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A novel construction of quino-fused tropone skeleton: first synthesis of 12*H*-benzo[4,5]cyclohepta[1,2-*b*]quinolin-12-one derivatives

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ABSTRACT

In the present investigation, the incorporation of both quinoline moiety and tropone ring in a molecule frame work in fused form leading to a series of structurally novel and biologically intriguing quinoline/tropone hybrids 12*H*-benzo[4,5]cyclohepta[1,2-*b*]quinolin-12-one derivatives has been first achieved through a simple, and economical two-step procedure, involving the one-pot synthesis of (*E*)-2-(arylvinyl)quinoline-3-carboxylic acids followed by intramolecular Friedel–Crafts acylation reaction using polyphosphoric acid (PPA).

1. Introduction

The cyclohepta-2,4,6-trienone, better known under the common name tropone, is a pharmaceutically important structural unit. Compounds bearing this moiety possess a broad spectrum of biological activities.[1–3] Especially, some tropones fused to aromatic or heteroaromatic rings are an important class of compounds, which represent privileged moieties in medicinal chemistry,[4] and are ubiquitous sub-structure associated with biologically active natural products, such as Colchicine (**I**, Fig. 1),[5] Caulersine (**II**, Fig. 1),[6] Tintamine (**III**, Fig. 1),[7] and Pareitropone (**IV**, Fig. 1).[8] Recent studies have suggested that some heterocycles with the combination of a tropone ring could increase their biological activities or create new medicinal properties due to the different electronic distribution and the additional basic character of the tropone ring.[9,10] In addition, the tropone moiety also plays an important role in molecular assemblies for a faster and efficient lead generation towards the new drug discovery.[11–13] Despite featuring only seven ring carbon atoms and no stereocentres, the synthesis of structurally novel ring-fused is still a considerable synthetic challenge as tropone derivatives are scarce in nature,[14] occurring only in lower plants and fungi,[15] and limited information is available on these compounds. On account of these facts, extensive synthetic efforts have been devoted surrounding the tropone ring to design and synthesize novel ring-fused tropone systemes.[16–19]

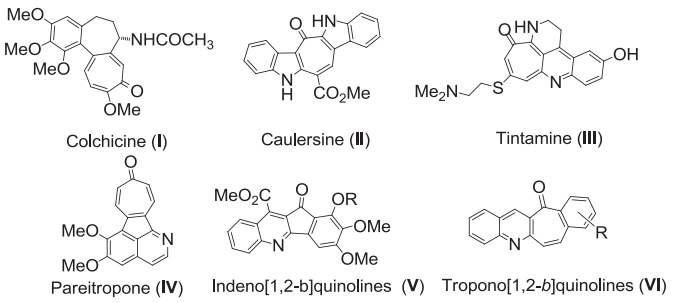

Fig. 1. Examples of hetero-fused tropones (**I**–**VI**).

On the other hand, it has been well-established that planar polycyclic-fused quinoline system, especially tri- or tetracyclic-fused frame work could intercalate into base pairs of DNA as an intercalator to induce topoisomerase II dependent DNA cleavage,[20,21] thereby exhibiting significant biological properties, such as antitumoral, anti-cancer,[22] anti-inflammatory,[23] antituberculosis,[24] and antiplasmodial activities.[25] For example, tetracyclic indenoquinoline derivatives (**V**, Fig. 1) were reported to show potent antiproliferative activities against breast (MCF-7), lung epithelial (A-549), and cervical (HeLa) adenocarcinoma cells.[26] As a consequence, the remarkable bioactivities along with the unique structural arrays displayed by these tetracyclic-fused quinoline systems have made them a particularly appealing target for the synthetic efforts.[27–30]

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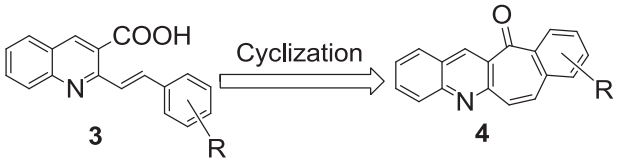
Considering the above valid points, and in view of structural diversity playing a prominent role in medicinal and combinatorial chemistry,[31] we conceived that the incorporation of the tropone nucleus into the planar tetracyclic-fused quinoline systems leading to new prototypes, as possible drug-like candidates for pharmacological studies, would be of synthetic importance. Therefore, in the context of our ongoing studies concerning the synthesis of potential biologically active hybrid molecules,[32–38] we wish to report, herein, a facile and inexpensive procedure for the preparation of planar linearly tetracyclic-fused benzotroponoquinoline systems, wherein the tropone ring is fused at its 2,3-position to the b-position of quinoline ring to give a compact structure like the compounds **VI** in Fig. 1. To the best of our knowledge, this type of polycyclic-fused structure is still unprecedented.

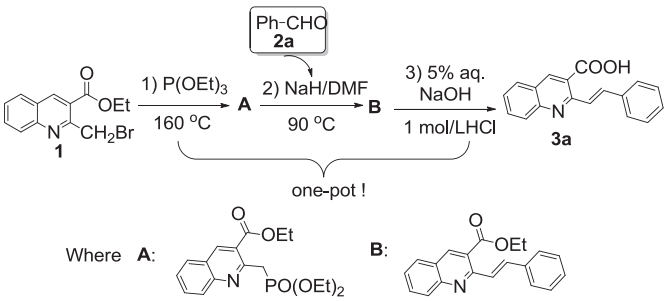
2. Results and discussion

It is well known that the intramolecular Friedel–Crafts acylation reaction of some appropriate aryl- or heteroarylcarboxylic acids has been particularly useful in synthetic organic chemistry,[39–41] since this reaction could result in the construction of an extra ring by generation of a new C–C bond, including seven-membered ring construction.[42,43] For example, Karcher and co-worker reported the intramolecular Friedel–Crafts acylation reaction of 2-styrylnicotinic acid for the synthesis of benzotroponopyridine derivatives.[9] In this regard, we recently reported the intramolecular Friedel–Crafts acylation reaction of 2-aryloxymethylquinoline-3-carboxylic acids for the construction of polycyclic-fused benzo[6,7]oxepino[3,4-*b*]quinolin-13(6*H*)-ones.[32,38] Taking these observations into account, we reasoned that if we could achieve the facile synthesis of suitably 2-styrylquinoline-3-carboxylic acid derivatives (**3**) as the tetracyclic precursors, it might be possible to convert them into the desired tetracyclic quino-fused tropone systems **4** via the intramolecular cyclization strategy as shown in Scheme 1.



Scheme 1. Possible construction of quino-fused tropone systems via Friedel–Crafts cyclization reaction.

