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Camphorsulfonic Acid Catalysed One-Pot Three Component Reaction for the Synthesis of Fused Quinoline and Benzoquinoline Derivatives

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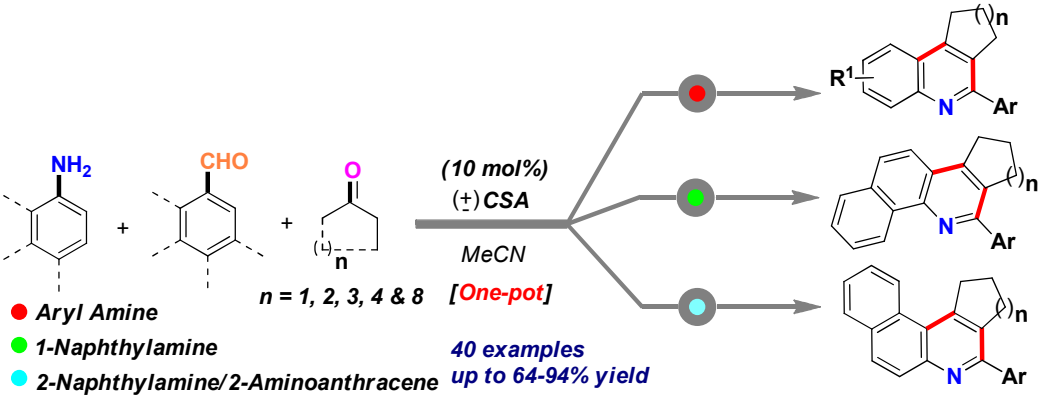


ABSTRACT: A simple and an efficient one-pot three component reaction of arylamines, aromatic aldehydes and cyclic ketones was described for the synthesis of various fused quinoline, benzoquinoline and napthoquinoline derivatives by using camphorsulfonic acid as a catalyst. The exploitation of pregnenolone steroid for benzoquinolines and terephthalaldehyde for bis-benzoquinolines synthesis was achieved with 68-75% yields. The reactivity of aryl amines and the mechanistic study for the formation of benzoquinoline was described precisely. The present protocol offers a great potential for atom-economy under mild condition.

INTRODUCTION

N-heterocyclics are an important class of compounds in biological, medicinal and material chemistry. Of these, quinoline, benzoquinoline derivatives are an interesting class of heterocyclic compounds having a large scope to be investigated by the synthetic chemists because of their natural occurrence and having medicinal value.[1-3] These scaffolds are found to be having several applications in agrochemicals, pharmaceuticals, dyestuffs and functional materials.[4] They have wide range of biological activities including antitubercular,[5a] anticancer,[5b,c] antipsychotics,[5d] antimicrobial,[6a] anti-HIV,[6b] and for the treatment of

neurodegenerative diseases.[7] Marinoquinolines are a class of fused quinolines isolated from the marine bacteria having antibacterial and antifungal activities. Fused quinolines and benzoquinolines core units are found in various alkaloids[8a] and commercial drugs[8b] as shown in Figure 1.

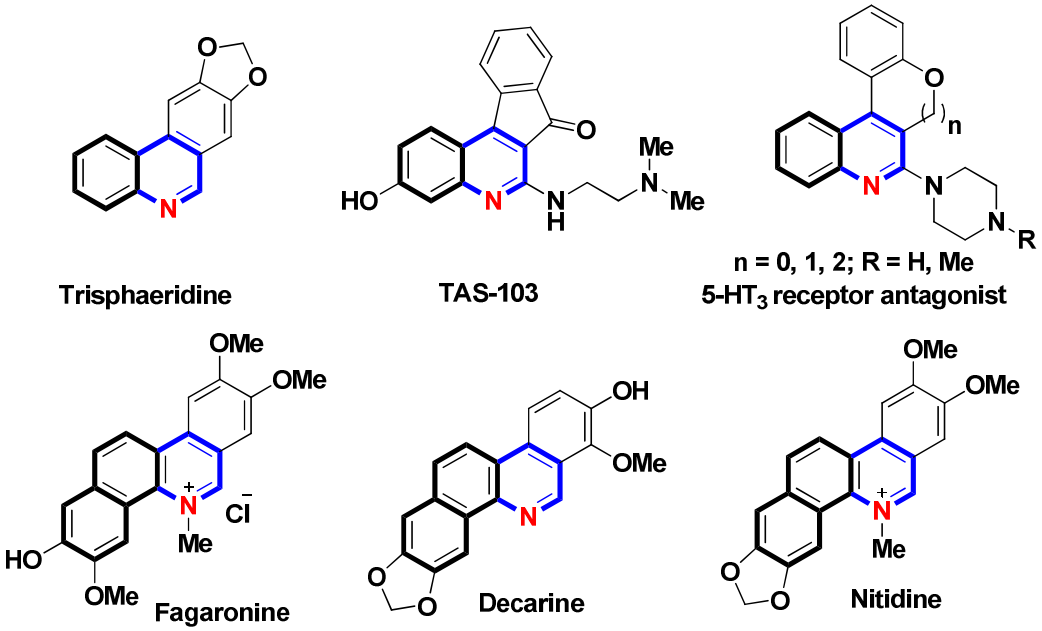


Figure 1. Biologically active Quinoline and Benzoquinoline core units

Quinolines act as effective ligands in cross coupling reaction[9a] and it also plays a crucial role in asymmetric synthesis as a catalyst.[9b,c] In addition they are also used as ligands for preparation of OLED complexes[10a] and with conjugated polymers acting as chemo-sensors of metal ions.[10b,c] Due to its potential biological activity and tremendous applications, chemists have developed various classical methods for the synthesis of quinolines such as Combes reaction,[11] Skraup reaction,[12] Doebner-von Miller,[13] Conrad-Limpach[14] and Knorr synthesis[15] which involve the formation of new *C-C* bond as shown in (Figure 2, 1a) whereas, in Pfitzinger[16] and Friedlander[17] reactions new *C-C* and *C-N* bonds were formed as shown in (Figure 2, 1b). In traditional approach there are new strategies emerged for the synthesis of quinolines through intramolecular cyclisation that involve formation of new *C-N* bond[18] (Figure 2, 1c), *N-C* bond[19] (Figure 2, 1d) and new *C-C* bond[20a] through Cross dehydrogenative coupling,[20b-d] Dual oxidative coupling,[20e] and Oxidative tandem reactions.[20f] The formation of new *C-C* or *C-N*/*N-C* bond is an interesting and challenging one for the synthesis of heterocyclic compounds. Herein, we have focused on the synthesis of fused quinolines derivatives through MCR strategy.

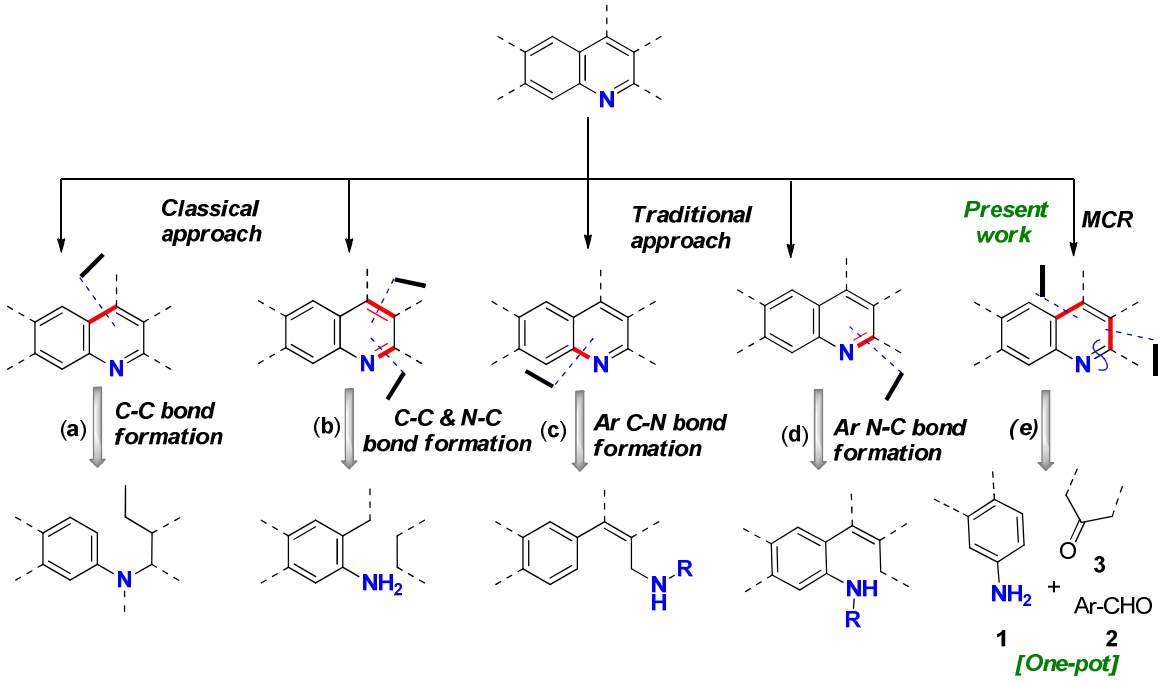
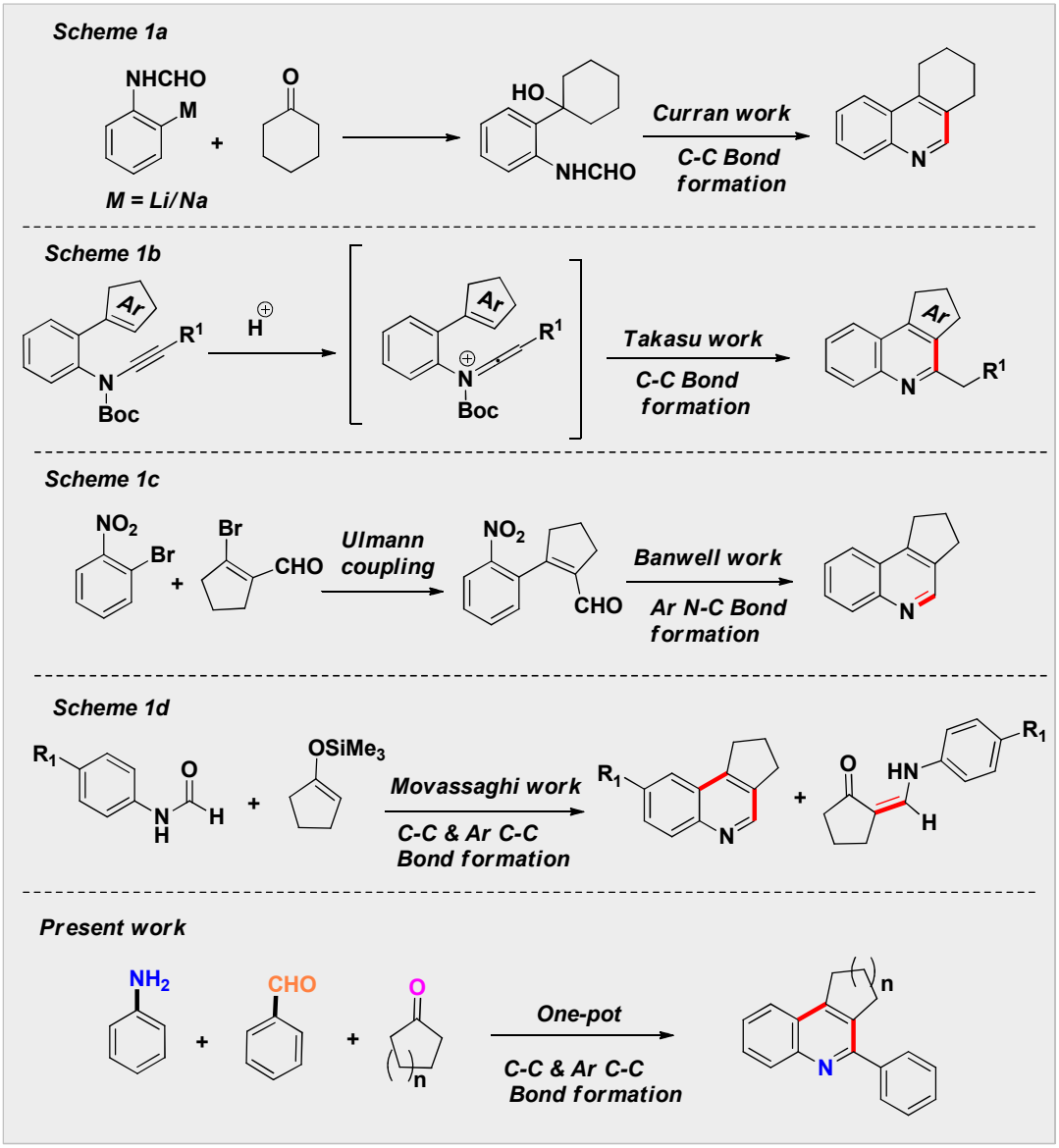


Figure 2. The various approaches of substituted quinoline synthesis with present work

In earlier, Currian *et.al* developed fused quinoline through formation of new *C-C* bond by involving cyclization of in situ generated *o*-vinyl anilides (Scheme 1a).[21a] Takasu *et.al* also explored quinoline through *C-C* bond formation from arene-ynamide cyclization *via* highly reactive keteniminium intermediate (Scheme 1b).[21b] Banwell and co-workers have developed fused quinoline involving a new *N-C* bond through reductive cyclisation of *β*-nitroaryl-enal (Scheme 1c).[21c] Movassaghi group synthesized fused quinoline by condensation of amide with trimethylsilyl enol ether (Scheme 1d).[21d] Wang[22a] *et.al* synthesized Benzo[*f*]quinoline derivatives using MCRs having a drawback, they were unable to synthesize the Quinoline and Benzo[*h*]quinoline from aniline and 1-naphthylamine because of low reactivity of the substrate in presence of iodine catalyst. Apart from these Kozlov[22b] obtained 1,2,3,4-tetrahydrobenzo[*a*]phenanthridine derivative along with byproduct benzo[*a*]acridines through reaction of aldehyde with initially formed enamine from 2-naphthylamine and cyclohexanone. More recently, Stryker[22c] and coworkers developed the synthesis of benzo/napthoquinoline containing steroidal biomarkers[22d,e] through condensation reaction.

Many of these reported methods suffers from drawbacks such as multistep[23a,b] process, difficult in isolation procedures, harsh reaction[23c] conditions, unsatisfactory yields, prolonged reaction time, complex starting materials and also less substrate scope. In this context, the development of new procedures for the synthesis of quinoline derivatives with structural

diversity involving readily available starting materials are challenging efforts to the modern synthetic organic chemists. Thus, we have focused on the development of a simple and an efficient method for the synthesis of fused quinoline and benzoquinoline derivatives through intermolecular cyclization of aryl amines, aromatic aldehydes and cyclic ketones in the presence 10 mol% CSA as shown in Scheme 1.



