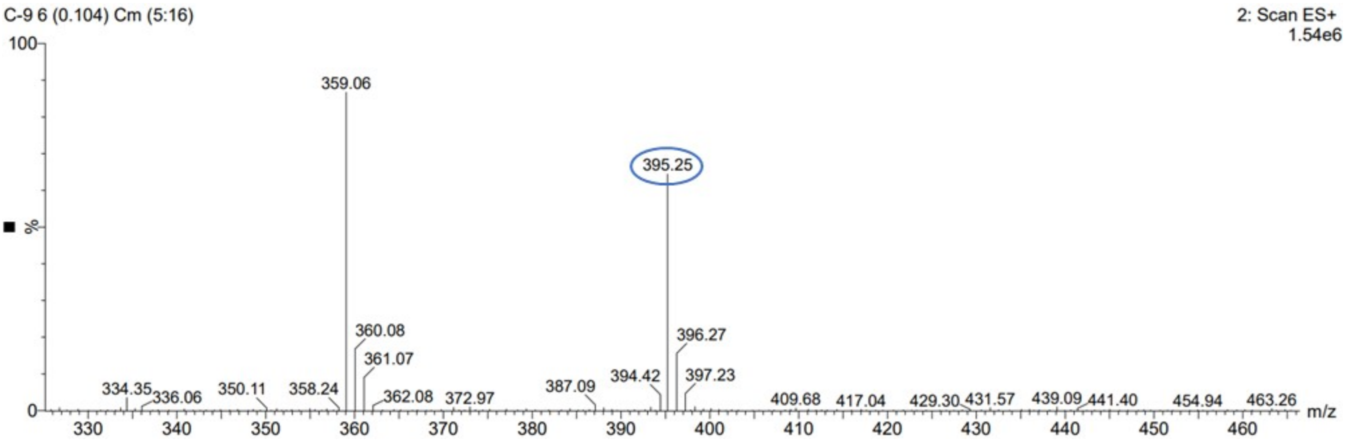
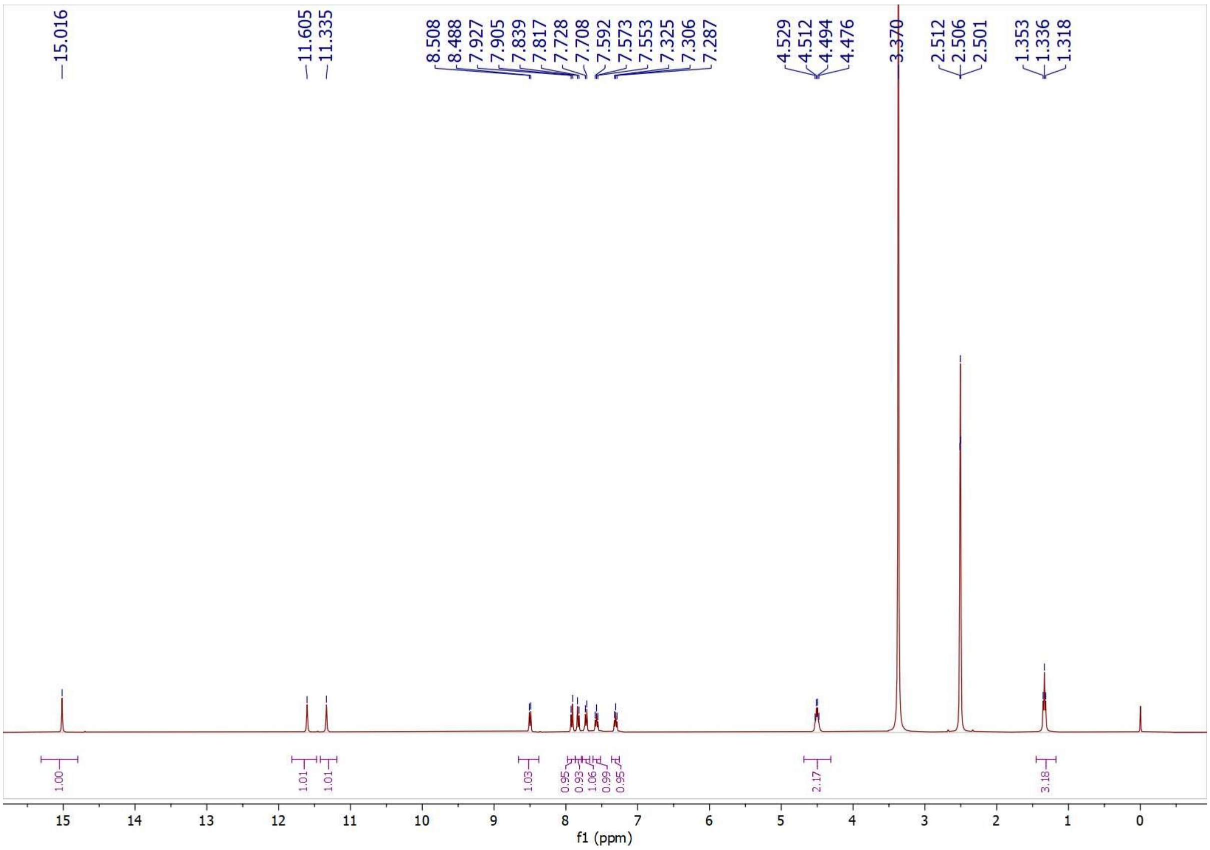


^{1}H-NMR of 5-(2-(9-ethyl-9H-carbazol-3-yl)hydrazineylidene)pyrimidine-2,4,6(1H,3H,5H)-trione **(9a)**