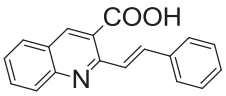
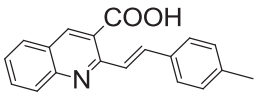
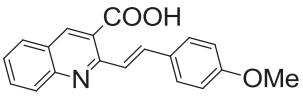
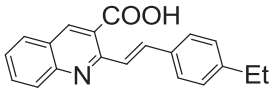
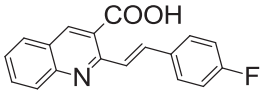
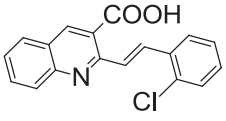
Thus, the key to implement our strategy was the realization of the facile preparation of the key substrates **3**. Prior to the current investigation, a few related examples involving the synthesis of 2-styrylpyridine3-carboxylic acids, structurally analogous to **3**, have been reported.[9,17] Although the two methodologies are elegant and impressive, our attempts to follow both routes to synthesize our 2-styrylquinoline-3-carboxylic acid derivatives were unfruitful, and no promising result was obtained. Therefore, we felt that there was a real need for the development of a direct and concise method to synthesize the required substrates **3**. To this end, we postulated an efficient and attractive one-pot reaction procedure. As outlined in Scheme 2, ethyl 2-(bromomethyl)quinoline-3-carboxylate (**1**) was first subjected to the Arbuzov reaction with triethyl phosphate at 160 °C. After the complete conversion of the starting material to the corresponding intermediate **A** (TLC), triethyl phosphate was evaporated to dryness under reduced pressure. Subsequently, we conducted the Horner–Emmons olefination reaction of **A** with benzaldehyde (**2a**) by adding directly a solution of 1.1 equiv of **2a** in DMF to the residue at 90 °C. We examined this reaction by using different bases (NaOH, K_2CO_3, Et_3N, EtONa, *t*-BuOK, NaH) and varying their equivalents, from one to three, separately. We found that the reaction could not occur upon using NaOH, K_2CO_3 or Et_3N, whereas an incomplete reaction was observed when using EtONa as base. The use of *t*-BuOK gave an intractable complex mixture that we could not separate any desired product in appreciable yield. To our delight, we discovered that 1.1 equiv of NaH were suitable to promote the reaction, which was completed within 2 h as TLC indicated the absence of intermediate **A**. Since the newly-formed olefination product **B** did not interfere with further ester hydrolysis reaction, purification at this stage was unnecessary. Accordingly, we simply added 5% aqueous NaOH solution directly to the reaction mixture and continued to reflux for 2 h. After the reaction was completed followed by an acidic work-up, the corresponding free carboxylic acid **3a** was obtained in a good overall yield of 76%. The stereochemistry of **3a** was established as an *E*-stereoisomer on the basis of its ^{1}H NMR spectrum, which showed the mutual coupling constant value J=15.6 Hz of the two arising vinylic protons CH=CH at 8.08 and 8.17 ppm, respectively.



Scheme 2. One-pot synthesis of 2-styrylquinoline-3-carboxylic acid (**3a**).

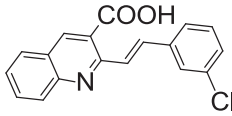
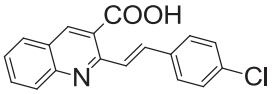
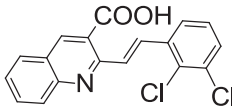
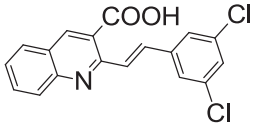
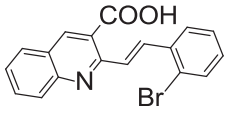
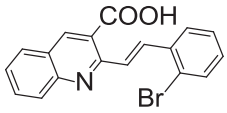
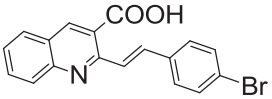
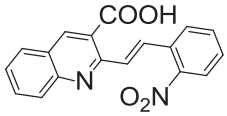
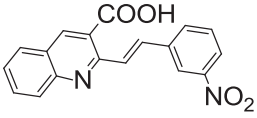
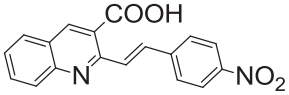
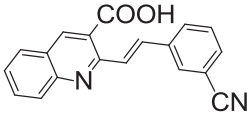
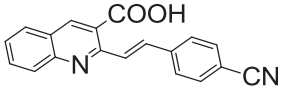
Thereafter, various aromatic aldehydes **2b–r** with differing electronic properties were subjected to the one-pot sequence under the same reaction conditions for the synthesis of a series of 2-styrylquinoline-3-carboxylic acid derivatives (**3b–r**). The reaction results were listed in Table 1.

Table 1
Synthesis of differently substituted (*E*)-2-(arylvinyl) quinoline-3-carboxylic acids (**3a–r**)

Entry	Product	3a–r	Yield[a] (%)
1		**3a**	76
2		**3b**	75
3		**3c**	83
4		**3d**	71
5		**3e**	74
6		**3f**	80

(*continued on next page*)

Table 1 (*continued*)

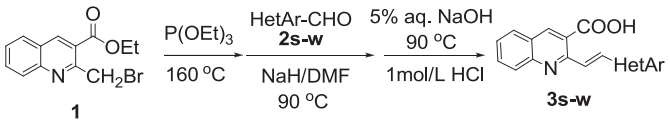
Entry	Product	3a–r	Yield[a] (%)
7		**3g**	73
8		**3h**	76
9		**3i**	70
10		**3j**	79
11		**3k**	74
12		**3l**	81
13		**3m**	79
14		**3n**	68
15		**3o**	72
16		**3p**	73
17		**3q**	70
18		**3r**	74

[a] Yield of isolated product.

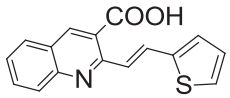
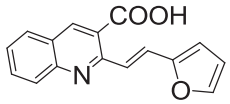
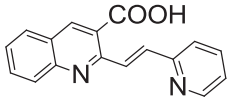
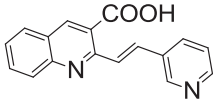
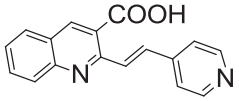
As shown in Table 1, various substituted 2-styrylquinoline-3-carboxylic acids (**3b**–**r**) were successfully synthesized with overall yields ranging from 68% to 83%. The nature and site of substituent present in the aromatic aldehydes did not seem to affect the one-pot reaction significantly, neither in product yield nor in reaction rate. In addition, it was worthy to mention that the halogen (F, Cl, Br), cyanogen, and nitro groups, which were sensitive to bases, were well tolerated in the one-pot process without any experimental difficulties.

Due to the simplicity and efficiency of the one-pot synthesis, we decided to further extend its scope to the preparation of 2-(hetarylvinyl)quinoline-3-carboxylic acids. To this purpose, an analogous series of reactions were performed using some heteroaromatic aldehydes viz., thiophene-2-carbaldehyde (**2s**), furan-2-carbaldehyde (**2t**), and pyridine aldehydes (**2u**–**w**) in place of aromatic aldehydes under similar reaction conditions (only varying the reaction time according to TLC monitoring). As shown in Table 2, all these heteroaromatic aldehydes were equally amenable to the one-pot reaction sequence, furnishing the expected *E*-configuration 2-(hetarylvinyl)quinoline-3-carboxylic acids (**3s**–**w**), albeit in slightly low yields of 52–61%.

Table 2
One-pot synthesis of (*E*)-2-(hetarylvinyl)quinoline-3-carboxylic acids (**3s**–**w**)

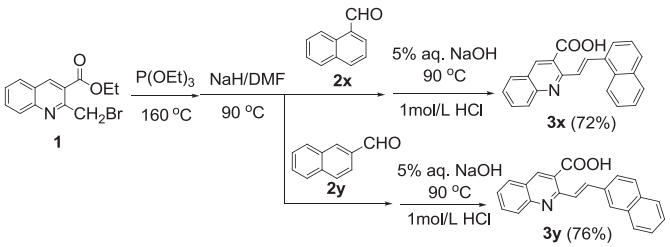


1 **3s-w**

Entry	Product	3s–w	Yield[a] (%)
1		**3s**	54
2		**3t**	61
3		**3u**	55
4		**3v**	56
5		**3w**	52

[a] Yield of isolated product.