Scheme 1. The main strategies of fused quinoline synthesis with present work

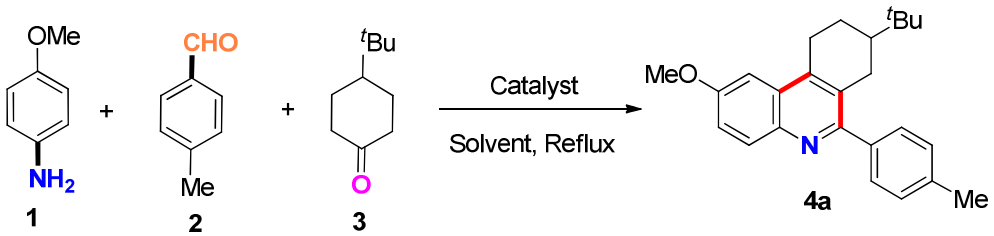
In general, quinolines preferentially undergo electrophilic substitution[24a] at the carbocyclic ring rather than the heterocyclic ring because sp^2-hybridized nitrogen atom decreases the reactivity by interacting with electrophiles. Whereas, Nucleophilic substitution occurs in presence of strong nucleophile, hence it is prerequisite to synthesize substitution on

heterocyclic ring rather than carbocyclic ring. We have focused on to synthesize substituted Quinolines by employing protic acid, Camphorsulfonic acid is a strong sulfur containing protic acid[24b-e] having broad scope in asymmetric synthesis, cyclisation reactions and monoalkylation of anilines which promoted us to employ this catalyst for the synthesis of fused quinoline and benzoquinoline derivatives.

RESULTS AND DISCUSSION

We initially, investigated on optimization study for the synthesis of fused quinoline using *p*-anisidine **1** (1.0 mmol), *p*-tolualdehyde **2** (1.0 mmol) and 4-(*tert*-butyl)cyclohexanone **3** (1.0 mmol) as model substrate under reflux condition and the results are summarized in Table 1. Primarily, when the reaction was carried out in the absence of catalyst proved futile (Table 1, entry 1). Next, the reaction was tested with various lewis acid catalysts. On screening the reaction with $Yb(OTf)_3$ (Table 1, entry 2) in CH_3CN resulted in isolation of the desired product **4a** in 54% yield. The product **4a** was confirmed through IR, ^1H, ^{13}C NMR and HRMS. The other lewis acids $Cu(OTf)_2$, $Zn(OTf)_2$, $In(OTf)_3$, AgOTf, $Bi(OTf)_3$ and $FeCl_3$ gave unsatisfactory yields (Table 1, entries 3-8). Whereas by employing iodine as a catalyst resulted in 54% and 48% yields of product **4a** in THF and CH_3CN respectively (Table 1, entries 9 and 10). Then, we observed on the protic acid catalysts like AcOH, TfOH and L-Proline the reaction were failed to obtain the desired product (Table 1, entries 11-13) but, PTSA resulted with satisfactory yields (Table 1, entry 14). Further for inferior results, the same set of reaction was executed with 10 mol% CSA and the desired product **4a** was isolated in 78% yield. (Table 1, entry 15).

Table 1. Optimization of Reaction Conditions[a]



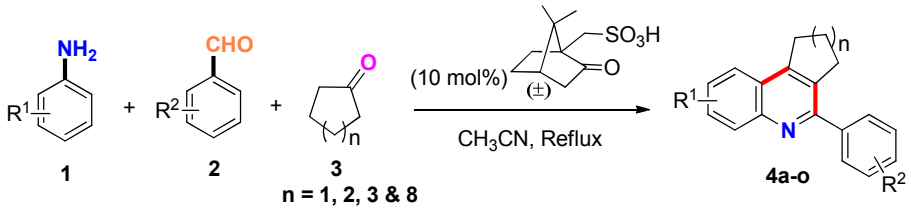
Entry	Catalyst	Mol %	Solvent	Time (h)	Yield **4a** (%)[b]
1	No catalyst	-	CH_3CN	24.0	NR
2	$Yb(OTf)_3$	10	CH_3CN	3.0	54
3	$Cu(OTf)_2$	10	CH_3CN	6.0	42
4	$Zn(OTf)_2$	10	CH_3CN	2.5	64
5	$In(OTf)_3$	10	CH_3CN	2.5	60
6	AgOTf	10	CH_3CN	3.0	62
7	$Bi(OTf)_3$	10	CH_3CN	2.5	36
8	$FeCl_3$	10	CH_3CN	12.0	30
9	Iodine	10	THF	4.0	54
10	Iodine	10	CH_3CN	4.0	48
11	AcOH	1 equiv	-	3.0	NR
12	TfOH	10	CH_3CN	24.0	NR
13	L-Proline	10	CH_3CN	24.0	NR
14	*p*-TSA	10	CH_3CN	6.0	68
15	**(±)-CSA**	**10**	**CH_3CN**	**1.5**	**78**
16	(±)-CSA	20	CH_3CN	1.5	78
17	(±)-CSA	05	CH_3CN	2.0	75
18	(±)-CSA	10	EtOH	2.0	72
19	(±)-CSA	10	MeOH	2.0	68
20	(±)-CSA	10	DMSO	24.0	20
21	(±)-CSA	10	DCE	12.0	35
22	(±)-CSA	10	DMF	24.0	NR
23	(±)-CSA	10	THF	12.0	NR
24	(±)-CSA	10	H_2O	12.0	NR
25	(±)-CSA	10	Toluene	8.0	NR

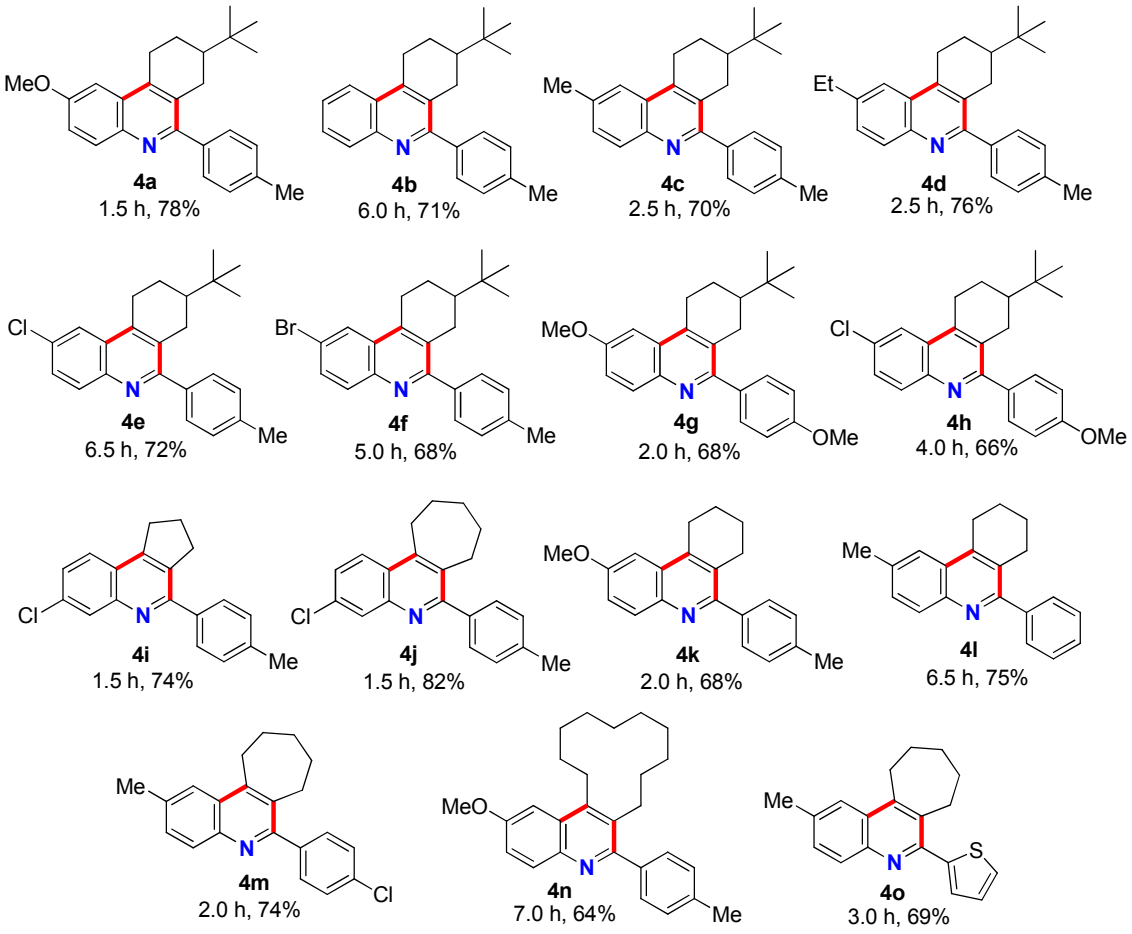
[a]All the reactions were performed using *p*-anisidine (1.0 mmol), *p*-tolualdehyde (1.0 mmol) and 4-(*tert*-butyl)cyclohexanone (1.0 mmol). [b]Isolated yields.

In order to obtain better results, the reaction was also scrutinized with 20 mol% and 5 mol% CSA, but the increment in yield was not observed (Table 1, entries 16 and 17). However, the other solvents such as EtOH, MeOH, DMSO and DCE gave lower yields (Table 1, entries 18-21), whereas DMF, THF, H_2O and toluene failed to give the desired product **4a** (Table 1,

entries 22-25). Thus, it was noted that 10 mol% CSA in CH_3CN under reflux condition is the optimized condition for our present protocol in terms of reaction time and yield.

Table 2. Substrate scope of aniline[a,b]



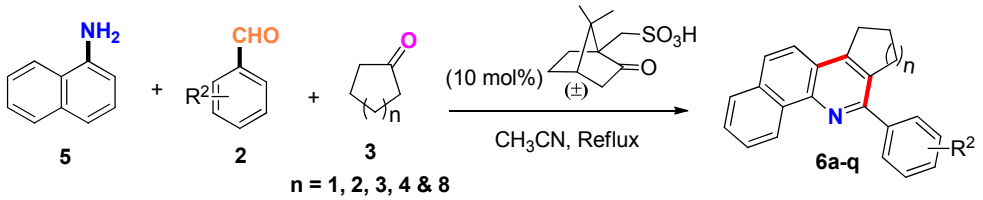


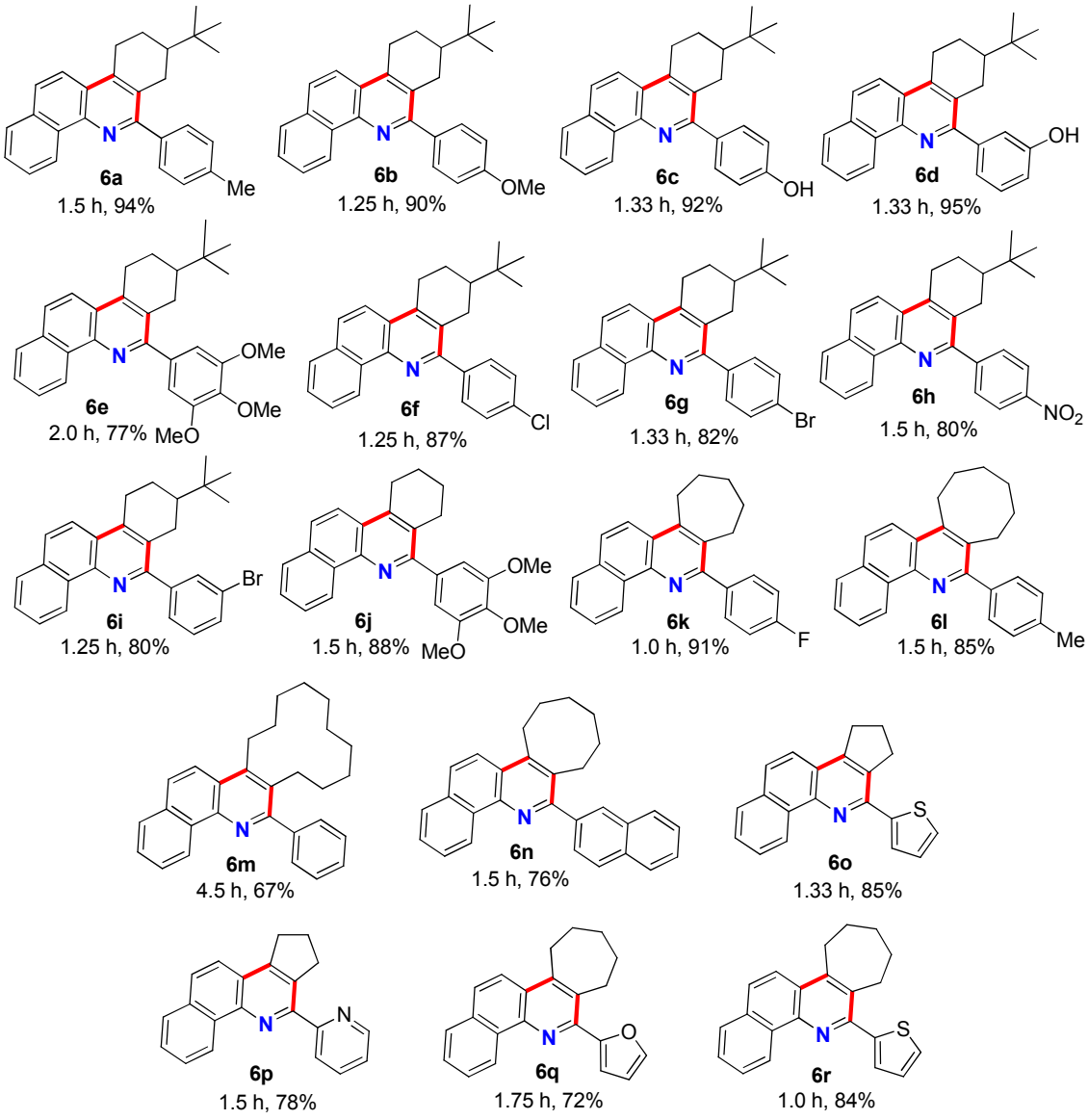
[a]The reactions were carried out using anilines (1.0 mmol), aldehydes (1.0 mmol) and cyclic ketones (1.0 mmol) in CH_3CN. [b]Isolated yields.

With standard optimisation reaction condition, the scope of the reaction was investigated with 4-(*tert*-butyl)cyclohexanone, aromatic aldehydes (4-Me and 4-OMe) and various anilines having *para* substituents on aromatic ring such as -Me, -Et, -Cl, -Br and -OMe which gave the products **4b-h** in 66-78% yield (Table 2). The aniline derivatives such as 4-

NO_2, 2-NO_2, 2-I and 2,4-Me failed to produce desired product which might be due to the strong withdrawing nature and steric crowding at ortho position.