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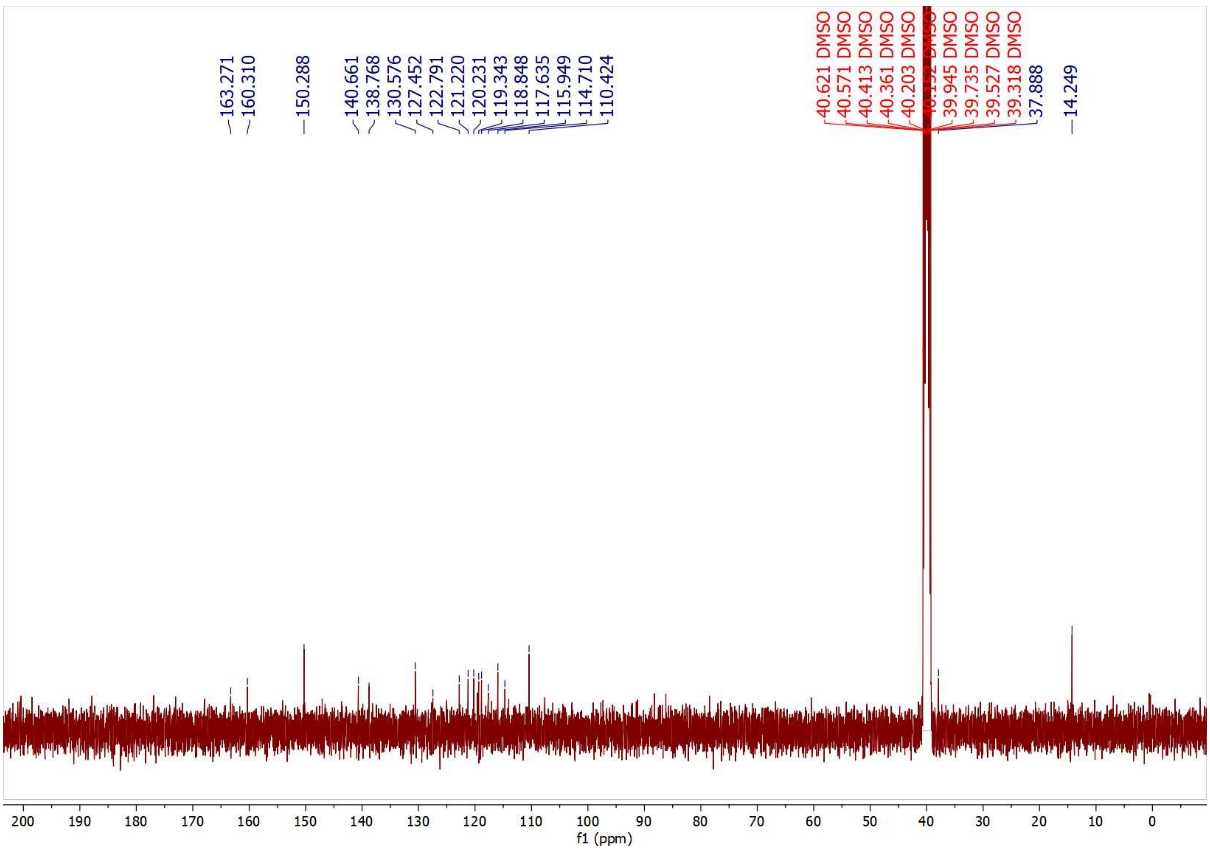

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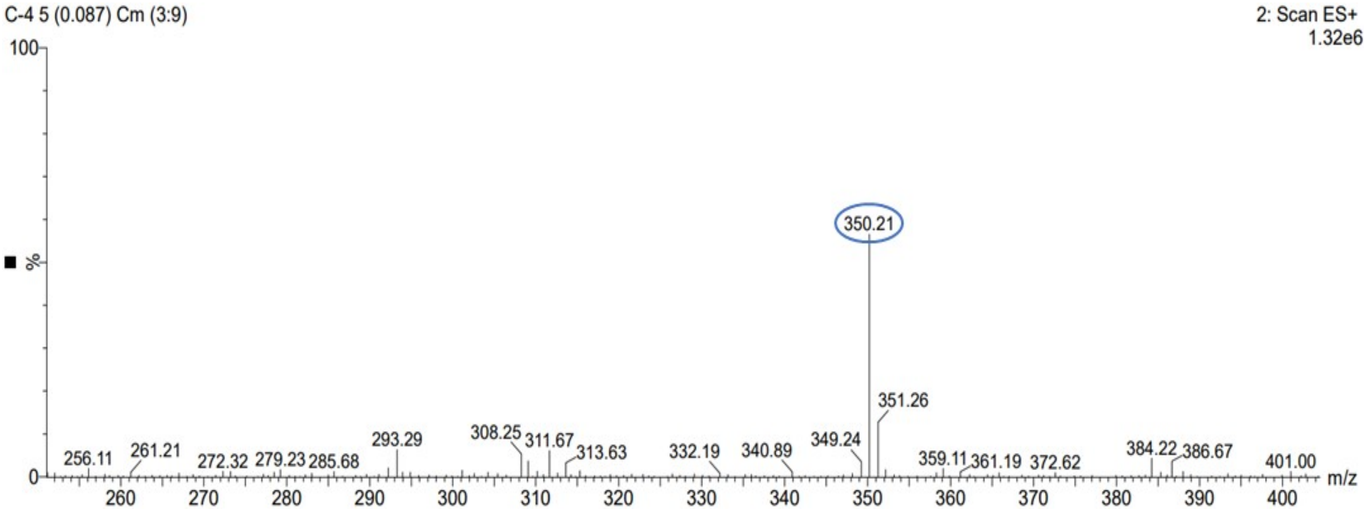
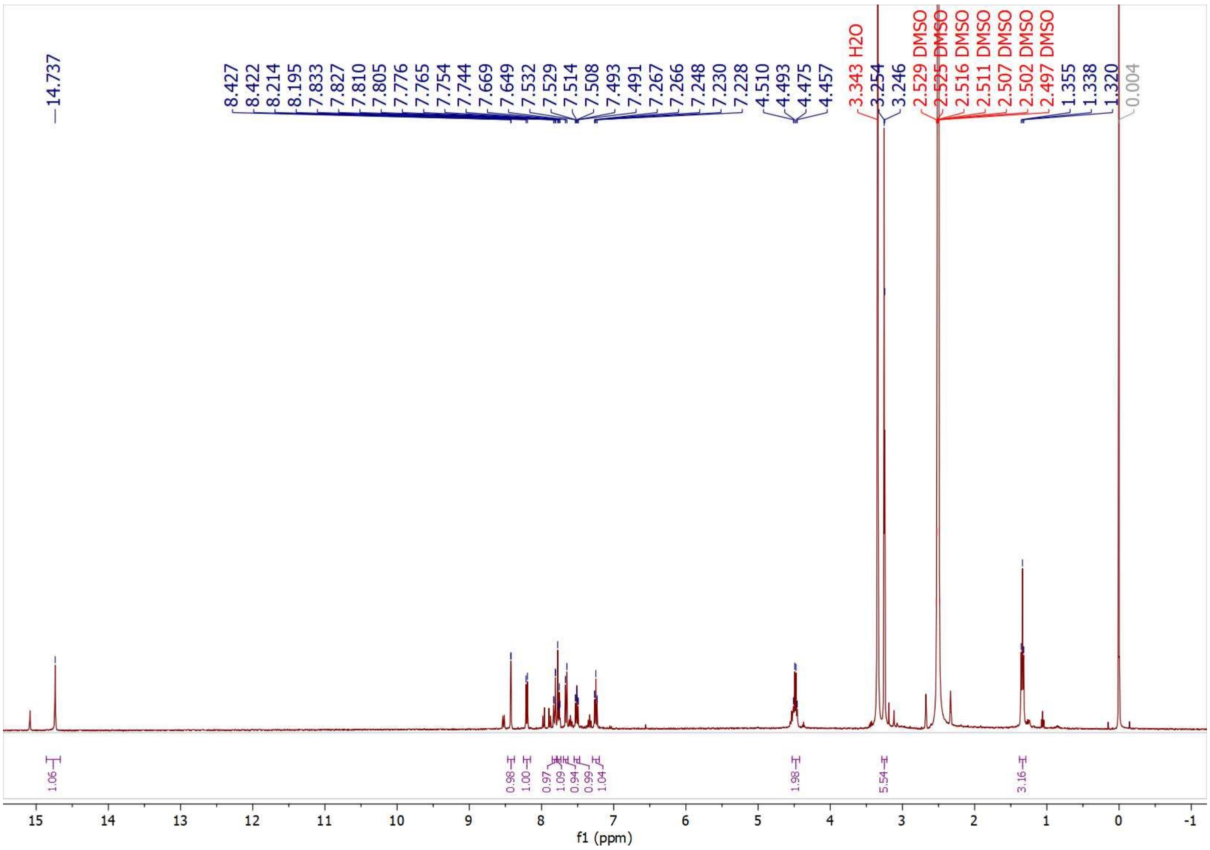
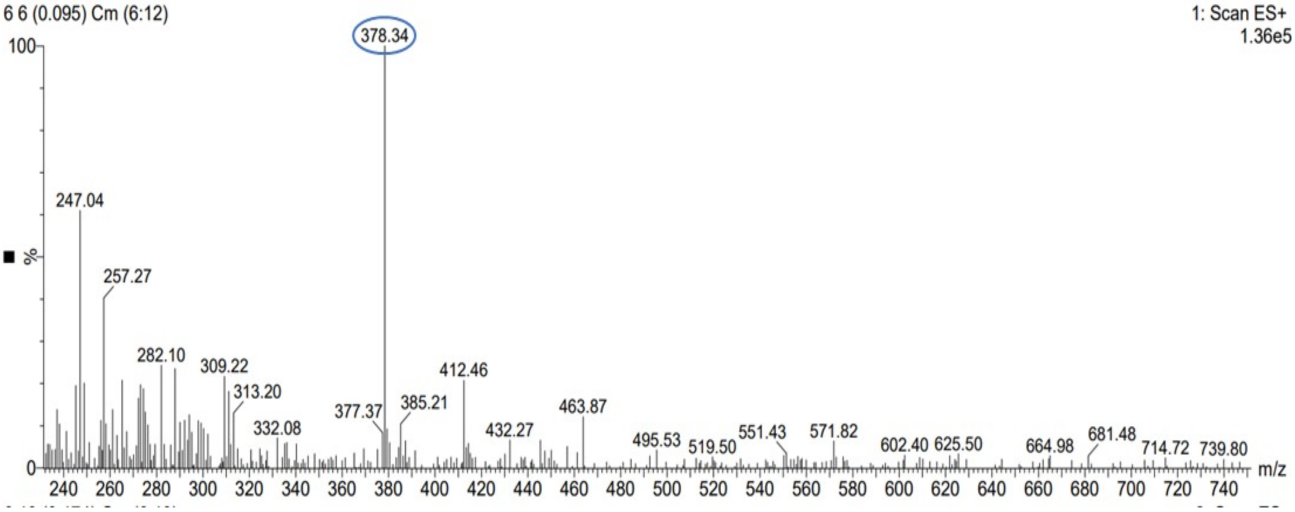


