HETEROCYCLES, Vol. 85, No. 7, 2012, pp. 1629 - 1653. © 2012 The Japan Institute of Heterocyclic Chemistry
Received, 19th April, 2012, Accepted, 21st May, 2012, Published online, 24th May, 2012
DOI: 10.3987/COM-12-12494

AN EFFICIENT ONE-POT THREE-COMPONENT SYNTHESIS OF HIGHLY FUNCTIONALIZED COUMARIN FUSED INDENODIHYDROPYRIDINE AND CHROMENO[4,3-*b*]QUINOLINE DERIVATIVES

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Abstract – An efficient one-pot, three-component synthesis method of highly functionalized coumarin fused 7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]-phenanthrene and chromeno[4,3-*b*]quinoline derivatives was accomplished using aromatic aldehyde, 4-aminocoumarin and cyclic 1,3-dione in acetic acid at reflux temperature. Environmental-friendly protocol has advantages of high yields, creating three new bonds and one stereocenter in single operation. Further, XRD and DFT study confirmed the molecular structure, stability and different interaction in the crystal packing.

INTRODUCTION

Multi-component reactions (MCRs) provide a wide range of opportunities for the formation of carbon-carbon and carbon-heteroatoms bonds in a single step for many complex and heterocyclic molecules. MCRs are highly useful in terms of products purifications, reaction time and less use of reagents and solvents.[1] Heterocyclics have played ubiquitous scaffolds in biological, medicinal, pharmaceutical and natural products.[2] For example, many dihydropyridyl and indeno dihydropyridyl derivatives are used as drugs in the treatment of cardiovascular diseases (calcium channel modulators) such as amlodipine, nicardipine, s-niguldipine, 4-aza-podophyllotoxin and nifedipine (Figure 1) and some other dihydropyridyl derivatives used as antihypertensive agents.[2] Moreover, dihydropyridine derivatives possess a variety of biological activities such as vasodilator, bronchodilator, antiatherosclerotic, antitumor,

gastroeroprotective, hepatoprotective, and antidiabetic activities[3] and various medicinal importance such as neuroprotectant, platelet anti-aggregatory activity, cerebral anti-ischemic activity in the treatment of Alzheimer's disease and chemosensitizer in tumor therapy.[4] In recent years, much attention has been focused on the synthesis of 1,4-dihydropyridyl compounds due to their significant biological activity.[2] 4-Aryl-1,4-dihydropyridines an analogue of NADH coenzymes have been explored for their calcium channel activity, potentiation of antitumoral, vasodilator, bronchodilator, anti-atherosclerotic, antitumor, hepatoprotective, antidiabetic agents and antimetastatic activity of some common cytotoxic drugs.[4] A slight structural modifications on DHP rings gave a remarkable change in pharmacological effects.[5] Therefore, various reaction approaches are explored using different catalysts and solvents like [bmim]OH,[6] HPAs,[7] TMGT,[8] MgO,[9] DAHP,[10] TBAB,[11] DBU,[12] $KAl(SO_4)_2.12H_2O$,[13] $H_6P_2W_{18}O_{62}.18H_2O$,[14] HY-Zeolite,[15] ionic liquids, PTSA, (±)lactic acid,[16] and MW-irradiation[17] *via* MCRs concept. However, some of these methods have limitations as longer reaction time, elevated temperature, intolerance of functional groups, low yields and tedious workups. Therefore, an efficient and versatile method is still required.

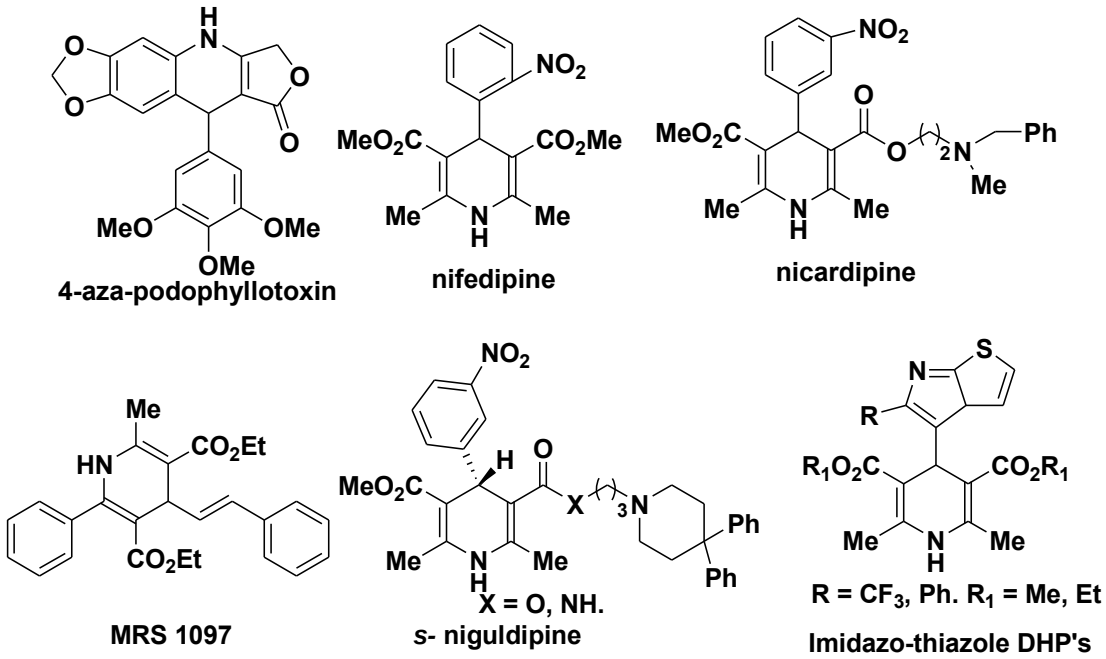


Figure 1. Biologically active of dihydopyridines

Similarly, coumarin and their derivatives represent most active class of compounds possessing a wide range of biological activities. 4-Aminocoumarin and their derivatives have received considerable attention due to different types of biological, industrial and pharmacological importance such as antibacterial, anticancer, anti-HIV, anticoagulant, antioxidant, and spasmolytic activities. Also, 1,3-indanedione and their

derivatives have bioactivities including antioxidants, anticoagulants, antibacterial, Cyclin-Dependent Kinases (CDK) inhibitors, neuroprotective agent, potential antitumor agents and binding the kinase ATP pockets.[18-20] Recently, there has been incredible interest in the synthetic manipulation of biologically active and functionalized indanedione derivatives.[18-20] Previous works have also shown that fusing an indeno moiety to the core structure of a natural products enhanced the pharmacologic potential of a target molecule. Based on this veracity, different derivatives have been synthesized as potential drug candidates. Therefore, different groups have tried for the synthesis of coumarin fused dihydropyridine molecules.[16a,b] A few reports are also available for the synthesis of coumarin fused indenodihydropyridines and chromeno quinolines. For example, Miri et al have synthesized chromeno[4,3-*b*]quinolines in multi-steps reaction using high temperature *via* Michael addition followed by cyclization and dehydration.[16c] Recently, DHPs synthesis has been reported using ethyl-L-lactate (solvent) and (±) lactic acid (organocatalyst) which gave moderate yields.[16d] Similarly, Khan et al have synthesized DHPs using 20 mol% *p*-toluenesulfonic acid (PTSA) as a catalyst in EtOH.[16c,d] However, reaction time is longer (7-8 h) and the product yields are moderate to good (72-82%) at refluxed. Indeed, we need to develop an efficient and green protocol due to the growing awareness about environmental concerns. Therefore, the organic chemists are under increasing pressure to alter current working practices for the sustainable development in academia and industry research and to find environmentally benign and greener alternatives.

Enormous biological important of these compounds as antagonist properties against estrogenic, tumor, hypertensive, microbial, allergic, high affinity retinoic acid receptor and vasodilator activities and agonist properties in potassium channel opening, fungicide and hypotensive activities motivated us to develop a more efficient and atom-economical protocol for high yields in shorter reaction time. Herein, we describe a simple and efficient multi-component reaction using aromatic aldehyde, 4-aminocoumarin, cyclic 1,3-diketones/indanone at reflux in acetic acid without adding catalyst or promoter to provide a series of coumarin based DHP's derivatives (Scheme 1).

RESULTS AND DISCUSSION

To find the optimal conditions in the synthesis of dihydropyridines, indenodihydropyridines and chromeno quinolines, a mixture of benzaldehyde (0.8 mmol), indanone (0.8 mmol) and 4-aminocoumarin (0.8 mmol) was refluxed for 24 h in the presence of solvents like benzene, toluene and 1,4-dioxane, methanol, ethanol, tetrahydrofuran (THF), acetonitrile (MeCN), dimethylformamide (DMF), *n*-butanol and dimethyl sulfoxide (DMSO) which gave trace amount of desired product either at room temperature or at reflux. Reaction was further carried out in a mixture of solvents like toluene: acetic acid (9:2) & (9:1), benzene: acetic acid (9:1), MeOH: acetic acid (9:2) ethanol:acetic acid (9:2) and acetic acid:glycol (2:1) where acetic acid used for catalyst, gave poor to moderate product yields (Table 1, entries 12-18).

We also tried in solvent free condition but failed to get the product. Finally, the reaction was carried out in acetic acid at room temperature which gave trace amount of desired product, but the yields were serendipitously increased at reflux temperature (Table 1, entries 19-20).

Table 1. Optimization of reaction conditions of **3b**

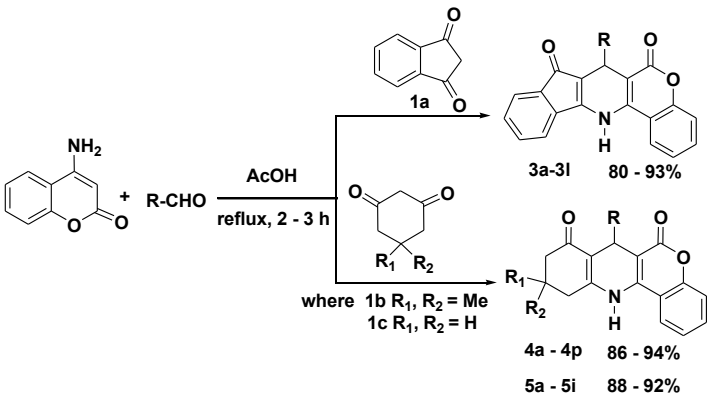
S.No	Solvents	Time (h) & Temp (^{o}C)	Yield (%)
1	solvent free	24, 100	0
2	*n*-BuOH	30-40, 85	0
3	toluene	24, 90	trace[a]
4	benzene	24, 90	trace[a]
5	1,4-dioxane	24, 90	trace[a]
6	MeCN	30-40, 85	10[a]
7	THF	30-40, 85	15[a]
8	DMSO	30-40, 100	17[a]
9	MeOH	30-40, 85	16[a]
10	EtOH	30-40, 85	15[a]
11	DMF	30-40, 100	14[a]
12	benzene:AcOH(9:1)	24, 90	8[a]
13	toluene:AcOH(9:1)	24, 90	6[a]
14	toluene:AcOH(9:2)	24, 90	10[a]
15	MeOH:AcOH(9:1)	24, 90	20[a]
16	MeOH:AcOH(9:2)	24, 90	25[a]
17	EtOH:AcOH(9:2)	30-40, 85	25[a]
18	AcOH:glycol (2:1)	24, 110	35[a]
19	AcOH	24, rt	6
20	**AcOH**	**2-3, 110**	**>90**

[a]reaction was carried out at rt and indicated temperature.