Table 3. Substrate scope of 1-naphthylamine[a,b]

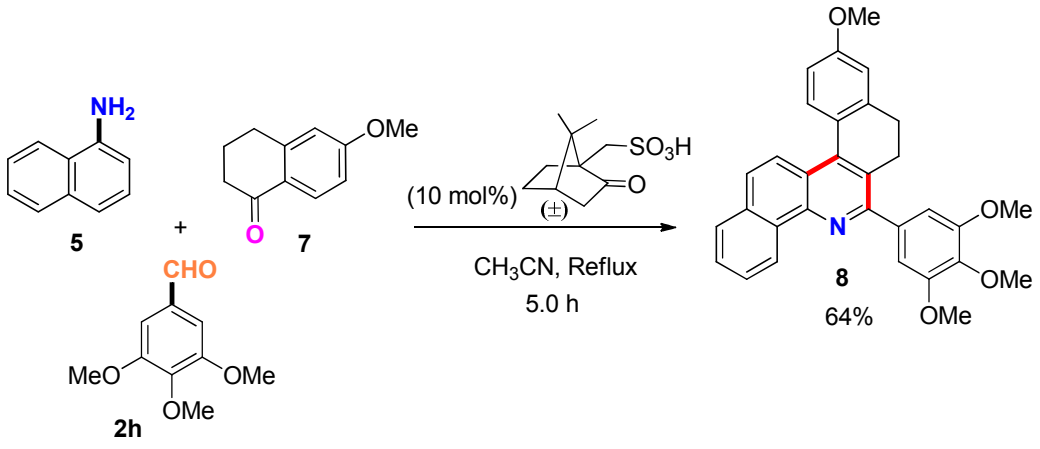




[a]The reactions were carried out using aldehydes (1.0 mmol), cyclic ketones (1.0 mmol) and 1-naphthylamine (1.0 mmol) in CH_3CN. [b]Isolated yields.

On the other hand, the reaction of *m*-chloroaniline, *p*-tolualdehyde and different cyclic ketones like cyclopentanone and cycloheptanone lead to the isolation of products **4i-j** in 74-82% yield. Since the formation of other tautomer was not observed in *meta*-substituted aniline due to steric hindrance on ortho postion, it is to be considered as a regiospecfic reaction. Next, the reaction was extended with various other cyclic ketones namely cyclohexanone, cycloheptanone and cyclododecanone all the reactions proceeded smoothly to produce the products **4k-n**. In addition, the heterocyclic aldehyde, thiophene-2-aldehyde on reaction with *p*-toluidine and cycloheptanone to afford the product **4o** in 69% yield.

All the products were characterized by recording IR, ^{1}H and ^{13}C NMR spectra and HRMS. The structure of the compound **4a** was further confirmed by single-crystal X-ray crystallographic data (see the Supporting Information).

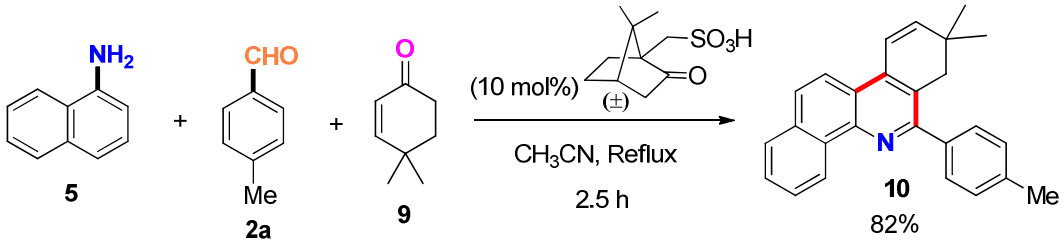


Scheme 2. Reaction of 1-naphthylamine with 6-methoxytetralone

Inspired by the above transformations, we have further explored the generality of the reaction with 1-naphthylamine **5** instead of anilines which produced fused benzo[*h*]quinoline derivatives and the results are summarised in Table 3. When the reaction was carried out with 1-naphthylamine **5** (1.0 mmol), *p*-tolualdehyde **2** (1.0 mmol) and 4-(*tert*-butyl)cyclohexanone **3** (1.0 mmol) under similar reaction condition induced the product **6a** in 94% yield without any column chromatographic separation. Substituted aromatic aldehydes with electron donating and electron withdrawing groups such as 4-OMe, 4-OH, 3-OH, 3,4,5-OMe, 4-Cl, 4-Br, 4-NO_2 and 3-Br underwent reaction with 4-(*tert*-butyl)cyclohexanone to generate the products **6b-i** in 77-95% yields.

The reaction was also extended with various substituted benzaldehydes and cyclic ketones such as cyclohexanone, cycloheptanone, cyclooctanone and cyclododecanone which

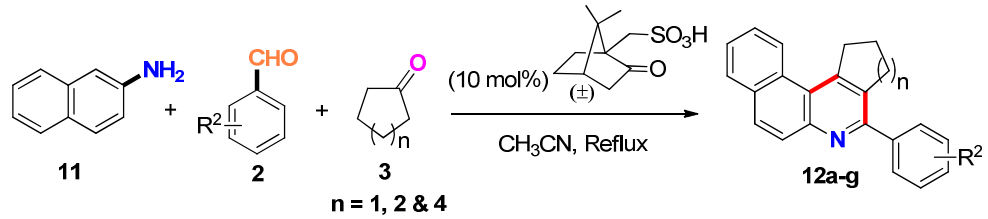
lead to the formation of desired products **6j-m** in 67-91% yields. The reaction with 2-naphthaldehyde and cycloheptanone furnished the product **6n** in 76% yield whereas heteroaromatic aldehydes, thiophene-2-aldehyde and pyridine-2-carbaldehyde on reaction with cyclopentanone gave the products **6o-p** in 78-85% yields while, 2-furfural and thiophene-2-aldehyde on reaction with cycloheptanone deliver the products **6q** and **6r** in 72% and 84% yields respectively.

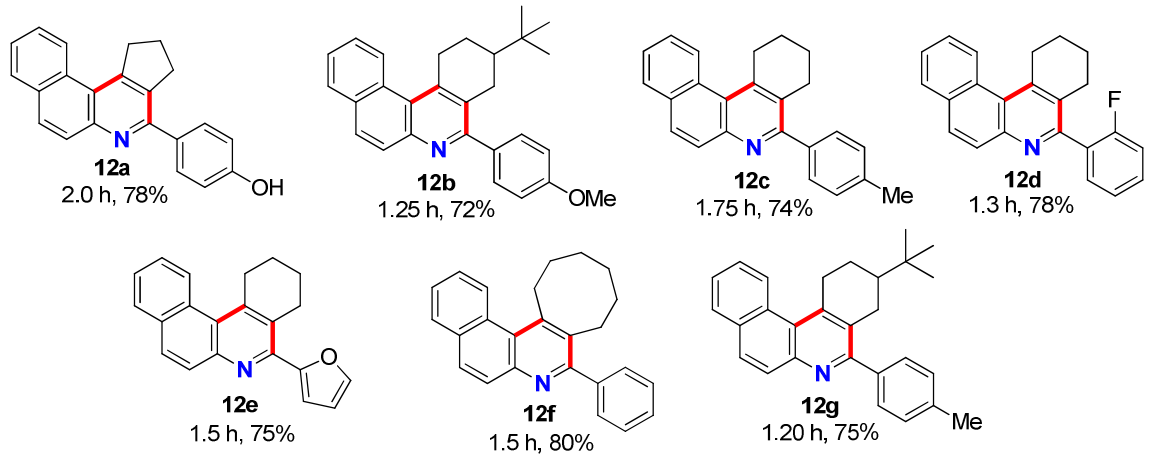


Scheme 3. Reaction of 1-naphthylamine, *p*-tolualdehyde and 4,4-Dimethylcyclohexenone

In addition, we have applied our present methodology for the synthesis of 3-methoxy-14-(3,4,5-trimethoxyphenyl)-5,6-dihydrodibenzo[*c*,*i*]phenanthridine (**8**) by employing 1-naphthylamine (**5**), 3,4,5-trimethoxybenzaldehyde (**2h**) and 6-methoxytetralone (**7**) in the presence of 10 mol% CSA under similar reaction conditions as shown in Scheme 2.

Table 4. Substrate scope of 2-naphthylamine[a,b]



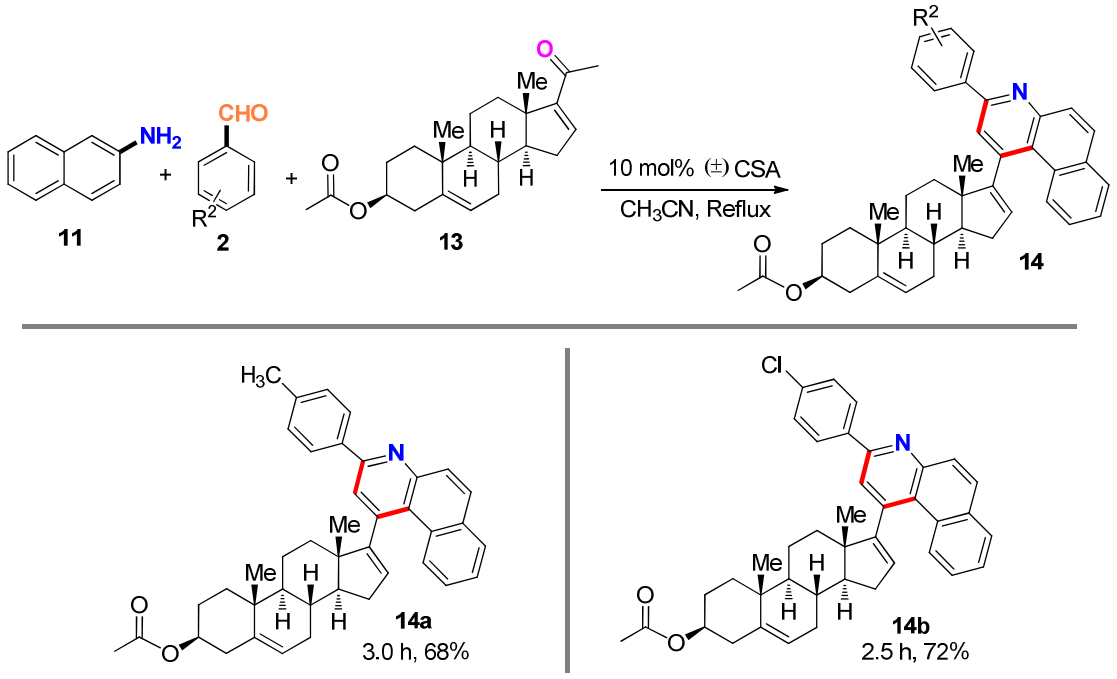


[a]The reactions were performed using aldehydes (1.0 mmol), cyclic ketones (1.0 mmol) and 2-naphthylamine (2.0 mmol) in CH_3CN. [b]Isolated yields.

The reactivity of other α,β-unsaturated cyclic ketone was investigated by performing the reaction with 1-naphthylamine **5**, *p*-tolualdehyde **2a** and 4,4-Dimethyl-2-cyclohexen-1-one **9** in the presence of 10 mol% CSA under reflux condition to give 8,8-dimethyl-6-(*p*-tolyl)-7,8-dihydrobenzo[*c*]phenanthridine **10** in 82 % yield as shown in Scheme 3.

The present protocol was further explored for the synthesis of fused benzoquinoline derivatives using 2-naphthylamine (**11**), with different substituted aromatic aldehydes (**2**) and cyclic ketones (**3**) in the presence of catalytic amount of CSA under identical reaction conditions to offer the corresponding products **12a-g** with 72-80% yields as depicted in Table 4.

Table 5. Reaction of 16-dehydro-pregnenolone acetate with aldehyde and 2-naphthylamine[a,b]

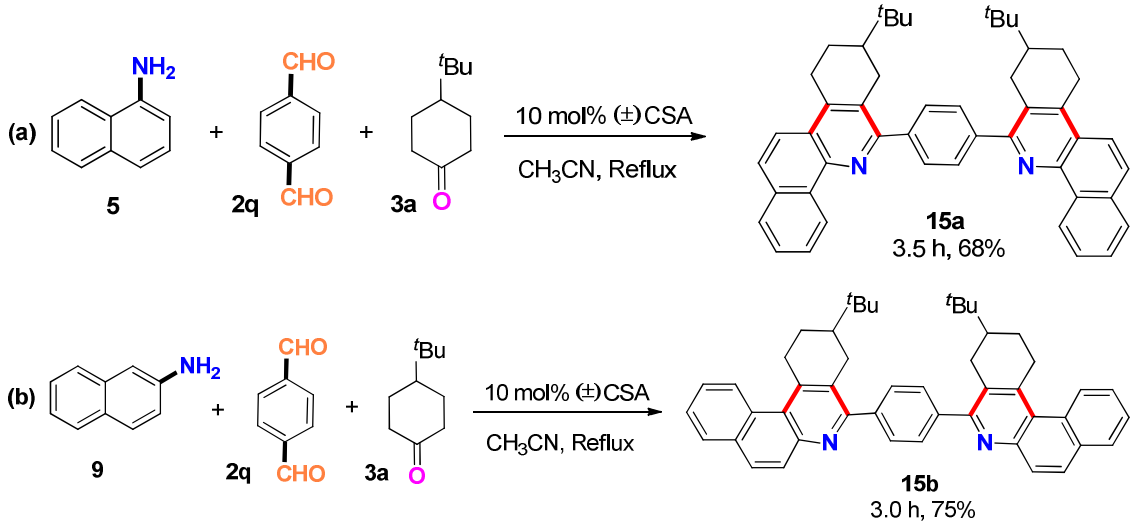


[a]The reactions were performed using aldehyde (1.0 mmol), 16-dehydro-pregnenolone acetate (1.0 mmol) and 2-naphthylamine (2.0 mmol) in CH_3CN. [b]Isolated yields.

Next, we put our forward effort for the synthesis of steroid substituted benzo[*f*]quinoline derivatives from 16-dehydro-pregnenolone acetate (**13**), 2-naphthylamine (**11**) and 4-Me/4-Cl benzaldehydes using 10 mol% CSA under identical reaction condition which offered the desired products **14a-b** in 68 and 72% yields as shown in Table 5.

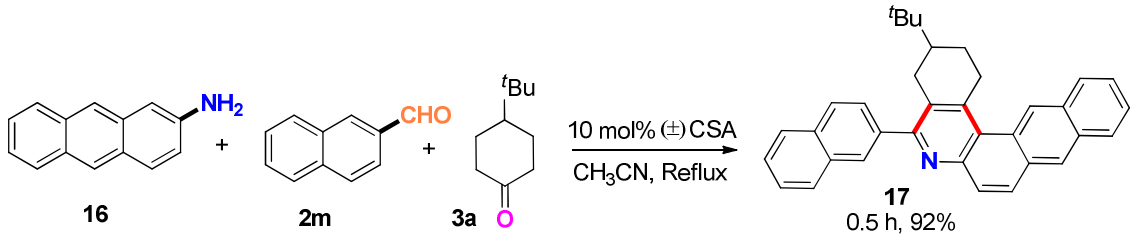
Next, our protocol was well applied for the synthesis of fused bis-benzoquinoline derivatives by using 1-naphthylamine/2-naphthylamine (1.0 mmol), terephthalaldehyde (0.5 mmol) and 4-(*tert*-butyl)cyclohexanone (1.0 mmol) in presence of 10 mol% CSA catalyst under similar

reaction condition and the successful results are shown in Scheme 4 along with their reaction time and yields. Unfortunately, *p*-anisidine failed to give the desired product under identical reaction condition.