Encouraged by these results, we also attempted the reaction of **1** with 1-naphthaldehydes (**2x**) and 2-naphthaldehydes (**2y**) under similar reaction conditions with the aim of diversifying our work on the synthesis of novel precursor compounds of quino-fused tropones. As expected, this one-pot reaction proceeded smoothly, and gave the corresponding (*E*)-2-(2-(naphthalen-1-yl)vinyl) quinoline-3-carboxylic acid (**3x**) and (*E*)-2-(2-(naphthalen-2-yl)vinyl) quinoline-3-carboxylic acid (**3y**) in 72% and 76% yields, respectively (Scheme 3).

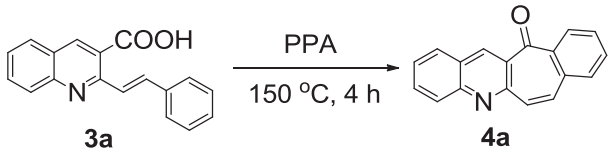


1

Scheme 3. One-pot synthesis of (*E*)-2-(2-(naphthalenyl)vinyl)quinoline-3-carboxylic acids (**3x** and **3y**).

From these results, it may be concluded that the novel one-pot method provides an efficient, straightforward, and general access to the construction of a wide variety of novel (*E*)-2-((aryl/hetaryl) vinyl) quinoline-3-carboxylic acids (**3a**–**y**) with good yields. The beauty of this one-pot reaction procedure is that three chemical transformations [i.e., Arbuzov reaction, Horner–Wadsworth–Emmons reaction, and ester hydrolysis] take place in one-pot procedure, thereby simplifying reaction handling and product purification, improving synthetic efficiency, and reducing solvent consumption and disposal.

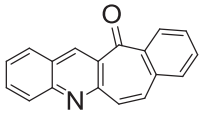
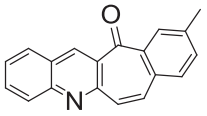
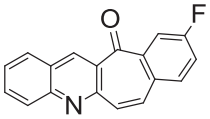
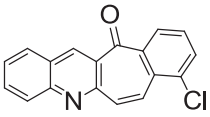
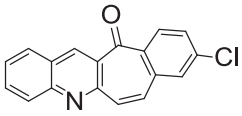
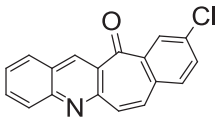
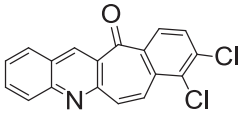
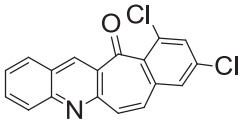
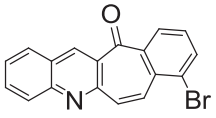
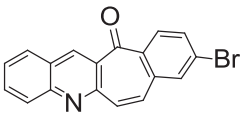
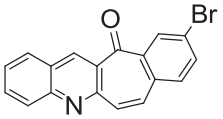
Having in hand a series of the newly synthesized substrates **3a**–**y**, our attention was transferred to their intramolecular Friedel–Crafts acylation reaction for building the desired tetracyclic quino-fused tropone systems. At this stage, we first investigated the intramolecular Friedel–Crafts reaction of the representative 2-styrylquinoline-3-carboxylic acid (**3a**) using Eaton's reagent as the cyclizing agent. Our recent work has proved that the use of Eaton's reagent is very efficient for the construction of polycyclic-fused quinoline systems.[44,45] However, in the present case, we found that it failed to promote the reaction efficiently and the corresponding cyclized product 12*H*-benzo[4,5]cyclohepta[1,2-*b*]quinolin-12-one (**4a**) was obtained in a very low yield (15%). Other attempts by varying the reaction temperature and the amount of Eaton's reagent used also failed. Additionally, we also attempted to use other cyclization reagents, such as sulfuric acid, hydrogen fluoride, trifluoroacetic anhydride, methanesulfonic acid, PPA–P_2O_5, and TFA–TfOH, but they produced either low yielding mixtures or no identifiable products. Upon using PPE (polyphosphate ester), no formation of product was observed and the starting material was recovered unchanged. The reaction using $POCl_3$ as cyclization reagent was also investigated according to the method reported recently by Meesala et al.[46] Unfortunately, the ^{1}H HMR spectrum of the reaction mixture showed that **4a** was not formed even in a trace amount. After these fruitless attempts, we decided to focus on the use of PPA (polyphosphoric acid) as the cycling agent. To our delight, we found that the cyclization reaction of **3a** could be performed smoothly at 150 °C as shown in Scheme 4. After the reaction was complete within 4 h, the reaction mixture was poured into cold water followed by neutralization with $NaHCO_3$ solution. TLC examination of the crude reaction mixture revealed the presence of a fast running major component contaminated with dark base line material, thereby rendering the purification of the resulting product by flash chromatography easy. Thus, the cyclized product **4a** was obtained in a good yield of 78%. In this reaction, the reaction temperature highly affected the product yield, and the yield significantly decreased when the reaction temperature was below 150 °C. Although the higher reaction temperature shortened the reaction time from 4 h to 1 h, tarry byproducts were formed, which significantly reduced the yield of the desired products. As far as the amount to PPA was concerned, the use of 15 g PPA to 1 mmol of **3a** was found most suitable to provide maximum yield and there was no further improvement in the yield with increasing the amount of PPA.



Scheme 4. Synthesis of 12*H*-benzo[4,5]cyclohepta[1,2-*b*]quinolin-12-one (**4a**).

Encouraged by the successful synthesis of compound **4a**, we tested this protocol for the intramolecular cyclization of other substrates **3b**–**y** in a similar fashion. The substrates **3a**, **b**, **e**–**m** could be smoothly transformed to the desired cyclized products 12*H*-areno[4,5]cyclohepta[1,2-*b*]quinolin-12-ones (**4a**, **b**, **e**–**m**) in good yields, ranging from 65 to 80% as shown in Table 3. Their structures were confirmed via spectroscopic data and elemental analyses with the results being in full agreement with the proposed structures. As an example, in the IR spectrum of **4a**, the disappearance of OH and C=O stretching peaks of its carboxyl group at 3421 cm^{-1} and 1716 cm^{-1}, and the appearance of the tropone C=O stretching frequency at a decreased wave number of 1650 cm^{-1}

Table 3
Synthesis of 12*H*-areno[4,5]cyclohepta[1,2-*b*]quinolin-12-ones (**4a**, **b**, **e**–**m**)

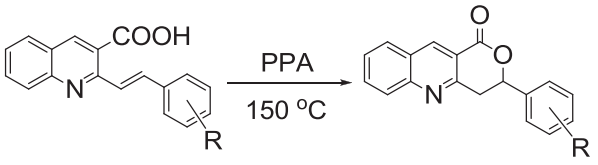
Entry	Product	**4a**, **b**, **e**–**m**	Yield[a] (%)
1		**4a**	78
2		**4b**	80
3		**4e**	66
4		**4f**	78
5		**4g**	76
6		**4h**	72
7		**4i**	65
8		**4j**	76
9		**4k**	70
10		**4l**	79
11		**4m**	74

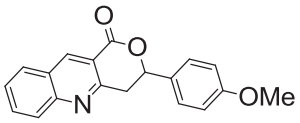
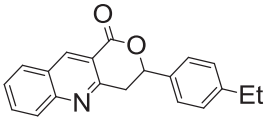
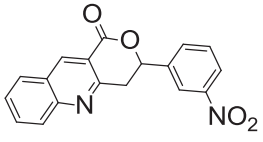
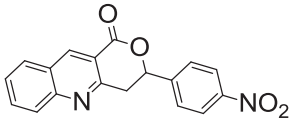
[a] Yield of isolated product.