For the verification of generality of the optimal condition, different diones like indanone, dimedone and 1,3-cyclohexadione and substituted aromatic aldehydes like *o*-methoxybezaldehyde, 3,4,5-trimethoxybezaldehye, 2-nitrobenzaldehyde, 2,3-dimethoxybenzaldehydes, naphthaldehyde, cinnamaldehyes and hetero-aromatic aldehydes like thiophene, furfuraldehyde were applied under identical reaction conditions to provide the desired coumarin fused indenodihydropyridines and chromeno[3,4-*b*]quinoline products (Table 2, entries 1–37). In the case of hetero-aromatic aldehydes (furfuraldehyde and thiophene) we got good yields (Table 2, entries 12, 24, 27, 34 & 36). However, nitrogen containing hetero-aromatic aldehydes, aliphatic aldehydes and ortho-methoxynaphthaldehydes (Table 2, entries 38-41) were failed to give the desired product which might be due to proton (acetic acid)-nitrogen interacting and steric hindrance in ortho-methoxynaphthaldehydes.

A pure product was obtained by recrystallization in EtOH or DMSO from the crude product in all the reactions. All products were confirmed by their spectral analysis (IR, ^{1}H- and ^{13}C-NMR, and ESI-HRMS)

and others compared with reported data in the literature.[16] For example, *7-phenyl-7,13-dihydro-5-oxa-13-aza-indeno[2,1-b]phenanthrene-6,8-dione* **3a**, the IR spectral peaks at 3439, 1692 cm^{-1} observed due to NH and carbonyl groups respectively. The ^1H NMR spectrum contained peak at δ 4.86 ppm (s, 1H) indicated for C-4 attached dihyropyridine ring proton and δ 10.41 ppm (s, br, D_2O exchangeable, 1H) indicated for N*H* of dihyropyridine ring proton. The ^{13}C NMR spectrum gave peaks at δ 191.1 ppm for the characteristic carbonyl carbon of indanone, δ 163.9 ppm for the characteristic carbonyl carbon of cyclic ester and δ 35.2 ppm for C-4 dihyropyridine ring carbon. Further, HRMS-ESI showed the molecular ion peak at 400.0900 [$M^{+\cdot}$+Na] for the compound **3a**. *10,10-Dimethyl-7–phenyl-7,10,11,12-tetrahydro-9H-chromeno[4,3-b]quinoline-6,8-dione* **4a**, the IR spectral peaks at 3307, 1681 cm^{-1} observed due to NH and carbonyl groups respectively. The ^1H NMR spectrum contained peak at δ 4.95 ppm (s, 1H) indicated for C-4 attached DHP's ring proton and δ 9.68 ppm (s, br, D_2O exchangeable, 1H) indicated for N*H* of dihydropyridine ring proton. The ^{13}C NMR spectrum gave peaks at δ 195.0 ppm for the characteristic carbonyl carbon of indanone, δ 161.7 ppm for the characteristic carbonyl carbon of cyclic ester, δ 34.8 ppm for C-4 dihyropyridine ring carbon and δ 29.5 & 26.9 ppm for two methyl carbons. Further, HRMS-ESI showed the molecular ion peak at 394.1386 [$M^{+\cdot}$+Na] for the compound. Similarly, other derivatives **3b-3l, 4b-4p & 5a-5i** were confirmed on their spectral analysis (experimental section). The structure of one of the representative compounds such *as* 7-(thiophen-2-yl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione **(3l)** and 10,10-dimethyl-7-(4-chlorophenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione **(4b)** was further confirmed unambiguously by single crystal X-ray diffraction analysis and DFT calculations to varify the different kind of interactions and packing.



Scheme 1. Synthesis of coumarin fused dihydropyridine derivatives

Table 2. Derivatives of coumarin fused dihydropyridine compounds

S.No	1,3-Diketone	R	Time & Temp	Product	Yield(%)[a]
1	**1a**	benzaldehyde (**2a)**	2.5 h, 110 ^{o}C	**3a**	92
2	**1a**	p-cholrobenzaldehyde **(2b)**	2.2 h, 110 ^{o}C	**3b**	90
3	**1a**	p-tolualdehyde **(2c)**	2.3 h, 110 ^{o}C	**3c**	93
4	**1a**	4-methoxybenzaldehyde **(2d)**	2.7 h, 110 ^{o}C	**3d**	92
5	**1a**	2-methoxybenzaldehyde **(2e)**	2.9 h, 110 ^{o}C	**3e**	90
6	**1a**	1-naphthaldehyde **(2f)**	2.5 h, 110 ^{o}C	**3f**	90
7	**1a**	4-hydroxybenzaldehyde **(2g)**	2.8 h, 110 ^{o}C	**3g**	93
8	**1a**	3,4-dimethoxybenzaldehyde **(2h)**	2.9 h, 110 ^{o}C	**3h**	90
9	**1a**	3,4,5-trimethoxybenzaldehyde **(2i)**	3.0 h, 110 ^{o}C	**3i**	80
10	**1a**	2-nitrobenzaldehyde **(2j)**	2.7 h, 110 ^{o}C	**3j**	91
11	**1a**	3-nitrobenzaldehyde **(2k)**	2.9 h, 110 ^{o}C	**3k**	87
12	**1a**	thiophene-2-carbaldehyde **(2l)**	2.4 h, 110 ^{o}C	**3l**	90
13	**1b**	benzaldehyde **(2a)**	2.0 h, 110 ^{o}C	**4a**	90
14	**1b**	p-cholrobenzaldehyde **(2b)**	2.1 h, 110 ^{o}C	**4b**	94
15	**1b**	p-tolualdehyde **(2c)**	2.3 h, 110 ^{o}C	**4c**	92
16	**1b**	4-methoxybenzaldehyde **(2d)**	2.9 h, 110 ^{o}C	**4d**	89
17	**1b**	2-methoxybenzaldehyde **(2e)**	2.9 h, 110 ^{o}C	**4e**	86
18	**1b**	1-naphthaldehyde **(2f)**	2.5 h, 110 ^{o}C	**4f**	90
19	**1b**	4-hydroxybenzaldehyde **(2g)**	2.8 h, 110 ^{o}C	**4g**	91
20	**1b**	3,4-dimethoxybenzaldehyde **(2h)**	3.0 h, 110 ^{o}C	**4h**	88
21	**1b**	3,4,5-trimethoxybenzaldehyde **(2i)**	3.0 h, 110 ^{o}C	**4i**	86
22	**1b**	2-nitrobenzaldehyde **(2j)**	2.7 h, 110 ^{o}C	**4j**	87
23	**1b**	3-nitrobenzaldehyde **(2k)**	2.8 h, 110 ^{o}C	**4k**	89
24	**1b**	thiophene-2-carbaldehyde **(2l)**	2.4 h, 110 ^{o}C	**4l**	90
25	**1b**	2-nitrobenzaldehyde **(2m)**	2.7 h, 110 ^{o}C	**4m**	90
26	**1b**	2-hydroxybenzaldehyde **(2n)**	2.9 h, 110 ^{o}C	**4n**	92
27	**1b**	furan-2-carbaldehyde **(2o)**	2.6 h, 110 ^{o}C	**4o**	91
28	**1b**	cinnamaldehyde **(2p)**	3.0 h, 110 ^{o}C	**4p**	91
29	**1c**	benzaldehyde **(2a)**	2.2 h, 110 ^{o}C	**5a**	92
30	**1c**	1-naphthaldehyde **(2f)**	2.3 h, 110 ^{o}C	**5b**	90
31	**1c**	4-hydroxybenzaldehyde **(2g)**	2.8 h, 110 ^{o}C	**5c**	91
32	**1c**	3,4,5-trimethoxybenzaldehyde **(2i)**	3.0 h, 110 ^{o}C	**5d**	89
33	**1c**	3-nitrobenzaldehyde **(2k)**	2.8 h, 110 ^{o}C	**5e**	90
34	**1c**	thiophene-2-carbaldehyde **(2l)**	2.8 h, 110 ^{o}C	**5f**	91
35	**1c**	2-hydroxybenzaldehyde **(2n)**	2.9 h, 110 ^{o}C	**5g**	88
36	**1c**	furan-2-carbaldehyde **(2o)**	2.7 h, 110 ^{o}C	**5h**	90
37	**1c**	cinnamaldehyde **(2p)**	3.0 h, 110 ^{o}C	**5i**	91
38	**1a, 1b, 1c**	2-methoxy-1-naphthaldehyde **(2q)**	30-40 h, rt-110 ^{o}C	**---**[b]	0
39	**1a, 1b, 1c**	1H-pyrrole-2-carbaldehyde **(2r)**	30-40 h, rt-110 ^{o}C	**---**[b]	0
40	**1a, 1b, 1c**	nicotinaldehyde **(2s)**	30-40 h, rt-110 ^{o}C	**---**[b]	0
41	**1a, 1b, 1c**	MeCHO **(2t)**	24 h, rt-110 ^{o}C	**---**[b]	0

[a] Isolated yield of the DHP's. [b] No product formation even increase in reaction time.