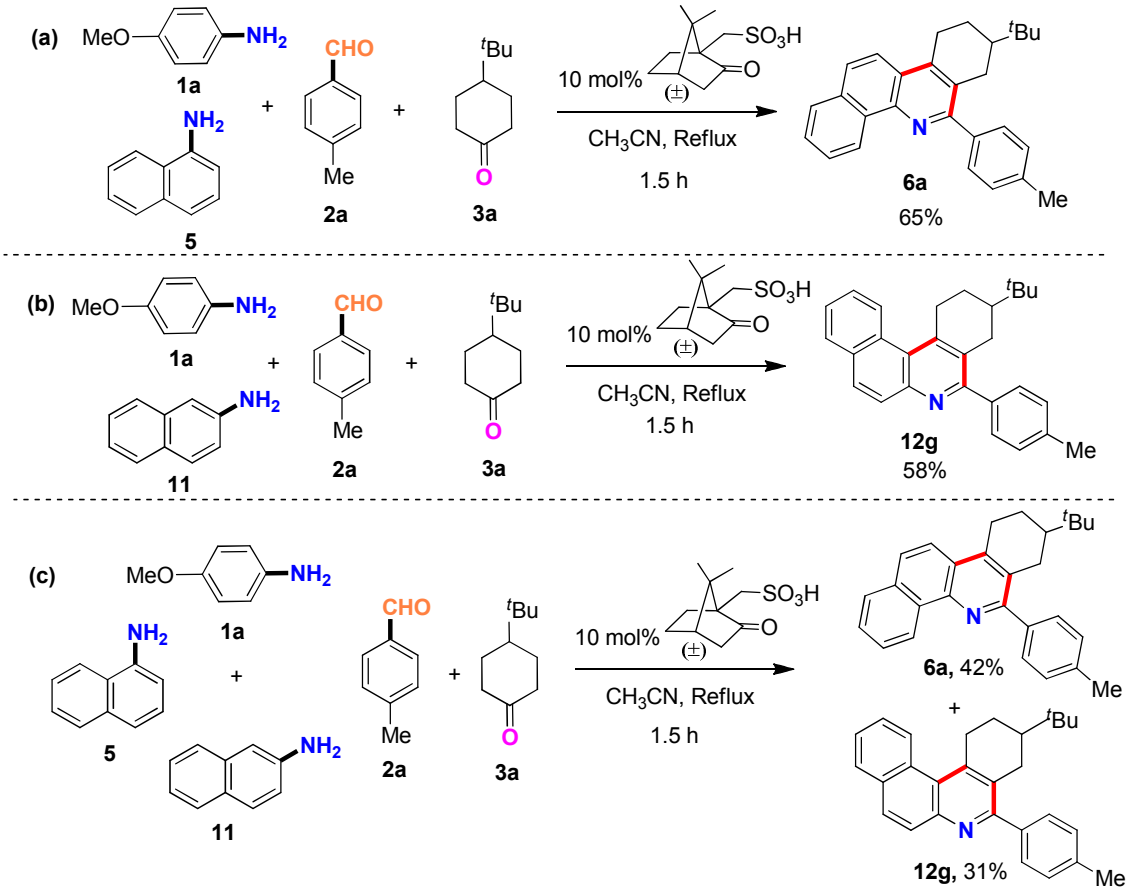
Scheme 4. Reaction scope of Terephthalaldehyde

Finally, 2-Aminoanthracene **16** (1.0 mmol) on reaction with 2-naphthaldehyde **2m** (1.0 mmol) and 4-(*tert*-butyl)cyclohexanone **3a** (1.0 mmol) in presence of 10 mol % CSA under reflux condition gave the product 3-(*tert*-butyl)-5-(naphthalen-2-yl)-1,2,3,4-tetrahydronaphtho[2,3-*a*]phenanthridine **17** as shown in Scheme 5. All the synthesised products were characterized by IR, ^{1}H and ^{13}C NMR spectra and HRMS. In addition, the structure of the compounds **6r, 8, 12e** and **14b** were further confirmed by single-crystal X-ray crystallographic data (see the Supporting Information).



Scheme 5. Reaction scope of 2-Aminoanthracene

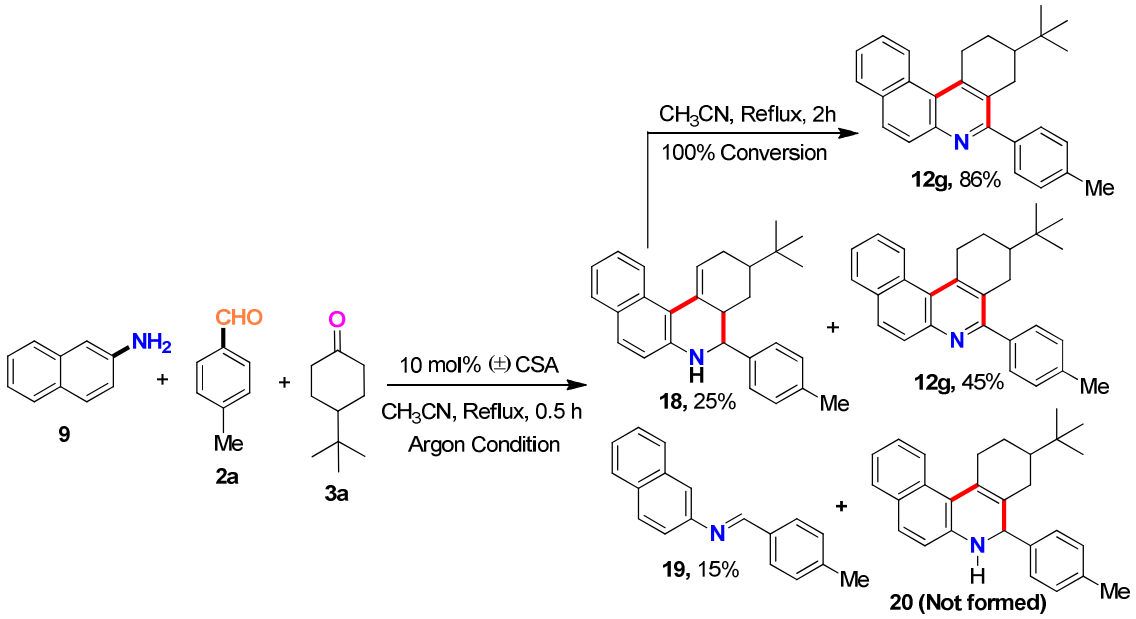
To understand the reactivity of aryl amines, we carried out three sets of reactions. Initially, *p*-anisidine (1.0 mmol), 1-naphthylamine (1.0 mmol), *p*-tolualdehyde (1.0 mmol), and 4-(*tert*-butyl)cyclohexanone (1.0 mmol) under same reaction condition produced single product **6a**. Next, the reaction of *p*-anisidine (1.0 mmol), 2-naphthylamine (1.0 mmol), *p*-tolualdehyde (1.0 mmol) and 4-(*tert*-butyl)cyclohexanone (1.0 mmol) gave only product **12g**.



Scheme 6. The reactivity of arylamines

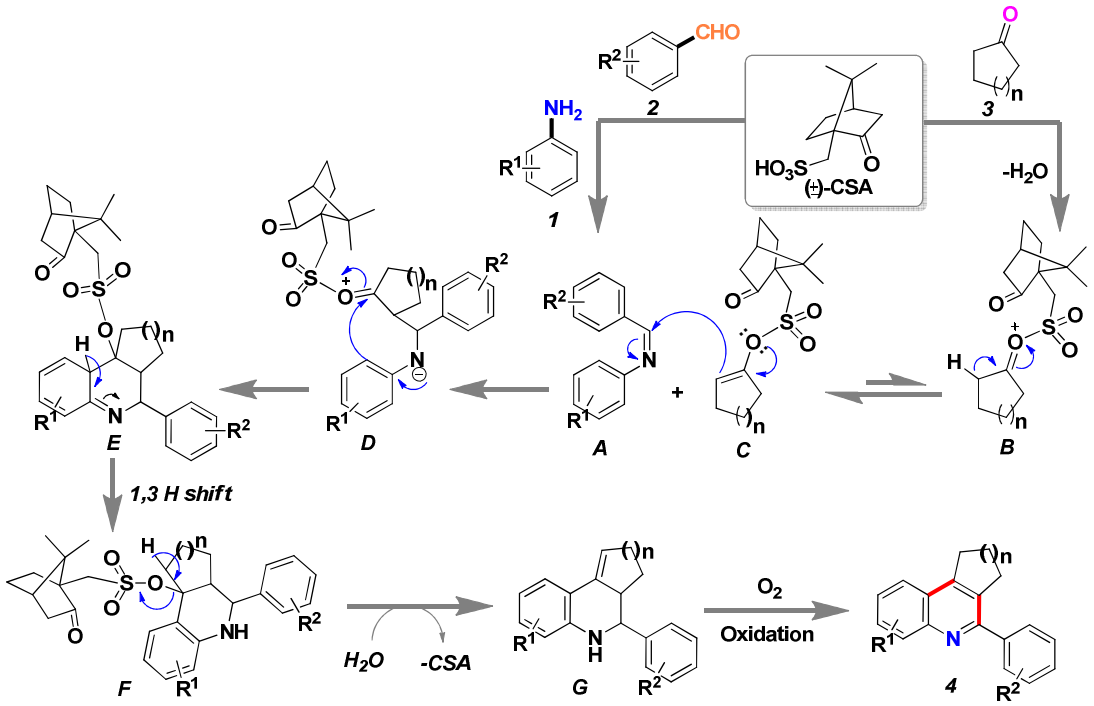
Finally, a mixture of *p*-anisidine (1.0 mmol), 1-naphthylamine (1.0 mmol), 2-naphthylamine (1.0 mmol), *p*-tolualdehyde (1.0 mmol) and 4-(*tert*-butyl)cyclohexanone (1.0 mmol) afforded products **6a** and **12g**. The product **4a** was not observed, due to poor reactivity of *p*-anisidine in presence of 1-naphthylamine and 2-naphthylamine and the results are represented in Scheme 6.

To study the mechanism, we performed one pot three component reaction using 2-naphthylamine, *p*-tolualdehyde and 4-(*tert*-butyl)cyclohexanone in the presence of 10 mol% CSA under reflux condition at argon atmosphere as shown in Scheme 7. As expected, we have observed the formation of **19** in 15% yield, which on readily reacted with 4-(*tert*-butyl)cyclohexanone **3a** to give the corresponding products **18** and **12g** in 25% and 45% yield respectively after 0.5 h. In addition, the product **18** was further refluxed with 2 mL CH_3CN in open atmosphere without any catalyst resulted aromatized product **12g** with 100% conversion in 86% yield in 2 h, where as in room temperature reaction time prolonged up to 24 h to produce compound **12g** with 100% conversion of 84% yield.



Scheme 7. Experiment for mechanistic pathway

From the literature,[22a] the intermediate **20** is expected to be formed but we have not observed such dihydroquinoline. All the compounds are isolated and characterised individually by IR, ^{1}H and ^{13}C NMR spectra and HRMS. In addition, product **18** was confirmed by single crystal XRD (see the Supporting Information).



Scheme 8. Proposed Reaction Mechanism Pathway

The plausible mechanism for the formation of fused quinoline is described as shown in Scheme 8. Initially, the aryl amine **1** reacts with aldehyde **2** to form the imine **A** and the cyclic ketone **3** to form an active species **B** which on tautomerize to most stable enol form **C** in the presence of camphorsulfonic acid. The generated imine **A** further reacted with **C** to form Micheal type addition product **D**, which subsequently undergoes an intramolecular cyclization to give dihydroquinoline **G** which undergoes oxidative aromatization to give the desired product **4**.

CONCLUSION

In summary, we have developed a simple and an efficient method for the synthesis of fused quinoline and benzoquinoline derivatives from readily available starting materials aryl amine, aromatic aldehyde and cyclic ketone through one pot three component reaction using camphor sulphonic acid as a catalyst. The protocol offers several advantages which include commercially available cheap catalyst, less reaction time, mild reaction condition, simple isolation procedure, wide range of substrate scope, eco-friendly with high atom economy in one pot with two new *C*-*C* bond formations. Along with these, we have developed the utility of pregnenolone acetate and terephthalaldehyde for the synthesis of steroid substituted benzo[*f*]quinoline and bis-benzo[*f*]quinoline respectively. To the best of our knowledge, these quinoline and benzoquinoline derivatives were reported first time in the literature using camphor sulphonic acid as a catalyst.

EXPERIMENTAL SECTION

l. General Information and Methods

Melting points were determined on a melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on 400 & 600 MHz and 100 & 150 MHz NMR spectrometer. TMS as internal reference; chemical shifts (δ scale) are reported in parts per million (ppm). ^{1}H NMR Spectra are reported in the order: multiplicity, coupling constant (*J* value) in hertz (Hz) and no. of protons; signals were characterized as s (singlet), d (doublet), t (triplet), m (multiplet) and bs (broad). IR spectra were recorded on IR spectrophotometer. HRMS spectra were recorded using ESI and APCI (TOF) mode. The X-ray crystal structures were determined using a single XRD diffractometer.

II. General Procedure for Synthesis of cycloalkyl fused quinolines 4

Into a dry 25 mL round bottem flask a mixture aniline **1** (1.0 mmol), aromatic aldehyde **2** (1.0 mmol) and cyclic ketone **3** was taken in 5 mL acetonitrile. Camphorsulfonic acid (0.023 g, 0.10 mmol) was added into it and stirring under reflux condition. The progress of the

reaction was monitered by TLC, after completion of the reaction the solvent was removed under reduced pressure and it was extracted with DCM (2 x 25 mL). The organic extract was dried over sodium sulphate and concentrated under reduced pressure. Finally, the residue was purified through silica gel (60-120 mesh) column chromatography with petroleum ether/ethyl acetate (9.5 : 0.5, v/v) to obtain the pure product **4**.

III. General Procedure for Synthesis of cycloalkyl fused benzoquinolines 6, 8, 10 & 12

To a mixture 1-naphthylamine (1.0 mmol), aromatic aldehyde **2** (1.0 mmol) and cyclic ketone **3**, camphorsulfonic acid (0.023 g, 0.10 mmol) 5 mL acetonitrile was added allowed to stir at reflux condition. After completion of the reaction indicated by TLC. The reaction mixture was allowed to cool at room temperature for complete precipitation. Then, the solid precipitate was filtered off through a Büchner funnel, washed with acetonitrile and dried under reduced pressure to obtain the pure products **6**. The similar reaction procedures were followed for the synthesis of products **8, 10** & **12**.

IV. General procedure for synthesis of steroid substituted benzo[*f*]quinoline 14

Into a 25 mL round bottom flask a mixture of aromatic aldehyde **2**, 2-naphthylamine (**11**) and 16-dehydro-pregnenolone acetate (**13**) were taken in 5 mL acetonitrile. Then, camphorsulfonic acid (0.023 g, 0.10 mmol) was added into the above reaction mixture and refluxed for 2.5 to 3.0 h until the completion of the starting materials indicated by TLC. The reaction mixture was allowed to cool at room temperature. The solvent was removed under reduced pressure and extracted with DCM (2 x 25 mL), dried over sodium sulphate and concentrated under reduced pressure. Then, the crude residue was purified through silica gel (60-120) column chromatography with petroleum ether-ethylacetate (9.5 : 0.5, v/v) to get the pure product **14**.