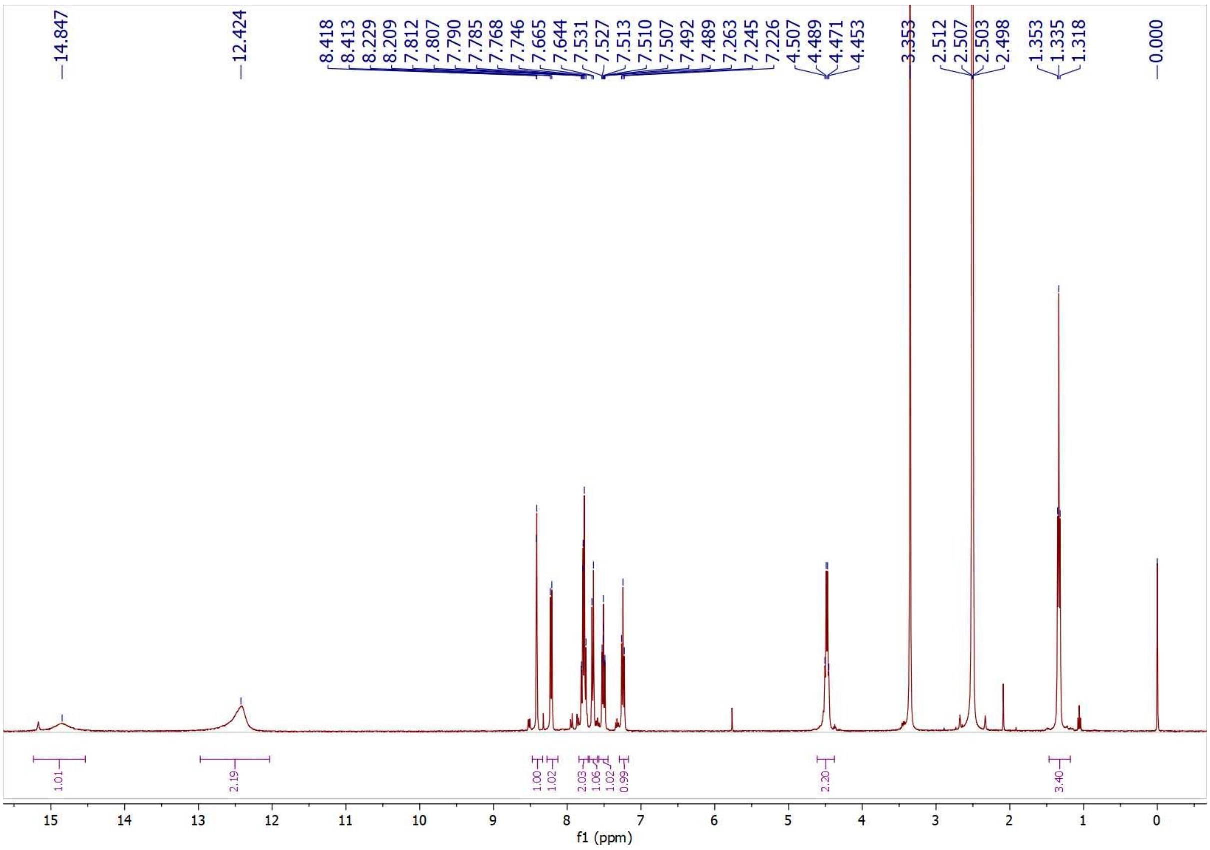
[1]H-NMR of 5-(2-(9-ethyl-9H-carbazol-3-yl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione **(9b)**