Comparison of Experimental and Computational Structures

To evaluate the stereochemical quality of the X-ray structures, the optimized structures of the compounds are generated using density functional theory (DFT). The full unconstrained geometry optimizations are carried out with the B3LYP/6-311++G(d,p) hybrid DFT method using the GAUSSIAN 98 suite of programs.[21] A combination of Becke's three-parameter hybrid exchange functional,[22] as implemented in GAUSSIAN 98,[23] and the Lee-Yang-Parr correlation functional[24] gives the B3LYP functional. The most attractive DFT method - B3LYP was generally found capable of generating reliable geometries of the large systems containing several aromatic rings.[25,26]

The X-ray and computational structures of the compound containing sulphur are given in Figure 2. The estimated energies showed that the DFT structure is more stable by about 39.72 kcal/mol than the experimental one. The major structural distinction is the different spatial orientation of the S-containing aromatic ring with respect to the remainder of the molecule (Figure 2). A close inspection of the structural parameters given in Table 5 illustrates that the structural difference is not obvious by only considering the bond lengths and the interatomic angles. However, values of several critical dihedral angles, such as C25-C24-C11-C12, C25-C24-C11-C7, S28-C24-C11-C7 and S28-C24-C11-C12 (Table 5), rationalize the structural deviations of these two structures.

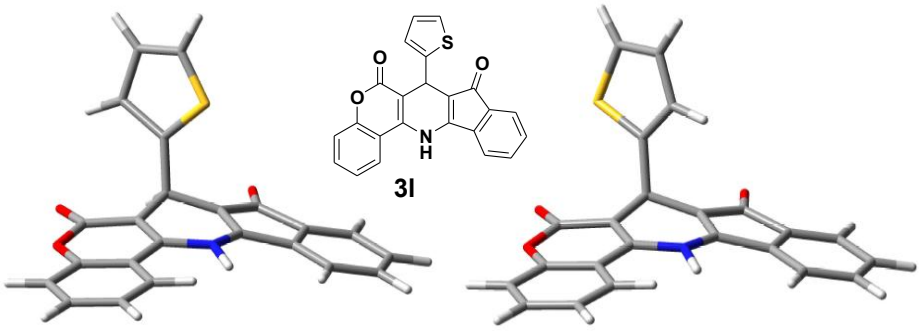


Figure 2. Experimental X-ray (left) and Computational - B3LYP/6-311++G(d,p) (right) 3D models of 7-(Thiophen-2-yl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione **(3l)**

The X-ray and computational structures of the compound containing chlorine are given in Figure 3. The evaluated energies demonstrate that the experimental structure is energetically less favorable by about 204.57kcal/mol than the DFT structure. The bonding distances in the DFT 3D model are in general larger than the experimental ones (Table 6). The major structural distinction is the different spatial orientation of one of the two methyl groups relative to the rest of the molecule (Figure 3). A close inspection of the structural parameters given in Table 6 illustrates that the reported values of several critical dihedral angles rationalize the structural deviations between these two structures.

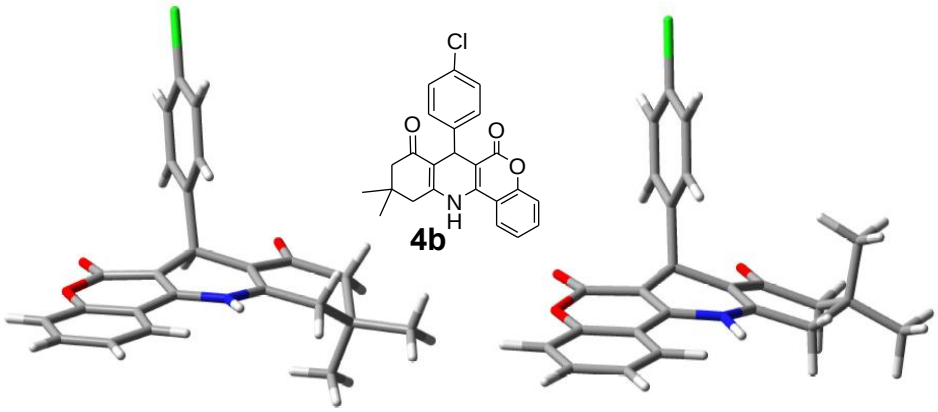


Figure 3. Experimental X-ray (left) and Computational - B3LYP/6-311++G(d,p) (right) 3D models of 10,10-Dimethyl-7-(4-chlorophenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (**4b**)

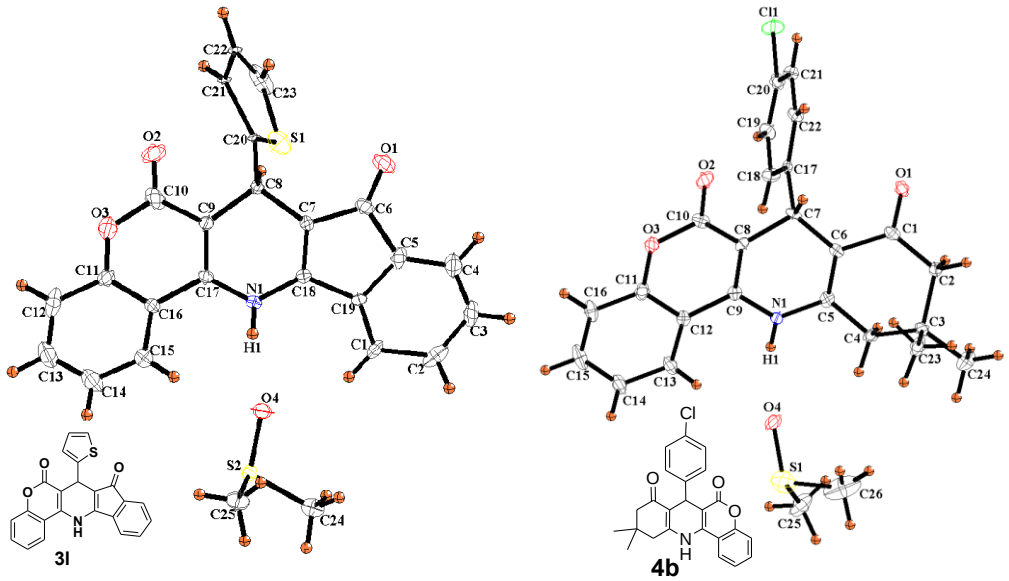


Figure 4. ORTEP diagrams of 7-(Thiophen-2-yl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (**3l**) and 10,10-Dimethyl-7-(4-chlorophenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]-quinoline-6,8-dione (**4b**)

Description of crystal structure:

Compounds **3l** and **4b** crystallize with one solvent molecule of DMSO in asymmetric unit (Figure 4). The crystal packing of **3l** shows that two organic molecules are hydrogen bonded with two molecules of DMSO *via* strong N1-H1···O4, 1.959(20) Å; and weak S2···O1, 3.304(48) Å non-covalent interactions, while in **4b**, one molecule strongly interacted with one molecule of DMSO through N1-H1···O4, 2.050(13) Å hydrogen bond interactions (Figure 5).

Table 3. Selected hydrogen-bond parameters

D-H···A	d(D-H)	d(H-A)	d(D-A)	<(DHA)>
Figure 3 **(3l)**				
N1-H1···O4	0.860	1.959(20)	2.807	168.4
Figure 3 **(4b)**				
N1-H1···O4	0.861	2.050(13)	2.891	165.5

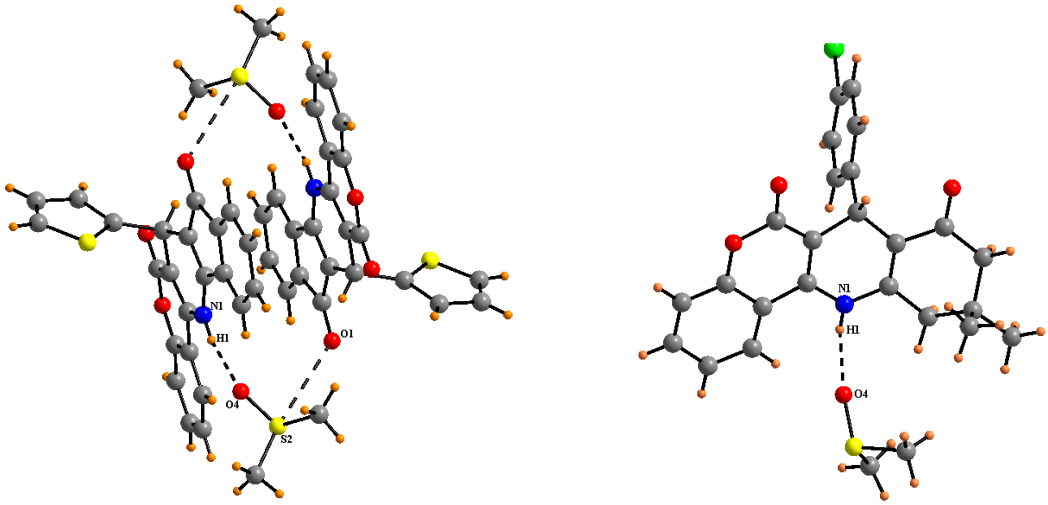
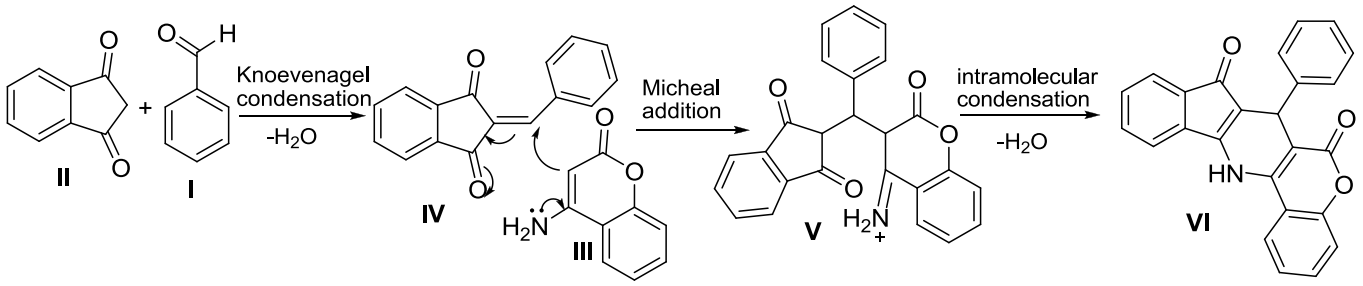


Figure 5. Intramolecular hydrogen-bonding between solvent and molecule of **3l and 4b**

The possible mechanism is given in Scheme 2. Initially, the condensation of aromatic aldehyde (**I**) with 1,3-diketone (**II**) gave Knoevenagel product, benzylidenecyclohexane-1,3-dione (**IV**), which may act as Michael acceptor. Then, intermediate **IV** reacts with 4-aminocoumarin (**III**) to provide reactive intermediate (**V**), which undergoes intramolecular ring closure followed by dehydration to give the desired coumarin fused indenodihydropyridines or chromeno [4,3-*b*]quinoline derivatives (**VI**).