were clear evidences for the intramolecular cyclization occurring. The main feature of its ^{1}H NMR spectrum was the appearance of two aromatic protons representing the peaks at 7.28 and 7.48 ppm, respectively, as *ortho* coupled doublets with a coupling constant J=12.5 Hz, which was characteristic of *ortho*-proton coupling of tropone ring protons. The other synthesized compounds exhibited similar spectral characteristics. Herein, it is worthy to mention that most of these newly synthesized quino-fused tropone systems contain one or two halogen substituents, which make them particularly appealing, since these functional groups could provide ample opportunities for further synthetic manipulation by cross coupling reactions to obtain more complex ring-fused systems. An example that is particularly relevant to the present discussion is described in the literature,[12] where the structural analogs of tricyclic 7-bromo-3-chloro-5*H*-benzo[4,5]cyclohepta[1,2-*b*]pyridin-5-one could be served as valuable synthetic intermediate for the synthesis of MK-8033, a specific c-Met/Ron dual kinase inhibitor.[12]

However, to our surprise, the substrates **3c**, **3d**, **3o** and **3p** displayed a different reactivity pattern, where the predicted tetracyclic quino-fused tropone products were not observed and instead, unexpected lactones **4c**, **4d**, **4o** and **4p** were formed as the main component in this intramolecular Friedel–Crafts reaction as shown in Table 4. Their structures were easily deduced from their ^{1}H NMR spectra. For example, the ^{1}H NMR spectrum of **4c** revealed the presence of two unequivalent methylene protons at 3.42 and 3.80 coupled with each other with a geminal coupling constant J=16.8 Hz, and in turn with the vicinal methine proton at 5.88 ppm, along with the signals for 9 aromatic protons exactly matching its structure in the range of aromatic region. The spectral pattern in our case was very similar to some structurally analogous lactones.[47,48]

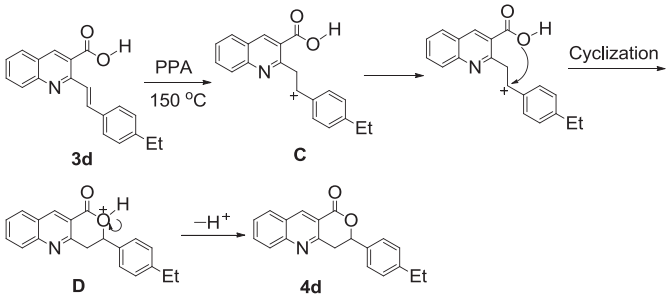
Table 4
An unexpected synthesis of 3-phenyl-3,4-dihydro-1*H*-pyrano[4,3-*b*]quinolin-1-ones



Entry	Product		Yield[a] (%)
1		**4c**	71
2		**4d**	69
3		**4o**	66
4		**4p**	62

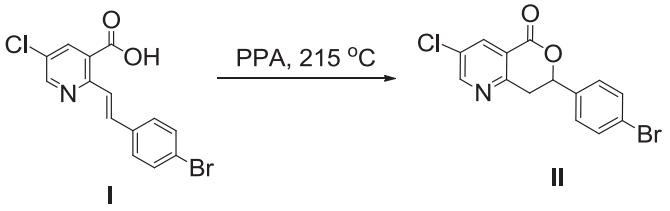
[a] Yield of isolated product.

Although we have not yet established the mechanism for formation of the lactone structure and the detailed experimental evidences are still elusive at the current stage, taking into consideration the entire outcome, this might be explained by the assumption that these substrates may be protonated at the carbon position of the olefinic group under the action of PPA. Importantly, the formation of this type of protonation of the styryl group has been already reported by Klumpp et al.[49–51] Thus, a tentative hypothesis is depicted in Scheme 5 using ethyl substrate **3d** as an example. The reaction presumably involves the protonation of **3d** at the olefinic group to form the carbocation **C**. It has been reported intramolecular acylation methods that directly use carboxylic acids as the electrophile often suffered from the poor leaving group ability of the –OH moiety.[52] Thus, the carbocation **C** might be trapped through intramolecular attack of the –OH oxygen leading to efficient cyclization to **D**. Subsequently, the elimination of hydrogen ion from **D** afforded the product **4d**.



Scheme 5. A tentative hypothesis to formation of the lactone **4d**.

But the question about why protonation of these substrates is positioned at the styryl group still remains unclear and elusive at the current stage. Given our present state of knowledge, the reaction results are difficult to guess prior to performing the actual experiments. It was pertinent to note that there was a similar report where the intramolecular Friedel–Crafts reaction of (*E*)-2-(4-bromostyryl)-5-chloronicotinic acid (**I**) by the treatment with PPA at 210 °C also resulted in the formation of a lactone **II** (Scheme 6).[17] But in this literature no detailed mechanistic studies have been carried out, and there is no consensus of opinion regarding the formation of the structure of lactone. Further research to explore its reaction mechanism represents an intriguing goal that we are currently contemplating.



Scheme 6. Formation of the lactone **II** from the intramolecular Friedel–Crafts acylation reaction.

Unfortunately, our similar endeavors to cyclize the substrates **3n** and **3q**–**y** did not meet any success. TLC and ^{1}H NMR spectroscopy of the reaction mixture showed a combination of starting materials and an intractable mixture of products, from which neither the desired quino-fused tropones nor the cyclized lactones could be isolated. Furthermore, our attempts to increase the amount of PPA or use other cyclization reagents were also unsatisfactory. Work is currently ongoing to extend the scope of intramolecular Friedel–-Crafts acylation reaction, and more studies toward screening catalysts and additives etc. will be part of our future efforts.

3. Conclusions

In conclusion, we have succeeded in achieving the first construction of structurally novel and biologically intriguing tetracyclic-fused quinoline–tropone systems 2*H*-areno[4,5]cyclohepta[1,2-*b*]quinolin-12-ones by the intramolecular Friedel–Crafts acylation reaction of (*E*)-2-(arylvinyl)quinoline-3-carboxylic acids, albeit there is still a demand for expanding the scope of the acylation reaction. In view of the synergism of both the medium-sized seven-membered tropone ring and quinoline unit in a molecular frame work, the newly synthesized compounds would likely possess significant biological activities and be potentially applied for the development of biologically and pharmaceutically important drugs. Our further work focusing on intramolecular Friedel–Crafts acylation reaction in the synthesis of quino-fused tropones is currently ongoing, and more studies toward screening catalysts and additives etc. is being actively pursued in our laboratory.

4. Experimental section

4.1. General

The chemical used in this work was obtained from Fluka and were used without purification. Melting points (uncorrected) were determined by using WRS-1B melting points apparatus. ^{1}H NMR spectra were recorded on a Brucker AVANCE NMR spectrometer using $CDCl_3$ or DMSO-d_6 as the solvent. The reported chemical shifts (δ values) are given in parts per million downfield from tetramethylsilane (TMS) as the internal standard. The progress of reactions was monitored by thin-layer chromatography (TLC) on silica gel GF_{254} using Ethyl acetate/petroleum ether (1:3) as eluent.