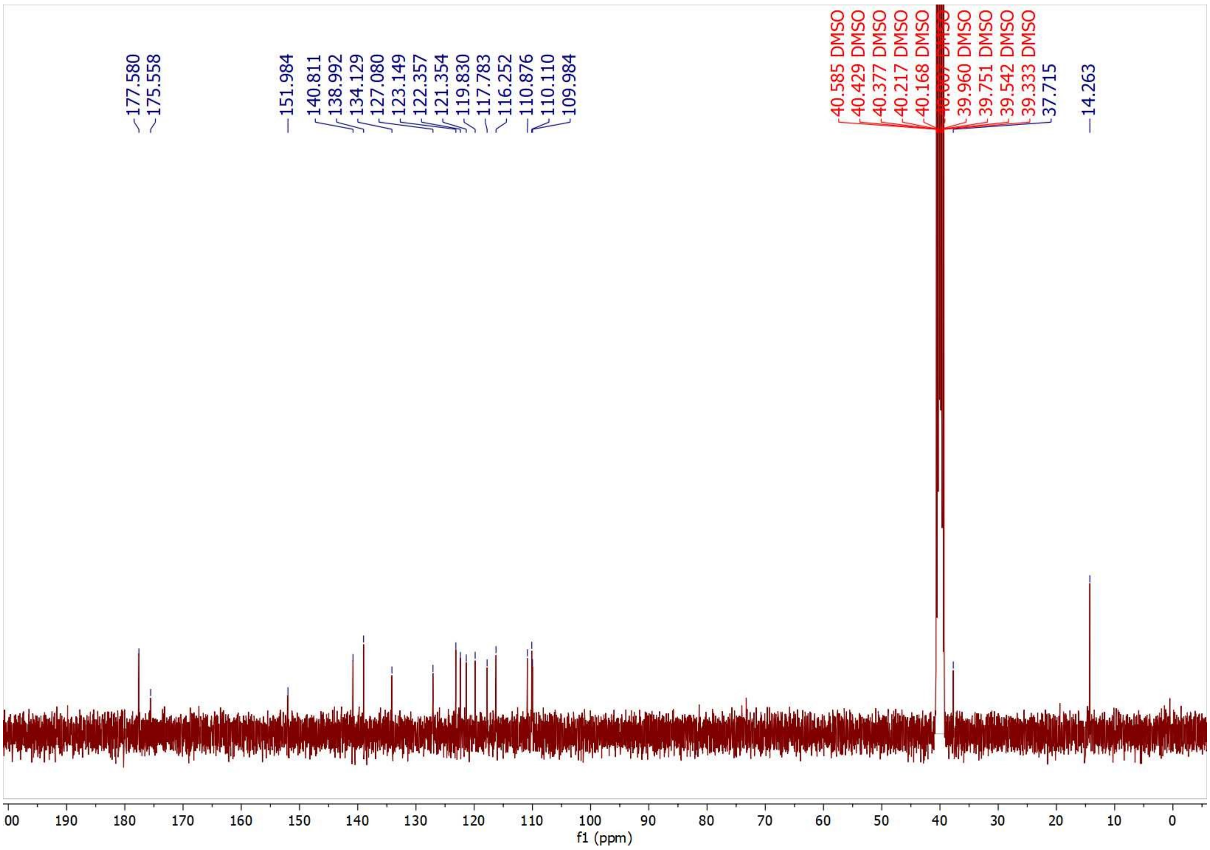
Mass of 5-(2-(9-ethyl-9H-carbazol-3-yl)hydrazineylidene)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione **(9b)**



[1]H-NMR of 5-(2-(9-ethyl-9H-carbazol-3-yl)hydrazineylidene)-2-thioxodihydropyrimidine-4,6(1H,5H)-dione **(9c)**



^{13}H-NMR of 5-(2-(9-ethyl-9H-carbazol-3-yl)hydrazineylidene)-2-thioxodihydropyrimidine-4,6(1H,5H)-dione **(9c)**



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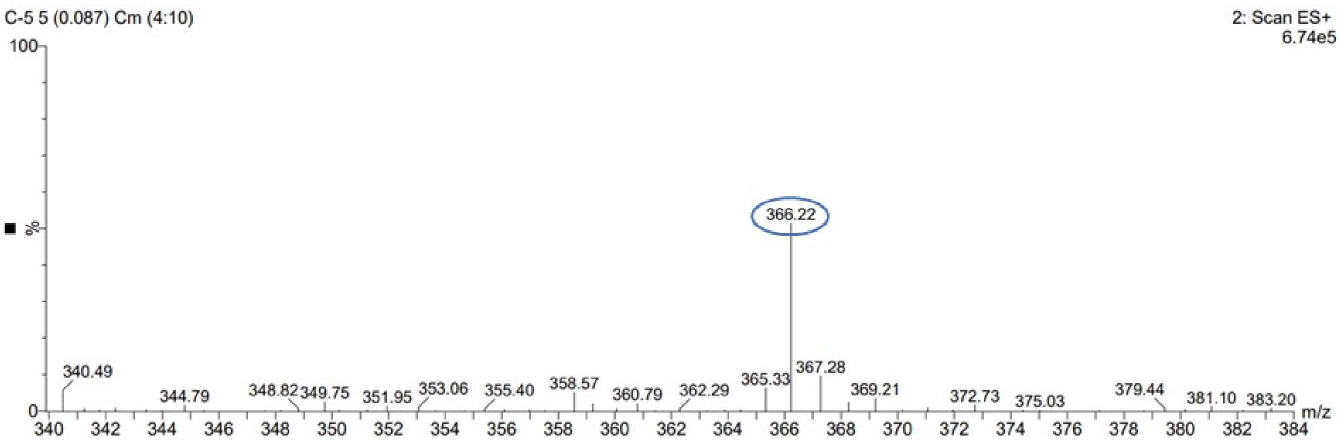

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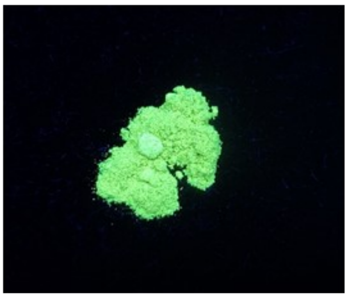

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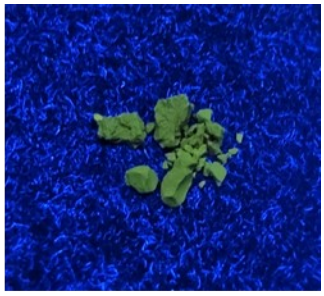

