Supporting Information

Tungsten Oxide: Green and Sustainable Heterogeneous Nanocatalyst for Synthesis of Bioactive Heterocyclic Compounds

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General procedure for the WO_3 catalysed reaction for C-3 Alkylation of 4 hydroxycoumarin

In a dry round bottom flask WO_3 (10 mol%), secondary benzyl alcohol (1mmol), 4-hydroxycoumarin (1mmol) were mixed and the reaction mixture was stirred at 100℃ for specified time (see **Table 2**). The progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was dissolved in ethanol and boiled. The undissolved WO_3 catalyst was separated by simple filtration method. The filtrate was cooled down to 0-5 ℃ to precipitate the desired product which was separated again by simple filtration

method. The obtained product was washed 2-3 times by ethanol to afford corresponding pure product.

General procedure for the heterogeneous WO_3 catalysed multicomponent reaction for synthesis of chromenes

In a dry round bottom flask, WO_3 (10 mol%), Dimedone (1mmol), aromatic aldehyde (1mmol) and malanonitrile (1mmol) were mixed and stirred at 70℃ for specified time (Table 3). The progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was dissolved in ethanol and boiled. The undissolved WO_3 catalyst was separated by simple filtration method. The filtrate was cooled down to 0-5℃ to precipitate the desired product which was separated again by simple filtration method. The obtained product was washed 2-3 times by ethanol to afford corresponding pure product.

General procedure for the heterogeneous WO_3 catalysed reaction for synthesis of xanthene

In a dry round bottom flask, WO_3 (10 mol%), Dimedone (1mmol), aromatic aldehyde (1mmol) were mixed and stirred at 70℃, for specified time (Table 4). The progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was dissolved in ethanol and boiled. The undissolved WO_3 catalyst was separated by simple filtration method. The filtrate was cooled down to 0-5℃ to precipitate the desired product which was separated again by simple filtration method. The obtained product was washed 2-3 times by ethanol to afford corresponding pure chromene derivatives.

Table S1: Comparative catalysts activity study of WO_3 NRs with commercially available WO_3 for C-3 Alkylation of 4-hydroxycoumarin derivative 3a.

Sr. No.	Catalyst (10 mol%)	Solvent	Temp. (°C)	Time (min)	Yield[b] (%)
1	Commercial WO_3	Solvent free	Heat (100 °C)	60	94
2	WO_3 NPs	Solvent free	Heat (100 °C)	70	92
3	WO_3 Nanospheres	Solvent free	Heat (100 °C)	75	93
4	WO_3 Nanorods	Solvent free	Heat (100 °C)	60	95

[a]Reaction conditions: 4-hydroxycoumarin (100 mg), Secondary benzyl Alcohol (1 equivalent), different forms of WO_3 (10 mol%), with continuous stirring under thermal condition, solvent free, [b]Isolation yield.

Table S2: Assessment of reported catalysts catalytic activity with WO_3 NRs for C-3 Alkylation of 4-hydroxycoumarin.

Sr. no.	Cat (mol.%)	Solvent	Temp (°C)	Time (h)	Yield[b] (%)	ref
1	$Bi(OTf)_3$ (1)	$MeNO_2$	90	4	85	1
2	$BiCl_3$ (1)	$MeNO_2$	90	7	30	1
3	$BiBr_3$ (1)	$MeNO_2$	90	7	10	1
4	TfOH (3)	$MeNO_2$	90	4	70	1
5	I_2 (20)	$MeNO_2$	50	3	75	2
6	$Bi(NO_3)_3.5H_2O$ (10)	[BMIM][PF_6]	30	1	90	3
7	Amberlite IR 120 (50 mg)	CH_3CN	Reflux	1.5	73	4
8	A-TiO_2 (20 mg)	Solvent free	70	5	95	5
9	SO_4^{-}/SnO_2 (10 mg)	CH_3COOH	Reflux	5	75	6

10	WO_3 (10 mol %)	Solvent free	100	1	95	This work

[a]Reaction conditions: 4-hydroxycoumarin (100 mg), Secondary benzyl Alcohol (1 equivalent), different catalysts, with continuous stirring under thermal condition, solvent free, [b]Isolation yield.

Table S3: Assessment of reported catalysts other than WO_3 NRs for the synthesis of chromenes.

Entry	**Catalyst**	**Catalyst loading**	**Solvent**	**Temp. (ºC)**	**Time (Min)**	**Yield [b] (%)**	**Ref.**
1	No catalyst	-	EtOH:H_20	Reflux	--	--	--
2	ZnO NPs	10 mol%	EtOH	Reflux	20	83	7
3	Urea	10 mol%	EtOH:H_20	Reflux	480	85	8
4	Na_2CO_3	10 mol%	EtOH:H_20	120	100	95	9
5	Aq PEG-400	1ml	EtOH:H_20	Reflux	180	85	10
6	Cerium (III)chloride	10 mol%	EtOH:H_20	Reflux	80	83	11
7	Piperidine		H_20	Reflux	380	75	12
8	S-Proline	10 mol%	EtOH:H_20	Reflux	180	80	13
9	CuO NPs	15 mol%	H_20	100	420	90	14
10	DBSA		H_20		280	92	15
11	TBAF	10 mol%	H_20	Reflux	55	93	16
12	I_2	10 mol%	DMSO	120	250	82	17
13	DMAP		EtOH	--	180	75	18
14	Lactose		EtOH:H_20	--	30	65	19
15	$CaHPO_4$	10 mol%	EtOH:H_20	80	150	88	20
16	TBAB	10 mol%	H_20	reflux	100	85	21

17	POPINO	7.5 mol%	H_20	reflux	70	90	22
18	Starch solution	4ml	No solvent	50	80	95	23
19	AP-SiO_2		H_20	70	150	89	24
20	WO_3	10 mol%	EtOH:H_20	reflux	--	97	This work
21	WO_3	10 mol%	Solvent free	70	--	97	This work

[a]Reaction conditions: Dimedone (100 mg), benzaldehyde (1 equivalent), malononitrile (1 equivalent), WO_3 NRs, different catalysts with continuous stirring at 70℃, [b]Isolation yield.

Table S4: Assessment of reported catalysts in addition to WO_3 NRs for the synthesis of xanthenes.

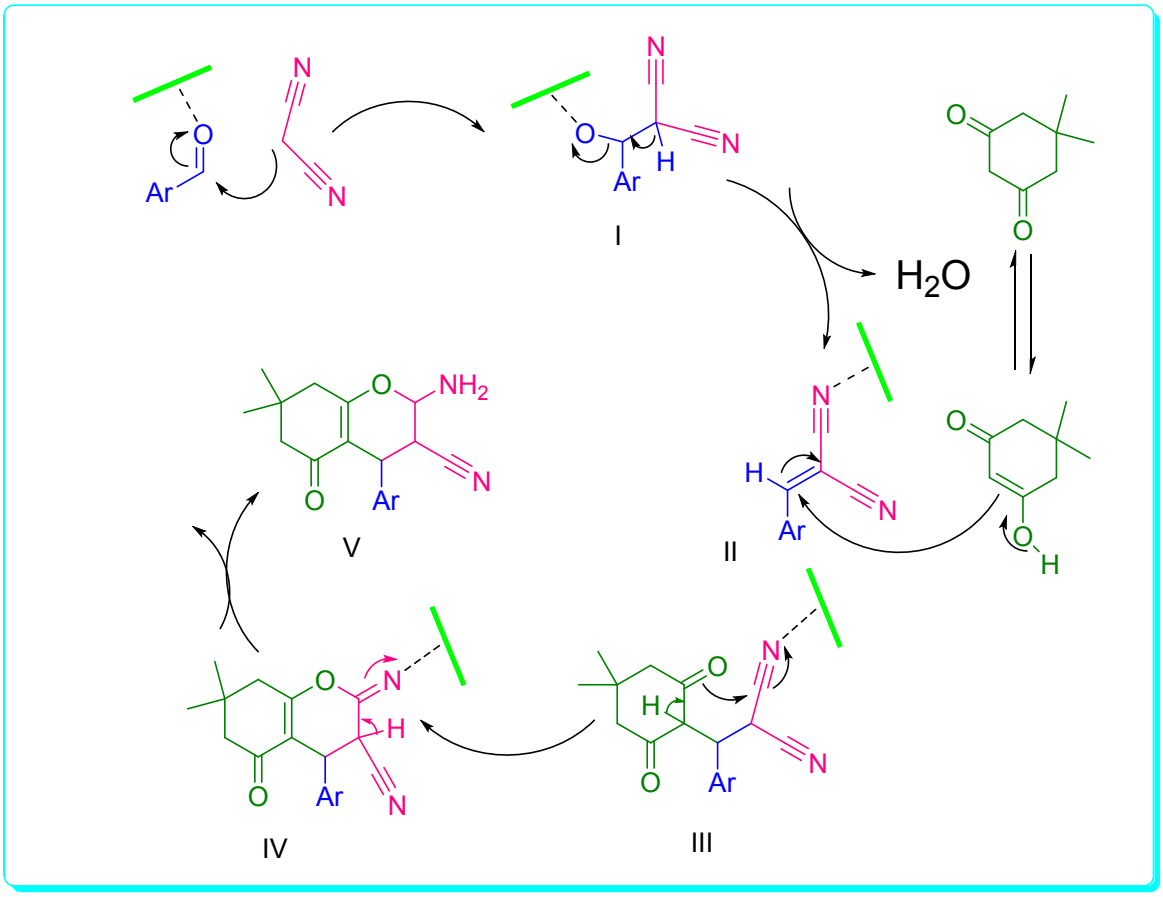
Sr. no.	**Catalyst**	**Solvent**	**Temp. (°C)**	**Time (h)**	**Yield[b] (%)**	**Ref.**
1	$InCl_3$	[bmim]BF_4	80	5	93	25
2	PANI-PTSA	H_2O	Reflux	6	70	26
3	Amberlyst-15	CH_3CN	Reflux	5	90	27
4	DABCO-Bromine	H_2O	Reflux	2	90	28
5	ZnO NPs (10 mg)	Solvent free	80	1/2	90	29
6	CuO NPs (10 mg)	Solvent free	80	1/2	92	30
7	$SmCl_3$ (20 mol%)	Solvent free	120	8	95	31
8	Fe_3O_4@SiO_2-Imid-PMA (30 mg)	EtOH	Reflux	1	92	32
9	I_2	Solvent free	90	2.5	91	33
10	CAN (5 mol%)	2-Propanol (ultrasound)	50	1/2	96	34

11	$CaCl_2$ (20 mol%)	DMSO	90	4	83	35
12	Cu(II)-Fur-APTES/GO (20 mg)	H_2O:EtOH	50	1/2	96	36
13	Boric acid (0.5 mol%)	Solvent free	120	1/2	97	37
14	WO_3	Solvent free	70	1/2	97	This work

[a]Reaction conditions: benzaldehyde (1 equivalent), Dimedone (2 equivalent) WO_3 NRs (10 mol%), H_2O/EtOH solvent system with continuous stirring at 70℃, [b]Isolation yield.

Plausible reaction mechanism for the formation of chromenes derivatives

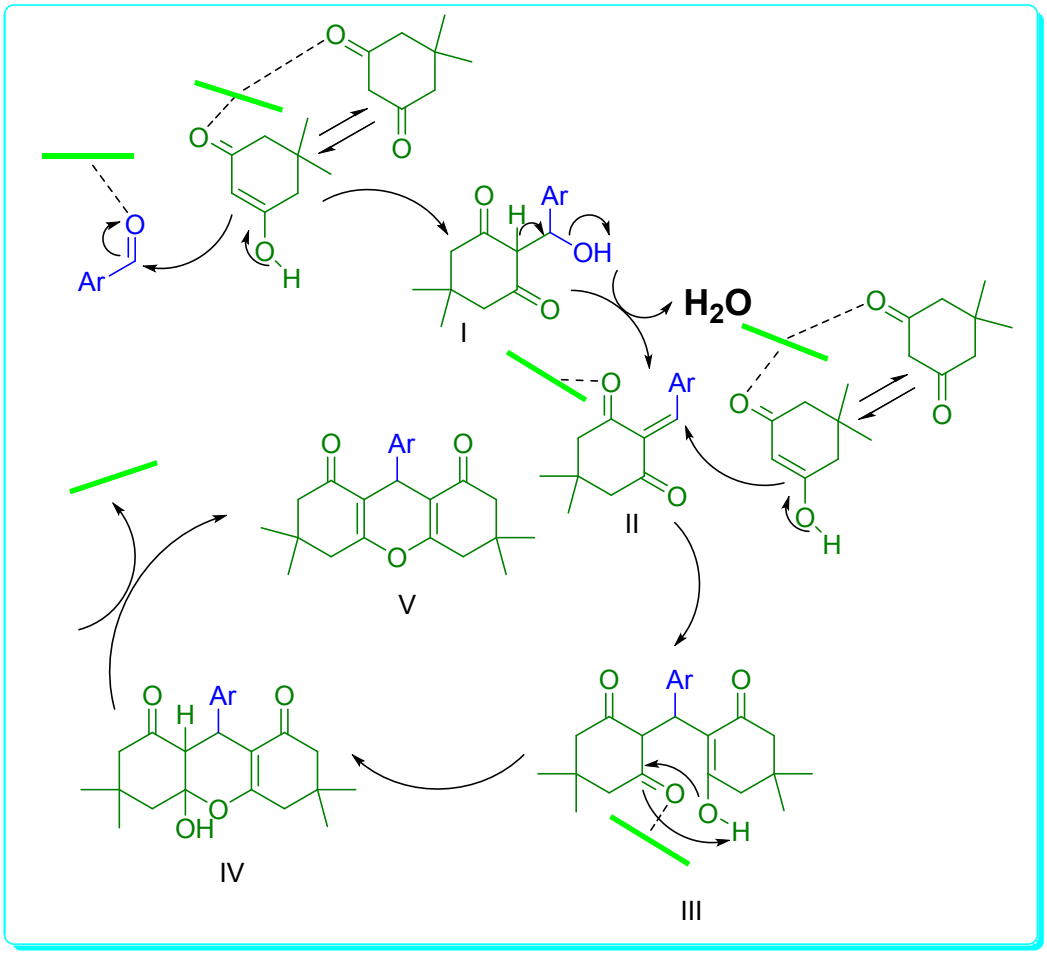
It considers the aldehyde–catalyst surface interaction. A plausible first step for the reaction cascade is the thermal energy induced activation of the carbonyl carbon of aromatic aldehyde followed by reaction with Malanonitrile *via* Knoevenagel condensation to form intermediate **I**. After losing water, **I** give intermediate **II**. The enol form of dimedone undergoes Michael addition with intermediate **II** to produce intermediate **III**. Finally, product **V** is formed by intramolecular cyclization of **III** and tautomerization of **IV** (**Scheme S1**).