Scheme 2. Plausible mechanism

CONCLUSION

In conclusion, we have demonstrated a simple and highly efficient method for the synthesis of coumarin fused DHP's in a one-pot, three components reaction protocol. The current environmentally benign procedure is a near absolute green protocol as follows: (i) it does not require the any use of catalysts and purification steps such as column chromatography; (ii) it requires less time to obtain the products; (iii) it incorporates the reactants into the final product to a maximum possible extent without any side products. We also reported XRD study and calculated DFT 3D models of computational studies of products **3l** and **4b** for the molecular structure, stability and different interactions in the crystal packing.

EXPERIMENTAL

General Methods: Commercially available reagents were used without further purification unless mentioned. All reactions were monitored by TLC using pre-coated silica gel aluminum plates. Visualization of TLC plates was accomplished with UV lamp or in iodine chamber. Melting points were recorded on perfit apparatus and are uncorrected. IR spectra of the compounds were expressed as wave numbers (cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively. ^{1}H NMR spectra were recorded in DMSO-d_6 and it self an internal standard. Chemical shifts of ^{1}H NMR spectra were given in parts per million and the coupling constant *J* was measured in Hz. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet). Mass spectra were recorded by HRMS-ESI. The X-ray data collection were performed on a Bruker Kappa Apex four circle-CCD diffractometer using graphite monochromated MoK_{α} radiation (λ = 0.71070 Å) at 100 K. Images were created in the crystal lattice with DIAMOND software.

General Procedure *(a) Synthesis of indenodihydropyridine:* A mixture of a selected aldehyde (0.8 mmol), 4-aminocoumarin (0.8 mmol), and indanone (0.8 mmol) was suspended in 6 mL acetic acid. The suspension was slowly dissolved and converted into a yellow solution upon heating at 110 ^{o}C. After 1.2 h, a bright orange precipitate started to form. After 2-3 h of heating the reaction mixture is cooled to room temperature and the orange precipitate is filtered off. Then, it was washed with 6 mL of EtOH followed by 3 mL Et_2O. Pure products were obtained in 80-94% yields after crystallization in EtOH or DMSO.

(b) Synthesis of 4-aminocoumarins: A mixture of well powdered 4-hydroxycoumarin (1.07 g, 0.066 mol) and ammonium acetate (7.87 g, 0.1 mol) was melted in an oil bath (max. 130 ºC). Liquid mixture was stirred for 3 h and was left to cool to ambient temperature. After cooling, water was added and the crude product was isolated as yellow crystals by simple filtration. Further purification was done by dissolving the crystals in EtOH followed by water addition gave the precipitate, filtered and dried under vacuum.

7-Phenyl-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (3a):

Orange colour solid. Yield: 92%. Mp 330-332 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3439 (NH str), 2942 (aromatic C-H str), 1692 (C=O str), 1628, 1503 (aromatic, C=C str), 1402, 1128. ^{1}H-NMR (DMSO-*d*$_6$, 500 M Hz) δ (ppm): 10.41 (s, br, D_2O exchangeable, 1H), 8.53 (d, *J*=8.0 Hz, 1H), 8.09 (d, *J*=6.5 Hz, 1H), 7.99 (m, 1H), 7.68 (d, *J*=8.0 Hz, 1H), 7.51 (t, *J*=8.0 Hz, 2H), 7.42 (d, *J*=7.5 Hz, 1H), 7.39 (d, *J*=7.0 Hz, 1H), 7.29 (d, *J*=6.5 Hz, 2H), 7.13 (d, *J*=8.5 Hz, 3H), 4.86 (s, 1H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz) δ (ppm): 191.1, 163.9, 154.1, 151.9, 144.8, 143.0, 138.0, 136.4, 132.5, 132.2, 130.2, 128.2, 127.85, 126.49, 125.41, 123.83, 120.51, 116.80, 116.73, 114.49, 113.39, 109.93, 103.86, 35.23. HRMS-ESI (m/z): [$M^{+\cdot}$+Na] calcd for $C_{25}H_{15}NO_3$: 400.0950; found 400.0900.

7-(4-Chlorophenyl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (3b):

Orange colour solid. Yield: 90%. Mp 325-327 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3439 (NH str), 2977 (aromatic C-H str), 1693 (C=O str), 1623, 1581 (aromatic, C=C str), 1511, 1425, 1161, 1058. ^{1}H-NMR (DMSO-V, 500 MHz) δ (ppm): 10.43 (s, br, D_2O exchangeable, 1H), 8.29 (d, *J*=7.5 Hz, 1H), 8.01 (d, *J*=7.5 Hz, 1H), 7.69 (t, *J*=7.5 Hz, 1H), 7.51 (m, 2H), 7.42 (d, *J*=8.0 Hz, 1H), 7.37 (t, *J*=8.0 Hz, 1H), 7.30 (m, 5H), 4.84 (s, 1H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz) δ (ppm): 191.1, 160.1, 153.7, 151.9, 143.7, 143.3, 136.3, 132.4, 132.2, 132.1, 130.3, 129.8, 128.1, 124.2, 123.6, 120.8, 120.7, 116.9, 113.4, 109.4, 103.4, 34.9. HRMS-ESI (m/z): [$M^{+\cdot}$] calcd for $C_{25}H_{14}NClO_4$: 411.0662; found 411.0652.

7-(p-Tolyl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (3c):

Orange colour solid. Yield: 93%. Mp above 360 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3432 (NH str), 2953 (aromatic C-H str), 1690 (C=O str), 1627, 1503 (aromatic, C=C str), 1401, 1183, 1129, 1003. ^{1}H-NMR (DMSO-*d*$_6$, 500 MHz) δ (ppm): 10.34 (s, br, D_2O exchangeable, 1H), 8.52 (d, *J*=8.0 Hz, 1H), 8.00 (d, *J*=7.0 Hz, 1H), 7.69 (t, *J*=7.5 Hz, 1H), 7.51 (t, *J*=7.5 Hz, 2H), 7.42 (d, *J*=8.0 Hz, 2H), 7.37 (t, *J*=7.5 Hz, 1H), 7.30 (d, *J*=7.0 Hz, 2H),7.17 (d, *J*=7.5 Hz, 1H), 7.03 (d, *J*=7.5 Hz, 1H), 4.85 (s, 1H), 2.20 (s, 3H). ^{13}C NMR (DMSO-*d*$_6$, 125 MHz) δ (ppm): 191.2, 160.2, 153.5, 151.9, 142.9, 141.9, 136.4, 135.6, 132.6, 132.5, 132.2, 132.1, 130.2, 128.7, 127.7, 124.0, 123.5, 116.8, 113.5, 110.0, 104.0, 34.8, 20.5. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{26}H_{17}NO_3$: 414.1106; found 414.1075.

7-(4-Methoxyphenyl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (3d):

Orange colour solid. Yield: 92%. Mp 310-312 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3422 (NH str), 3157, 2957 (aromatic C-H str), 1691 (C=O str), 1627, 1502 (aromatic, C=C str), 1400, 1130, 1004. ^{1}H-NMR (DMSO-*d*$_6$, 500 MHz) δ (ppm): 10.41 (s, br, D_2O exchangeable, 1H), 8.53 (d, *J*=7.5 Hz, 1H), 8.00 (d, *J*= 6.5 Hz, 1H), 7.69 (d, *J*=8.0 Hz, 1H), 7.52 (t, *J*=8.0 Hz, 2H), 7.43 (d, *J*=7.5 Hz, 1H), 7.36 (d, *J*=7.0 Hz, 1H), 7.30 (d, *J*=6.5 Hz, 1H), 7.19 (d, *J*=6.5 Hz, 2H), 6.79 (d, *J*=7.5 Hz, 2H), 4.82 (s, 1H), 3.66 (s, 3H).

^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 191.4, 160.2, 157.9, 153.4, 151.8, 142.7, 137.0, 136.4, 132.4, 132.2, 130.2, 128.9, 124.1, 123.4, 120.8, 120.5, 116.8, 113.6, 113.4, 110.1, 104.2, 54.9, 34.3. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{26}H_{17}NO_4$: 430.1055; found 430.1035.

7-(2-Methoxyphenyl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (3e):
Orange colour solid. Yield: 90%. Mp 332-334 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3427 (NH str), 2954 (aromatic C-H str), 1701 (C=O str), 1655, 1611 (aromatic, C=C str), 1451, 1354, 1100. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 10.35 (s, br, D_2O exchangeable, 1H), 8.53 (d, *J*=7.5 Hz, 1H), 7.98 (d, *J*=6.5 Hz, 1H), 7.67 (d, *J*=8.0 Hz, 1H), 7.51 (t, *J*=8.0 Hz, 2H), 7.41 (d, *J*=7.5 Hz, 1H), 7.35 (t, *J*=7.0 Hz, 1H), 7.24 (d, *J*=6.5 Hz, 1H), 7.20 (d, *J*=6.5 Hz, 1H), 7.11 (d, *J*=6.5 Hz, 1H), 6.90 (d, *J*=7.5 Hz, 1H), 6.82 (d, *J*=6.5 Hz, 1H), 5.10 (s, 1H), 3.64 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 191.4, 160.4, 157.9, 154.5, 152.3, 143.8, 136.9, 133.0, 132.9, 132.4, 132.3, 130.7, 130.4, 128.3, 124.4, 123.7, 120.9, 120.6, 120.6, 117.2, 113.8, 109.7, 103.9, 56.3, 31.7. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{26}H_{17}NO_4$: 430.1055; found 430.1025.

7-(Naphthalen-1-yl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (3f):
Orange solid. Yield: 90%. Mp above 360 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3430 (NH str), 2946 (aromatic C-H str), 1679 (C=O str), 1541 (aromatic, C=C str), 1436, 1342, 1128, 1037. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 10.45 (s, br, D_2O exchangeable, 1H), 8.64 (d, *J*=8.0 Hz, 1H), 8.59 (dd, *J*=8.0, 1.0 Hz, 1H), 8.02 (d, *J*=7.5 Hz, 1H), 7.87 (d, *J*=15.0 Hz, 1H), 7.71 (m, 2H), 7.59 (t, *J*=7.0 Hz, 1H), 7.52 (m, 3H), 7.49 (d, *J*= 8.0 Hz, 1H), 7.34 (m, 3H), 7.71 (d, *J*=7.0 Hz, 1H), 5.66 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 191.4, 160.5, 153.3, 152.3, 143.4, 136.9, 133.3, 132.8, 132.6, 132.5, 131.2, 130.5, 128.4, 127.4, 126.1, 126.0, 125.1, 124.4, 123.9, 120.9, 117.2, 113.8, 111.5, 105.6, 34.2. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{29}H_{17}NO_3$: 450.1106; found 450.1063.