4.2. General procedure for synthesis of (*E*)-2-((aryl/hetaryl)vinyl) quinoline-3-carboxylic acids (3a–y)

Ethyl 2-bromomethylquinoline-3-carboxylate (**1**) (0.294 g, 1 mmol) was dissolved in triethyl phosphate (4 mL). The resulting reaction mixture was stirred at 160 °C for about 1 h. The conversion was monitored by TLC. After the reaction was complete, the excessive triethyl phosphate was removed in vacuo, and a solution of aromatic or heteroaromatic aldehyde **2a–y** (1.1 mmol) in DMF (5 mL) and NaH (0.026 g, 1.1 mmol) were added to the residue, respectively. The mixture was stirred for about 1 h at room temperature and stirred further at 90 °C for 1 h. After completion (TLC), 5% aqueous solution of sodium hydroxide (5 mL) was added to the reaction mixture and continued to stir at the temperature for 2 h. The mixture was cooled to room temperature followed by acidification with 1 mol/L HCl. The resulting crude product was purified by recrystallization from ethanol to give **3** with yields ranging from in 52–83%.

*4.2.1. (E)-2-Styrylquinoline-3-carboxylic acid (**3a**).* Pale yellow needles, mp 190–191 °C; FT-IR (KBr) ν_{max}: 3421, 1716, 1625, 1586, 1488, 1453, 1384, 1264, 1202, 1066, 963 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.51 (s, br, 1H, COOH), 9.13 (s, 1H, ArH), 8.32 (d, *J*=8.1 Hz, 1H, ArH), 8.22 (d, *J*=8.1 Hz, 1H, Quino–H), 8.17 (d, *J*=15.6 Hz, 1H, –CH=CH–), 8.08 (d, *J*=15.6 Hz, 1H, –CH=CH–), 7.99 (t, *J*=8.1 Hz, 1H, ArH), 7.73 (t, *J*=8.1 Hz, 3H, ArH), 7.39–7.50 (m, 3H, ArH); MS (FAB) *m*/*z*: 276.1 ([M+H]$^+$, 100). Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09%. Found: C, 78.71; H, 4.94; N, 5.02%.

*4.2.2. (E)-2-(4-Methylstyryl)quinoline-3-carboxylic acid (**3b**).* Pale yellow needles, mp 232–234 °C; FT-IR (KBr) ν_{max}: 3421, 1716, 1624, 1587, 1488, 1453, 1415, 1384, 1346, 1262, 1197, 1065, 979 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.56 (s, br, 1H, COOH), 9.17 (s, 1H, Quino–H), 8.36 (d, *J*=8.1 Hz, 1H, Quino–H), 8.23 (d, *J*=8.1 Hz, 1H, Quino–H), 8.14 (d, *J*=15.6 Hz, 1H, –CH=CH–), 8.08 (d, *J*=15.6 Hz, 1H, –CH=CH–), 8.01 (t, *J*=8.1 Hz, 1H, Quino–H), 7.75 (t, *J*=8.1 Hz, 1H, Quino–H), 7.62 (d, *J*=8.1 Hz, 2H, Ph–H), 7.30 (d, *J*=8.1 Hz, 2H, Ph–H), 2.37 (s, 3H, Me); MS (FAB) *m*/*z*: 290.1 ([M+H]$^+$, 100). Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84%. Found: C, 78.58; H, 5.12; N, 4.78%.

*4.2.3. (E)-2-(4-Methoxystyryl)quinoline-3-carboxylic acid (**3c**).* Pale yellow needles, mp 170–171 °C; FT-IR (KBr) ν_{max}: 3421, 1716, 1625, 1585, 1453, 1385, 1346, 1264, 1202, 1066, 964 cm^{-1}; ^{1}H NMR (DMSO-d_6, 600 MHz): δ 13.49 (s, br, 1H, COOH), 8.88 (s, 1H, Quino–H), 8.07–8.09 (m, 2H, Quino–H), 8.05 (d, *J*=15.6 Hz, 1H, –CH=CH–), 7.97 (d, *J*=15.6 Hz, 1H, –CH=CH–), 7.86 (t, *J*=7.8 Hz, 1H, Quino–H), 7.64 (d, *J*=8.4 Hz, 2H, Ph–H), 7.61 (t, *J*=7.8 Hz, 1H, Quino–H), 7.02 (d, *J*=8.4 Hz, 2H, Ph–H), 3.82 (s, 3H, OMe); MS (FAB) *m*/*z*: 306.1 ([M+H]$^+$, 100). Anal. Calcd for $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.59%. Found: C, 74.95; H, 5.09; N, 4.44%.

*4.2.4. (E)-2-(4-Ethylstyryl)quinoline-3-carboxylic acid (**3d**).* Pale yellow prisms, mp 208–210 °C; FT-IR (KBr) ν_{max}: 3421, 1716, 1624, 1587, 1489, 1453, 1416, 1385, 1347, 1222, 1197, 1065, 980 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 13.50 (s, br, 1H, COOH), 9.24 (s, 1H, Quino–H), 8.46 (d, *J*=8.4 Hz, 1H, Quino–H), 8.27 (d, *J*=8.1 Hz, 1H, Quino–H), 8.20 (d, *J*=15.9 Hz, 1H, –CH=CH–), 8.00–8.06 (m, 2H, ArH and –CH=CH–), 7.77 (t, *J*=8.1 Hz, 1H, Quino–H), 7.67 (d, *J*=8.4 Hz, 2H, Ph–H), 7.04 (d, *J*=8.4 Hz, 2H, Ph–H), 4.10 (q, *J*=6.9 Hz, 2H, –CH_2CH$_3$), 1.36 (t, *J*=6.9 Hz, 3H, –CH$_2$$CH_3$); MS (FAB) *m*/*z*: 304.1 ([M+H]$^+$, 100). Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62%. Found: C, 79.48; H, 5.45; N, 4.51%.

*4.2.5. (E)-2-(4-Fluorostyryl)quinoline-3-carboxylic acid (**3e**).* Pale yellow needles, mp 161–163 °C; FT-IR (KBr) ν_{max}: 3440, 1737, 1632, 1598, 1554, 1508, 1422, 1379, 1230, 1159, 972 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.62 (s, br, 1H, COOH), 8.95 (s, 1H, Quino–H), 8.15 (d, *J*=15.7 Hz, 1H, –CH=CH–), 8.08–8.12 (m, 2H, ArH), 7.97 (d, *J*=15.7 Hz, 1H, –CH=CH–), 7.90 (t, *J*=7.4 Hz, 1H, ArH), 7.71–7.78 (m, 2H, ArH), 7.65 (t, *J*=7.6 Hz, 1H, ArH), 7.26–7.32 (m, 2H, ArH); MS (FAB) *m*/*z*: 294.1 ([M+H]$^+$, 100). Anal. Calcd for $C_{18}H_{12}FNO_2$: C, 73.71; H, 4.12; N, 4.78%. Found: C, 73.94; H, 4.37; N, 4.63%.

*4.2.6. (E)-2-(2-Chlorostyryl)quinoline-3-carboxylic acid (**3f**).* Pale yellow needles, mp 231–232 °C; FT-IR (KBr) ν_{max}: 3373, 1715, 1630, 1491, 1471, 1429, 1247, 1197, 1135, 1058, 973 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.59 (s, br, 1H, COOH), 8.95 (s, 1H, Quino–H), 8.30 (d, *J*=15.6 Hz, 1H, –CH=CH–), 8.23 (d, *J*=15.7 Hz, 1H, –CH=CH–), 8.14 (d, *J*=8.0 Hz, 1H, ArH), 8.09 (d, *J*=8.6 Hz, 1H, ArH), 7.87–7.93 (m, 2H, ArH and –CH=CH–), 7.66 (t, *J*=7.8 Hz, 1H, ArH), 7.56 (dd, *J*=7.5, 7.6 Hz, 1H, ArH), 7.38–7.49 (m, 2H, ArH); MS (FAB) *m*/*z*: 310.1 ([M+H]$^+$, 100), 312.1 (35). Anal. Calcd for $C_{18}H_{12}ClNO_2$: C, 69.80; H, 3.90; N, 4.52%. Found: C, 69.49; H, 3.96; N, 4.22%.