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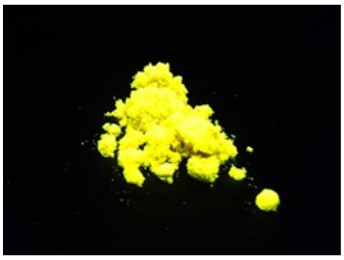

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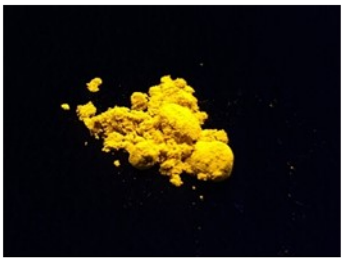

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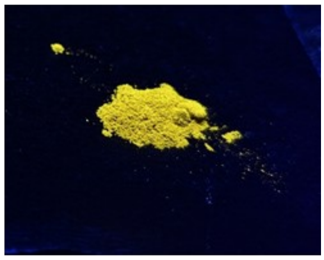
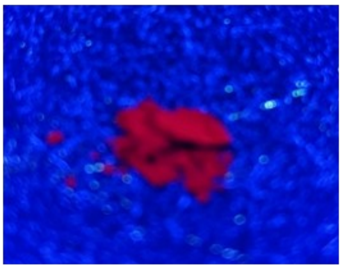


8f



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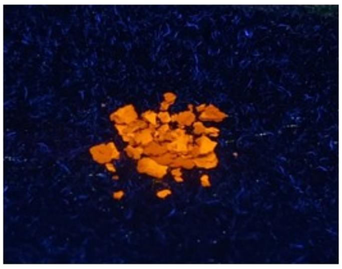
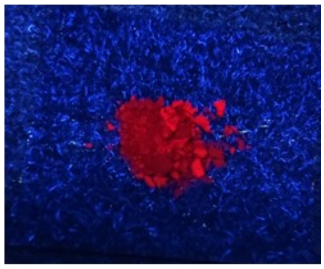


9b



9c

Figure S1: AIE of compounds **8a-f** and compounds **9a-c** in solid state under long UV light.

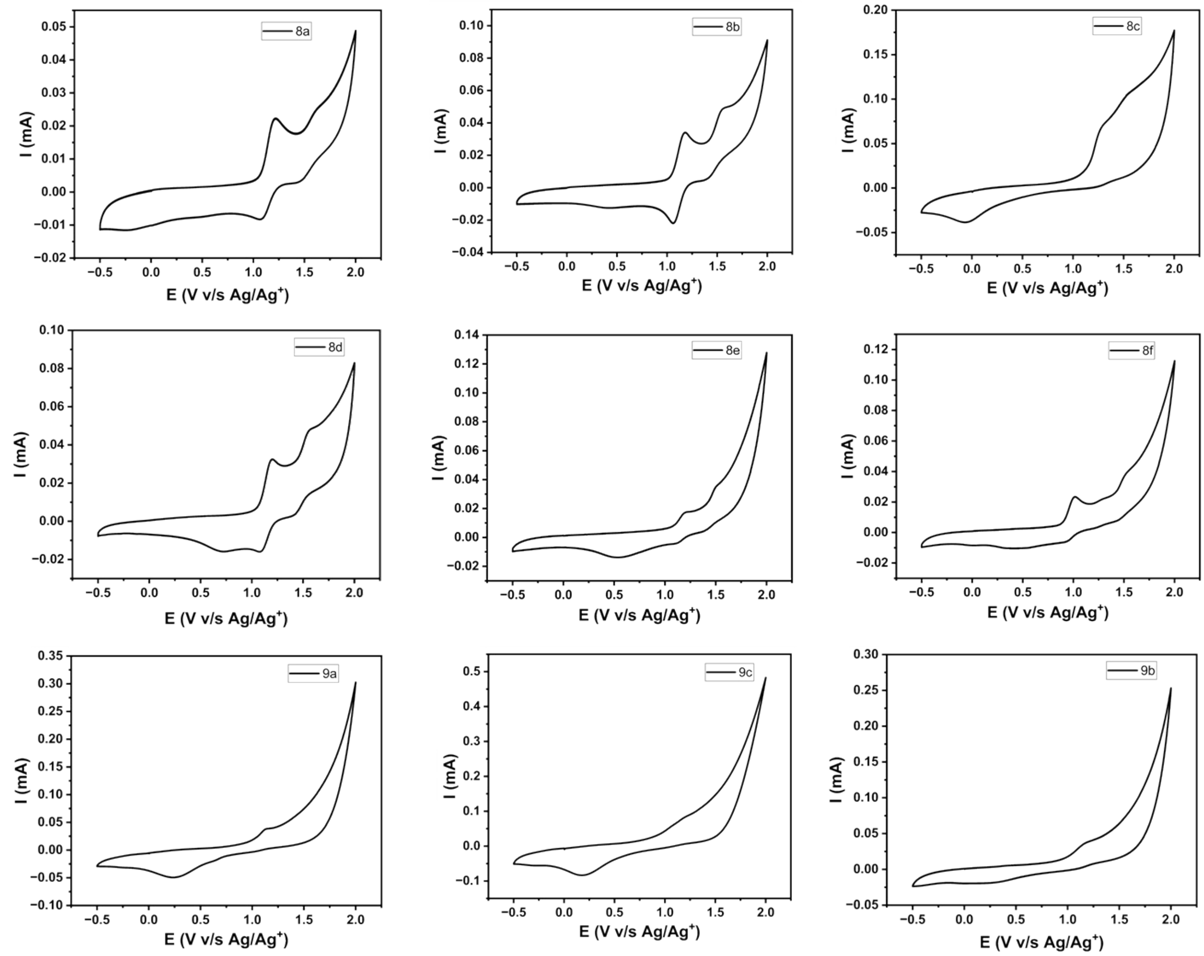


Figure S2: Cyclic voltammetry data of compounds **8a-f** and **9a-c.**

Table S1:

Compd		λ_{abs}[a]	λ_{emi}[b]	$\Delta\nu$[c]
		nm	nm	nm
8d	**Acetone**	343	435	92
	ACN	343	485	**142**
	$CHCl_3$	347	435	88
	DMSO	347	485	138
8e	**Acetone**	403	521	118
	ACN	403	530	**127**
	$CHCl_3$	409	511	102
	DMSO	410	537	**127**
8f	**Acetone**	396	501	105
	ACN	398	540	**142**
	$CHCl_3$	396	502	106
	DMSO	403	504	101

[a]Absorption maxima; [b]Emission maxima; [c]Stokes shift;