Scheme S1: Plausible reaction mechanism for the formation of chromenes derivatives.

A plausible reaction pathway for the formation of xanthenes derivatives

WO_3NRs catalysed plausible reaction pathway for the formation of xanthenes **Scheme S2** and considers the aldehyde surface interaction which is believed to be responsible for the absorption of visible light. The first step of the cascade reaction is the light-induced activation of carbonyl carbon of aromatic aldehyde with enol form of dimedone forming the intermediate **I**, this intermediate after losing water gives intermediate **II.** Enol form of second molecule of dimedone undergoes Michael addition with intermediate **II** to form intermediate **III**. Finally, the product **V** was formed by intramolecular cyclization of **III** with subsequent removal of water from **IV**.



Scheme S2: Reaction mechanism for the formation of Xanthenes derivatives.

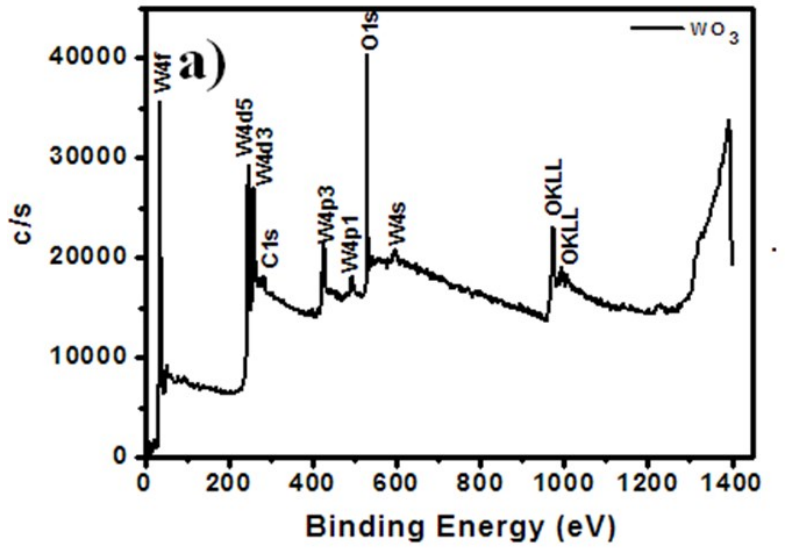


Fig. S1: XPS survey spectrum of WO_3 NRs.

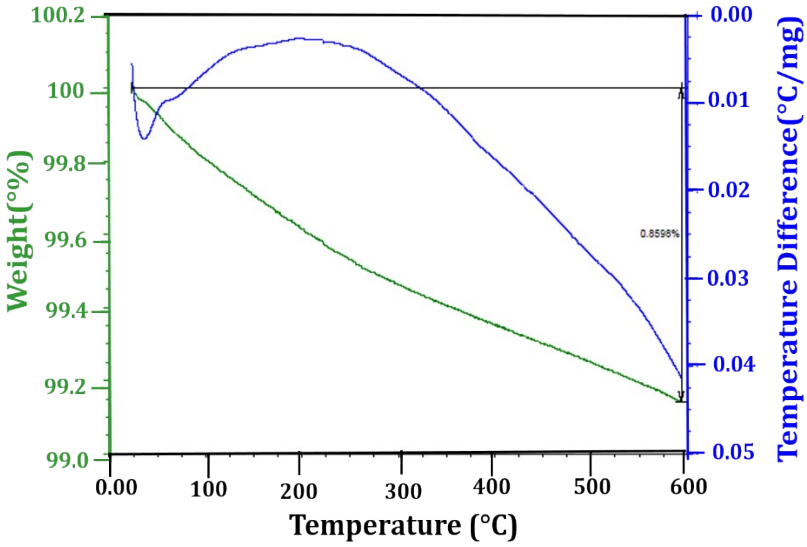
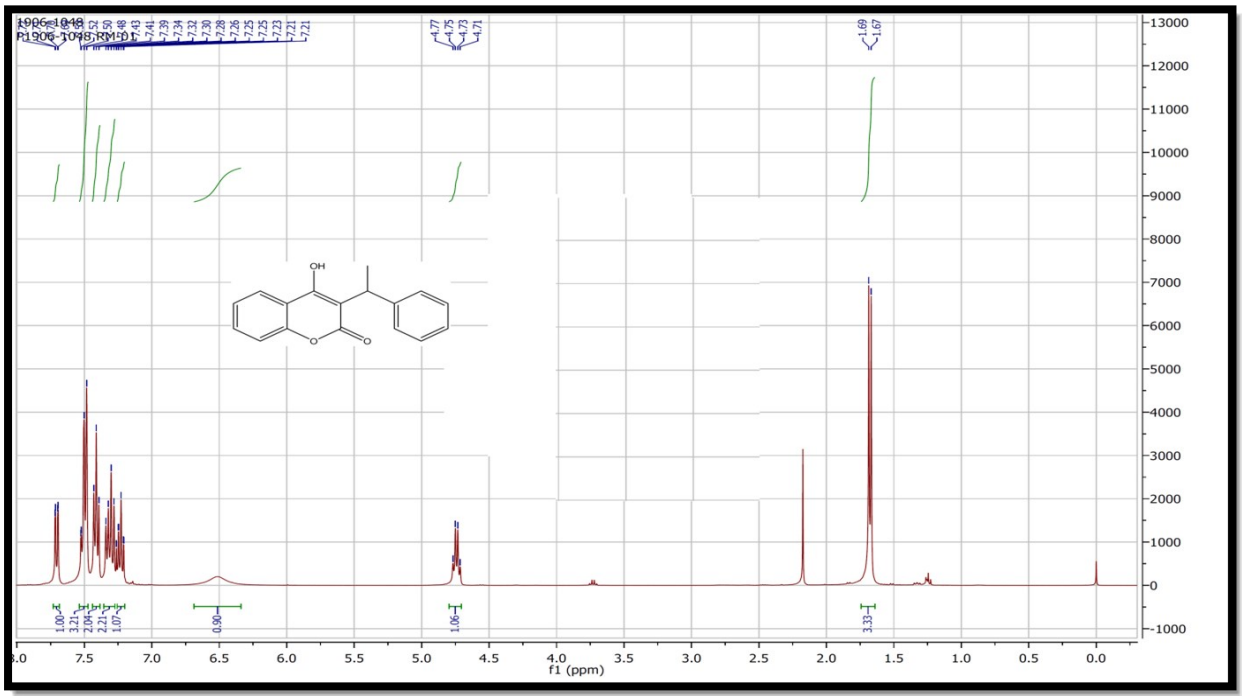


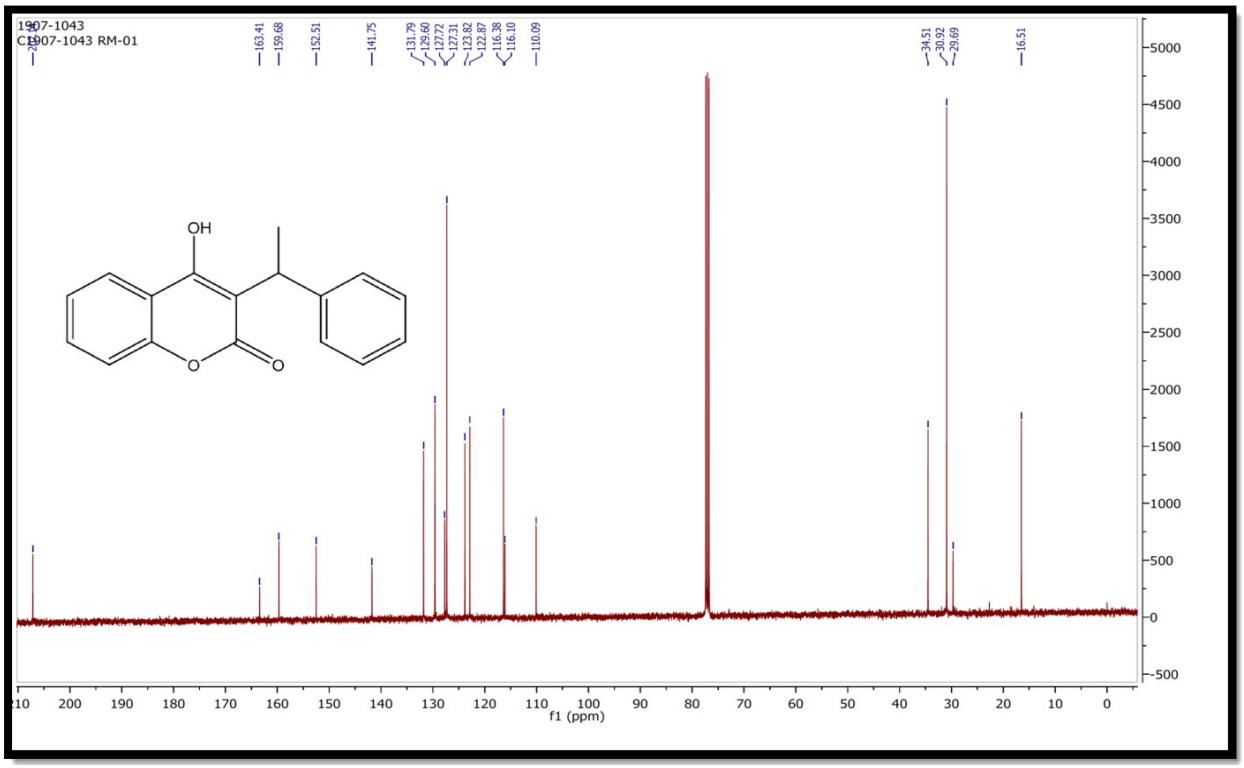
Fig. S2 Thermal analysis (TGA/DTA) of WO_3 NRs

The TGA/DTA plot confirms that the ammonium paratungstate decomposes through loss of water molecules and the formation of WO_3 could affirm at around 500°C. Based on this information an annealing temperature to produced WO_3 NRs was 500°C.[38]