*4.2.7. (E)-2-(3-Chlorostyryl)quinoline-3-carboxylic acid (**3g**).* Pale yellow needles, mp 205–206 °C; FT-IR (KBr) ν_{max}: 3443, 1698, 1617, 1561, 1491, 1455, 1379, 1232, 1199, 1138, 957 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.55 (s, br, 1H, COOH), 8.93 (s, 1H, Quino–H), 8.12 (d, *J*=7.9 Hz, 1H, ArH), 8.08 (t, *J*=8.1 Hz, 1H, ArH), 8.22 (d, *J*=15.7 Hz, 1H, –CH=CH–), 7.93 (d, *J*=15.7 Hz, 1H, –CH=CH–), 7.86–7.91 (m, 1H, ArH), 7.75 (s, 1H, Ph–H), 7.63–7.68 (m, 2H, ArH), 7.48 (t, *J*=7.5 Hz, 1H, ArH), 7.42 (d, *J*=8.1 Hz, 1H, ArH); MS (FAB) *m*/*z*: 310.0 ([M+H]$^+$, 100), 312.0 (32). Anal. Calcd for $C_{18}H_{12}ClNO_2$: C, 69.80; H, 3.90; N, 4.52%. Found: C, 69.97; H, 3.76; N, 4.75%.

*4.2.8. (E)-2-(4-Chlorostyryl)quinoline-3-carboxylic acid (**3h**).* Pale yellow needles, mp 189–190 °C; FT-IR (KBr) ν_{max}: 3400, 1625, 1624, 1584, 1491, 1411, 1379, 1269, 1220, 1090, 1012, 973 cm^{-1}; ^{1}H NMR

(DMSO-d_6, 300 MHz) δ: 13.57 (s, br, 1H, COOH), 9.01 (s, 1H, Quino–H), 8.20 (d, J=15.8 Hz, 1H, –CH=CH–), 8.13–8.16 (m, 2H, Quino–H), 7.98 (d, J=15.7 Hz, 1H, –CH=CH–), 7.91 (d, J=8.0 Hz, 1H, Quino–H), 7.72 (d, J=8.4 Hz, 2H, Ph–H), 7.69 (d, J=8.1 Hz, 1H, Quino–H), 7.52 (d, J=8.4 Hz, 2H, Ph–H); MS (FAB) m/z: 310.0 ([M+H]$^+$, 100), 312.0 (38). Anal. Calcd for $C_{18}H_{12}ClNO_2$: C, 69.80; H, 3.90; N, 4.52%. Found: C, 69.51; H, 3.68; N, 4.31%.

*4.2.9. (E)-2-(2,3-Dichlorostyryl)quinoline-3-carboxylic acid (**3i**).* Pale yellow needles, mp 251–252 °C; FT-IR (KBr) ν_{max}: 3412, 1696, 1615, 1564, 1491, 1449, 1406, 1380, 1249, 1188, 1142, 1061, 964 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.60 (s, br, 1H, COOH), 8.97 (s, 1H, Quino–H), 8.25 (d, J=15.6 Hz, 1H, –CH=CH–), 8.21 (d, J=15.7 Hz, 1H, –CH=CH–), 8.14 (d, J=8.0 Hz, 1H, ArH), 8.11 (d, J=8.4 Hz, 1H, ArH), 7.84–7.93 (m, 2H, ArH), 7.65–7.70 (m, 2H, ArH), 7.47 (t, J=7.9 Hz, 1H, ArH); MS (FAB) m/z: 344.1 ([M+H]$^+$, 100), 346.0 (72), 348.0 (12). Anal. Calcd for $C_{18}H_{11}Cl_2NO_2$: C, 62.81; H, 3.22; N, 4.07%. Found: C, 62.53; H, 3.33; N, 3.78%.

*4.2.10. (E)-2-(3,5-Dichlorostyryl)quinoline-3-carboxylic acid (**3j**).* Pale yellow prisms, mp 243–244 °C; FT-IR (KBr) ν_{max}: 3410, 1719, 1615, 1584, 1561, 1488, 1414, 1320, 1274, 1203, 1131, 1068, 969 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.56 (s, br, 1H, COOH), 8.94 (s, 1H, Quino–H), 8.24 (d, J=15.7 Hz, 1H, –CH=CH–), 8.13 (d, J=8.0 Hz, 1H, Quino–H), 8.06 (d, J=8.4 Hz, 1H, Quino–H), 7.85–7.93 (m, 2H, Quino–H), 7.76 (s, 1H, Ph–H), 7.75 (s, 1H, Ph–H), 7.66 (t, J=7.5 Hz, 1H, Quino–H), 7.59 (s, 1H, Ph–H); MS (FAB) m/z: 306.1 (54), 344.0 ([M+H]$^+$, 100), 346.0 (66), 348.0 (12). Anal. Calcd for $C_{18}H_{11}Cl_2NO_2$: C, 62.81; H, 3.22; N, 4.07%. Found: C, 62.46; H, 3.47; N, 3.75%.

*4.2.11. (E)-2-(2-Bromostyryl)quinoline-3-carboxylic acid (**3k**).* Pale yellow powder, mp 244–245 °C; FT-IR (KBr) ν_{max}: 3446, 1716, 1616, 1558, 1558, 1490, 1466, 1426, 1378, 1247, 1197, 1134, 1056, 972 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.59 (s, br, 1H, COOH), 8.96 (s, 1H, Quino–H), 8.26 (d, J=15.6 Hz, 1H, –CH=CH–), 8.08–8.16 (m, 3H, ArH and –CH=CH–), 7.86–7.93 (m, 2H, ArH), 7.74 (d, J=8.1 Hz, 1H, ArH), 7.67 (dd, J=7.8, 7.5 Hz, 1H, ArH), 7.50 (t, J=7.5 Hz, 1H, ArH), 7.33 (t, J=7.8 Hz, 1H, ArH); MS (FAB) m/z: 200.1 (27), 354.0 ([M+H]$^+$, 100), 356.0 (90). Anal. Calcd for $C_{18}H_{12}BrNO_2$: C, 61.04; H, 3.41; N, 3.95%. Found: C, 60.70; H, 3.11; N, 3.58%.

*4.2.12. (E)-2-(3-Bromostyryl)quinoline-3-carboxylic acid (**3l**).* Pale yellow powder, mp 219–220 °C; FT-IR (KBr) ν_{max}: 3447, 1703, 1615, 1552, 1487, 1426, 1400, 1210, 1130, 1058, 980 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.55 (s, br, 1H, COOH), 8.93 (s, 1H, Quino–H), 8.22 (d, J=15.7 Hz, 1H, –CH=CH–), 8.12 (d, J=7.8 Hz, 1H, ArH), 8.07 (d, J=8.4 Hz, 1H, ArH), 7.87–7.94 (m, 3H, ArH and –CH=CH–), 7.63–7.72 (m, 2H, ArH), 7.56 (d, J=7.9 Hz, 1H, ArH), 7.42 (t, J=7.8 Hz, 1H, ArH); MS (FAB) m/z: 200.1 (38), 354.0 ([M+H]$^+$, 88), 356.0 (92). Anal. Calcd for $C_{18}H_{12}BrNO_2$: C, 61.04; H, 3.41; N, 3.95%. Found: C, 60.89; H, 3.37; N, 3.87%.