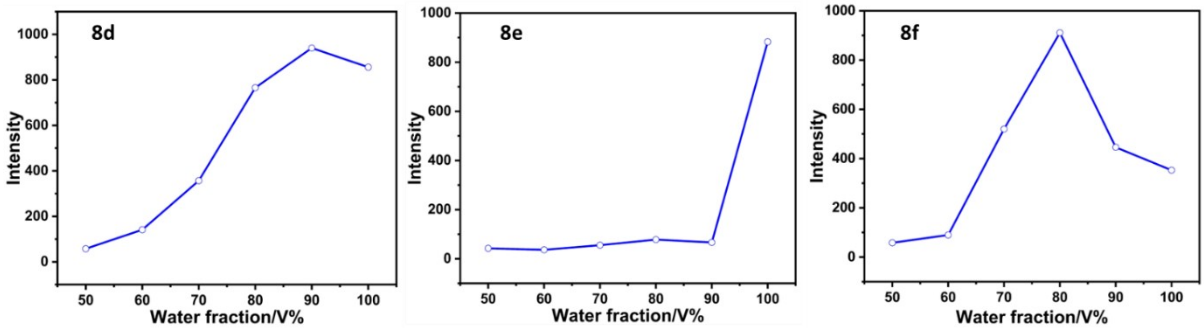


Figure S3: AIEE data of compounds **8b**, **8d** and **8f** at different fractions of water in DMSO.

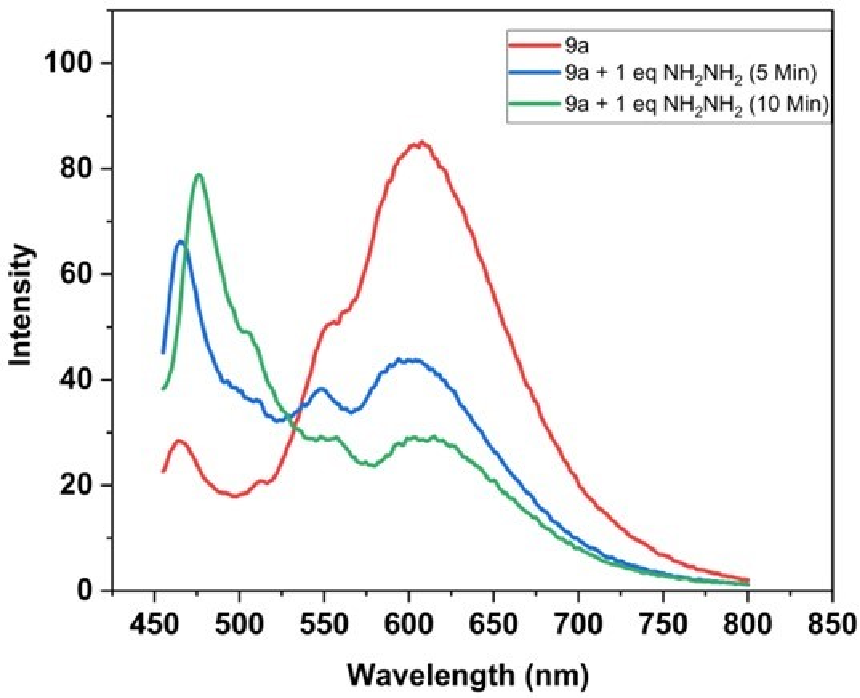


Figure S4: Change in fluorescence data of compounds **9a** with 1.0 eq of hydrazine in DMSO from time = 5 min and 10 min.

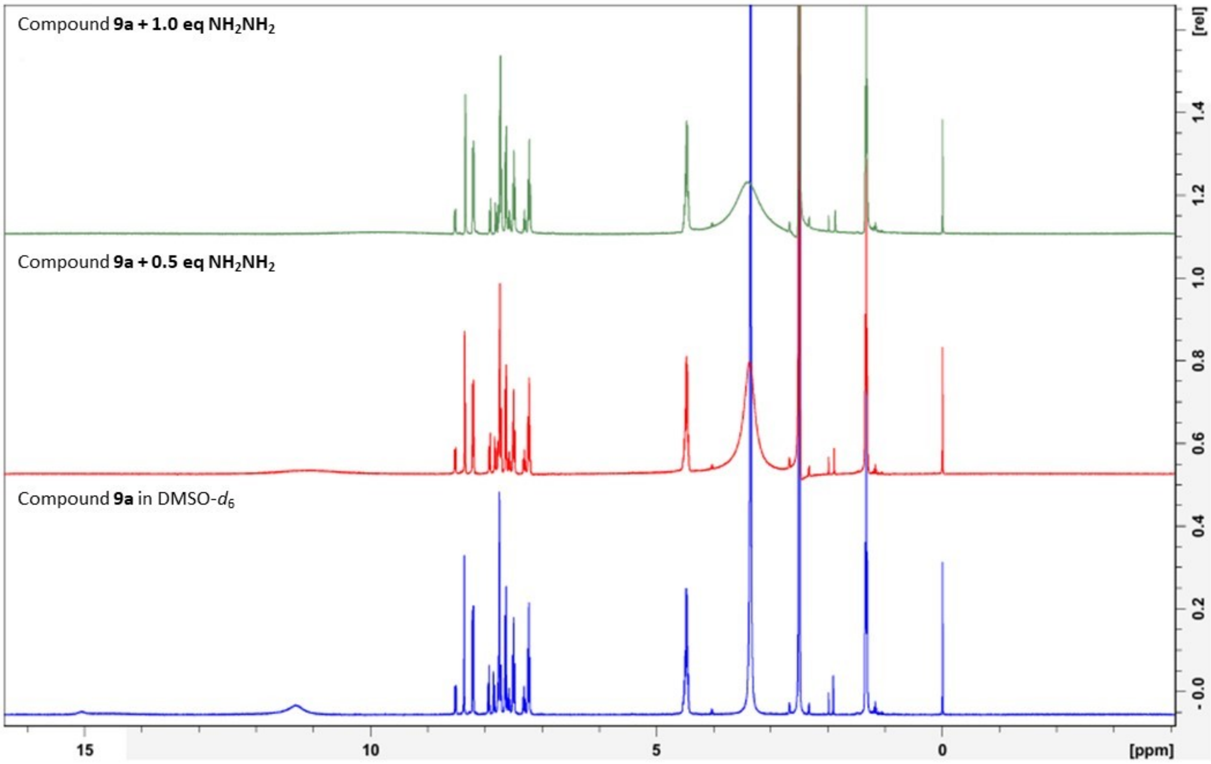


Figure S5: [1]H- NMR spectral changes of compound **9a** in DMSO-d_6 upon subsequent addition of hydrazine