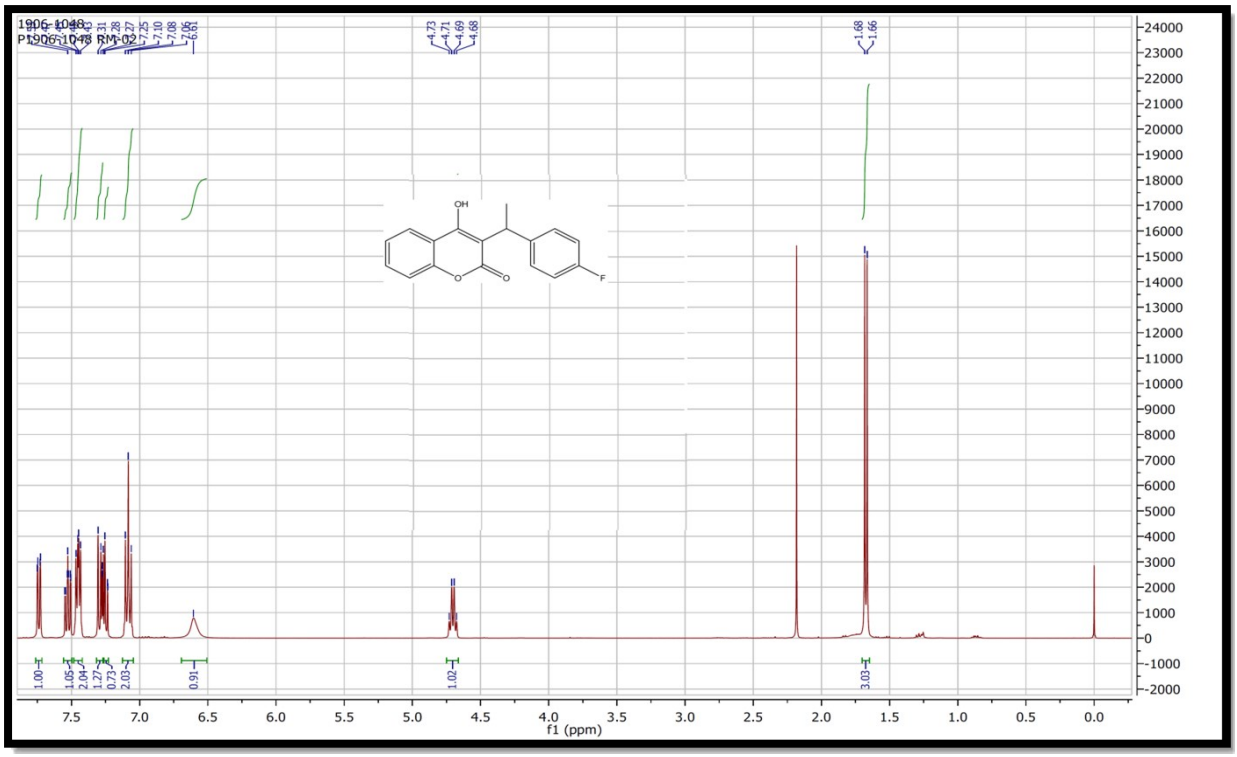
^{1}H-NMR of 4-hydroxy-3-(1-phenylethyl)-2H-chromen-2-one (3a)



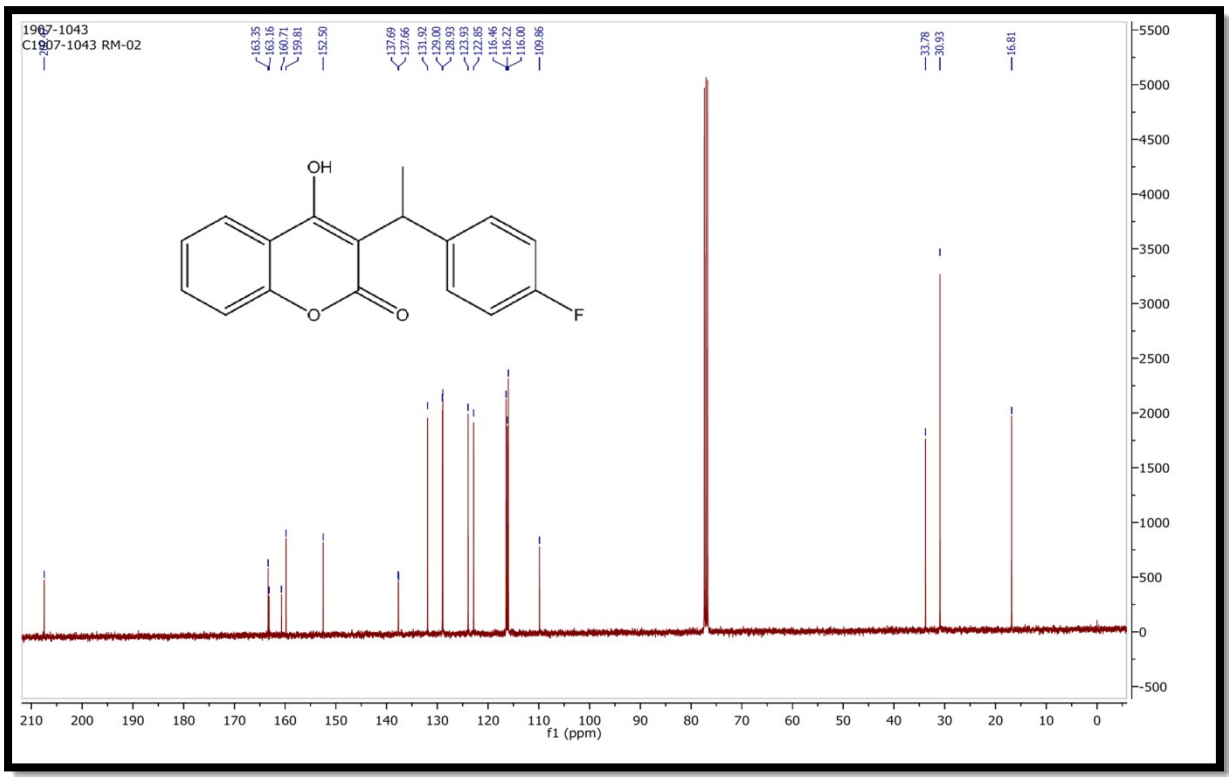
^{13}C-NMR of 4-hydroxy-3-(1-phenylethyl)-2H-chromen-2-one (3a)



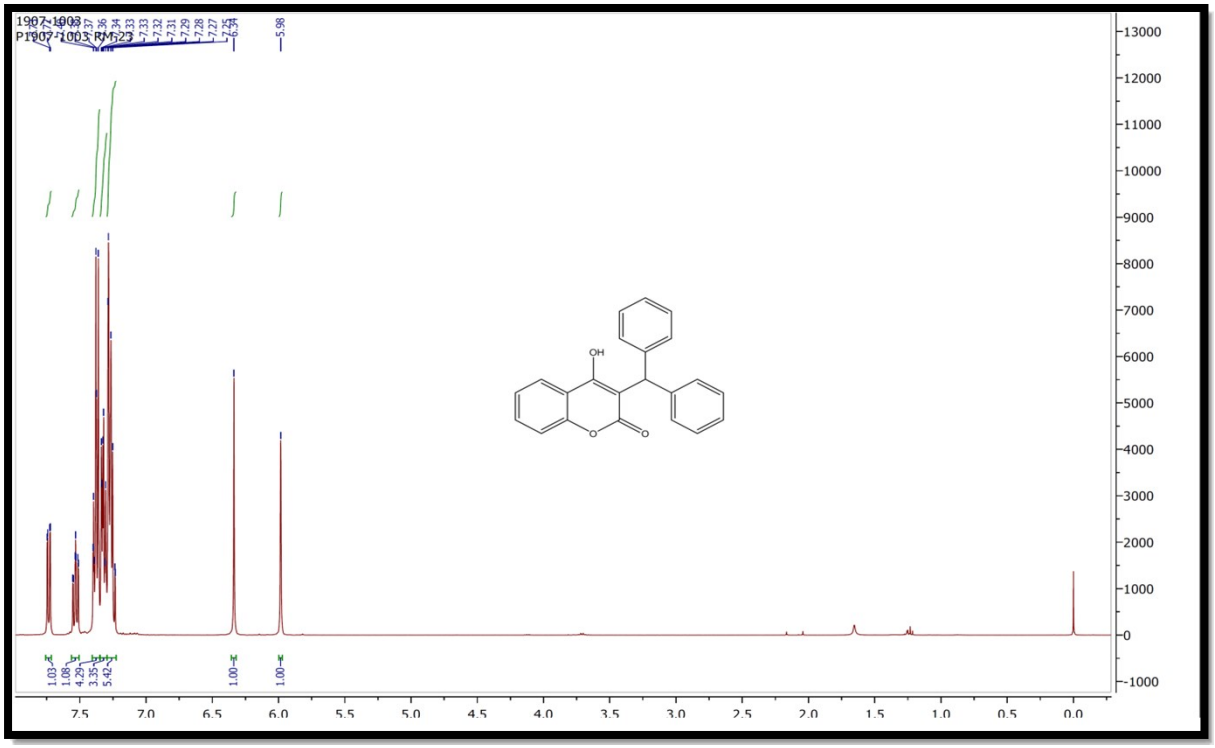
2) ^{1}H-NMR of3-(1-(4-fluorophenyl)ethyl)-4-hydroxy-2H-chromen-2-one (3b)



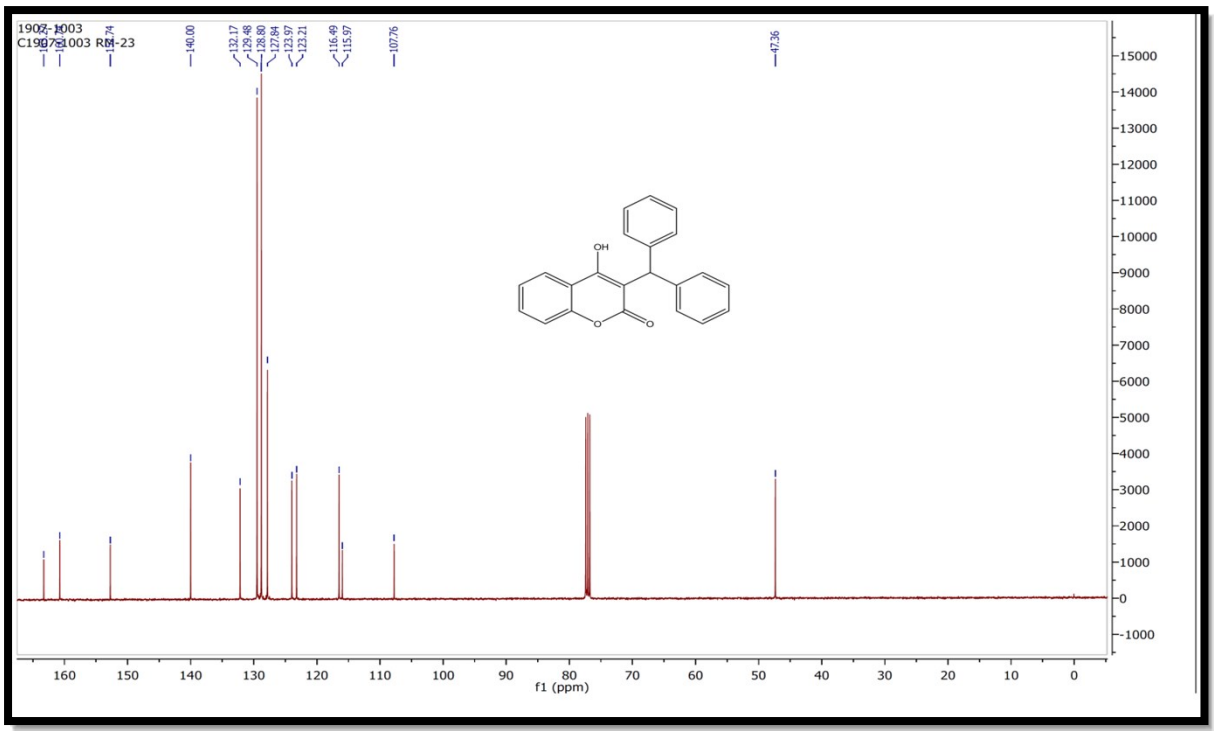
^{13}C-NMR of3-(1-(4-fluorophenyl)ethyl)-4-hydroxy-2H-chromen-2-one (3b)



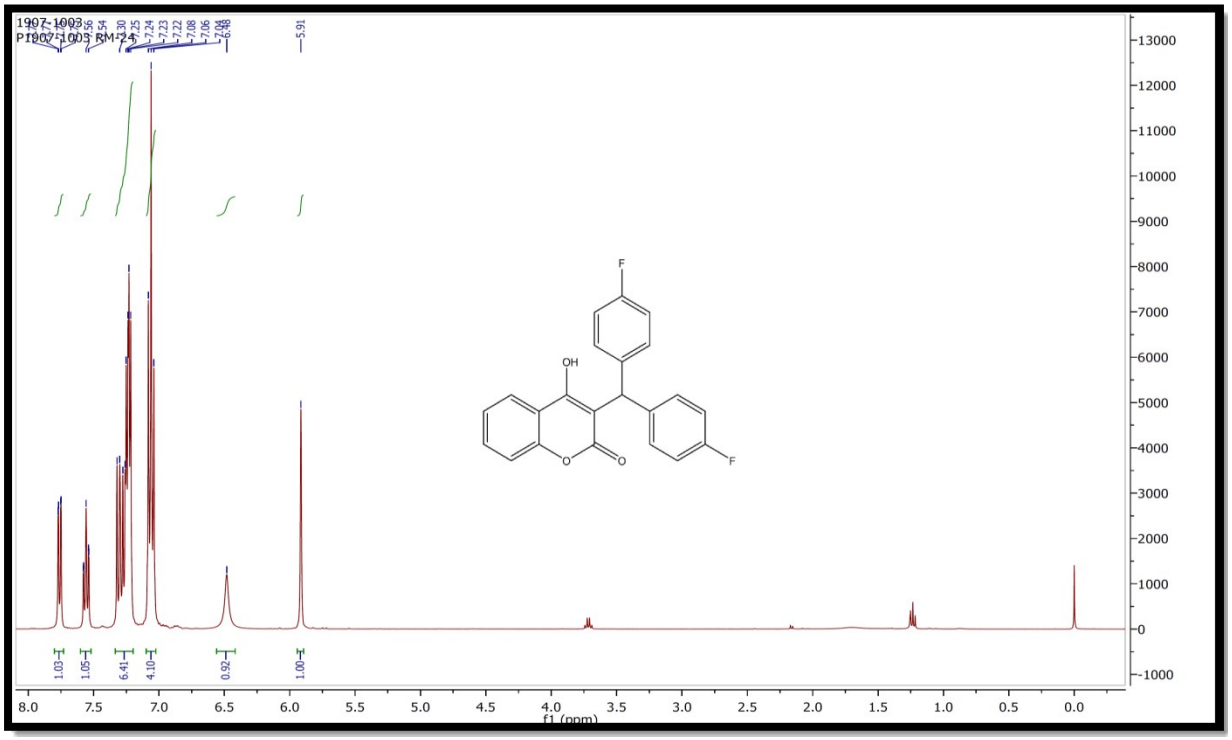
3) ^{1}H-NMR of 3-benzhydryl-4-hydroxy-2H-chromen-2-one (3c)