7-(4-Hydroxyphenyl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (3g):
Orange colour solid. Yield: 93%. Mp above 360 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3422, 3410 (NH str), 2951 (aromatic C-H str), 1698 (C=O str), 1635, 1528 (aromatic, C=C str), 1417, 1140, 1031. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 10.37 (s, br, D_2O exchangeable, 1H), 9.24 (s, br, D_2O exchangble, 1H), 8.52 (d, *J*=8.0 Hz, 1H), 7.99 (d, *J*=6.5 Hz, 1H), 7.69 (d, *J*=8.0 Hz, 1H), 7.52 (t, *J*=8.0 Hz, 2H), 7.43 (d, *J*=7.5 Hz, 1H), 7.36 (d, *J*=7.0 Hz, 1H), 7.30 (d, *J*=6.5 Hz, 1H), 7.05 (d, *J*=8.5 Hz, 2H), 6.61 (d, *J*=8.5 Hz, 2H), 4.76 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 191.7, 160.6, 156.4, 153.7, 152.3, 142.9, 136.9, 135.8, 132.9, 132.5, 130.5, 129.2, 124.4, 123.8, 121.1, 120.8, 117.2, 115.3, 113.9, 110.7, 104.7, 34.6. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{25}H_{15}NO_4$: 416.0899; found 416.0817.

7-(3,4-Dimethoxyphenyl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (3h):
Orange colour solid. Yield: 90%. Mp 306-308 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3439 (NH str), 2941 (aromatic C-H str), 1692 (C=O str), 1628, 1503 (aromatic, C=C str), 1403, 1129. ^{1}H-NMR (DMSO-d_6, 500 M Hz) δ (ppm): 10.43 (s, br, D_2O exchangeable, 1H), 8.53 (d, *J*=7.5 Hz, 1H), 8.00 (d, *J*=7.0 Hz, 1H), 7.71 (d, *J*= 8.0 Hz, 1H), 7.54 (t, *J*=7.5 Hz, 2H), 7.44 (d, *J*=8.0 Hz, 1H), 7.38 (t, *J*=7.5 Hz, 1H), 7.32 (d, *J*=7.0 Hz, 1H), 6.94 (m, 1H), 6.79 (d, *J*=8.5 Hz, 1H), 6.70 (dd, *J*=8.5, 2.0 Hz, 1H), 4.83 (s, 1H), 3.69 (s, 3H), 3.65 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 191.4, 160.2, 151.9, 148.3, 147.6, 137.5, 132.2, 130.2, 124.1, 123.5, 120.8, 120.5, 119.6, 116.8, 112.1, 111.8, 55.5, 34.6. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{27}H_{19}NO_5$: 460.1161; found 460.1181.

7-(3,4,5-Trimethoxyphenyl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (3i):
Orange colour solid. Yield: 80%. Mp 346-348 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3423 (NH str), 3134, 2955 (aromatic C-H str), 1692 (C=O str), 1635, 1590 (aromatic, C=C str), 1500, 1455, 1177, 1123. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 10.47 (s, br, D_2O exchangeable, 1H), 8.52 (d, *J*=7.5 Hz, 1H), 7.99 (d, *J*= 7.0 Hz, 1H), 7.70 (t, *J*=7.5 Hz, 1H), 7.53 (t, *J*=7.5 Hz, 1H), 7.44 (d, *J*=8.0 Hz, 1H), 7.38 (t, *J*=8.0 Hz, 2H), 7.32 (d, *J*=7.0 Hz, 1H), 6.54 (s, 2H), 4.85 (s, 1H), 3.67 (s, 6H), 3.58 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 191.3, 160.3, 152.6, 151.9, 140.3, 136.4, 136.3, 132.5, 132.3, 132.2, 130.3, 124.0, 123.6, 120.8, 120.6, 116.8, 113.4, 109.6, 105.3, 103.5, 59.8, 55.8, 35.4. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{28}H_{21}NO_6$: 490.1267; found 490.1235.

7-(2-Nitrophenyl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (3j):
Orange colour solid. Yield: 91%. Mp above 360 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3425 (NH str), 2985 (aromatic C-H str), 1703 (C=O str), 1624, 1522 (aromatic, C=C str), 1479, 1358, 1197, 1033. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 10.44 (s, br, D_2O exchangeable, 1H), 8.55 (d, *J*=8.0 Hz, 1H), 8.05 (d, *J*=7.0 Hz, 1H), 7.86 (d, *J*=8.0 Hz, 1H), 7.70 (t, *J*=7.5 Hz, 1H), 7.57-7.51 (m, 4H), 7.40-7.37 (m, 3H), 7.29 (m, 1H), 5.84 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 190.7, 160.1, 152.0, 148.6, 143.6, 138.8, 136.2, 133.4, 132.5, 132.2, 131.4, 130.5, 127.7, 124.1, 123.9, 123.7, 120.8, 116.9, 113.2, 108.6, 103.5, 30.5. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{25}H_{14}N_2O_5$: 416.0899; found 416.0817.

7-(3-Nitrophenyl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (3k):
Orange colour solid. Yield: 87%. Mp above 360 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3435 (NH str), 2938 (aromatic C-H str), 1691 (C=O str), 1614, 1515 (aromatic, C=C str), 1400, 1347, 1187, 1029. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 10.52 (s, br, D_2O exchangeable, 1H), 8.57 (d, *J*=6.0 Hz, 1H), 8.10 (d, *J*= 6.5 Hz, 1H), 8.05 (m, 2H), 7.81 (d, *J*=8.0 Hz, 1H), 7.73 (m, 1H), 7.56 (d, *J*=6.0 Hz, 1H), 7.45 (d, *J*=7.5

Hz, 1H), 7.41 (m, 2H), 7.34 (m, 2H), 5.10 (s, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 191.0, 160.1, 153.9, 152.1, 147.7, 146.6, 143.7, 136.1, 134.7, 132.5, 132.3, 132.2, 130.4, 129.7, 124.1, 123.7, 122.4, 121.4, 120.9, 120.8, 116.9, 113.3, 108.8, 102.9, 35.5. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{25}H_{14}N_2O_4$: 445.0800; found 445.0790.

7-(Thiophen-2-yl)-7,13-dihydro-5-oxa-13-aza-indeno[2,1-*b*]phenanthrene-6,8-dione (3l):

Orange colour solid. Yield: 90%. Mp 330-332 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3422 (NH str), 2968 (aromatic C-H str), 1690 (C=O str), 1627, 1502 (aromatic, C=C str), 1401, 1181, 1130, 1003. ^{1}H-NMR (DMSO-d_6, 500 M Hz) δ (ppm): 10.58 (s, br, D_2O exchangeable, 1H), 8.50 (d, *J*=8.0 Hz, 1H), 8.00 (d, *J*=7.0 Hz, 1H), 7.71 (t, *J*=8.0 Hz, 1H), 7.53 (t, *J*=7.0 Hz, 2H), 7.40 (d, *J*=8.0 Hz, 1H), 7.37 (d, *J*=7.0 Hz, 2H), 7.27 (d, *J*=7.0 Hz, 1H), 6.89 (m, 2H), 5.19 (d, *J*=2.0 Hz, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 191.1, 160.3, 151.8, 148.5, 132.5, 132.3, 130.5, 127.0, 124.7, 124.5, 124.2, 123.5, 121.1, 120.8, 116.9, 109.1, 103.6, 54.8, 29.6. HRMS-ESI (m/z): [$M^{+\cdot}$] calcd for $C_{23}H_{13}NSO_3$: 383.0616; found 383.0601.

10,10-Dimethyl-7-phenyl-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4a):

Light yellow solid. Yield: 90%. Mp 290-292 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3307 (NH str), 2956 (aromatic C-H str), 1681 (C=O str), 1505 (aromatic, C=C str), 1473, 1356, 1195, 1051. ^{1}H-NMR (DMSO-d_6, 500 M Hz) δ (ppm): 9.68 (s, br, D_2O exchangeable, 1H), 8.30 (d, *J*=8.0 Hz, 1H), 7.62 (t, *J*=8.0 Hz, 1H), 7.42 (t, *J*=8.0 Hz, 1H), 7.36 (d, *J*=7.5 Hz, 1H), 7.24-7.10 (m, 4H), 7.09 (t, *J*=7.0 Hz, 1H), 4.95 (s, 1H), 2.65 (m, 2H), 2.26 (d, *J*=16.0 Hz, 1H), 2.07 (d, *J*=16.0 Hz, 1H), 1.06 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.0, 161.7, 152.4, 150.0, 146.2, 132.3, 128.4, 128.1, 126.6, 124.4, 123.3, 117.3, 113.4, 111.2, 50.5, 34.8, 32.6, 29.5, 26.9. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{24}H_{21}NO_3$: 394.1419; found 394.1406.

10,10-Dimethyl-7-(4-chlorophenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4b):

Light yellow solid. Yield: 94%. Mp 216-218 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3422 (NH str), 2957 (aromatic C-H str), 1705 (C=O str), 1606 (aromatic, C=C str), 1476, 1365, 1195, 1045. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.73 (s, br, D_2O exchangeable, 1H), 8.32 (d, *J*=8.0 Hz, 1H), 7.65 (t, *J*=8.0 Hz, 1H), 7.46 (t, *J*=8.0 Hz, 1H), 7.39 (d, *J*=8.0 Hz, 1H), 7.28-7.24 (m, 4H), 4.96 (s, 1H), 2.66 (d, *J*=8.0 Hz, 1H), 2.10 (d, *J*=8.0 Hz, 1H), 1.08 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.0, 160.6, 152.5, 150.2, 145.1, 142.7, 132.4, 131.2, 130.0, 128.3, 124.4, 123.4, 117.3, 113.3, 110.9, 101.8, 50.4, 34.6, 32.5, 29.4, 26.9. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{24}H_{20}NClO_3$: 428.1029; found 428.1004.