V. General procedure for synthesis of cycloalkyl fused bis-benzoquinolines 15 and 3-(tert-butyl)-5-(naphthalen-2-yl)-1,2,3,4-tetrahydronaphtho[2,3-*a*]phenanthridine 17

To a mixture naphthylamine (1.0 mmol), terephthalaldehyde **2q** (0.5 mmol) and 4-(*tert*-butyl)cyclohexanone **3a** (1.0 mmol) in 3 mL acetonitrile camphorsulfonic acid (0.023 g, 0.10 mmol) was added and allowed to stir at reflux for 1.0-4.5 h. After completion of the reaction indicated by TLC. The reaction mixture was allowed to cool at room temperature to obtain the solid product. Then, the pure solid product **15a-b** were obtained after washing with acetonitrile and dried under reduced pressure. The NMR of products were analysed by disolving in 2-3 drops of CF_3COOH in $CDCl_3$. The similar reaction procedures was followed for the synthesis of 3-(*tert*-butyl)-5-(naphthalen-2-yl)-1,2,3,4-tetrahydronaphtho[2,3-*a*]phenanthridine **17**.

8-(tert-butyl)-2-methoxy-6-(p-tolyl)-7,8,9,10-tetrahydrophenanthridine (4a): Yield 78% (280 mg), white solid, mp 180-181˚C, ^{1}H NMR (600 MHz, $CDCl_3$):δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J*= 7.8 Hz, 2H), 7.31-7.29(m, 1H), 7.27-7.26 (m, 2H), 7.18 (m, 1H), 3.95 (s, 3H), 3.76 (dd, *J* = 17.4, 4.8 Hz, 1H), 2.99 (m, 1H), 2.74 (d, *J* = 16.8 Hz, 1H), 2.53 (t, *J* = 12.6 Hz, 1H), 2.42 (s, 3H), 2.20-2.19 (m, 1H), 1.49-1.44 (m, 1H), 1.40-1.36 (m, 1H), 0.90 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.7, 157.8, 138.4, 137.7, 131.6, 129.4, 129.1, 128.9, 127.7, 120.3, 101.4, 55.7, 44.7, 32.6, 30.5, 27.6, 27.5, 23.9, 21.5; IR (KBr)ν_{max} 3051, 2957, 2867, 1585, 1497, 1068, 1031, 957 cm^{-1}; HRMS (ESI) Calcd For $C_{25}H_{30}NO$ 360.2322 (M + H$^+$); Found 360.2323.

8-(tert-butyl)-6-(p-tolyl)-7,8,9,10-tetrahydrophenanthridine (4b): Yield 71% (233 mg), brown solid, mp 145-146˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 3.48 (dd, *J* = 18.0, 4.2 Hz, 1H), 3.07 (m, 1H), 2.76 (d, *J* = 16.2 Hz, 1H), 2.55 (t, *J* = 12.0 Hz, 1H), 2.43 (s, 3H), 2.23-2.20 (m, 1H), 1.51-1.45 (m, 1H), 1.42-1.37 (m, 1H), 0.91 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.5, 158.3, 157.7, 141.8, 140.7, 133.9, 131.6, 130.3, 129.4, 127.6, 120.2, 113.8, 101.3, 55.7, 44.8, 32.5, 30.6, 27.6, 27.5, 23.9; IR (KBr)ν_{max} 3059, 3029, 2984, 2867, 1683, 1585, 1559, 1110, 1040, 1016 cm^{-1}; HRMS (APCI) Calcd For $C_{24}H_{28}N$ 330.2216(M + H$^+$); Found 330.2205.

8-(tert-butyl)-2-methyl-6-(p-tolyl)-7,8,9,10-tetrahydrophenanthridine (4c): Yield 70% (240 mg), white solid, mp 182-183˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.72 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 3.44 (dd, *J* = 18.0, 4.8 Hz, 1H), 3.02 (m, 1H), 2.74 (d, *J* = 16.2 Hz, 1H), 2.56 (s, 3H), 2.52 (d, *J* = 16.2 Hz, 1H), 2.42 (s, 3H), 2.21-2.18 (m, 1H), 1.47-1.42 (m, 1H), 1.39-1.35 (m, 1H), 0.90 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.8, 143.6, 142.2, 138.0, 137.6, 136.2, 130.8, 129.3, 129.1, 128.9, 126.7, 121.8, 44.7, 32.5, 32.4, 30.4, 27.4, 23.8, 22.2, 21.5; IR (KBr)ν_{max} 3043, 3016, 2941, 2864, 1646, 1585, 1471, 1102, 1010, 922 cm^{-1}; HRMS (APCI) Calcd For $C_{25}H_{30}N$ 344.2373 (M + H$^+$); Found 344.2361.

8-(tert-butyl)-2-ethyl-6-(p-tolyl)-7,8,9,10-tetrahydrophenanthridine (4d): Yield 76% (271 mg), white solid, mp 135-136˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.73 (s, 1H), 7.53-7.51 (m, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 3.45 (dd, *J* = 17.4, 4.8 Hz, 1H), 3.07-3.03 (m, 1H), 2.85 (m, 2H), 2.75 (d, *J* = 16.8 Hz, 1H), 2.54 (t, *J* = 12.0 Hz, 1H), 2.42 (s, 3H), 2.19 (m, 1H), 1.49-1.44 (m, 1H), 1.44-1.39 (m, 1H), 1.35 (t, *J* = 7.8 Hz, 3H), 0.91 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.0, 144.1, 142.4, 142.1, 138.1, 137.9, 129.7, 129.6, 129.1, 129.0, 128.9, 126.8, 120.5, 44.7, 32.6, 32.5, 30.4, 29.5, 27.4, 23.8,

21.5, 15.9; IR (KBr)ν_{max} 3048, 3024, 2964, 2867, 1612, 1585, 1112, 1058, 1016, 932 cm^{-1}; HRMS (ESI) Calcd For $C_{26}H_{32}N$ 358.2530 ($M + H^+$); Found 358.2540.

8-(tert-butyl)-2-chloro-6-(p-tolyl)-7,8,9,10-tetrahydrophenanthridine (4e): Yield 72% (261 mg), white solid, mp 230-231˚C,^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 1.8 Hz, 1H), 7.56 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 3.37 (dd, *J* = 18.0, 5.4 Hz, 1H), 3.02-2.96 (m, 1H), 2.74 (d, *J* = 16.8 Hz, 1H), 2.54 (t, *J* = 16.8 Hz, 1H), 2.42 (s, 3H), 2.21- 2.18 (m, 1H), 1.47-1.42 (m, 1H), 1.39-1.35 (m, 1H), 0.90 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.4, 144.2, 141.4, 138.2, 138.0, 132.0, 131.7, 130.7, 130.2, 129.2, 128.8, 127.6, 121.9, 44.6, 32.5, 30.5, 27.4, 27.3, 23.7, 21.5; IR (KBr)ν_{max} 3042, 2948, 2922, 2863, 1586, 1062, 1011, 942 cm^{-1}; HRMS (ESI) Calcd For $C_{24}H_{27}ClN$ 364.1827 ($M + H^+$); Found 364.1835.

2-bromo-8-(tert-butyl)-6-(p-tolyl)-7,8,9,10-tetrahydrophenanthridine (4f): Yield 68% (276 mg), white solid, mp 237-238˚C,^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.14 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 2H), 3.41 (dd, *J* = 18.0, 4.2 Hz, 1H), 3.03 (m, 1H), 2.75 (d, *J* = 16.8 Hz, 1H), 2.56 (t, *J* = 12.6 Hz, 1H), 2.43 (s, 3H), 2.23-2.20 (m, 1H), 1.51-1.44 (m, 1H), 1.38 (t, *J* = 10.2 Hz, 1H), 0.90 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.0, 143.5, 142.4, 138.6, 136.8, 132.2, 131.2, 130.4, 129.2, 128.9, 128.1, 125.3, 120.7, 44.5, 32.5, 30.4, 27.5, 27.4, 23.6, 21.6; IR (KBr)ν_{max} 3043, 2947, 2896, 2864, 1584, 1182, 1072, 1016, 976 cm^{-1}; HRMS (ESI) Calcd For $C_{24}H_{27}BrN$ 408.1322 ($M + H^+$); Found 408.1336.

8-(tert-butyl)-2-methoxy-6-(4-methoxyphenyl)-7,8,9,10-tetrahydrophenanthridine (4g): Yield 68% (255 mg), brown solid, mp 145-146˚C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 9.2 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.29 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.17 (d, *J* = 2.4 Hz, 1H), 6.92 (d, *J* = 6.0 Hz, 2H), 3.95 (s, 3H), 3.87 (s, 3H), 3.35 (dd, *J* = 17.6, 5.2 Hz, 1H), 3.03-2.94 (m, 1H), 2.75 (d, *J* = 16.8 Hz, 1H), 2.50 (t, *J* = 11.6 Hz, 1H), 2.22-2.04 (m, 1H), 1.51-1.39 (m, 1H), 1.38-1.34 (m, 1H), 0.91 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 158.3, 157.7, 141.8, 140.7, 133.9, 131.6, 130.3, 129.4, 127.6, 120.2, 113.8, 101.3, 55.7, 55.5, 44.8, 32.5, 30.6, 27.6, 27.5, 23.9; IR (KBr)ν_{max} 3042, 2955, 2867, 2828, 1620, 1581, 1174, 1106, 1034, 958 cm^{-1}; HRMS (APCI) Calcd For $C_{25}H_{30}NO_2$ 376.2271 ($M + H^+$); Found 376.2256.

8-(tert-butyl)-2-chloro-6-(4-methoxyphenyl)-7,8,9,10-tetrahydrophenanthridine (4h): Yield 66% (250 mg), white solid, mp 202-203˚C,^{1}H NMR (600 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.94 (s, 1H), 7.58 (d, *J* = 9.0 Hz,1H), 7.52 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H), 3.41-3.37(m, 1H), 3.04-2.98 (m, 1H), 2.76 (d, *J* = 16.8 Hz, 1H), 2.56 (t, *J* = 12.0 Hz, 1H), 2.23-2.19 (m, 1H), 1.51-1.44 (m, 1H), 1.39-1.35 (m, 1H), 0.90 (s, 9H); ^{13}C NMR (100

MHz, $CDCl_3$): δ 160.4, 160.2, 143.1, 142.7, 135.4, 132.4, 130.9, 130.6, 130.5, 129.7, 127.6, 122.0, 114.0, 55.9, 44.6, 32.6, 30.6, 27.5, 27.4, 23.6; IR (KBr)ν_{max} 3005, 2952, 2917, 2864, 1608, 1573, 1558, 1149, 1082, 1035, 950 cm^{-1}; HRMS (ESI) Calcd For $C_{24}H_{27}ClNO$ 380.1776 ($M + H^+$); Found 380.1778.

7-chloro-4-(p-tolyl)-2,3-dihydro-1H-cyclopenta[*c*]quinoline (4i): Yield 74% (216 mg), white solid, mp 127-128˚C, ^1H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.41 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 3.23 (m, 4H), 2.45 (s, 3H), 2.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 151.4,147.9, 138.9, 137.5, 135.4, 134.3, 129.2, 128.9, 128.8, 126.9, 125.6, 123.7, 33.9, 31.4, 25.1, 21.5; IR (KBr)ν_{max} 3025, 2970, 2919, 2849, 1605, 1575, 1559, 1070, 1042, 969 cm^{-1}; HRMS (ESI) Calcd For $C_{19}H_{17}ClN$ 294.1044 ($M + H^+$); Found 294.1050.

3-chloro-6-(p-tolyl)-8,9,10,11-tetrahydro-7H-cyclohepta[*c*]quinoline (4j): Yield 82% (263 mg), white solid, mp 146-147˚C, ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 2.4 Hz, 1H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.41-7.38 (m, 3H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.24 (t, *J* = 4.8 Hz, 2H), 2.95 (t, *J* = 5.6 Hz, 2H), 2.41 (s, 3H), 1.89 (t, *J* = 6.0 Hz, 2H), 1.73 (t, *J* = 4.8 Hz, 2H), 1.62 (t, *J* = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 149.6, 146.9, 138.7, 137.9, 134.7, 134.1, 129.1, 129.0, 128.9, 126.9, 124.7, 124.6, 31.9, 30.8, 28.3, 27.0, 26.1, 21.4; IR (KBr)ν_{max} 3048, 2978, 2919, 2852, 1637, 1576, 1489, 1069, 1019, 964 cm^{-1}; HRMS (ESI) Calcd For $C_{21}H_{21}ClN$ 322.1357 ($M + H^+$); Found 322.1359.

2-methoxy-6-(p-tolyl)-7,8,9,10-tetrahydrophenanthridine (4k): Yield 68% (206 mg), brown solid, mp 135-136˚C, ^1H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 9.0 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.31-7.30 (m, 1H), 7.30-7.29 (m, 1H), 7.26 (d, *J* = 6.0 Hz, 1H), 7.19 (s, 1H), 3.96 (s, 3H), 3.13 (t, *J* = 6.0 Hz, 2H), 2.73 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 1.98 (t, *J* = 5.4 Hz, 2H), 1.77 (t, *J* = 5.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.5, 157.8, 141.8, 140.8, 138.5, 137.8, 131.7, 129.1, 128.9, 127.9, 120.3, 101.2, 55.7, 29.0, 26.1, 22.9, 22.5, 21.5; IR (KBr)ν_{max} 3041, 2933, 2859, 1668, 1655, 1220, 1093, 946 cm^{-1}; HRMS (ESI) Calcd For $C_{21}H_{22}NO$ 304.1696 ($M + H^+$); Found 304.1703.

2-methyl-6-phenyl-7,8,9,10-tetrahydrophenanthridine (4l): Yield 75% (204 mg), yellow liquid, ^1H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.74 (s, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.49-7.45 (m, 3H), 7.41 (t, *J* = 7.2 Hz, 1H), 3.18 (t, *J* = 5.4 Hz, 2H), 2.72 (t, *J* = 5.4 Hz, 2H), 2.57 (s, 3H), 1.97 (t, *J* = 4.8 Hz, 2H), 1.79-1.77 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.0, 144.4, 141.5, 141.5, 136.1, 130.6, 129.9, 128.9, 128.5, 128.4, 128.1, 127.1, 121.7, 28.9, 25.9, 22.9, 22.5, 22.2; IR (KBr)ν_{max} 3055, 3025, 2932, 2859, 1733, 1621, 1582,

1095, 1029, 1001, 988 cm^{-1}; HRMS (APCI) Calcd For $C_{20}H_{20}N$ 274.1590 ($M + H^+$); Found 274.1573.

6-(4-chlorophenyl)-2-methyl-8,9,10,11-tetrahydro-7H-cyclohepta[*c*]quinoline (4m): Yield 74% (237 mg), white solid, mp 192-193˚C, ^1H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.87 (s, 1H), 7.49 (d, *J* = 9.0 Hz, 1H), 7.46-7.43 (m, 4H), 3.29 (t, *J* = 4.8 Hz, 2H), 2.92 (t, *J* = 5.4 Hz, 2H), 2.57 (s, 3H), 1.93-1.90 (m, 2H), 1.77 (m, 2H), 1.63 (t, *J* = 4.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.7, 149.0, 145.1, 140.5, 136.1, 134.1, 133.9, 130.9, 130.6, 130.1, 128.5, 126.3, 122.1, 32.1, 30.8, 28.1, 27.1, 26.2, 22.2; IR (KBr)ν_{max} 3061, 2991, 2972, 2921, 2851, 1682, 1105, 1090, 1012, 965 cm^{-1}; HRMS (ESI) Calcd For $C_{21}H_{21}ClN$ 322.1357 ($M + H^+$); Found 322.1371.