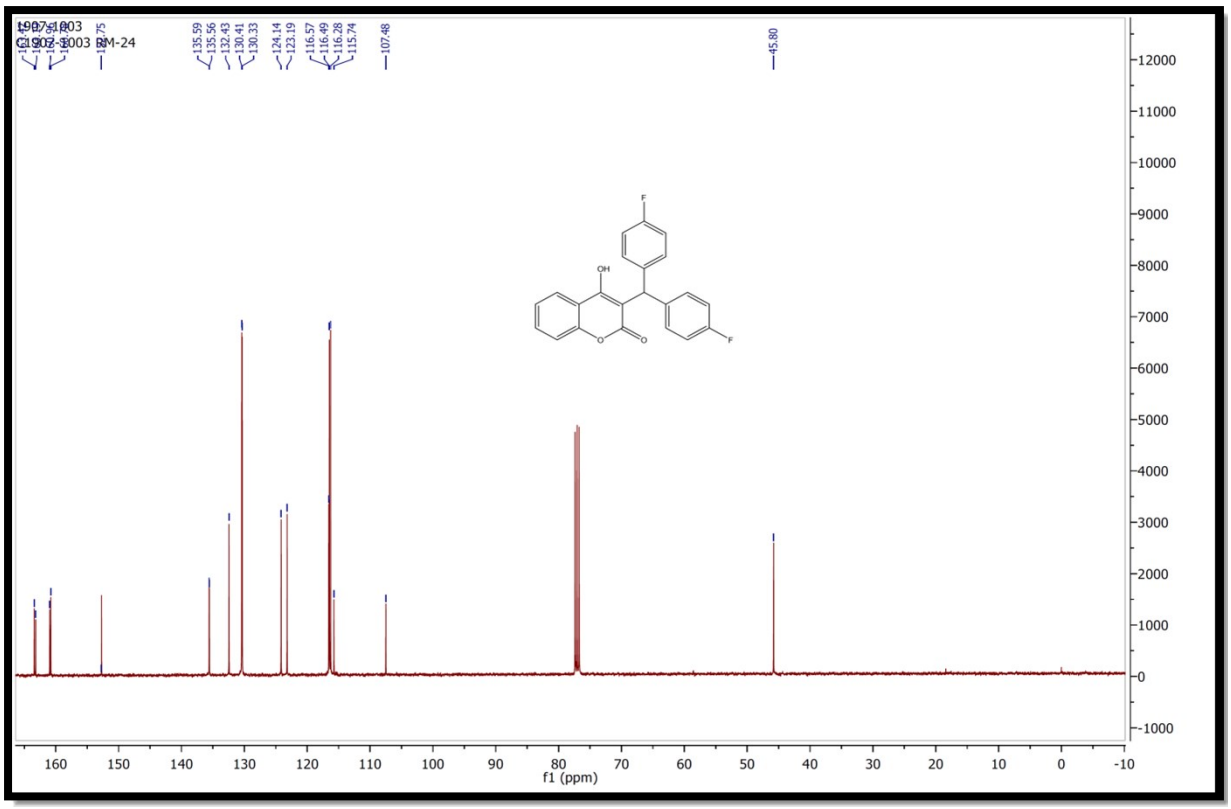
^{13}C-NMR of 3-benzhydryl-4-hydroxy-2H-chromen-2-one (3c)



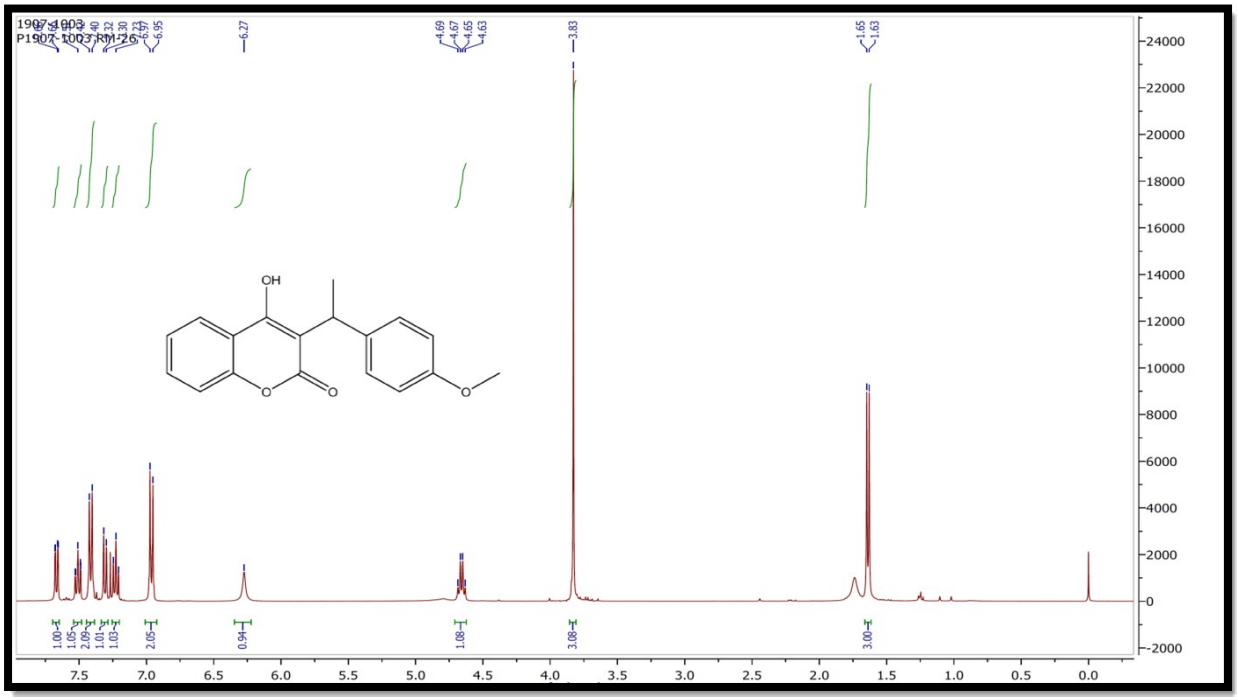
4) ^{1}H-NMR of 3-(bis(4-fluorophenyl)methyl)-4-hydroxy-2H-chromen-2-one (3d)



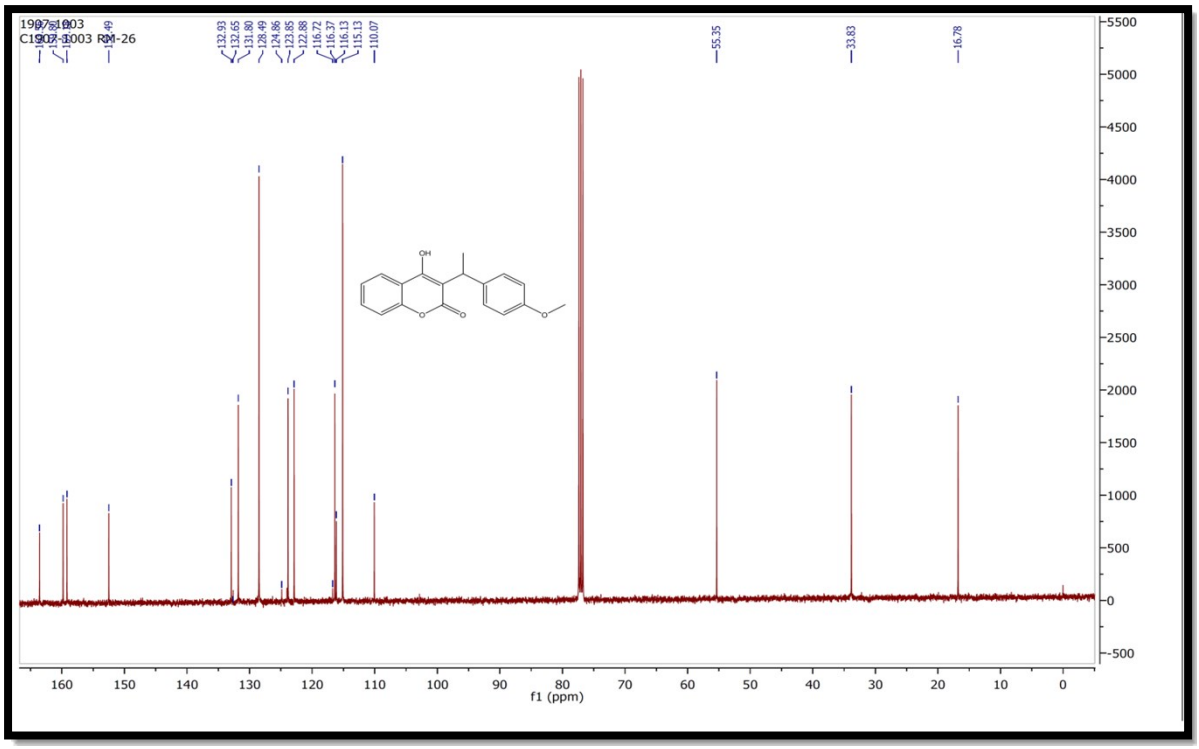
^{13}C-NMR of 3-(bis(4-fluorophenyl)methyl)-4-hydroxy-2H-chromen-2-one (3d)



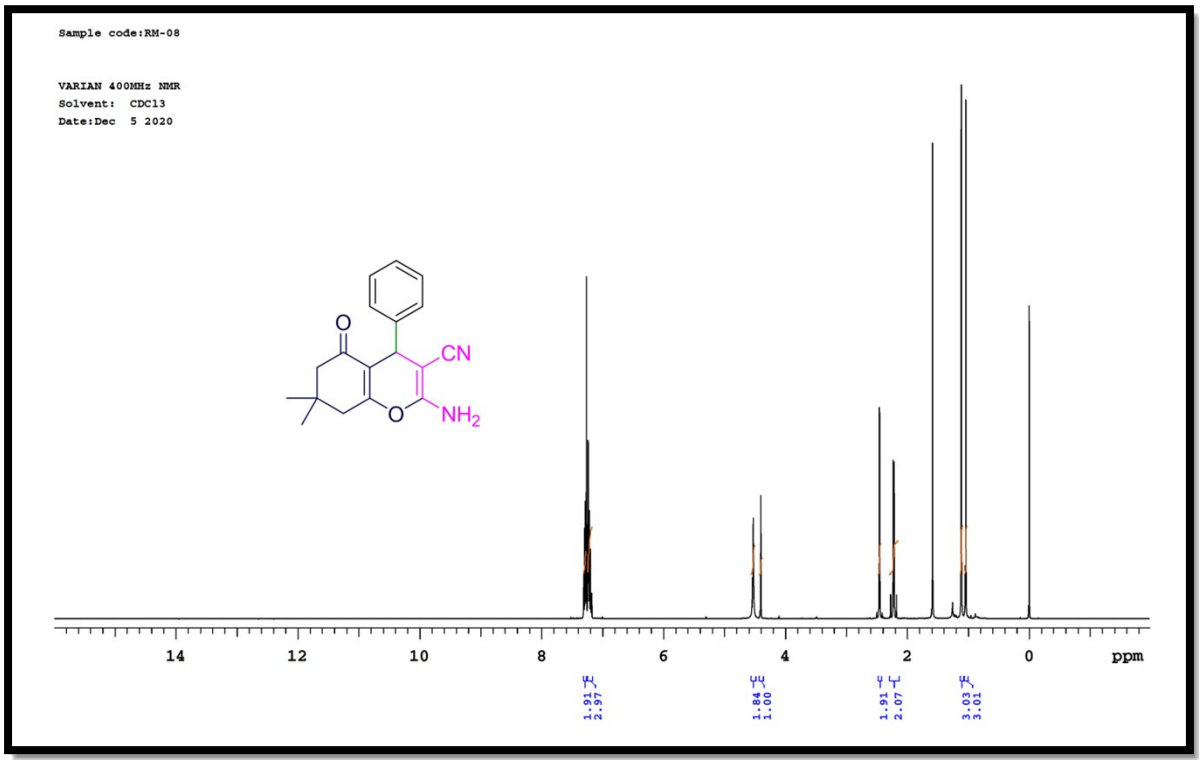
5) ^{1}H-NMR of4-hydroxy-3-(1-(4-methoxyphenyl)ethyl)-2H-chromen-2-one (3e)