10,10-Dimethyl-7-(p-tolyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione(4c):

Light yellow colour solid. Yield: 92%. Mp 330-332 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3445 (NH str), 3128, 2985 (aromatic C-H str), 1685 (C=O str), 1640, 1593 (aromatic, C=C str), 1505, 1463, 1152, 1093. ^{1}H-NMR (DMSO-d_6, 500 M Hz) δ (ppm): 9.65 (s, br, D_2O exchangeable, 1H), 8.29 (d, *J*=7.5 Hz, 1H), 7.63 (t, *J*=8.0 Hz, 1H), 7.43 (t, *J*=7.5 Hz, 1H), 7.37 (d, *J*=7.5 Hz, 1H), 7.10 (d, *J*=8.0 Hz, 2H), 6.99 (d, *J*=8.0 Hz, 2H), 4.90 (s, 1H), 2.65 (m, 2H), 2.25 (d, *J*=16.0 Hz, 1H), 2.18 (s, 3H), 2.06 (d, *J*=16.0 Hz, 1H), 1.06 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 194.8, 160.3, 151.9, 149.5, 142.9, 141.9, 135.4, 131.9, 128.5, 127.6, 124.0, 122.8, 116.8, 112.9, 110.9, 101.9, 50.1, 33.9, 32.1, 29.2, 26.5, 20.5. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{25}H_{23}NO_3$: 408.1576; found 408.1509.

10,10-Dimethyl-7-(4-methoxyphenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4d):

Light yellow solid. Yield: 89%. Mp 260-262 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3444 (NH str), 2946 (aromatic C-H str), 1656 (C=O str), 1511 (aromatic, C=C str), 1471, 1367, 1192, 1040. ^{1}H-NMR (DMSO-d_6, 500 M Hz) δ (ppm): 9.65 (s, br, D_2O exchangeable, 1H), 8.29 (d, *J*=8.0 Hz, 1H), 7.62 (d, *J*=8.5 Hz, 1H), 7.43 (m, 1H), 7.37 (d, *J*=8.0 Hz, 1H), 7.13 (d, *J*=8.5, 2H), 6.75 (d, *J*=8.5 Hz, 2H), 4.88 (s, 1H), 3.65 (s, 3H), 2.64 (m, 2H), 2.25 (d, *J*=16.0 Hz, 1H), 2.07 (d, *J*=16.0 Hz, 1H), 1.06 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.1, 160.7 (C=O), 158.0, 152.4, 149.8, 142.2, 138.5, 132.3, 129.1, 124.4, 123.3, 117.2, 113.7, 113.4, 111.4, 102.5, 55.3, 50.5, 33.9, 32.6, 29.5, 26.9. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{25}H_{23}NO_4$: 424.1525; found 424.1505.

10,10-Dimethyl-7-(2-methoxyphenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4e):

Light yellow solid. Yield: 86%. Mp 302-304 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3435 (NH str), 3296, 2950 (aromatic C-H str), 1704 (C=O str), 1602 (aromatic, C=C str), 1476, 1358, 1242, 1192, 1016. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.62 (s, br, D_2O exchangeable, 1H), 8.29 (d, *J*=7.0 Hz, 1H), 7.60 (m, 1H), 7.43 (m, 1H), 7.33 (d, *J*=8.5 Hz, 1H), 7.26 (dd, *J*=7.5 Hz, 1.5 Hz, 1H), 7.08 (d, *J*=6.0 Hz, 1H), 6.84 (d, *J*=8.5 Hz, 1H), 6.79 (m, 1H), 5.04 (s, 1H), 3.62 (s, 3H), 2.67 (m, 2H), 2.23 (d, *J*=16.0 Hz, 1H), 1.98 (d, *J*=16.0 Hz, 1H), 1.05 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 194.85, 160.46 (C=O), 158.4, 152.4, 150.4, 142.9, 132.7, 132.1, 132.0, 127.9, 124.3, 123.1, 119.8, 117.1, 113.5, 111.8, 109.6, 100.8, 55.7, 50.6, 33.5, 32.4, 29.7, 26.3. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{25}H_{23}NO_4$: 424.1525; found 424.1501.

10,10-Dimethyl-7-(naphthalen-1-yl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione

(4f):

Light yellow solid. Yield: 90%. Mp 320-322 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3445 (NH str), 2958 (aromatic C-H str), 1677 (C=O str), 1510 (aromatic, C=C str), 1472, 1362, 1194, 1055. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.76 (s, br, D_2O exchangeable, 1H), 8.79 (d, *J*= 8.0 Hz, 1H), 8.36 (d, *J*=8.0 Hz, 1H), 7.81 (d, *J*=8.0 Hz, 1H), 7.68 (d, *J*=8.0 Hz, 1H), 7.61 (d, *J*=7.0 Hz, 1H), 7.56 (d, *J*=8.0 Hz, 1H), 7.49-7.44, (m, 2H), 7.35 (t, *J*=7.0 Hz, 3H), 5.73 (s, 1H), 2.70 (m, 2H), 2.24 (d, *J*=8.0 Hz, 1H), 1.97 (d, *J*=8.0 Hz, 1H) 1.07 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.1, 160.7, 152.2, 149.5, 145.5, 142.2, 133.2, 132.2, 131.2, 128.0, 127.2, 126.9, 126.0, 125.9, 125.9, 125.7, 124.4, 123.3, 117.2, 113.5, 112.9, 103.8, 50.4, 32.5, 29.6, 26.7. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{28}H_{23}NO_3$: 444.1576; found 444.1505.

10,10-Dimethyl-7-(4-hydroxyphenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4g):

Light yellow solid. Yield: 91%. Mp 346-348 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3270 (NH str), 2957 (aromatic C-H str), 1672 (C=O str), 1619 (aromatic, C=C str), 1469, 1366, 1197, 1046. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.62 (s, br, D_2O exchangeable, 1H), 9.12 (s, br, D_2O exchangeable, 1H), 8.27 (d, *J*=8.0 Hz, 1H), 7.61 (d, *J*=7.5 Hz, 1H), 7.44 (d, *J*=8.0 Hz, 1H), 7.37 (d, *J*=8.5 Hz, 1H), 7.01 (d, *J*=8.5 Hz, 2H), 6.57 (d, *J*=8.5 Hz, 2H), 4.84 (s, 1H), 2.63 (m, 2H), 2.24 (d, *J*=16.0 Hz, 1H), 2.08 (d, *J*=16.0 Hz, 1H), 1.06 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.1, 160.7 (C=O), 156.1, 152.3, 149.6, 142.0, 136.9, 132.1, 129.1, 124.3, 123.2, 117.2, 115.1, 113.5, 111.6, 102.7, 50.6, 33.7, 32.5, 29.5, 26.9. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{24}H_{23}NO_4$: 410.1368; found 410.1311.

10,10-Dimethyl-7-(3,4-dimethoxyphenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4h):

Light yellow solid. Yield: 88%. Mp 288-290 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3444 (NH str), 3231, 2947 (aromatic C-H str), 1681 (C=O str), 1609 (aromatic, C=C str), 1402, 1361, 1236, 1171, 1026. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.67 (s, br, D_2O exchangeable, 1H), 8.27 (d, *J*=8.0 Hz, 1H), 7.61 (m, 1H), 7.42 (m, 1H), 7.35 (d, *J*=8.5 Hz, 1H), 6.85 (m, 1H), 6.67 (d, *J*=8.5 Hz, 1H), 6.69 (d, *J*=8.0 Hz, 1H), 4.89 (s, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.66 (m, 2H), 2.11 (d, *J*=16.0 Hz, 1H), 1.91 (d, *J*=16.0 Hz, 1H), 1.07 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.2, 160.5 (C=O), 152.4, 149.9, 148.5, 147.7, 142.2, 138.8, 132.2, 124.4, 123.3, 119.9, 117.2, 113.5, 112.3, 111.9, 111.2, 102.4, 55.7, 55.7, 50.5, 34.0, 32.5, 29.5, 26.8. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{26}H_{25}NO_5$: 454.1630; found 454.1611.

10,10-Dimethyl-7-(3,4,5-trimethoxyphenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-

6,8-dione (4i):

Light yellow solid. Yield: 86%. Mp 300-302 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3436 (NH str), 3227, 2940 (aromatic C-H str), 1705 (C=O str), 1622 (aromatic, C=C str), 1474, 1359, 1122, 1013. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.73 (s, br, D_2O exchangeable, 1H), 8.27 (d, *J*=8.0 Hz, 1H), 7.63 (t, *J*=8.0 Hz, 1H), 7.43 (t, *J*=8.0 Hz, 1H), 7.37 (d, *J*=7.5 Hz, 1H), 6.52 (s, 2H), 4.92 (s, 1H), 3.67 (s, 6H), 3.57 (s, 3H), 2.69 (d, *J*=5.0 Hz, 2H), 2.28 (d, *J*=16.0 Hz, 1H), 2.10 (d, *J*=16.0 Hz, 1H), 1.09 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.1, 160.8 (C=O), 152.8, 152.3, 150.4, 142.2, 141.6, 136.5, 132.3, 124.4, 123.3, 117.2, 113.4, 110.7, 105.4, 102.2, 60.2, 56.1, 50.5, 34.7, 32.5, 29.6, 26.8. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{27}H_{27}NO_6$: 484.1736; found 484.1712.

10,10-Dimethyl-7-(2-nitrophenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4j):

Yellow colour solid. Yield: 87%. Mp 260-262 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3439 (NH str), 2942 (aromatic C-H str), 1693 (C=O str), 1622, 1510 (aromatic, C=C str), 1475, 1363, 1120, 1031. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.69 (s, br, D_2O exchangeable, 1H), 8.32 (d, *J*=8.0 Hz, 1H), 7.79 (d, *J*=8.0 Hz, 1H), 7.65 (t, *J*=7.5 Hz, 1H), 7.53 (t, *J*=8.0 Hz, 1H), 7.45 (t, *J*=8.0 Hz, 2H), 7.35 (m, 2H), 5.83 (s, 1H), 2.62 (m, 2H), 2.22 (m, 1H), 2.01 (m, 1H), 1.05 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 190.7, 160.0, 152.0, 148.6, 138.8, 136.2, 133.3, 132.5, 132.2, 130.5, 127.7, 124.1, 123.9, 123.7, 120.8, 116.8, 108.6, 103.5, 35.2, 30.6, 25.9, 21.0. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{24}H_{20}N_2O_5$: 439.1270; found 439.1216.