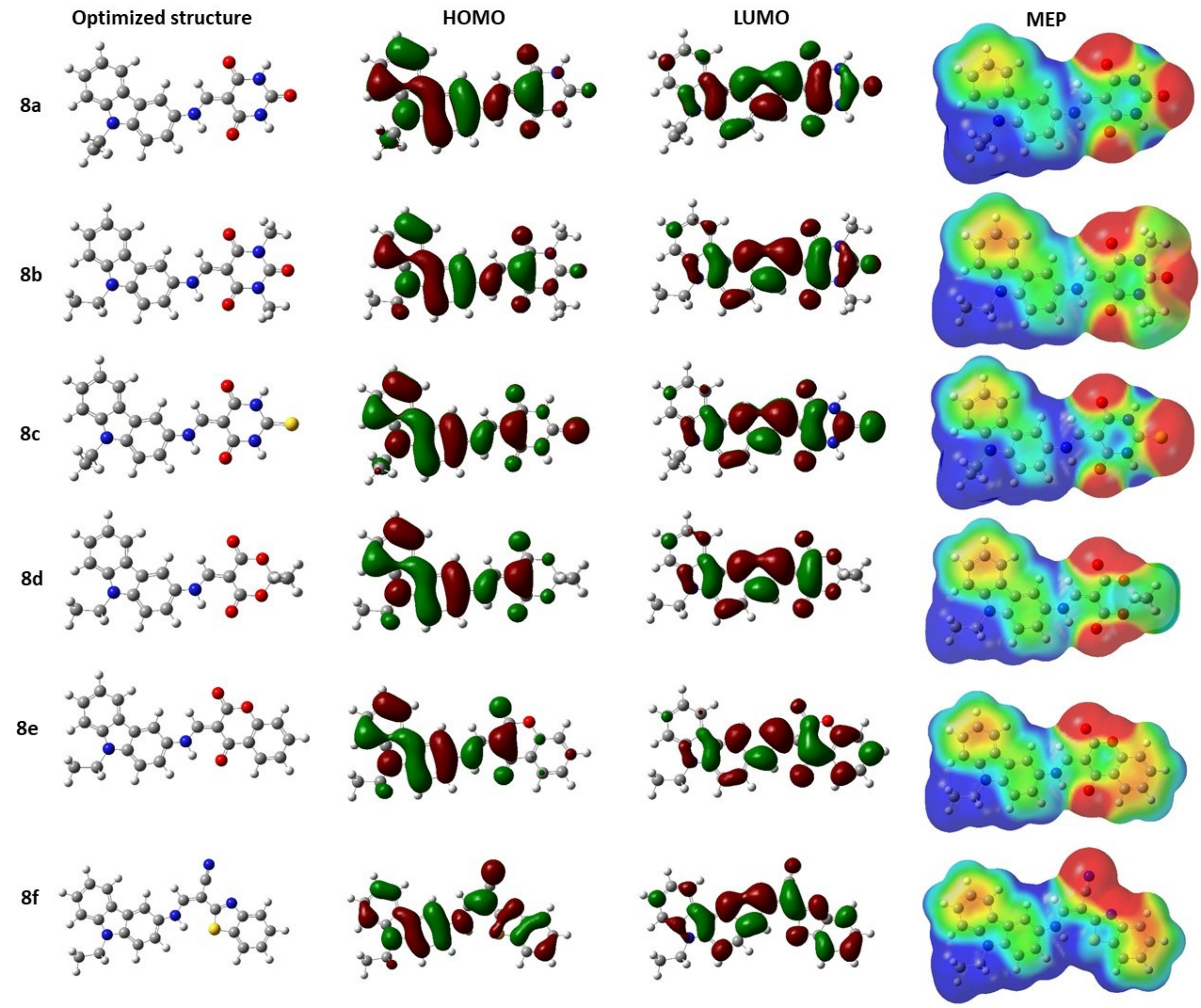


Figure S6: For compounds **8a-f** (a) Optimized ground state structure **(**b**)** Frontiers molecular orbitals (HOMO and LUMO) diagrams obtained from DFT calculations at B3LYP/6–311 G ++ (d,p) level **(c)** Electrostatic potentials calculated in the range from -2.0 x 10^{-3} (red) to 2.0x 10^{-3} (blue) using optimized ground state structures

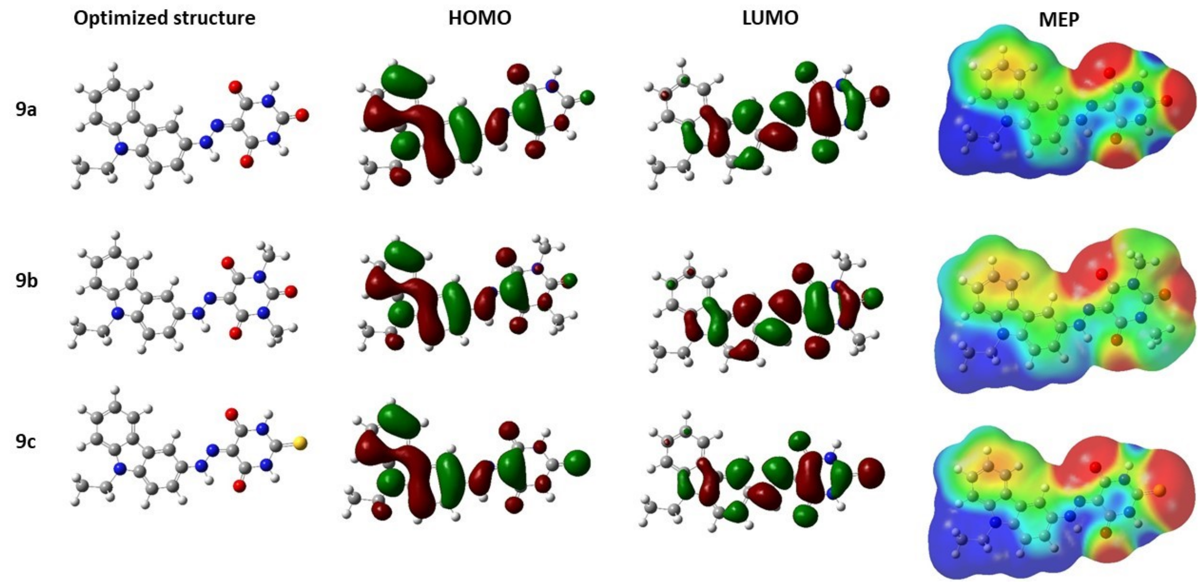


Figure S7: For compounds **9a-c (**a**)** Optimized ground state structure **(**b**)** Frontiers molecular orbitals (HOMO and LUMO) diagrams obtained from DFT calculations at B3LYP/6–311 G ++ (d,p) level **(c)** Electrostatic potentials calculated in the range from -2.0 x 10^{-3} (red) to 2.0x 10^{-3} (blue) using optimized ground state structures