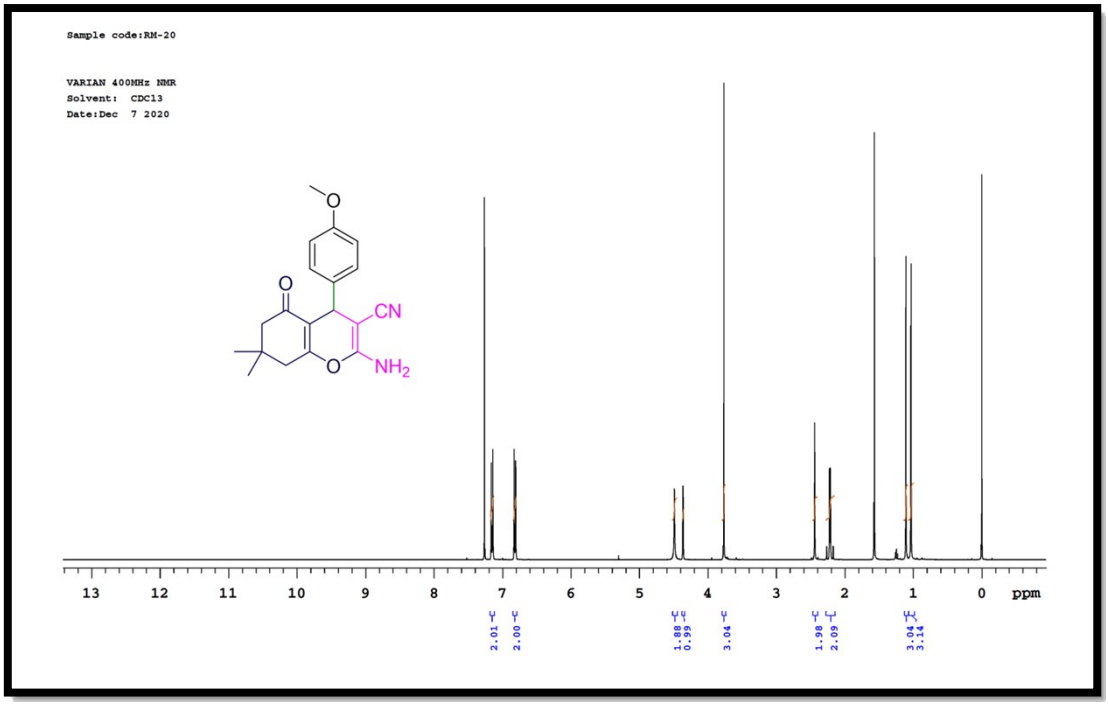
^{13}C-NMR of 4-hydroxy-3-(1-(4-methoxyphenyl)ethyl)-2H-chromen-2-one (3e)



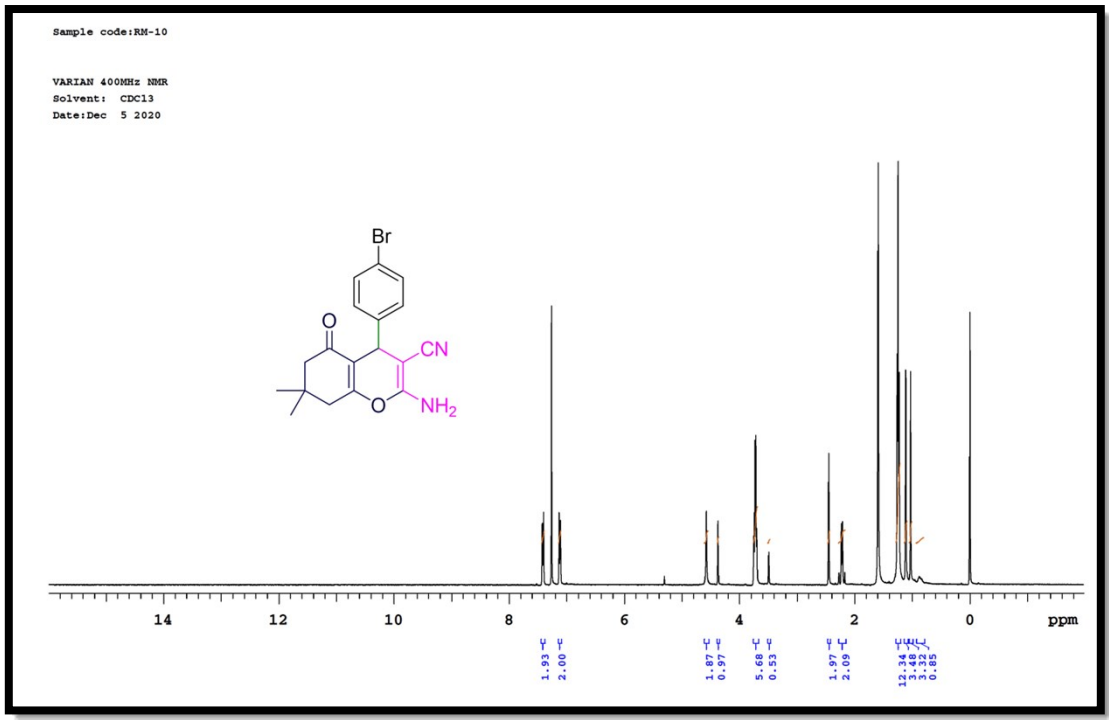
6) ^{1}H-NMR of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7a)



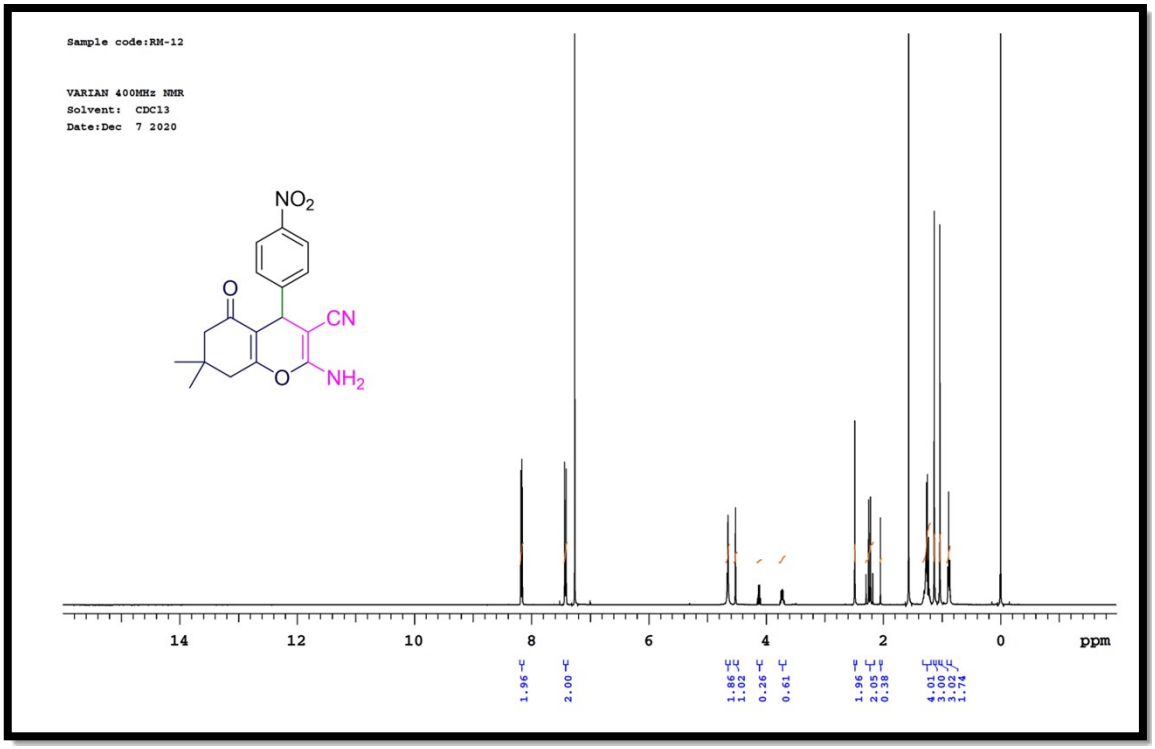
7) ^{1}H-NMR of 2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7b)



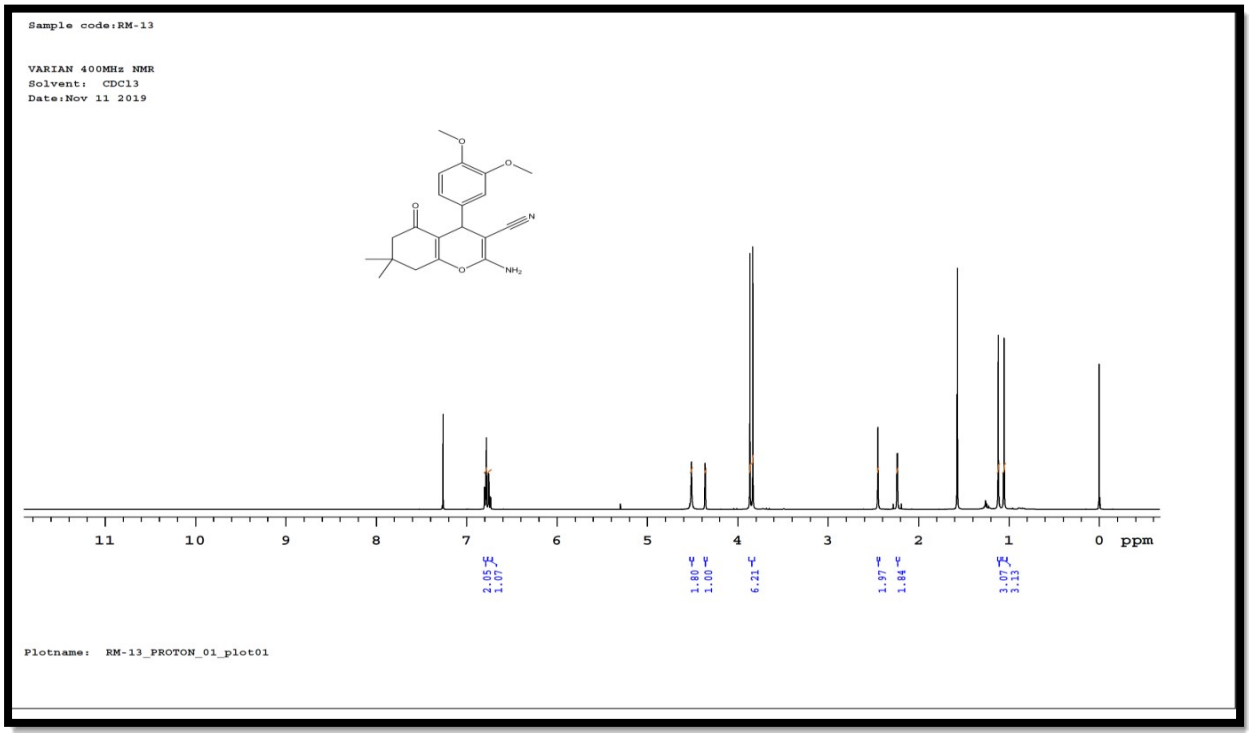
8)^{1}H-NMR of 2-amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7C)



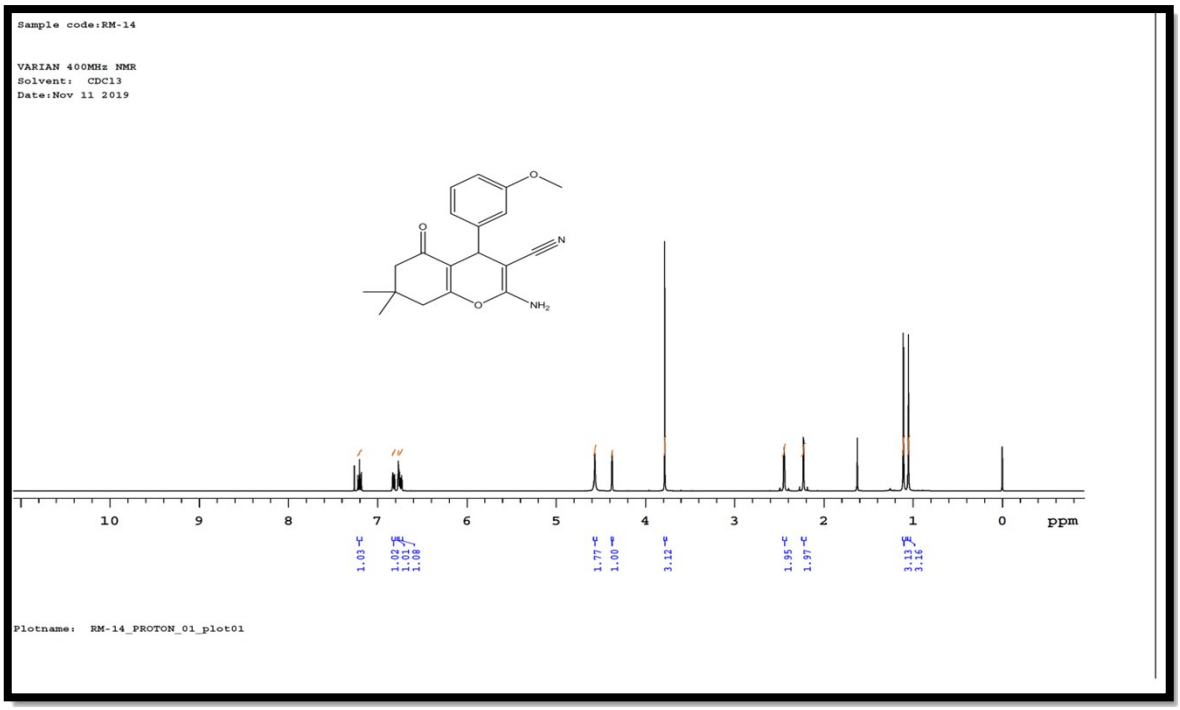
9)^{1}H-NMR of 2-amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7d)