10,10-Dimethyl-7-(3-nitrophenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4k):

Light yellow solid. Yield: 89%. Mp 282-284 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3424 (NH str), 3125, 2947 (aromatic C-H str), 1657 (C=O str), 1517 (aromatic, C=C str), 1472, 1357, 1187, 1051. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.84 (s, br, D_2O exchangeable, 1H), 8.32 (d, *J*=8.5 Hz, 1H), 8.05 (d, *J*=8.5 Hz, 1H), 7.99 (m, 1H), 7.72 (d, *J*=8.0 Hz, 1H), 7.67 (m, 1H), 7.52 (m, 1H), 7.44 (m, 1H), 7.39 (m, 1H), 5.07 (s, 1H), 2.69 (d, *J*=4.0 Hz, 2H), 2.28 (d, *J*=16.0 Hz, 1H), 2.08 (d, *J*=16.0 Hz, 1H), 1.08 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.2, 160.6 (C=O), 152.5, 150.8, 148.1, 147.9, 135.0, 132.7, 129.9, 124.5, 123.5, 122.6, 121.8, 117.3, 113.2, 110.4, 101.3, 99.9, 50.3, 35.4, 32.6, 29.4, 26.8. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{24}H_{20}N_2O_5$: 439.1270; found 439.1230.

10,10-Dimethyl-7-(thiophen-2-yl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4l):

Light yellow solid. Yield: 90%. Mp 294-296 °C. IR ν_{max} (KBr, cm^{-1}): 3427 (NH str), 2954 (aromatic C-H str), 1708 (C=O str), 1602 (aromatic, C=C str), 1472, 1361, 1192, 1046. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.84 (s, br, D_2O exchangeable, 1H), 8.28 (dd, *J*=8.0, 1.0 Hz, 1H), 7.64 (d, *J*=7.5 Hz, 1H), 7.43 (m, 2H), 7.22 (dd, *J*=5.0, 1.0 Hz, 1H), 6.83 (dd, *J*=5.0, 3.5 Hz, 1H), 6.78 (d, *J*=3.0 Hz, 1H), 5.28 (s, 1H), 2.65 (m, 2H), 2.30 (d, *J*=16.0 Hz, 1H), 2.17 (d, *J*=16.0 Hz, 1H), 1.08 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 194.9, 160.6 (C=O), 152.38, 150.3, 149.6, 142.5, 132.5, 127.0, 124.5, 124.4, 124.0, 123.3, 117.3, 113.3, 110.7, 101.5, 50.4, 32.5, 29.5, 29.4, 26.9. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{22}H_{19}NSO_3$: 400.0983; found 400.0913.

10,10-Dimethyl-7-(4-nitrophenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4m):

Yellow colour solid. Yield: 90%. Mp 318-320 °C. IR ν_{max} (KBr, cm^{-1}): 3419 (NH str), 2957 (aromatic C-H str), 1689 (C=O str), 1641, 1514 (aromatic, C=C str), 1472, 1352, 1151, 1053. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.80 (s, br, D_2O exchangeable, 1H), 8.32 (d, *J*=8.0 Hz, 1H), 8.09 (d, *J*=9.0 Hz, 2H), 7.64 (t, *J*=7.5 Hz, 1H), 7.51 (d, *J*=9.0 Hz, 2H), 7.45-7.37 (m, 3H), 5.06 (s, 1H), 2.67 (m, 2H), 2.26 (m, 1H), 2.10 (m, 1H), 1.07 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 194.6, 160.1, 153.0, 152.1, 150.2, 145.9, 142.7, 132.2, 129.1, 124.1, 123.2, 123.1, 116.9, 112.8, 109.9, 100.7, 49.9, 35.2, 32.1, 28.9, 26.6. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{24}H_{20}N_2O_5$: 439.1270; found 439.1210.

10,10-Dimethyl-7-(2-hydroxyphenyl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4n):

Light yellow solid. Yield: 92%. Mp 308-310 °C. IR ν_{max} (KBr, cm^{-1}): 3427 (NH str), 2954 (aromatic C-H str), 1665 (C=O str), 1603 (aromatic, C=C str), 1477, 1367, 1199, 1050. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.75 (s, br, D_2O exchangeable, 1H), 9.20 (s, br, D_2O exchangeable, 1H), 8.32 (d, *J*=8.0 Hz, 1H), 7.64 (t, *J*=7.0 Hz, 1H), 7.45 (t, *J*=8.0 Hz, 1H), 7.38 (d, *J*=8.0 Hz, 1H), 7.05 (dd, *J*=7.0, 1.5 Hz, 1H), 6.95 (m, 1H), 6.67 (m, 2H), 5.02 (s, 1H), 2.63 (m, 2H), 2.29 (d, *J*=16.0 Hz, 1H), 2.09 (d, *J*=16.0 Hz, 1H), 1.07 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 196.3, 160.8 (C=O), 155.0, 152.3, 151.3, 143.0, 132.2, 132.1, 130.6, 127.7, 124.3, 123.2, 119.4, 117.2, 116.9, 113.4, 110.3, 101.5, 50.3, 32.4, 31.2, 29.5, 26.6. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{24}H_{21}NO_4$: 410.1368; found 410.1314.

10,10-Dimethyl-7-(furan-2-yl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4o):

Greay colour solid. Yield: 91%. Mp 308-310 °C. IR ν_{max} (KBr, cm^{-1}): 3431 (NH), 2942 (aromatic C-H str), 1711 (C=O str), 1603 (aromatic, C=C str), 1469, 1363, 1150, 1025. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.78 (s, br, D_2O exchangeable, 1H), 8.29 (d, *J*=8.0 Hz, 1H), 7.65 (m, 1H), 7.44-7.37 (m, 3H), 6.26 (dd, *J*=3.0, 2.0 Hz, 1H), 6.00 (d, *J*=3.0 Hz, 1H), 5.13 (s, 1H), 2.63 (m, 2H), 2.28 (d, *J*=8.0 Hz, 1H), 2.15

(d, *J*=8.0 Hz, 1 Hz), 1.08 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 194.5, 160.0, 156.4, 151.9, 150.4, 142.6, 141.3, 132.1, 124.0, 122.8, 116.9, 112.9, 110.4, 107.8, 105.1, 50.0, 32.1, 29.0, 27.9, 26.3. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{22}H_{19}NO_4$: 384.1212; found 384.1180.

10,10-Dimethyl-7-((*E*)-styryl)-7,10,11,12-tetrahydro-9*H*-chromeno[4,3-*b*]quinoline-6,8-dione (4p):
Light yellow solid. Yield: 91%. Mp 202-204 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3431 (NH str), 2956 (aromatic C-H str), 1681 (C=O str), 1509 (aromatic, C=C str), 1473, 1371, 1196, 1054. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.64 (s, br, D_2O exchangeable, 1H), 8.27 (d, *J*=7.0 Hz, 1H), 7.65 (m, 1H), 7.44 (dd, *J*=12, 7.5 Hz, 2H), 7.29-7.22 (m, 4H), 7.17 (d, *J*=7.0 Hz, 1H), 6.22 (m, 2H), 4.60 (d, *J*=5.5 Hz, 1H), 2.62 (m, 2H), 2.26 (m, 2H), 1.08 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.2, 160.8 (C=O), 152.5, 150.6, 143.1, 137.1, 132.3, 131.4, 129.3, 128.9, 127.6, 126.4, 124.3, 123.2, 117.3, 113.5, 109.4, 100.2, 50.5, 32.6, 31.5, 29.3, 27.2. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{26}H_{23}NO_3$: 420.1576; found 420.1521.

7-Phenyl-8,9,10,12-tetrahydro-7*H*-chromeno[4,3-*b*]quinoline-6,8-dione (5a):
Yellow colour solid. Yield: 92%. Mp 324-326 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3435 (NH str), 2938 (aromatic C-H str), 1703 (C=O str), 1634, 1508 (aromatic, C=C str), 1467, 1363, 1174, 1032. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.74 (s, br, D_2O exchangeable, 1H), 8.31 (d, *J*=8.0 Hz, 1H), 7.63 (m, 1H), 7.43 (t, *J*= 8.0 Hz, 1H), 7.37 (d, *J*=8.0 Hz, 1H), 7.24-7.18 (m, 4H), 7.09 (t, *J*=7.0 Hz, 1H), 5.00 (s, 1H), 2.84 (m, 1H), 2.71 (m, 1H), 2.30 (m, 2H), 2.00 (m, 1H), 1.90 (m, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 194.9, 160.3, 152.0, 151.6, 145.9, 142.0, 131.9, 128.0, 127.6, 126.1, 123.9, 122.9, 116.8, 113.0, 111.8, 101.7, 36.6, 34.1, 26.3, 20.7. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{22}H_{17}NO_3$: 366.1106; found 366.1086.

7-(Naphthalen-1-yl)-8,9,10,12-tetrahydro-7*H*-chromeno[4,3-*b*]quinoline-6,8-dione (5b):
White solid. Yield: 90%. Mp 328-330 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3433 (NH str), 2950 (aromatic C-H str), 1707 (C=O str), 1602 (aromatic, C=C str), 1470, 1359, 1176, 1029. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.84 (s, br, D_2O exchangeable, 1H), 8.82 (d, *J*=9.0 Hz, 1H), 8.38 (d, *J*=8.0 Hz, 1H), 7.81 (d, *J*=8.0 Hz, 1H), 7.69 (d, *J*=7.0 Hz, 1H), 7.63 (t, *J*=7.0 Hz, 1H), 7.57 (t, *J*=8.0 Hz, 1H), 7.47 (dd, *J*=13.0, 7.5 Hz, 2H), 7.35 (dd, *J*=4.5, 11.0 Hz, 2H), 5.76 (s, 1H), 2.86 (m, 1H), 2.74 (m, 1H), 2.25 (dd, *J*=11.0, 5.0 Hz, 1H), 2.16 (m, 1H), 1.98 (m, 1H), 1.85 (m, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.0, 160.3, 151.8, 151.1, 141.7, 132.7, 131.8, 130.7, 127.6, 126.8, 126.5, 125.7, 125.6, 125.3, 123.9, 122.9, 116.8, 113.8, 113.1, 103.5, 36.6, 29.6, 26.5, 20.6. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{26}H_{19}NO_3$: 416.1263; found 416.1210.

7-(4-Hydroxyphenyl)-8,9,10,12-tetrahydro-7*H*-chromeno[4,3-*b*]quinoline-6,8-dione (5c):

Yellow colour solid. Yield: 91%. Mp 338-340 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3442 (NH str), 2930 (aromatic C-H str), 1672 (C=O str), 1630, 1511 (aromatic, C=C str), 1469, 1366, 1178, 1037. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.66 (s, br, D_2O exchangeable, 1H), 9.14 (s, br, D_2O exchangeable, 1H), 8.28 (d, *J*= 8.0 Hz, 1H), 7.58 (t, *J*=8.5 Hz, 1H), 7.40 (d, *J*=8.0 Hz, 1H), 7.34 (d, *J*=8.0 Hz, 1H), 7.02 (d, *J*=8.5 Hz, 2H), 6.59 (d, *J*=8.5 Hz, 2H), 4.89 (s, 1H), 2.81 (m, 1H), 2.68 (m, 1H), 2.28 (m, 2H), 1.99 (m, 1H), 1.91 (m, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 194.9, 160.4, 155.7, 151.9, 151.2, 141.6, 136.6, 131.7, 128.6, 123.8, 122.8, 116.7, 114.7, 113.0, 112.2, 102.2, 36.7, 33.0, 26.3, 20.7. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{22}H_{17}NO_4$: 382.1055; found 382.1011.