2-methoxy-6-(p-tolyl)-7,8,9,10,11,12,13,14,15,16-decahydrocyclododeca[*c*]quinoline (4n): Yield 64% (247 mg), brown solid, mp 149-150 ˚C, ^1H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, *J* = 9.0 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.30-7.28(m, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 3.96 (s, 3H), 3.16 (t, *J* = 7.8 Hz, 2H), 2.81 (t, *J* = 7.8 Hz, 2H), 2.41 (s, 3H), 1.89-1.88 (m, 2H), 1.67-1.64 (m, 4H), 1.53-1.52 (m, 2H), 1.52-1.45 (m, 6H), 1.25-1.24 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.4, 157.6, 145.0, 142.2, 139.6, 137.4, 132.4, 131.7, 128.9, 128.6, 128.1, 120.1, 102.9, 55.7, 28.9, 28.6, 28.5, 28.4, 28.0, 27.6, 27.4, 26.9, 22.8, 21.5; IR (KBr)ν_{max} 3058, 2924, 2851, 1621, 1571, 1034, 968 cm^{-1}; HRMS (ESI) Calcd For $C_{27}H_{34}NO$ 388.2635 ($M + H^+$); Found 388.2654.

2-methyl-6-(thiophen-2-yl)-8,9,10,11-tetrahydro-7H-cyclohepta[*c*]quinoline (4o): Yield 69% (202 mg), white solid, mp 130-131˚C, ^1H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.82 (s, 1H), 7.47 (d, *J* = 9.0 Hz, 1H), 7.43 (d, *J* = 4.8 Hz, 1H), 7.26 (s, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 3.30 (t, *J* = 4.8 Hz, 2H), 3.18 (t, *J* = 5.4 Hz, 2H), 2.55 (s, 3H), 1.95-1.94 (m, 2H), 1.78-1.77 (m,2H), 1.73-1.72 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 151.9, 149.2, 145.3, 144.5, 136.2, 134.4, 130.9, 130.1, 127.6, 127.2, 126.9, 126.2, 122.1, 32.1, 30.7, 28.1, 27.0, 26.4, 22.3; IR (KBr)ν_{max} 3070, 2995, 2917, 2852, 1637, 1568, 1056, 1019 cm^{-1}; HRMS (APCI) Calcd For $C_{19}H_{20}NS$ 294.1311($M + H^+$); Found 294.1325.

8-(tert-butyl)-6-(p-tolyl)-7,8,9,10-tetrahydrobenzo[*c*]phenanthridine (6a): Yield 94% (356 mg), white solid, mp 211-212˚C, ^1H NMR (600 MHz, $CDCl_3$): δ 9.37 (d, *J* = 6.6 Hz, 1H), 7.91-7.87 (m, 2H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.64-7.62 (m, 4H), 7.32 (d, *J* = 7.8 Hz, 2H), 3.56-3.50 (m, 1H), 3.15-3.11 (m, 1H), 2.91-2.88 (m, 1H), 2.69 (t, *J* = 12.0 Hz, 1H), 2.47 (s, 3H), 2.25-2.22 (m, 1H), 1.57-1.49 (m, 1H), 1.43-1.39 (m, 1H), 0.94 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.7, 143.4, 142.3, 138.9, 137.9, 133.2, 132.3, 129.7, 129.6, 128.9, 127.6, 127.2, 126.8, 125.2, 124.1, 120.9, 44.7, 32.6, 30.6, 27.8, 27.5, 24.1, 21.6; IR (KBr)ν_{max} 3045,

3022, 2955, 2867, 2837, 1573, 1099, 1019 cm^{-1}; HRMS (ESI) Calcd For $C_{28}H_{30}N$ 380.2373 ($M + H^+$); Found 380.2376.

8-(tert-butyl)-6-(4-methoxyphenyl)-7,8,9,10-tetrahydrobenzo[*c*]phenanthridine (6b): Yield 90% (355 mg), brown solid, mp 270-271˚C, ^1H NMR (400 MHz, $CDCl_3$): δ 9.34 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 9.2 Hz, 2H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.64 (t, *J* = 6.4 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 3.51-3.46 (m, 1H), 3.12-3.03 (m, 1H), 2.87 (d, *J* = 16.0 Hz, 1H), 2.68 (t, *J* = 12.0 Hz, 1H), 2.21-2.19 (m, 1H), 1.53-1.43 (m, 1H), 1.36 (t, *J* = 10.0 Hz, 1H), 0.93 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 158.2, 143.3, 142.4, 134.1, 133.1, 132.1, 131.0, 129.6, 127.7, 127.6, 127.1, 126.8, 125.1, 123.9, 120.8, 113.6, 58.5, 44.7, 32.5, 30.7, 27.8, 27.5, 23.9; IR (KBr)ν_{max} 3051, 2956, 2897, 1608, 1506, 1174, 1073, 1012 cm^{-1}; HRMS (ESI) Calcd For $C_{28}H_{30}NO$ 396.2322 ($M + H^+$); Found 396.2322.

4-(8-(tert-butyl)-7,8,9,10-tetrahydrobenzo[*c*]phenanthridin-6-yl)phenol (6c): Yield 92% (350 mg), white solid, mp 256-257˚C, ^1H NMR (400 MHz, $CDCl_3$): δ 9.35-9.33 (m, 1H), 7.91-7.87 (m, 2H), 7.81 (d, *J* = 9.6 Hz, 1H), 7.66-7.63 (m, 4H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.56-3.49 (m, 1H), 3.16-3.06 (m, 1H), 2.87 (d, *J* = 16.4 Hz, 1H), 2.69 (t, *J* = 12.4 Hz, 1H), 2.54-2.18 (m, 1H), 1.57-1.47 (m, 1H), 1.41-1.38 (m, 1H), 0.94 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 157.3, 142.8, 142.2, 132.9, 132.3, 131.7, 130.8, 129.5, 127.4, 127.3, 126.7, 126.5, 124.7, 123.6, 120.7, 115.1, 44.5, 32.3, 30.5, 27.6, 27.2, 23.8; IR (KBr)ν_{max} 3473, 3049, 2962, 2915, 2858, 1636, 1518, 1100, 1022 cm^{-1}; HRMS (ESI) Calcd For $C_{27}H_{28}NO$ 382.2166 ($M + H^+$); Found 382.2166.

3-(8-(tert-butyl)-7,8,9,10-tetrahydrobenzo[*c*]phenanthridin-6-yl)phenol (6d): Yield 95% (362 mg), white solid, mp 220-221˚C, ^1H NMR (600 MHz, $CDCl_3$): δ 9.32 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.65-7.61 (m, 2H), 7.29-7.27 (m, 1H), 7.13-7.12 (m, 2H), 6.86-6.84 (m, 1H), 3.46-3.42 (m, 1H), 3.07-3.01 (m, 1H), 2.78 (d, *J* = 6.2 Hz, 1H), 2.54 (t, *J* = 12.6 Hz, 1H), 2.18-2.15 (m, 1H), 1.45-1.38 (m, 1H), 1.35-1.31 (m, 1H), 0.89 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.4, 156.0, 143.5, 142.6, 141.9, 133.2, 131.4, 130.1, 129.4, 127.9, 127.8, 127.6, 127.1, 125.0, 124.4, 121.6, 120.7, 116.9, 115.8, 44.5, 32.5, 30.2, 27.9, 27.4, 23.8; IR (KBr)ν_{max} 3446, 3051, 2956, 2861, 1636, 1121, 996 cm^{-1}; HRMS (ESI) Calcd For $C_{27}H_{28}NO$ 382.2166 ($M + H^+$); Found 382.2161.

8-(tert-butyl)-6-(3,4,5-trimethoxyphenyl)-7,8,9,10-tetrahydrobenzo[*c*]phenanthridine (6e): Yield 77% (350 mg), white solid, mp 196-197˚C, ^1H NMR (600 MHz, $CDCl_3$): δ 9.41,(s, 1H), 7.90 (t, *J* = 3.6 Hz, 2H), 7.83, (d, *J* = 9.6 Hz, 1H), 7.71-7.64, (m, 2H), 6.95, (s,

2H), 3.96, (s, 3H), 3.94, (s, 6H), 3.54-3.51, (m, 1H), 3.15-3.09, (m, 1H), 2.93, (d, *J* = 16.2 Hz, 1H), 2.67, (t, *J* = 12.6 Hz, 1H), 2.24, (t, *J* = 4.2 Hz, 1H), 1.55-1.48,(m, 1H), 1.42 (t, *J* = 10.2 Hz, 1H), 0.95, (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.1, 153.1, 142.8, 141.4, 138.4, 136.5, 133.3, 131.6, 129.7, 127.9, 127.8, 127.7, 127.1, 125.3, 124.3, 120.7, 107.2, 61.2, 56.5, 44.7, 32.6, 30.6, 27.9, 27.5, 23.9; IR (KBr)ν_{max} 3042, 2997, 2956, 2886, 1637, 1585, 1127, 1006 cm^{-1}; HRMS (ESI) Calcd For $C_{30}H_{34}NO_3$ 456.2533 (M + H$^+$); Found 456.2527.

8-(tert-butyl)-6-(4-chlorophenyl)-7,8,9,10-tetrahydrobenzo[*c*]phenanthridine (6f): Yield 87% (347 mg), white solid, mp 217-218 ˚C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.40, (s, 1H), 7.90-7.89, (m, 2H), 7.85,(s, 1H), 7.67-7.66, (m, 4H), 7.51-7.50, (m, 2H), 3.53, (d, *J* = 17.2 Hz, 1H), 3.12-3.11, (m, 1H), 2.82, (d, *J* = 16.0 Hz, 1H), 2.65, (t, *J* = 12.8 Hz, 1H), 2.24-2.23, (m, 1H), 1.51, (d, *J* = 12.0 Hz, 1H),1.41,(d, *J* = 11.0 Hz, 1H), 0.94, (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 143.3, 143.0, 139.6, 134.4, 133.2, 131.7, 131.1, 129.6, 128.5, 127.9, 127.7, 127.1, 125.1, 124.4, 1207, 44.6, 32.6, 30.5, 27.8, 27.5, 23.9;.IR (KBr)ν_{max} 3022, 2958, 2873, 2840, 1652, 1573, 1123, 1090, 1014 cm^{-1}; HRMS (ESI) Calcd For $C_{27}H_{27}ClN$ 400.1827 (M + H$^+$); Found 400.1825.

6-(4-bromophenyl)-8-(tert-butyl)-7,8,9,10-tetrahydrobenzo[*c*]phenanthridine (6g): Yield 82% (363 mg), white solid, mp 215-216 ˚C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45 (s, 1H), 7.89(s, 2H), 7.87, (s, 1H), 7.68-7.66 (m, 4H), 7.61(s, 2H), 3.54 (d, *J* = 17.2 Hz, 1H), 3.14 (s, 1H), 2.82 (d, *J* = 16.0 Hz, 1H), 2.64 (t, *J* = 12.8 Hz, 1H), 2.23 (s, 1H), 1.51 (d, *J* = 11.6 Hz, 1H), 1.41 (d, *J* = 11.2 Hz, 1H), 0.94, (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 143.7, 142.8, 139.6, 133.3, 131.5, 131.4, 129.7, 128.1, 127.9, 127.8, 127.2, 125.2, 124.5, 122.8, 120.6, 44.5, 32.5, 30.4, 27.9, 27.4, 23.9; IR (KBr)ν_{max} 2953, 2869, 2840, 1573, 1122, 1099, 1073, 1010 cm^{-1}; HRMS (ESI) Calcd For $C_{27}H_{27}BrN$ 444.1322 (M + H$^+$); Found 444.1323.

8-(tert-butyl)-6-(4-nitrophenyl)-7,8,9,10-tetrahydrobenzo[*c*]phenanthridine (6h): Yield 80% (328 mg), yellow solid, mp > 350 ˚C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.27 (d, *J* = 8.8 Hz, 1H), 8.39 (d, *J* = 8.8 Hz, 2H), 7.93-7.89 (m, 4H), 7.86 (d, *J* = 9.2 Hz, 1H), 7.68 (t, *J* = 3.6 Hz, 2H), 3.56 (dd, *J* = 17.6, 5.2Hz, 1H), 3.18-3.09 (m, 1H), 2.79 (d, *J* = 15.2 Hz, 1H), 2.69 (t, *J* = 12.0 Hz, 1H), 2.26 (dd, *J* = 12.4, 5.6Hz, 1H), 1.57-1.49 (m, 1H), 1.44-1.39 (m, 1H), 0.93 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 148.2, 147.7, 143.6, 143.2, 133.3, 132.1,130.7, 129.3, 128.2, 128.0, 127.8, 127.2, 124.9, 124.7, 123.5, 120.7, 44.6, 32.6, 30.4, 27.8, 27.4, 23.9; IR (KBr)ν_{max} 3069, 2957, 2926, 2896, 2864, 1639, 1599, 1108, 1014 cm^{-1}; HRMS (APCI) Calcd For $C_{27}H_{27}N_2O_2$ 411.2067 (M + H$^+$); Found 411.2064.

6-(3-bromophenyl)-8-(tert-butyl)-7,8,9,10-tetrahydrobenzo[*c*]phenanthridine (6i): Yield 80% (354 mg), white solid, mp 185-186 ˚C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (d, *J* = 8.0 Hz, 1H), 7.96 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.76 (s, 2H), 7.68-7.61 (m, 4H), 7.38 (t, *J* = 8.0 Hz, 1H), 3.35-3.30 (m, 1H), 2.98-2.92 (m, 1H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.62-2.55 (m, 1H), 2.12 (d, *J* = 12.0 Hz, 1H), 1.37-1.30 (m, 2H), 0.94 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 143.6, 143.3, 142.6, 133.1,132.8, 132.0, 131.0, 129.5, 129.2, 128.1, 127.7, 127.6, 127.4, 126.9, 124.9, 124.2, 122.4, 120.7, 44.3, 32.4, 30.3, 27.5, 27.4, 23.7; IR (KBr)ν_{max} 3067, 3053, 2960, 2886, 1556, 1549, 1129, 1064, 1022, 997 cm^{-1}; HRMS (ESI) Calcd For $C_{27}H_{27}BrN$ 444.1321 (M + H$^+$); Found 444.1330.