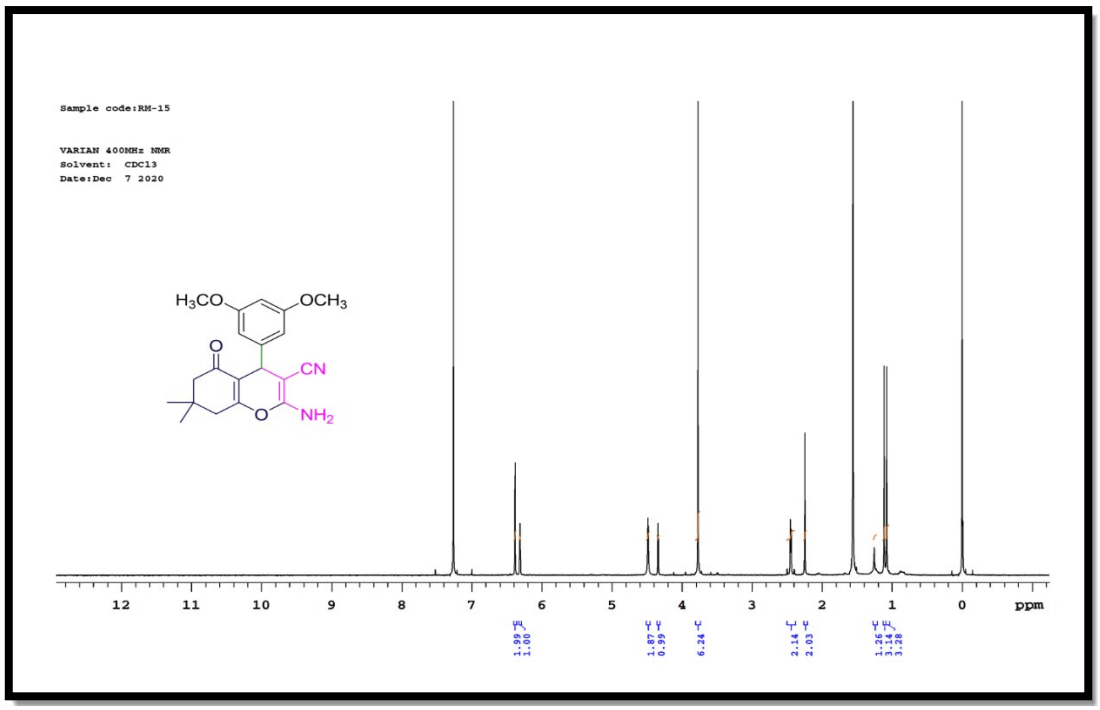
10)^{1}H-NMR of 2-amino-4-(3,4-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7e)



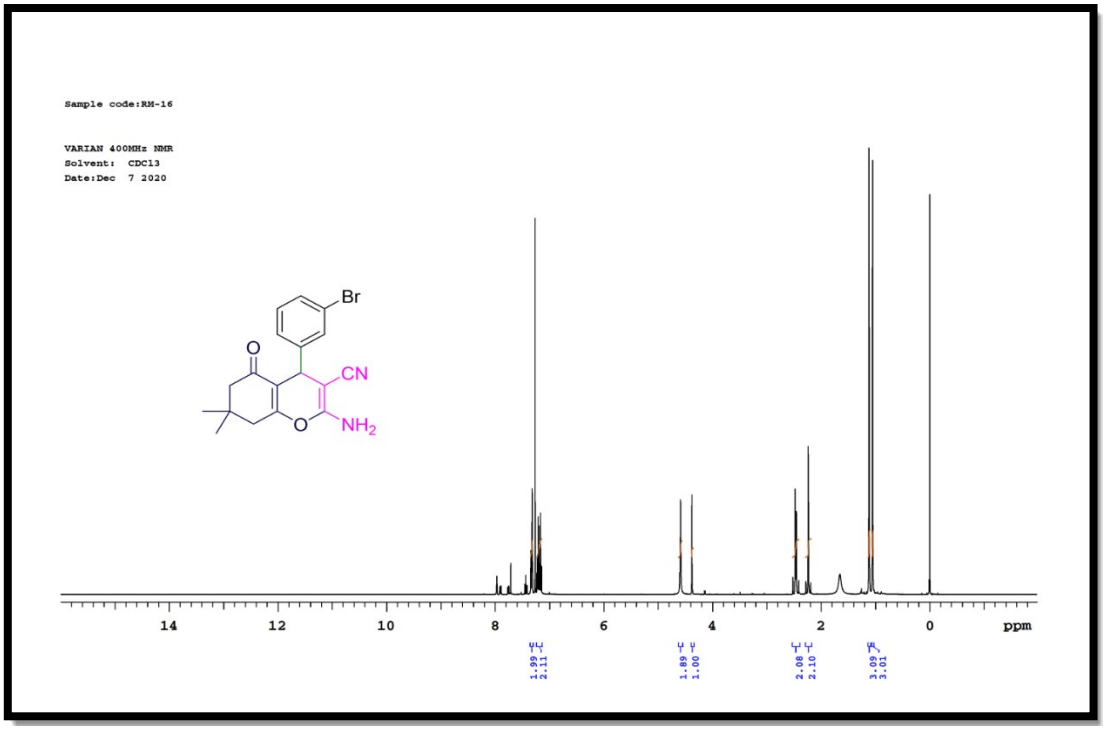
11)**^{1}H-NMR of 2-amino-4-(3-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7f)**



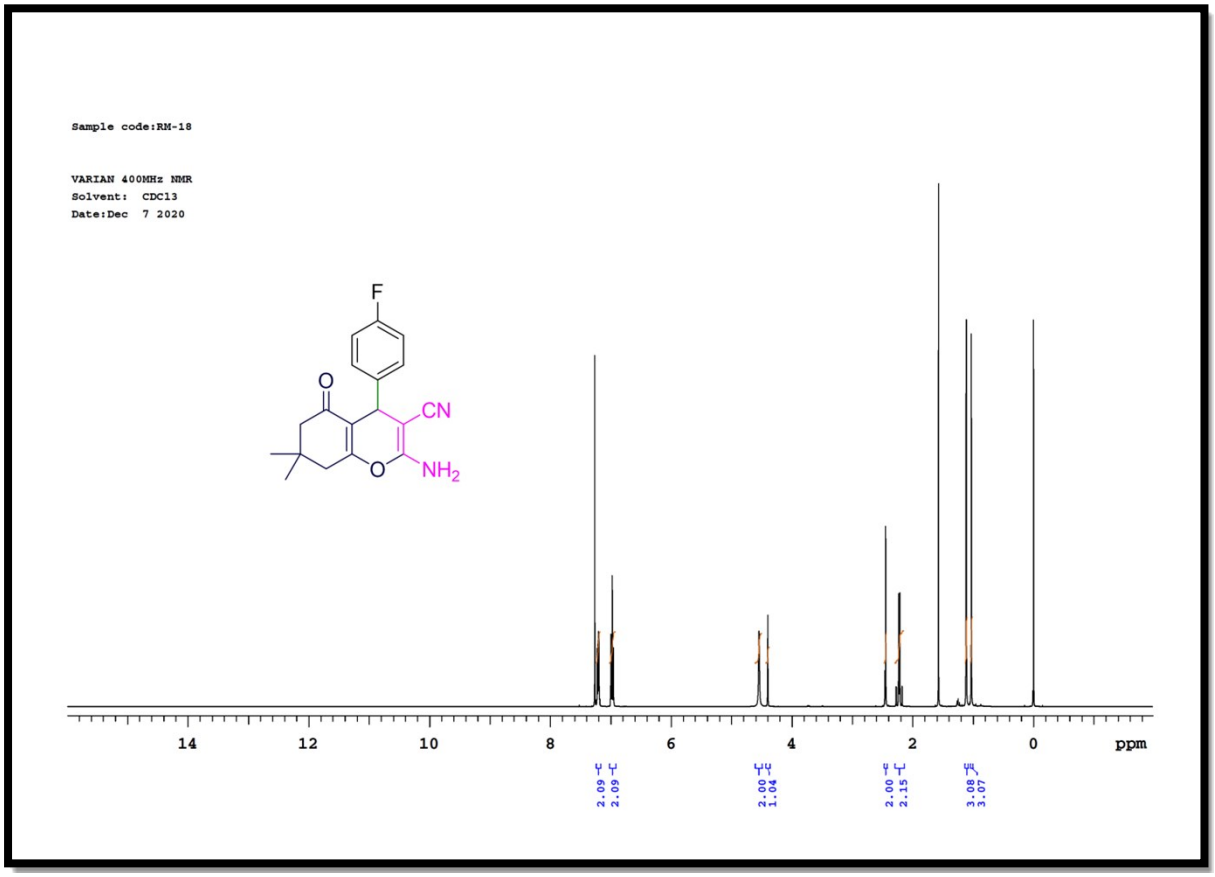
12) ^{1}H-NMR of 2-amino-4-(3,5-dimethoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7g)



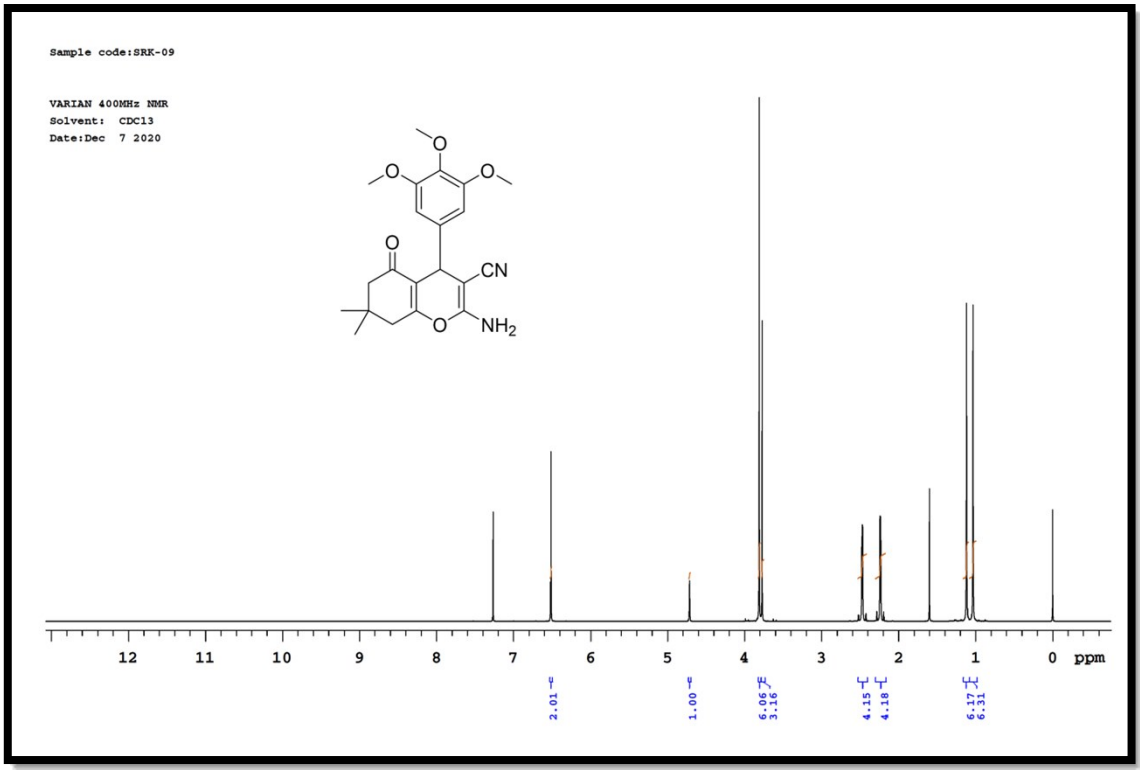
13) ^{1}H-NMR of 2-amino-4-(3-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7h).