7-(3,4,5-Trimethoxyphenyl)-8,9,10,12-tetrahydro-7*H*-chromeno[4,3-*b*]quinoline-6,8-dione (5d):

Yellow colour solid. Yield: 89%. Mp 290-292 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3406 (NH str), 2934 (aromatic C-H str), 1669 (C=O str), 1635, 1508 (aromatic, C=C str), 1414, 1366, 1183, 1042. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.78 (s, br, D_2O exchangeable, 1H), 8.28 (d, *J*=8.0 Hz, 1H), 7.62 (t, *J*=8.0 Hz, 1H), 7.42 (t, *J*=8.0 Hz, 1H), 7.37 (d, *J*=8.0 Hz, 1H), 6.51 (s, 2H), 4.99 (s, 1H), 3.67 (s, 6H), 3.57 (s, 3H), 2.89 (m, 1H), 2.72 (m, 1H), 2.32 (m, 2H), 2.04 (m, 1H), 1.94 (m, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.0, 160.5, 152.5, 151.9, 151.9, 141.8, 141.2, 131.9, 123.9, 122.9, 116.8, 113.0, 111.2, 104.9, 101.6, 59.8, 55.7, 36.7, 33.8, 26.3, 21.0. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{25}H_{23}NO_6$: 456.1423; found 456.1395.

7-(3-Nitrophenyl)-8,9,10,12-tetrahydro-7*H*-chromeno[4,3-*b*]quinoline-6,8-dione (5e):

Yellow colour solid. Yield: 90%. Mp 296-298 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3446 (NH str), 2945 (aromatic C-H str), 1702 (C=O str), 1604, 1517 (aromatic, C=C str), 1470, 1350, 1172, 1025. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.87 (s, br, D_2O exchangeable, 1H), 8.34 (d, *J*=8.0 Hz, 1H), 7.99 (d, *J*=8.0 Hz, 1H), 7.71 (d, *J*=8.0 Hz, 1H), 7.65 (t, *J*=7.5 Hz, 1H), 7.53 (d, *J*=8.0 Hz, 1H), 7.45 (t, *J*=8.5 Hz, 1H), 7.41 (d, *J*=7.0 Hz, 1H), 7.38 (d, *J*=8.0 Hz, 1H), 5.11 (s, 1H), 2.87 (m, 1H), 2.74 (m, 1H), 2.31 (m, 2H), 2.03 (m, 1H), 1.90 (m, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.0, 160.2, 152.3, 152.1, 147.8, 147.5, 142.5, 134.5, 132.2, 129.6, 124.0, 123.1, 122.2, 121.3, 116.9, 112.8, 111.0, 100.8, 36.5, 34.7, 26.3, 20.6. HRMS-ESI (m/z): [M+Na$^{+\cdot}$] calcd for $C_{22}H_{16}N_2O_5$: 411.0957; found 411.0901.

7-(Thiophen-2-yl)-8,9,10,12-tetrahydro-7*H*-chromeno[4,3-*b*]quinoline-6,8-dione (5f):

Light yellow solid. Yield: 91%. Mp 336-338 ^{o}C. IR ν_{max} (KBr, cm^{-1}): 3441 (NH str), 2962 (aromatic C-H str), 1683 (C=O str), 1532 (aromatic, C=C str), 1463, 1356, 1176, 1023. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.90 (s, br, D_2O exchangeable, 1H), 8.30 (d, *J*=8.0 Hz, 1H), 7.64 (d, *J*=8.0 Hz, 1H), 7.43 (q, *J*=

8.0 Hz, 2H), 7.21 (dd, *J*=5.0, 1.0 Hz, 1H), 6.83 (m, 1H), 6.77 (m, 1H), 5.30 (s, 1H), 2.82 (m, 1H), 2.70 (m, 1H), 2.35 (m, 2H), 2.03 (m, 1H), 1.91 (m, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.2, 160.7, 152.3, 152.2, 149.8, 142.3, 132.4, 127.0, 124.4, 123.9, 123.2, 117.2, 113.3, 111.7, 101.5, 37.0, 29.2, 26.7, 21.1. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{20}H_{15}NSO_3$: 372.0670; found 372.0611.

7-(2-Hydroxyphenyl)-8,9,10,12-tetrahydro-7*H*-chromeno[4,3-*b*]quinoline-6,8-dione (5g):

Yellow colour solid. Yield: 88%. Mp above 360 °C. IR ν_{max} (KBr, cm^{-1}): 3452 (NH str), 2934 (aromatic C-H str), 1683 (C=O str), 1629, 1601 (aromatic, C=C str), 1473, 1369, 1183, 1044. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.85 (s, br, D_2O exchangeable, 1H), 9.27 (s, br, D_2O exchangeable, 1H), 8.34 (d, *J*= 8.0 Hz, 1H), 7.64 (t, *J*=7.5 Hz, 1H), 7.45 (t, *J*=7.5 Hz, 1H), 7.38 (d, *J*=8.0 Hz, 1H), 6.96 (m, 2H), 6.67 (m, 2H), 5.04 (s, 1H), 2.78 (m, 1H), 2.69 (m, 1H), 2.33 (m, 2H), 1.99 (m, 1H), 1.90 (m, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 196.7, 160.4, 154.3, 153.1, 151.9, 142.6, 132.1, 131.9, 129.7, 127.4, 123.9, 122.9, 119.3, 116.8, 116.7, 112.9, 111.2, 101.2, 36.3, 30.1, 26.4, 20.5. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{22}H_{17}NO_4$: 382.1055; found 382.1007.

7-(Furan-2-yl)-8,9,10,12-tetrahydro-7*H*-chromeno[4,3-*b*]quinoline-6,8-dione (5h):

Gray colour solid. Yield: 90%. Mp 303-305 °C. IR ν_{max} (KBr, cm^{-1}): 3440 (NH str), 2951 (aromatic C-H str), 1673 (C=O str), 1639, 1510 (aromatic, C=C str), 1472, 1365, 1170, 1047. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.82 (s, br, D_2O exchangeable, 1H), 8.28 (d, *J*=8.0 Hz, 1H), 7.64 (t, *J*=7.5 Hz, 1H), 7.44-7.37 (m, 2H), 6.25 (dd, *J*=3.0, 2.0 Hz, 1H), 5.99 (d, *J*=3.0 Hz, 1H), 5.16 (s, 1H), 2.82 (m, 1H), 2.67 (m, 1H), 2.32 (m, 2H), 2.00 (m, 1H), 1.90 (m, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 194.7, 160.1, 156.5, 152.3, 152.0, 142.6, 141.3, 132.0, 124.0, 122.8, 116.9, 112.9, 110.3, 108.9, 105.2, 99.5, 98.7, 36.6, 27.9, 26.4, 20.7. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{20}H_{15}NO_4$: 356.0899; found 356.0821.

***(E)*-7-Styryl-8,9,10,12-tetrahydro-7*H*-chromeno[4,3-*b*]quinoline-6,8-dione (5i):**

Light yellow solid. Yield: 91%. Mp 164-166 °C. IR ν_{max} (KBr, cm^{-1}): 3448 (NH), 2946 (aromatic C-H str), 1682 (C=O str), 1638, 1508 (aromatic, C=C str), 1473, 1370, 1179, 1035. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ (ppm): 9.70 (s, br, D_2O exchangeable, 1H), 8.28 (d, *J*=8.0 Hz, 1H), 7.65 (d, *J*=8.0 Hz, 1H), 7.43 (m, 2H), 7.31 (d, *J*=7.0 Hz, 2H), 7.25 (m, 1H), 7.16 (d, *J*=7.0 Hz, 1H), 6.18 (t, *J*=7.0 Hz, 2H), 4.62 (d, *J*=5.5 Hz, 1H), 2.80 (m, 1H), 2.71 (m, 1H), 2.37 (m, 2H), 2.00 (m, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 195.0, 160.4, 152.2, 152.1, 142.5, 136.7, 131.9, 130.8, 128.6, 128.4, 127.2, 126.0, 123.9, 122.8, 116.9, 113.1, 109.8, 36.7, 31.0, 26.4, 20.8. HRMS-ESI (m/z): [M+$Na^{+\cdot}$] calcd for $C_{24}H_{19}NO_3$: 392.1263; found 392.1213.

X-Ray crystallography

The X-ray data collection were performed on a Bruker Kappa Apex four circle-CCD diffractometer using graphite monochromated MoK_α radiation (λ = 0.71070 Å) at 100 K. In the reduction of data Lorentz and polarization corrections, empirical absorption corrections were applied.[27] Crystal structures were solved by direct methods. Structure solution, refinement and data output were carried out with the SHELXTL program.[28,29] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions by using a riding model. Images were created in the crystal lattice with DIAMOND software.[30]

Table 4. Crystal data and details of structure refinement

S. No.	3l	4b
Chemical formula	$C_{25}H_{19}NO_4S_2$	$C_{26}H_{26}ClNO_4S$
Formula weight	461.55	484.00
Crystal system	Triclinic	Monoclinic
Space group	P-1	P 21/n
a (Å)	10.448(4)	16.187(6)
b (Å)	10.511(4)	8.223(3)
c (Å)	11.262(4)	17.723(6)
α (0)	88.55(2)	90.00
β (0)	65.14(2)	94.067(18)
γ (0)	76.46(2)	90.00
V(Å3)	1087.3(7)	2353.1(14)
Z	2	4
Temprature	296(2)	296(2)
DCalc (g/cm3)	1.410	1.366
μ(Mo Kα) (cm-1)	0.278	0.285
F(000)	480.0	1016.0
No. of measured reflections	3681	3885
No. of observed reflections	2787	2538
reflections/restraints/parameters	3681/2/279	3885/0/302
Goodness-of-fit	2.379	2.363
Final R indices[$I > 2(I)$ R1	0.1255	0.1471
wR2	0.3367	0.3668

ACKNOWLEDGEMENT

We thank Department of Chemistry, IIT Roorkee through MHRD, New Delhi for financial support.

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