Table S2: HOMO LUMO energy gap of compounds **8a-f** and **9a-c**

Compound	HOMO	LUMO	ΔE [c]
8a	5.60	2.09	3.51
8b	5.66	1.99	3.67
8c	5.80	2.31	3.49
8d	5.71	2.01	3.69
8e	5.69	2.28	3.41
8f	5.30	1.79	3.51
9a	5.84	2.66	3.18
9b	5.67	2.45	3.22
9c	5.84	2.78	3.06

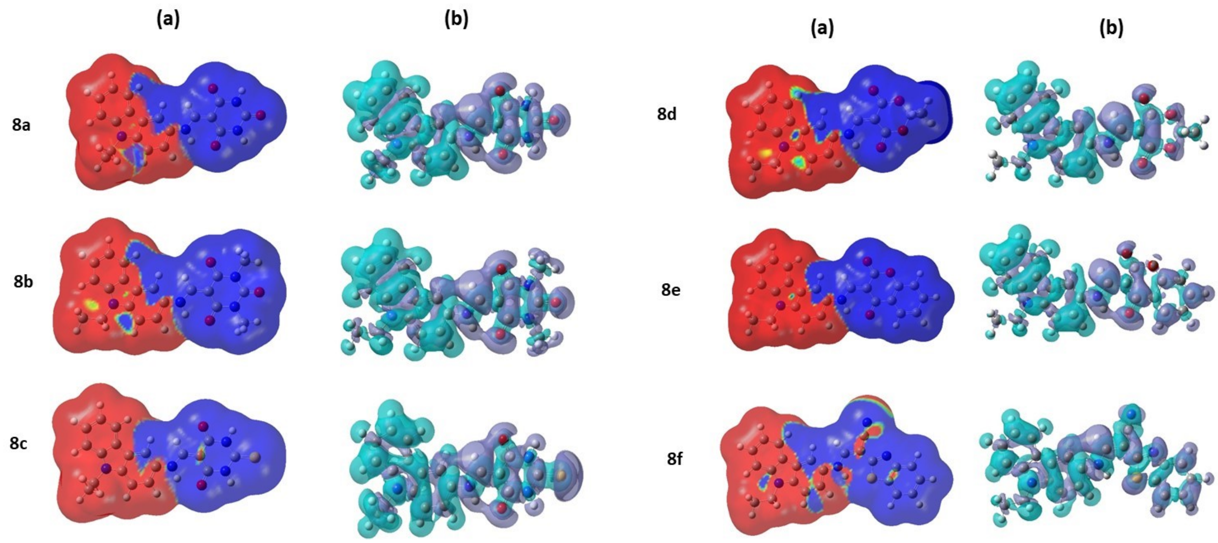


Figure S8: (a) Mapped surface for excitation-induced electron density difference Δρ(r) (iso-value = 0.001 a.u.) on total SCF electron density for compounds **8a-f**, red/blue corresponds to negative/positive Δρ(r); (b) Excitation-induced electron density difference (Δρ(r)) as calculated for the key excited state of compounds **8a-f** at TDDFT/B3LYP/6-311G level of approximation (iso-value = 0.001 a.u.) light/dark blue corresponds to negative/positive Δρ(r).

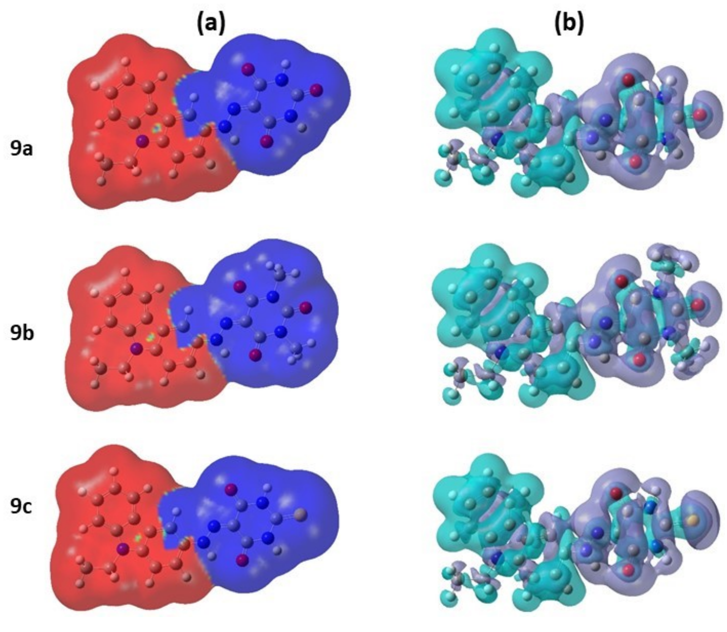


Figure S9: (a) Mapped surface for excitation-induced electron density difference Δρ(r) (iso-value = 0.001 a.u.) on total SCF electron density for compounds **9a-c**, red/blue corresponds to negative/positive Δρ(r); (b) Excitation-induced electron density difference (Δρ(r)) as calculated for the key excited state of compounds **9a-c** at TDDFT/B3LYP/6-311G level of approximation (iso-value = 0.001 a.u.) light/dark blue corresponds to negative/positive Δρ(r).

Table S3: Calculated first-order hyperpolarizability (β) values for compounds **8a-f** and **9a-c** using CAM-B3LYP/ 6-311G ++ (d,p) basis set in DMSO.

Comp.	**xxx**	**Xyy**	**xzz**	**yyy**	**yxx**	**yzz**	**zzz**	**zxx**	**zyy**	**β_tot**
8a	61.09	3.47	5.34	-2.89	-7.57	-2.34	-2.07	-20.19	-2.14	75.13
8b	-1.41	0.32	7.14	-1.96	0.77	-5.67	-38.69	-1.18	-6.37	47.13
8c	73.01	7.17	0.27	5.41	10.03	0.48	-0.06	1.06	0.1	82.02
8d	40.66	3.68	-0.4	6.25	3.44	0.21	0.11	-2.79	0.42	45.1
8e	81.8	6.2	-0.08	4.55	0.73	-0.25	0	-0.01	0	88.07
8f	56.07	10.74	-0.79	8.4	5.62	-0.55	-0.01	-0.04	0	67.38
9a	-156.4	-4.43	1.48	6.7	7.96	0.51	-0.17	2.58	0.13	160.09
9b	-142.36	-4.59	1.01	6.71	7.83	0.38	-0.18	1.99	0.05	146.72
9c	-209	-6.66	-0.28	6.42	10.2	0.59	-0.05	3.01	0.14	216.65