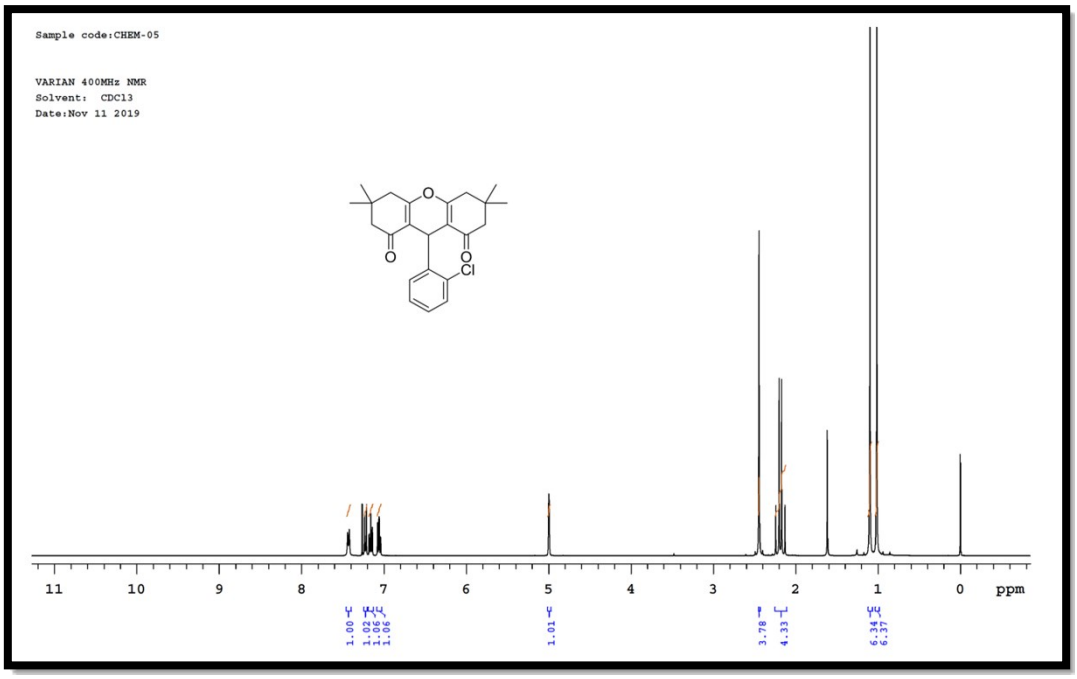
14) ^{1}H-NMR of 2-amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7i)



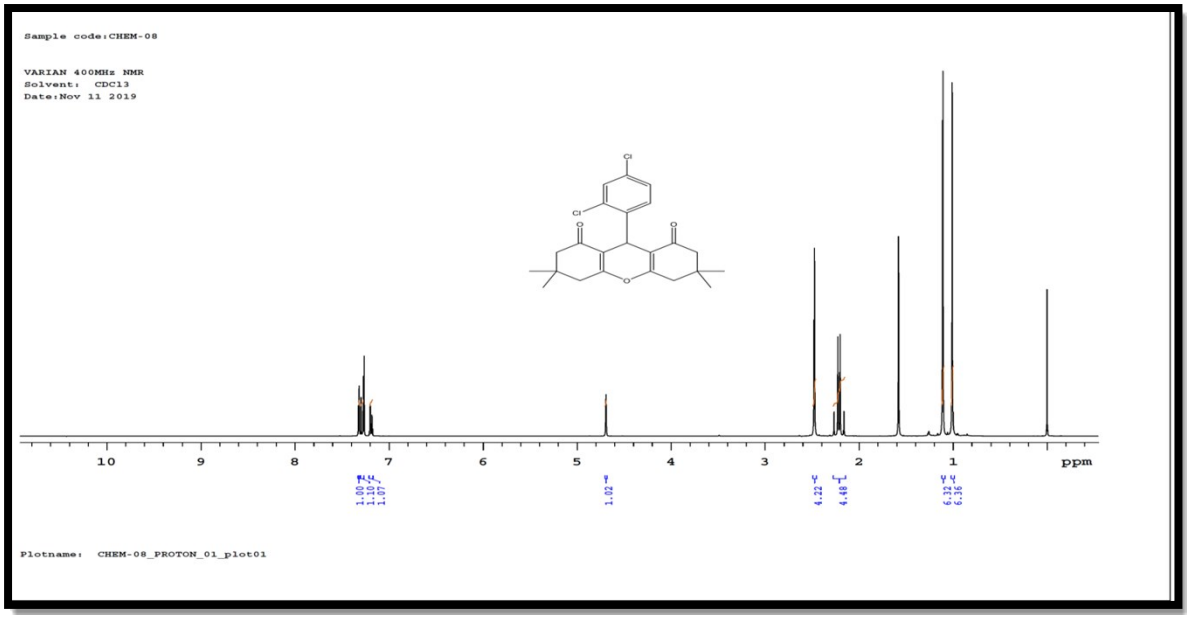
15)^{1}H-NMR of 2-amino-7,7-dimethyl-5-oxo-4-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (7j)



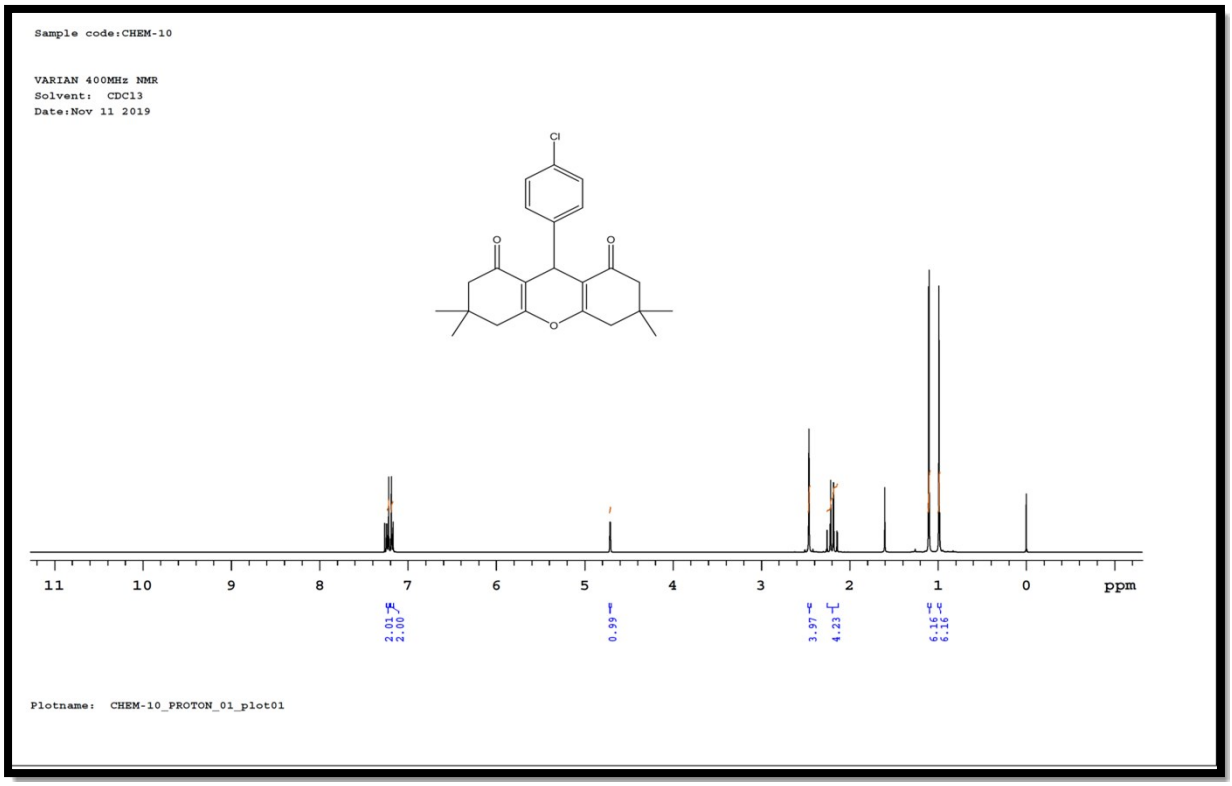
16) ^{1}H-NMR of 9-(2-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8a)



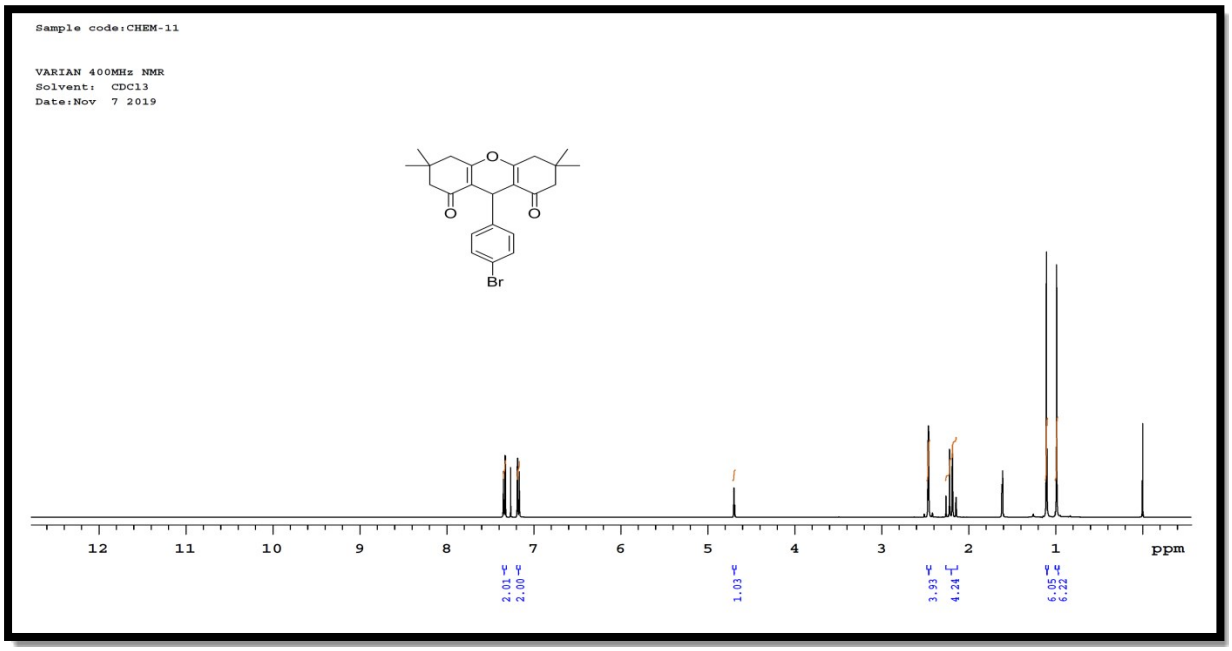
17) **^{1}H-NMR of 9-(2,4-dichlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8b)**



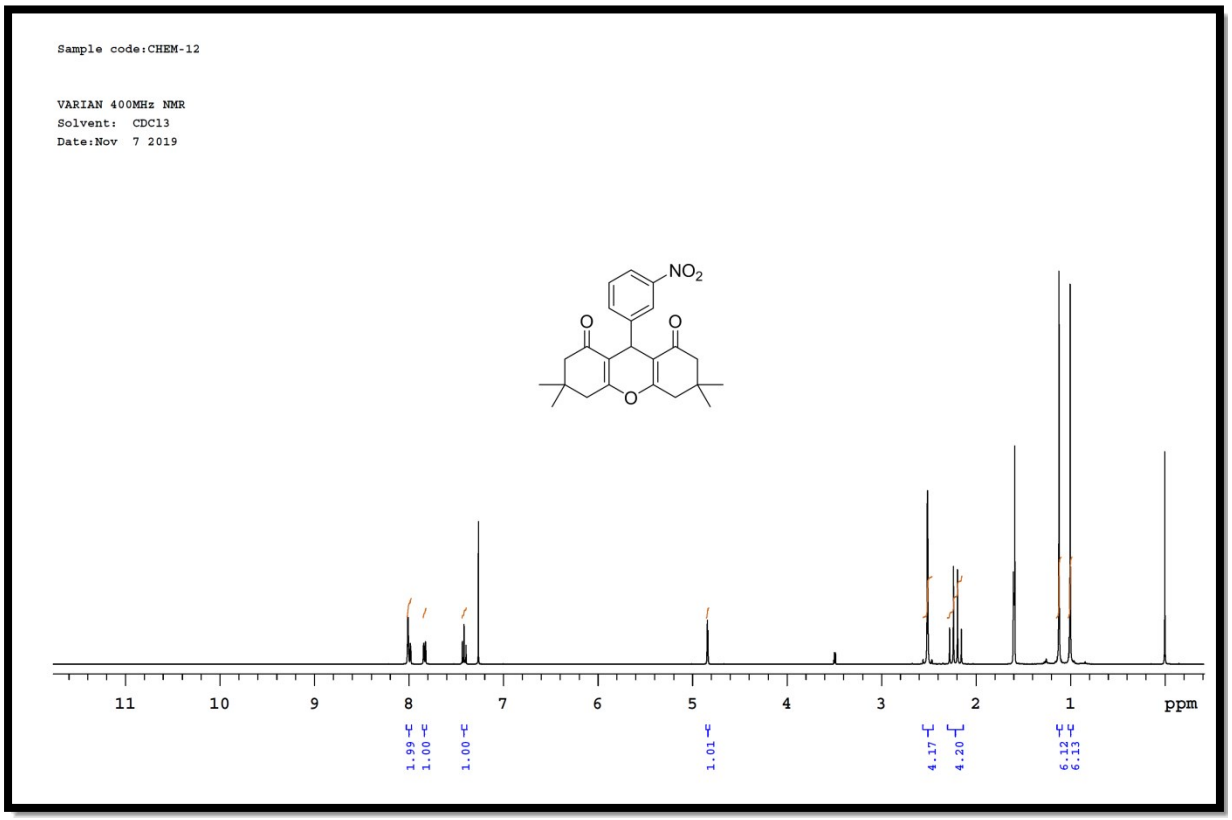
18) **^{1}H-NMR of 9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8c)**