6-(3,4,5-trimethoxyphenyl)-7,8,9,10-tetrahydrobenzo[*c*]phenanthridine (6j): Yield 88% (351 mg), brown solid, mp 138-139 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.37 (d, *J* = 7.2 Hz, 1H), 7.90 (t, *J* = 9.0 Hz, 2H), 7.83 (d, *J* = 9.6 Hz, 1H), 7.69-7.64 (m, 2H), 6.91 (s, 2H), 3.95 (s, 3H), 3.94 (s, 6H), 3.28 (t, *J* = 6.0 Hz, 2H), 2.89 (t, *J* = 6.0 Hz, 2H), 2.04-2.00 (m, 2H), 1.84-1.80 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.2, 153.2, 143.2, 143.0, 138.3, 136.6, 133.3, 131.7, 129.3, 127.9, 127.7, 127.6, 127.0, 125.3, 124.6, 120.6, 107.1, 61.2, 56.5, 29.1, 26.5, 22.9, 22.6; IR (KBr)ν_{max} 3051, 2996, 2936, 2860, 2834, 1622, 1584, 1170, 1126, 1006 cm^{-1}; HRMS (ESI) Calcd For $C_{26}H_{26}NO_3$ 400.1907 (M + H$^+$); Found 400.1927.

6-(4-fluorophenyl)-8,9,10,11-tetrahydro-7H-benzo[*h*]cyclohepta[*c*]quinoline (6k): Yield 91% (310 mg), white solid, mp 159-160 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.35 (d, *J* = 5.4 Hz, 1H), 8.04 (d, *J* = 9.6 Hz, 1H), 7.88-7.87 (m, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 768-7.64 (m, 4H), 7.21 (t, *J* = 8.4 Hz, 2H), 3.38 (t, *J* = 5.4 Hz, 2H), 3.08-3.06 (m, 2H), 1.97-1.93 (m, 2H), 1.84-1.81 (m, 2H), 1.73-1.69(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 161.6, 156.4, 150.0, 144.3, 138.2, 134.8, 133.2, 132.2, 131.7, 131.6, 128.0, 127.5, 127.4, 126.9, 125.2, 123.7, 121.2, 115.3, 115.1, 32.1, 30.9, 28.7, 27.5, 26.5; IR (KBr)ν_{max} 3046, 2981, 2936, 2910, 2875, 1635, 1538, 1052, 1014 cm^{-1}; HRMS (ESI) Calcd For $C_{24}H_{21}FN$ 342.1653 (M + H$^+$); Found 342.1659.

6-(p-tolyl)-7,8,9,10,11,12-hexahydrobenzo[*h*]cycloocta[*c*]quinoline (6l): Yield 85% (298 mg), white solid, mp 151-152 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.32-9.31 (m, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.88-7.86 (m, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.63-7.62 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 3.37-3.36 (m, 2H), 3.02 (t, *J* = 5.4 Hz, 2H), 2.46 (s, 3H), 1.94-1.93 (m, 2H), 1.64-1.63 (m, 2H), 1.46-1.45 (m, 2H), 1.39-1.38 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.8, 146.6, 144.2, 139.9, 137.5, 133.1, 132.4, 129.3, 128.8, 127.7, 127.5, 127.2, 126.8, 125.2, 123.8, 121.7, 32.1, 30.4, 28.8, 26.9, 26.8, 26.2, 21.5; IR (KBr)ν_{max}

3054, 2925, 2846, 1634, 1570, 1117, 1068, 1027 cm^{-1}; HRMS (APCI) Calcd For $C_{26}H_{26}N$ 352.2060 ($M + H^+$); Found 352.2074.

6-phenyl-7,8,9,10,11,12,13,14,15,16-decahydrobenzo[*h*]cyclododeca[*c*]quinoline (6m): Yield 67% (263 mg), white solid, mp 166-167 ˚C, ^1H NMR (400 MHz, $CDCl_3$): δ 9.31 (s, 1H), 7.96, (d, *J* = 9.2 Hz, 1H), 7.87 (s, 1H), 7.80 (d, *J* = 9.2 Hz, 1H), 7.63 (s, 4H), 7.50-7.45 (m, 3H), 3.25 (t, *J* = 6.8 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 1.92-1.91 (m, 2H), 1.67-1.66 (m, 4H), 1.58-1.48 (m, 8H), 1.35-1.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 146.7, 143.0, 133.1, 132.6, 132.4, 129.2, 128.2, 127.8, 127.5, 127.2, 126.8, 125.2, 124.8, 122.1, 29.1, 28.9, 28.6, 28.5, 28.4, 27.7, 27.4, 27.0, 22.8; IR (KBr)ν_{max} 3058, 2925, 2845, 1570, 1118, 1072, 1025 cm^{-1}; HRMS (ESI) Calcd For $C_{29}H_{32}N$ 394.2530 ($M + H^+$); Found 394.2530.

6-(naphthalen-2-yl)-7,8,9,10,11,12-hexahydrobenzo[*h*]cycloocta[*c*]quinoline (6n): Yield 76% (294 mg), white solid, mp 166-167 ˚C, ^1H NMR (600 MHz, $CDCl_3$): δ 9.36 (s, 1H), 8.09 (s, 1H), 8.02 (d, *J* = 9.6 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 3.0 Hz, 2H), 7.89 (t, *J* = 3.0 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.65 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.55 (dd, *J* = 5.4, 2.4 Hz, 2H), 3.41 (t, *J* = 5.4 Hz, 2H), 3.06 (t, *J* = 6.0 Hz, 2H), 1.97 (t, *J* = 5.4 Hz, 2H), 1.64-1.63 (m, 2H), 1.47-1.46 (m, 2H), 1.43-1.42 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.3, 147.5, 143.8, 139.6, 133.4, 133.2, 133.1, 133.0, 131.9, 128.7, 128.6, 128.0, 127.9, 127.8, 127.7, 127.6, 127.0, 126.4, 126.3, 125.3, 124.0, 121.6, 32.0, 30.5, 28.9, 27.1, 26.7, 26.3; IR (KBr)ν_{max} 3042, 2929, 2854, 1608, 1549, 1082, 1036, 1012, 956 cm^{-1}; HRMS (APCI) Calcd For $C_{29}H_{26}N$ 388.2060 ($M + H^+$); Found 388.2045.

6-(thiophen-2-yl)-8,9-dihydro-7H-benzo[*h*]cyclopenta[*c*]quinoline (6o): Yield 85% (255 mg), white solid, mp 166-167 ˚C, ^1H NMR (400 MHz, $CDCl_3$): δ 9.40 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 6.8 Hz, 1H), 7.69-7.67 (m, 2H), 7.63-7.62 (m, 1H), 7.61-7.56 (m, 1H), 7.51 (d, *J* = 18.8 Hz, 1H), 7.17 (t, *J* = 4.4 Hz, 1H), 3.29 (t, *J* = 7.6 Hz, 2H), 3.23 (t, *J* = 7.6 Hz, 2H), 2.31-2.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 147.5, 147.1, 144.6, 133.6, 133.5, 131.8, 128.2, 128.1, 127.9, 127.8, 127.1, 127.0, 126.7, 125.2, 122.6, 122.2, 33.8, 31.2, 24.5; IR (KBr)ν_{max} 3053, 2954, 2915, 2847, 1577, 1119, 1055, 1024 cm^{-1}; HRMS (ESI) Calcd For $C_{20}H_{16}NS$ 302.0998 ($M + H^+$); Found 302.1012.

6-(pyridin-2-yl)-8,9-dihydro-7H-benzo[*h*]cyclopenta[*c*]quinoline (6p): Yield 78% (230 mg), brown solid, mp 128-129 ˚C, ^1H NMR (600 MHz, $CDCl_3$): δ 9.45 (d, *J* = 8.4 Hz, 1H), 8.74 (d, *J* = 4.2 Hz, 1H), 8.67 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.75-7.71 (m, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 6.0 Hz, 1H), 3.68 (t, *J* = 7.2 Hz, 2H), 3.35 (t, *J* = 7.8 Hz, 2H), 2.33-2.28 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.1,

147.3, 144.8, 139.1, 137.2, 133.6, 132.1, 128.7, 128.1, 128.0, 127.4, 125.5, 124.6, 124.2, 123.7, 122.2, 34.2, 31.3, 25.1; IR (KBr)ν_{max} 3052, 2921, 2850, 1574, 1192, 1097, 1022, 987 cm^{-1}; HRMS (APCI) Calcd For $C_{21}H_{17}N_2$ 297.1386 ($M + H^+$); Found 297.1376.

6-(furan-2-yl)-8,9,10,11-tetrahydro-7H-benzo[*h*]cyclohepta[*c*]quinoline (6q): Yield 72% (225 mg), brown solid, mp 83-84 ˚C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.37 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 6.8 Hz, 1H), 7.68-7.65 (m, 2H), 7.08 (d, *J* = 3.2 Hz, 1H), 6.62-6.61 (m, 1H), 3.78 (t, *J* = 5.6 Hz, 2H), 3.31 (t, *J* = 5.2 Hz, 2H), 1.94 (d, *J* = 5.6 Hz, 2H), 1.79 (d, *J* = 3.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 150.4, 146.8, 144.6, 143.1, 134.6, 133.2, 132.2, 128.0, 127.5, 127.4, 127.0, 125.2, 123.7, 121.2, 111.6, 111.5, 31.9, 29.9, 28.3, 27.0, 26.6; IR (KBr)ν_{max} 3049, 2921, 2853, 1621, 1571, 1163, 1126, 1076, 1009 cm^{-1}; HRMS (ESI) Calcd For $C_{22}H_{20}NO$ 314.1540 ($M + H^+$); Found 314.1547.

6-(thiophen-2-yl)-8,9,10,11-tetrahydro-7H-benzo[*h*]cyclohepta[*c*]quinoline (6r): Yield 84% (276 mg), brown solid, mp 142-143 ˚C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 9.2 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.71 (t, *J* = 10.0 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 5.2 Hz, 1H), 7.40 (d, *J* = 2.8 Hz, 1H), 7.18 (t, *J* = 3.6 Hz, 1H), 3.55, (t, *J* = 5.2 Hz, 2H), 3.31 (t, *J* = 5.2 Hz, 2H), 1.97 (d, *J* = 4.8 Hz, 2H), 1.80, (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 150.1, 145.7, 144.2, 134.4, 133.2, 131.9, 128.1, 127.6, 127.6,127.5, 127.4, 127.4, 127.0, 125.3, 123.4, 121.1, 31.9, 30.4, 28.5, 27.0, 26.6; IR (KBr)ν_{max} 3062, 2966, 2923, 2853, 1683, 1652, 1101, 1079, 1027 cm^{-1}; HRMS (ESI) Calcd For $C_{22}H_{20}NS$ 330.1311 ($M + H^+$); Found 330.1311.

10-methoxy-6-(3,4,5-trimethoxyphenyl)-7,8-dihydrodibenzo[*c*,*k*]phenanthridine (8): Yield 64% (305 mg), brown solid, mp 208-209 ˚C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41 (d, *J* = 6.8 Hz, 1H), 8.33 (d, *J* = 8.8 Hz, 1H), 7.91 (t, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 9.6 Hz, 1H), 7.23-7.66 (m, 2H), 7.02 (s, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.97 (s, 1H), 3.96 (s, 3H), 3.94 (s, 6H), 3.92 (s, 3H), 3.03 (t, *J* = 6.4 Hz, 2H), 2.77 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 156.4, 153.2, 145.9, 142.5, 141.6, 138.5, 136.8, 133.2, 132.2, 131.3, 129.2, 128.1, 127.5, 127.2, 126.9, 125.6, 125.2, 123.5, 121.5, 113.6, 111.8, 107.3, 61.2, 56.5, 55.6, 30.2, 27.8; IR (KBr)ν_{max} 3062, 2935, 2834, 1607, 1584, 1123, 1064, 1034, 1005 cm^{-1}; HRMS (ESI) Calcd For $C_{31}H_{28}NO_4$ 478.2013 ($M + H^+$); Found 478.2014.

8,8-dimethyl-6-(p-tolyl)-7,8-dihydrobenzo[*c*]phenanthridine (10): Yield 82% (286 mg), brown solid, mp 174-175 ˚C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.37 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 12.0 Hz, 1H), 7.89-7.87 (m, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.68-7.63 (m, 3H), 7.36 (d, *J* =12.0 Hz, 2H), 7.25 (d, *J* = 12.0 Hz, 1H), 6.25 (d, *J* = 8.0 Hz, 1H), 4.45 (s, 1H), 2.96 (s,

2H), 2.48 (s, 3H), 1.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 145.1, 144.7, 138.2, 137.8, 136.6, 133.0, 131.9, 129.6, 128.8, 127.7, 127.4, 127.1, 126.7,124.9, 124.8, 120.5, 120.2, 120.1, 39.9, 32.0, 29.7, 27.2, 21.4; IR (KBr)ν_{max} 3029, 2956, 2918, 2895, 2857, 1627, 1583, 1564, 1115, 1024, 1000 cm^{-1}; HRMS (ESI) Calcd For $C_{26}H_{24}N$ 350.1903 (M + H$^+$); Found 350.1908.

4-(2,3-dihydro-1H-benzo[*f*]cyclopenta[*c*]quinolin-4-yl)phenol (12a): Yield 78% (242 mg), white solid, mp 308-309 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.42 (s, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 7.91-7.83 (m, 3H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.59-7.55 (m, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 3.65-3.62 (m, 2H), 3.18-3.16 (m, 2H), 2.17-2.15 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.9, 152.6, 149.5, 146.0, 134.9, 130.9, 129.6, 129.1, 128.9, 128.6, 127.6, 127.3, 125.3, 125.2, 125.1, 121.0, 114.0, 35.8, 31.8, 24.6; IR (KBr)ν_{max} 3446, 1636, 1607, 1548, 1145, 1104, 1018 cm^{-1}; HRMS (ESI) Calcd For $C_{22}H_{18}NO$ 312.1383 (M + H$^+$); Found 312.1382.

3-(tert-butyl)-5-(4-methoxyphenyl)-1,2,3,4-tetrahydrobenzo[*a*]phenanthridine (12b): Yield 72% (284 mg), brown solid, mp 206-207 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.76 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.95-7.94 (m, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.64-7.61 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H), 3.70 (d, *J* = 16.2 Hz, 1H), 3.63-3.61 (m, 1H), 3.01 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.56 (dd, *J* = 16.8, 11.4 Hz, 1H), 2.16 (dd, *J* = 12.6, 2.4 Hz, 1H), 1.64-1.63 (m, 1H), 1.26-1.22 (m, 1H), 0.90 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.6, 159.2, 146.6, 145.2, 133.9, 133.5, 130.4, 130.3, 130.1, 130.0, 129.4, 129.1, 128.5, 126.3, 125.7, 124.6, 113.9, 55.5, 44.3, 34.6, 32.7, 30.4, 27.2, 24.9; IR (KBr)ν_{max} 3016, 2948, 2858, 1635, 1609, 1109, 1033, 834 cm^{-1}; HRMS (ESI) Calcd For $C_{28}H_{30}NO$ 396.2322 (M + H$^+$); Found 396.2341.

5-(p-tolyl)-1,2,3,4-tetrahydrobenzo[*a*]phenanthridine (12c): Yield 74% (239 mg), white solid, mp 146-147 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.77 (d, *J* = 9.0 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.96-7.95 (m, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.66-7.61 (m, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 3.62 (t, *J* = 6.0 Hz, 2H), 2.89 (t, *J* = 6.6 Hz, 2H), 2.44 (s, 3H), 1.92-1.83 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.1, 146.3, 145.7, 138.0, 133.6, 130.4, 130.3, 129.3, 129.2, 129.1, 128.9, 128.6, 126.4, 125.8, 124.9, 33.5, 28.7, 23.3, 22.4, 21.5; IR (KBr)ν_{max} 3049, 3027, 2936, 2860, 1613, 1559, 1118, 1020 cm^{-1}; HRMS (ESI) Calcd For $C_{24}H_{22}N$ 324.1747 (M + H$^+$); Found 324.1746.