*4.2.13. (E)-2-(4-Bromostyryl)quinoline-3-carboxylic acid (**3m**).* Pale yellow needles, mp 217–218 °C; FT-IR (KBr) ν_{max}: 3446, 1698, 1616, 1590, 1562, 1491, 1472, 1379, 1258, 1200, 1140, 1066, 957 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 13.55 (s, br, 1H, COOH), 8.93 (s, 1H, Quino–H), 8.22 (d, J=15.6 Hz, 1H, –CH=CH–), 8.12 (d, J=8.1 Hz, 1H, ArH), 8.07 (d, J=8.4 Hz, 1H, ArH), 7.87–7.95 (m, 3H, ArH), 7.63–7.72 (m, 2H, ArH), 7.56 (d, J=7.8 Hz, 1H, ArH), 7.42 (t, J=7.8 Hz, 1H, Quino–H); MS (FAB) m/z: 200.1 (28), 354.0 ([M+H]$^+$, 100), 356.0 (90). Anal. Calcd for $C_{18}H_{12}BrNO_2$: C, 61.04; H, 3.41; N, 3.95%. Found: C, 61.25; H, 3.48; N, 3.89%.

*4.2.14. (E)-2-(2-Nitrostyryl)quinoline-3-carboxylic acid (**3n**).* Pale yellow solid, mp 214–216 °C; FT-IR (KBr) ν_{max}: 3441, 1708, 1627, 1605, 1560, 1526, 1451, 1439, 1339, 1249, 1197, 1135, 1060, 966, 860 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.60 (s, 1H, COOH), 8.97 (s, 1H, Quino–H), 8.26 (d, J=15.6 Hz, 1H, –CH=CH–), 8.18 (d, J=15.9 Hz, 1H, –CH=CH–), 8.15 (d, J=7.8 Hz, 1H, –CH=CH–), 8.07 (d, J=8.1 Hz, 2H, –CH=CH–), 7.97 (d, J=7.5 Hz, 1H, ArH), 7.90 (t, J=7.5 Hz, 1H, ArH), 7.82 (t, J=7.5 Hz, 1H, ArH), 7.61–7.69 (m, 2H, ArH); MS (FAB) m/z: 321.0 ([M+H]$^+$, 100). Anal. Calcd for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.75%. Found: C, 67.62; H, 3.71; N, 8.79%.

*4.2.15. (E)-2-(3-Nitrostyryl)quinoline-3-carboxylic acid (**3o**).* Pale yellow powder, mp 228–229 °C; FT-IR (KBr) ν_{max}: 3441, 1702, 1645, 1616, 1589, 1560, 1534, 1491, 1456, 1416, 1352, 1203, 1139, 1064, 993, 860 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.60 (s, br, 1H, COOH), 8.95 (s, 1H, Quino–H), 8.50 (s, 1H, Ph–H), 8.36 (d, J=15.7 Hz, 1H, –CH=CH–), 8.20 (d, J=8.0 Hz, 1H, ArH), 8.12–8.18 (m, 2H, ArH), 8.09 (d, J=8.1 Hz, 1H, ArH), 8.06 (d, J=15.7 Hz, 1H, –CH=CH–), 7.74 (t, J=8.0 Hz, 1H, ArH), 7.67 (t, J=7.5 Hz, 1H, ArH), 7.91 (dd, J=7.4, 8.0 Hz, 1H, ArH); MS (FAB) m/z: 276.1 (9), 321.1 ([M+H]$^+$, 100). Anal. Calcd for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.75%. Found: C, 67.64; H, 3.81; N, 8.57%.

*4.2.16. (E)-2-(4-Nitrostyryl)quinoline-3-carboxylic acid (**3p**).* Pale yellow solid, mp 248–249 °C; FT-IR (KBr) ν_{max}: 3446, 1731, 1650, 1604, 1573, 1515, 1496, 1396, 1329, 1267, 1213, 1158, 1064, 993, 840 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.57 (s, 1H, COOH), 8.99 (s, 1H, Quino–H), 8.39 (d, J=15.9 Hz, 1H, –CH=CH–), 8.29 (d, J=8.4 Hz, 2H, Ph–H), 8.11–8.17 (m, 2H, ArH), 8.05 (d, J=15.9 Hz, 1H, –CH=CH–), 7.90–7.97 (m, 3H, ArH), 7.69 (t, J=7.5 Hz, 1H, ArH); MS (FAB) m/z: 321.1 ([M+H]$^+$, 100). Anal. Calcd for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.75%. Found: C, 67.66; H, 3.74; N, 9.04%.

*4.2.17. (E)-2-(3-Cyanostyryl)quinoline-3-carboxylic acid (**3q**).* Yellow needles, mp 241–242 °C; FT-IR (KBr) ν_{max}: 3251, 1698, 1638, 1616, 1590, 1561, 1490, 1451, 1431, 1380, 1270, 1227, 1198, 1138, 1064, 957, 922 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.56 (s, br, 1H, COOH), 8.27 (d, J=15.9 Hz, 1H, –CH=CH–), 8.12 (d, J=8.1 Hz, 1H, ArH), 8.05–8.14 (m, 2H, ArH), 7.97 (s, 1H, Ph–H), 7.86–7.92 (m, 3H, ArH), 7.81 (d, J=7.8 Hz, 1H, ArH), 7.64 (t, J=7.8 Hz, 2H, ArH); MS (FAB) m/z: 301.0 ([M+H]$^+$, 100). Anal. Calcd for $C_{19}H_{12}N_2O_2$: C, 75.99; H, 4.03; N, 9.33%. Found: C, 76.15; H, 4.10; N, 9.12%.

*4.2.18. (E)-2-(4-Cyanostyryl)quinoline-3-carboxylic acid (**3r**).* Pale yellow plates, mp 246–247 °C; FT-IR (KBr) ν_{max}: 3243, 1724, 1615, 1603, 1554, 1488, 1458, 1422, 1357, 1245, 1192, 1126, 1052, 972, 933 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.86 (s, br, 1H, COOH), 8.95 (s, 1H, Quino–H), 8.34 (d, J=15.6 Hz, 1H, –CH=CH–), 8.13 (d, J=8.1 Hz, 1H, ArH), 8.08 (d, J=8.4 Hz, 1H, ArH), 7.99 (d, J=15.6 Hz, 1H, –CH=CH–), 7.84–7.92 (m, 5H, ArH), 7.66 (t, J=7.8 Hz, 1H, ArH); MS (FAB) m/z: 301.0 ([M+H]$^+$, 100). Anal. Calcd for $C_{19}H_{12}N_2O_2$: C, 75.99; H, 4.03; N, 9.33%. Found: C, 75.74; H, 3.96; N, 9.05%.

*4.2.19. (E)-2-(2-(Thiophen-2-yl)vinyl)quinoline-3-carboxylic acid (**3s**).* Yellow solid, mp 245–246 °C; FT-IR (KBr) ν_{max}: 3421, 1717, 1614, 1586, 1488, 1425, 1385, 1342, 1264, 1231, 1199, 1062, 969 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 12.51 (s, br, 1H, COOH), 9.07 (s, 1H, Quino–H), 8.29 (d, J=15.6 Hz, 1H, –CH=CH–), 8.17–8.24 (m, 2H, ArH), 7.98 (d, J=15.5 Hz, 1H, –CH=CH–), 7.93–7.97 (m, 1H, ArH), 7.67–7.72 (m, 2H, ArH), 7.49 (d, J=3.4 Hz, 1H, ArH), 7.16–7.19 (m, 1H, ArH); MS (FAB) m/z: 282.0 ([M+H]$^+$, 100). Anal. Calcd for $C_{16}H_{11}NO_2S$: C, 68.31; H, 3.94; N, 4.98%. Found: C, 68.15; H, 3.80; N, 4.82%.