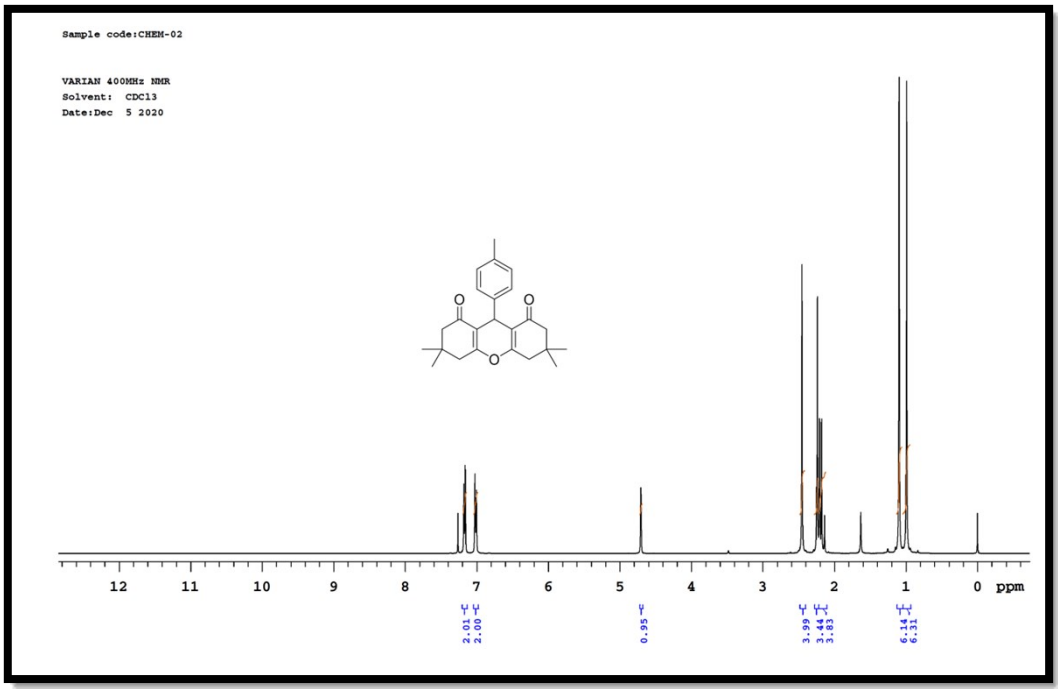
19) **^{1}H-NMR of9-(4-bromophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8d)**



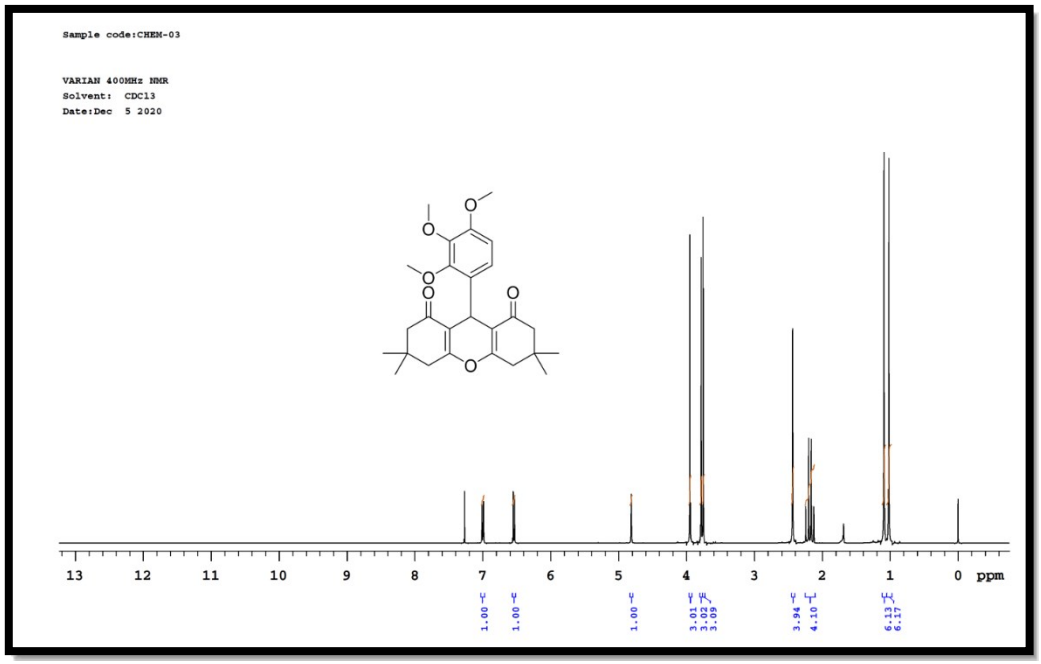
20) **^{1}H-NMR of 3,3,6,6-tetramethyl-9-(3-nitrophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8e)**



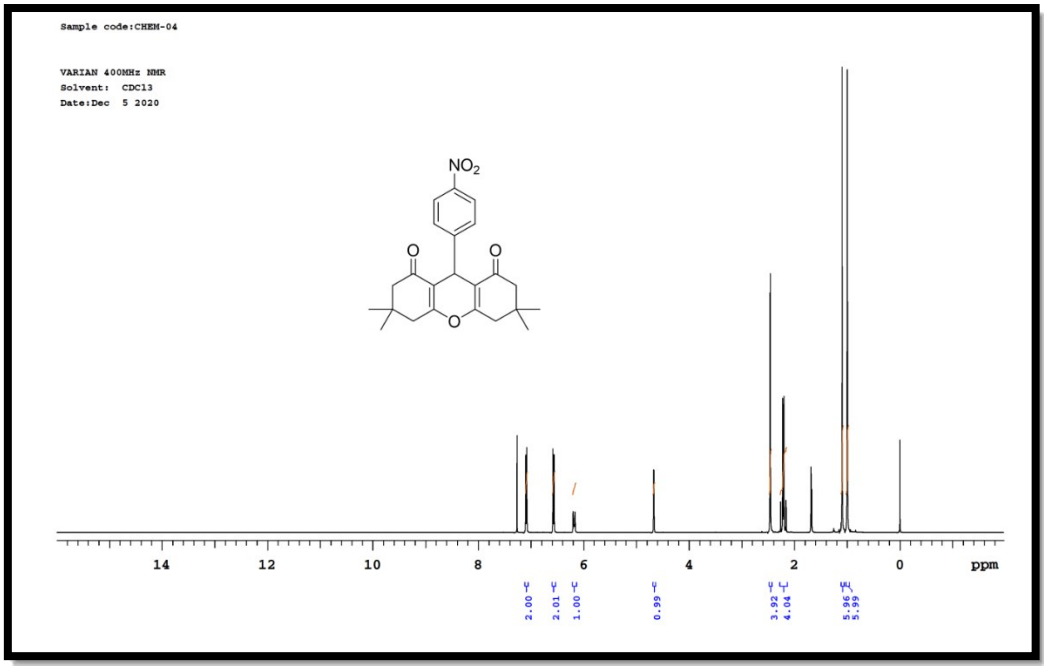
21)[1]H-NMR of 3,3,6,6-tetramethyl-9-p-tolyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8f)



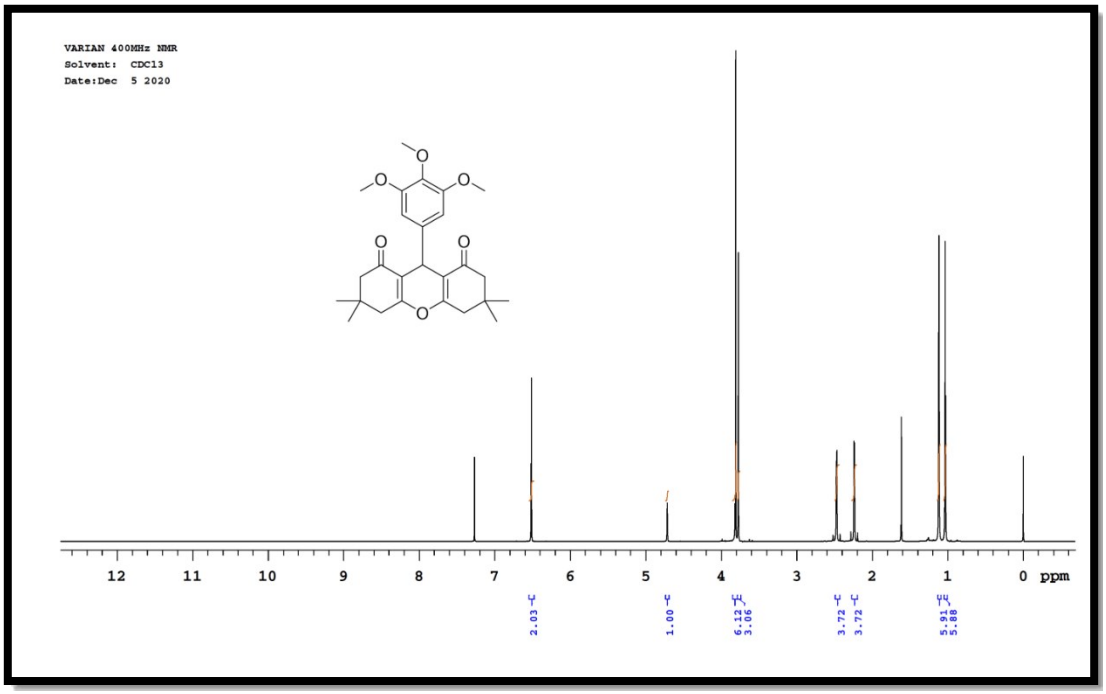
22) [1]H-NMR of 3,3,6,6-tetramethyl-9-(2,3,4-trimethoxyphenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8g)



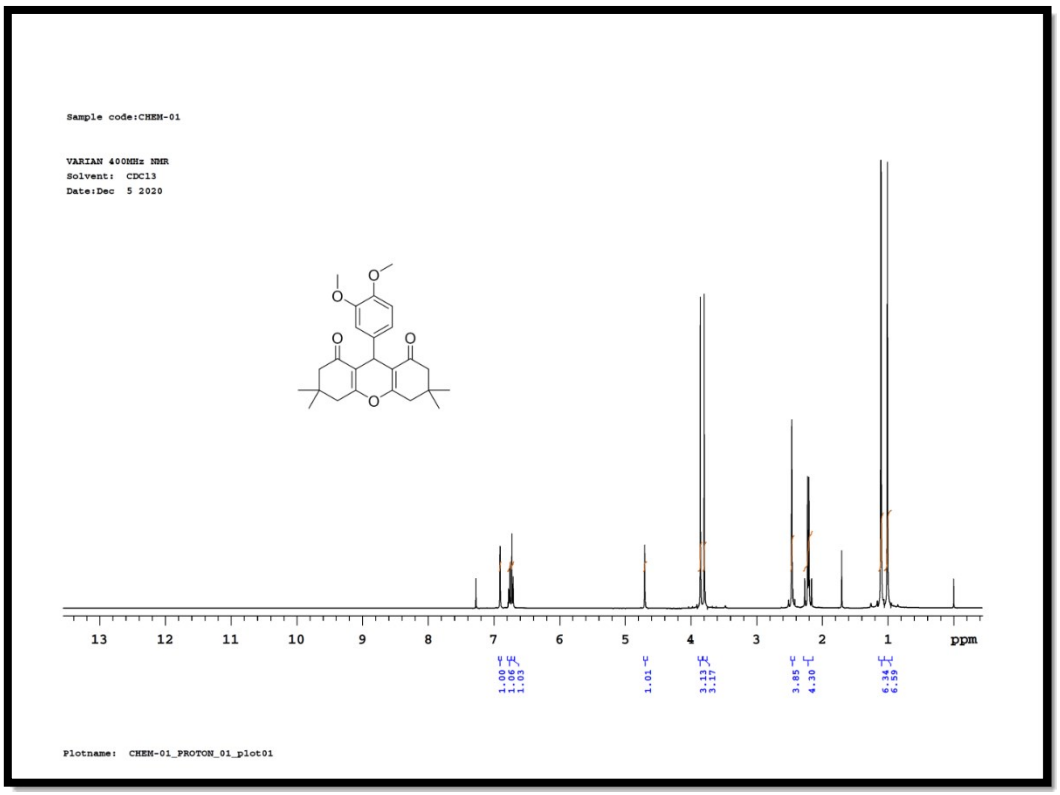
23)^{1}H-NMR of 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8h)



24)^{1}H-NMR of 3,3,6,6-tetramethyl-9-(3,4,5-trimethoxyphenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione. (8i)



25) ^{1}H-NMR of 9-(3,4-dimethoxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (8j)



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