5-(2-fluorophenyl)-1,2,3,4-tetrahydrobenzo[*a*]phenanthridine (12d): Yield 78% (255 mg), brown solid, mp 108-109 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.78-8.76 (m, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.96-7.94 (m, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.65-7.61 (m, 2H), 7.49-7.47 (m, 1H), 7.46-7.42 (m, 1H), 7.30 (t, *J* = 6.6 Hz, 1H), 7.21-6.98 (m, 1H), 3.62 (t, *J* = 5.4 Hz,

2H), 2.90-2.69 (m, 2H), 1.91-1.90 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.7, 159.1, 154.5, 146.7, 145.5, 133.6, 131.2, 131.1, 130.5, 130.3, 130.2, 129.1, 129.0, 128.6, 126.6, 125.8, 125.5, 124.8, 116.0, 115.9, 33.5, 27.4, 23.4, 22.2; IR (KBr)ν_{max} 3055, 2935, 2861, 1616, 1579, 1122, 1092, 1030, 1006 cm^{-1}; HRMS (ESI) Calcd For $C_{23}H_{19}FN$ 328.1496 (M + H^+); Found 328.1496.

5-(furan-2-yl)-1,2,3,4-tetrahydrobenzo[*a*]phenanthridine (12e): Yield 75% (224 mg), brown solid, mp 116-118 ˚C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74-8.72 (m, 1H), 8.00-7.98 (d, *J* = 8.0 Hz, 1H), 7.94-7.92 (m, 1H), 7.89-7.87 (d, *J* = 9.2 Hz, 1H), 7.68-7.67 (m, 1H), 7.62-7.59 (m, 2H), 7.06 (d, *J* = 3.6 Hz, 1H), 6.60-6.59 (m, 1H), 3.58 (t, *J* = 6.0 Hz, 2H), 3.22 (t, *J* = 6.8 Hz, 2H), 2.03-1.99 (m, 2H), 1.86-1.84 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.8, 147.9, 146.9, 145.8, 143.5, 133.7, 130.4, 130.3, 129.4, 129.1, 128.7, 128.6, 126.4, 125.8, 124.9, 112.7, 111.6, 33.9, 27.9, 23.2, 22.5; IR (KBr)ν_{max} 3054, 2962, 2905, 1944, 1605, 1543, 1096 cm^{-1}; HRMS (APCI) Calcd For $C_{21}H_{18}NO$ 300.1383 (M + H^+); Found 300.1391.

8-phenyl-9,10,11,12,13,14-hexahydrobenzo[*f*]cycloocta[*c*]quinoline (12f): Yield 80% (269 mg), brown solid, mp 128-129 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.83 (d, *J* = 8.4 Hz, 1H), 8.05 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.69-7.63 (m, 2H), 7.51-7.49 (t, *J* = 7.8 Hz, 4H), 7.47-7.43 (m, 1H), 3.62 (s, 2H), 2.97 (t, *J* = 6.0 Hz, 2H), 2.26 (t, *J* = 4.8 Hz, 2H), 1.72-1.71 (m, 2H), 1.70-1.64 (m, 2H), 1.54-1.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 148.8, 147.2, 142.1, 133.6, 133.2, 130.7, 130.3, 129.5, 129.4, 128.8, 127.9, 127.8, 126.4, 126.3, 124.8, 31.2, 31.1, 30.8, 28.5, 27.4, 26.0; IR (KBr)ν_{max} 3055, 2925, 2852, 1737, 1605, 1548, 1118, 1072, 1029, 1009 cm^{-1}; HRMS (ESI) Calcd For $C_{25}H_{24}N$ 338.1903 (M + H^+); Found 338.1903.

3-(tert-butyl)-5-(p-tolyl)-1,2,3,4-tetrahydrobenzo[*a*]phenanthridine (12g): Yield 75% (284 mg), white solid, mp 255-256 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.76 (d, *J* = 6.0 Hz, 1H), 7.99 (d, *J* = 12.0 Hz, 1H), 7.95 (d, *J* = 6.0 Hz, 1H), 7.89 (d, *J* = 6.0 Hz. 1H), 7.62-7.61 (t, *J* = 6.0 Hz, 2H), 7.46 (d, *J* = 12.0 Hz, 2H), 7.31 (d, *J* = 6.0 Hz, 2H), 3.71 (d, *J* = 18.0 Hz, 1H), 3.63 (d, *J* = 6.0 Hz, 1H), 3.0 (dd, *J* = 6.0, 12.0 Hz, 1H), 2.56 (t, *J* = 12.0 Hz, 1H), 2.45 (s, 3H), 2.17 (d, *J* = 12.0 Hz, 1H), 1.64 (s, 1H), 1.26-1.22 (m, 1H), 0.90 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.6, 146.6, 145.2, 138.5, 137.8, 133.5, 130.4, 130.1, 129.4, 129.2, 129.1, 128.9, 128.5, 126.3, 125.7, 124.7, 44.3, 34.6, 32.7, 30.3, 27.2, 24.9, 21.5; IR (KBr)ν_{max} 3016, 2931, 2868, 1619, 1554, 1180, 1121, 1016 cm^{-1}; HRMS (ESI) Calcd For $C_{28}H_{30}N$ 380.2373 (M + H^+); Found 380.2387.

(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-(3-(p-tolyl)benzo[f]quinolin-1-yl)-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (14a): Yield 68% (395 mg), white solid, mp 216-217 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.46 (d, *J* = 6.0 Hz, 1H), 8.11 (d, *J* = 6.0 Hz, 2H), 8.07 (d, *J* = 6.0 Hz, 1H), 7.95 (d, *J* = 12.0 Hz, 1H), 7.90 (d, *J* = 6.0 Hz, 1H), 7.59 (d, *J* = 6.0 Hz, 1H), 7.55 (s, 2H), 7.35(d, *J* = 6.0 Hz, 2H), 6.03 (s, 1H), 5.45 (s, 1H), 4.59 (s, 1H), 2.62 (d, *J* = 12.0 Hz, 1H), 2.44 (s, 3H), 2.37-2.25 (m, 3H), 2.16 (s, 1H), 2.03 (s, 3H), 1.97 (s, 1H), 1.80 (s, 3H), 1.71 (d, *J* = 12.0 Hz, 1H), 1.54 (t, *J* = 12.0 Hz, 1H), 1.37 (s, 1H), 1.27 (d, *J* = 18.0 Hz, 2H), 1.06 (t, *J* = 12.0 Hz, 3H), 0.99 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 157.7, 155.5, 149.3, 144.9, 140.3, 139.5, 136.7, 132.6, 131.2, 131.1, 129.7, 129.5, 128.6, 128.4, 128.1, 127.5, 126.9, 125.7, 123.8, 122.4, 122.2, 57.5, 51.7, 50.4, 38.3, 37.0, 33.2, 32.8, 32.0, 31.3, 27.9, 21.6, 21.5, 20.8, 19.4, 17.2; IR (KBr)ν_{max} 3157, 2967, 2722, 1647, 1567, 1167, 1102, 1019, 952 cm^{-1}; HRMS (ESI) Calcd For $C_{41}H_{44}NO_2$ 582.3367 (M + H$^+$); Found 582.3371.

(3S,8R,9S,10R,13S,14S)-17-(3-(4-chlorophenyl)benzo[*f*]quinolin-1-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[*a*]phenanthren-3-yl acetate (14b): Yield 72% (432 mg), white solid, mp 229-230 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.47 (d, *J* = 12.0 Hz, 1H), 8.17 (d, *J* = 6.0 Hz, 2H), 8.05 (d, *J* = 6.0 Hz, 1H), 7.96 (d, *J* = 12.0 Hz, 1H), 7.90, (d, *J* = 6.0 Hz, 1H), 7.61 (d, *J* = 6.0 Hz, 1H), 7.57 (d, *J* = 6.0 Hz, 1H), 7.54 (s, 1H), 7.51 (d, *J* = 6.0 Hz, 2H), 6.00 (s, 1H), 5.45 (s, 1H), 4.60 (s, 1H), 2.63 (d, *J* = 12.0 Hz, 1H), 2.37 (d, *J* = 6.0 Hz, 1H), 2.33-2.25 (m, 2H), 2.18 (d, *J* = 18.0 Hz, 1H), 2.03 (s, 3H), 1.99 (s, 1H), 1.85-1.81 (m, 3H), 1.71-1.69 (d, *J* = 18.0 Hz, 2H), 1.56-1.50 (m, 1H), 1.38-1.37 (m, 1H), 1.28 (s, 2H), 1.09-1.02 (m, 2H), 0.99 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.7, 157.5, 154.2, 149.4, 145.2, 140.3, 137.9, 135.6, 132.7, 131.4, 131.1, 129.3, 129.2, 128.8, 128.7, 128.4, 128.3, 127.1, 125.9, 124.1, 122.4, 121.9, 74.0, 57.5, 51.5, 50.4, 38.3, 36.9, 33.2, 32.8, 31.9, 31.3, 27.9, 21.6, 20.7, 19.4, 17.2; IR (KBr)ν_{max} 3047, 3028, 2926, 1689, 1653, 1589, 1030, 964 cm^{-1}; HRMS (ESI) Calcd For $C_{40}H_{41}ClNO_2$ 602.2820 (M + H$^+$); Found 602.2823.

1,4-bis(8-(tert-butyl)-7,8,9,10-tetrahydrobenzo[*c*]phenanthridin-6-yl)benzene (15a): Yield 68% (443 mg), pale yellow solid, mp > 350 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.00 (t, *J* = 12.0 Hz, 2H), 8.25 (d, *J* = 6.0 Hz, 2H), 8.17 (s, 4H), 7.98 (d, *J* = 6.0 Hz, 2H), 7.94 (s, 2H), 7.90 (s, 4H), 3.90 (d, *J* = 18.0 Hz, 2H), 3.47 (d, *J* = 12.0 Hz, 2H), 2.88 (d, *J* = 18.0 Hz, 2H), 2.67 (d, *J* = 12.0 Hz, 2H), 2.42 (s, 2H), 1.62 (d, *J* = 12.0 Hz, 4H), 0.93 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.7, 161.5, 161.2, 160.9, 158.2, 151.1, 135.2, 134.8, 134.2, 133.1, 132.8, 132.3, 130.2, 130.1, 129.9, 127.3, 122.8, 122.3, 119.4, 117.7, 115.8, 113.9,

111.9, 43.5, 32.5, 29.6, 29.5, 26.9, 22.9; IR (KBr)ν_{max} 3082, 2996, 2956, 2867, 1581, 1551, 1081, 1019, 999 cm^{-1}; HRMS (ESI) Calcd For $C_{48}H_{49}N_2$ 653.3890 (M + H^+); Found 653.3887.

1,4-bis(3-(tert-butyl)-1,2,3,4-tetrahydrobenzo[*a*]phenanthridin-5-yl)benzene (15b): Yield 75% (489 mg), pale yellow solid, mp > 350 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.93 (d, *J* = 8.0 Hz, 2H), 8.37-8.34 (m, 2H), 8.20-8.17 (m, 2H), 7.99-7.92 (m, 6H), 7.89-7.86 (m, 4H), 4.05-3.90 (m, 4H), 3.05-2.99 (m, 2H), 2.77-2.68 (m, 2H), 2.38 (d, *J* = 18.0 Hz, 2H), 1.79 (s, 2H), 1.48-1.38(m, 2H), 0.91 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 161.6, 161.2, 160.8, 160.4, 160.1, 149.3, 138.4, 138.3, 134.1, 133.5, 133.4, 130.9, 130.1, 129.9, 129.7, 128.7, 128.2, 127.4, 119.2, 117.5, 116.3, 113.5, 110.6, 43.3, 36.1, 32.6, 29.7, 26.7, 23.9; IR (KBr)ν_{max} 3136, 3080, 2968, 2874, 1683, 1555, 1057, 1021, 998 cm^{-1}; HRMS (APCI) Calcd For $C_{48}H_{49}N_2$ 653.3890 (M + H^+); Found 653.3897.

3-(tert-butyl)-5-(naphthalen-2-yl)-1,2,3,4-tetrahydronaphtho[2,3-*b*]phenanthridine (17): Yield 92% (428 mg), brown solid, mp 285-286 ˚C, ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.24 (s, 1H), 8.43 (s, 1H), 8.15-8.14 (m, 1H), 8.07-8.04 (m, 2H), 7.98-7.96 (m, 2H), 7.94-7.92 (m, 2H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 4.2 Hz, 2H), 7.54 (t, *J* = 4.2 Hz, 2H), 3.84-3.80 (m, 2H), 3.08 (dd, *J* = 16.8, 5.4Hz, 1H), 2.62 (dd, *J* = 16.8, 11.4 Hz, 1H), 2.24 (d, *J* = 12.0 Hz, 1H), 1.69 (t, *J* = 12.0 Hz, 2H), 0.85 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.9, 147.3, 145.9, 138.8, 133.7, 133.2, 131.9, 131.5, 131.4, 130.9, 130.3, 128.9, 128.7, 128.6, 128.5, 128.4, 128.1, 127.9, 127.7, 127.1, 127.0, 126.6, 126.4, 126.3, 126.1, 125.0, 44.4, 34.7, 32.8, 30.3, 27.2, 25.1; IR (KBr)ν_{max} 3064, 2926, 2847, 1639, 1558, 1105, 1017, 885 cm^{-1}; HRMS (ESI) Calcd For $C_{35}H_{32}N$ 466.2530 (M + H^+); Found 466.2532.

(4aR,5S)-3-(tert-butyl)-5-(p-tolyl)-2,3,4,4a,5,6-hexahydrobenzo[*a*]phenanthridine (18): Yield 25% (93.5 mg), brown solid, mp 120-121 ˚C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 4.0 Hz, 1H), 7.37-7.34 (m, 1H), 7.25-7.21 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.89-6.86 (m, 1H), 6.24 (s, 1H), 6.15 (d, *J* = 4.0 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 2.49-2.47 (d, *J* = 8.0 Hz, 1H), 2.31 (s, 3H), 2.23 (s, 1H), 2.16-2.08 (m, 1H), 1.45 (d, *J* = 12.0 Hz, 2H), 1.35 (dd, *J* = 12.0, 4.0 Hz, 2H), 0.81 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 140.6, 137.9, 132.8, 130.9, 129.4, 128.6, 128.1, 127.9, 126.3, 125.3, 123.7, 121.4, 116.8, 114.3, 110.1, 62.8, 39.4, 38.4, 32.4, 27.7, 27.4, 25.1, 21.4; IR (KBr)ν_{max} 3042, 2957, 2925, 2856, 1619, 1569, 1152, 1082, 1020, 968 cm^{-1}; HRMS (APCI) Calcd For $C_{28}H_{32}N$ 382.2529 (M + H^+); Found 382.2526.

ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C NMR, HRMS spectra and X-ray crystallography data of all compounds are available free of charge via the Internet at http://pubs.acs.org/.

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