*4.2.20. (E)-2-(2-(Furan-2-yl)vinyl)quinoline-3-carboxylic acid (**3t**).* Yellow plates, mp 241–242 °C; FT-IR (KBr) ν_{max}: 3313, 1699, 1609, 1586, 1489, 1450, 1373, 1345, 1319, 1276, 1221, 1154, 1067, 1017, 967, 928 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 13.54 (s, br, 1H, COOH), 8.98 (s, 1H, Quino–H), 8.09–8.15 (m, 2H, ArH), 8.02 (d, J=15.6 Hz,

1H, −CH=CH−), 7.89–7.93 (m, 2H, ArH and −CH=CH−), 7.85 (d, *J*=8.4 Hz, 1H, ArH), 7.66 (t, *J*=7.6 Hz, 1H, ArH), 6.86 (d, *J*=3.3 Hz, 1H, Furan−H), 6.64–6.66 (m, 1H, ArH); MS (FAB) *m*/*z*: 266.0 ($[M+H]^+$, 100). Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.18; N, 5.28%. Found: C, 72.30; H, 4.23; N, 5.12%.

*4.2.21. (E)-2-(2-(Pyridin-2-yl)vinyl)quinoline-3-carboxylic acid (**3u**).* Yellow solid, mp 208–210 °C; FT-IR (KBr) ν_{max}: 3410, 1696, 1615, 1591, 1563, 1486, 1430, 1377, 1322, 1288, 1149, 1056, 1013, 986, 934 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ 13.60 (s, br, 1H, COOH), 8.93 (s, 1H, Quino−H), 8.68 (d, *J*=4.0 Hz, 1H, Py−H), 8.65 (d, *J*=15.3 Hz, 1H, −CH=CH−), 8.12 (t, *J*=8.7 Hz, 2H, ArH), 8.02 (d, *J*=15.3 Hz, 1H, −CH=CH−), 7.84–7.93 (m, 2H, ArH), 7.64–7.70 (m, 2H, ArH), 7.36 (dd, *J*=6.6, 4.8 Hz, 1H, ArH); MS (FAB) *m*/*z*: 277.0 ($[M+H]^+$, 100). Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14%. Found: C, 73.67; H, 4.33; N, 10.03%.

*4.2.22. (E)-2-(2-(Pyridin-3-yl)vinyl)quinoline-3-carboxylic acid (**3v**).* Yellow prisms, mp 258–259 °C; FT-IR (KBr) ν_{max}: 3411, 1699, 1636, 1616, 1583, 1554, 1485, 1420, 1400, 1326, 1253, 1206, 1122, 1047, 968 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ 13.59 (s, br, 1H, COOH), 8.94 (s, 1H, Quino−H), 8.88 (d, *J*=1.5 Hz, 1H, Py−H), 8.55 (dd, *J*=4.2, 1.1 Hz, 1H, Py−H), 8.29 (d, *J*=15.8 Hz, 1H, −CH=CH−), 8.07–8.14 (m, 3H, ArH), 7.98 (d, *J*=15.8 Hz, 1H, −CH=CH−), 7.87–7.92 (m, 1H, ArH), 7.66 (t, *J*=7.6 Hz, 1H, ArH), 7.48 (dd, *J*=7.8, 7.8 Hz, 1H, ArH); MS (FAB) *m*/*z*: 277.0 ($[M+H]^+$, 100). Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14%. Found: C, 74.09; H, 4.29; N, 9.88%.

*4.2.23. (E)-2-(2-(Pyridin-4-yl)vinyl)quinoline-3-carboxylic acid (**3w**).* Yellow prisms, mp 219–220 °C; FT-IR (KBr) ν_{max}: 3412, 1716, 1609, 1557, 1506, 1451, 1419, 1378, 1275, 1206, 1128, 1056, 1028, 976, 958 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ 13.60 (s, br, 1H, COOH), 8.96 (s, 1H, Quino−H), 8.63 (d, *J*=4.2 Hz, 2H, Py−H), 8.42 (d, *J*=15.7 Hz, 1H, −CH=CH−), 8.14 (d, *J*=8.1 Hz, 1H, ArH), 8.09 (d, *J*=8.5 Hz, 1H, ArH), 7.90 (d, *J*=15.7 Hz, 1H, −CH=CH−), 7.65–7.70 (m, 2H, ArH), 7.64 (d, *J*=4.4 Hz, 2H, Py−H); MS (FAB) *m*/*z*: 277.0 ($[M+H]^+$, 100). Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14%. Found: C, 73.72; H, 4.32; N, 9.92%.

*4.2.24. (E)-2-(2-(Naphthalen-1-yl)vinyl)quinoline-3-carboxylic acid (**3x**).* Yellow needles, mp 211–213 °C; FT-IR (KBr) ν_{max}: 3442, 1707, 1616, 1588, 1559, 1489, 1396, 1346, 1253, 1187, 1133, 1060, 963 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ 13.57 (s, br, 1H, COOH), 8.95 (s, 1H, Quino−H), 8.77 (d, *J*=15.3 Hz, 1H, −CH=CH−), 8.36 (d, *J*=8.4 Hz, 1H, ArH), 8.26 (d, *J*=15.6 Hz, 1H, −CH=CH−), 8.13–8.17 (m, 2H, ArH), 8.00 (t, *J*=8.1 Hz, 2H, ArH), 7.88–7.94 (m, 2H, ArH), 7.58–7.68 (m, 4H, ArH); MS (FAB) *m*/*z*: 326.1 ($[M+H]^+$, 100). Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.30%. Found: C, 81.37; H, 4.59; N, 4.06%.

*4.2.25. (E)-2-(2-(Naphthalen-2-yl)vinyl)quinoline-3-carboxylic acid (**3y**).* Yellow powder, mp 239–241 °C; FT-IR (KBr) ν_{max}: 3441, 1712, 1616, 1558, 1492, 1453, 1436, 1379, 1248, 1186, 1135, 1057, 969, 819, 749 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ: 13.15 (s, br, 1H, COOH), 8.97 (s, 1H, Quino−H), 8.33 (d, *J*=16.0 Hz, 1H, −CH=CH−), 8.16 (d, *J*=15.6 Hz, 1H, −CH=CH−), 8.12–8.15 (m, 2H, ArH), 8.10 (s, 1H, ArH), 8.00 (d, *J*=8.4 Hz, 2H, ArH), 7.88–7.96 (m, 3H, ArH), 7.67 (t, *J*=8.0 Hz, 1H, ArH), 7.53–7.58 (m, 2H, ArH); MS (FAB) *m*/*z*: 326.1 ($[M+H]^+$, 100). Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.30%. Found: C, 80.99; H, 4.74; N, 4.33%.

4.3. General procedure for synthesis of the cyclized products 4a–n

(*E*)-2-Arylvinylquinoline-3-carboxylic acid (0.5 mmol) and PPA (83% P_2O_5, 7.5 g) were added to round flask (25 mL) and stirred at 150 °C for about 4 h. The conversion was monitored by TLC. Then the reaction mixture was poured slowly into cold saturated sodium hydrogen carbonate solution. The crude products were obtained after filtration, and purified by flash chromatography (petroleum ether/EtOAc, 1:1).

*4.3.1. 12H-Benzo[4,5]cyclohepta[1,2-b]quinolin-12-one (**4a**).* White solid, mp 204–205 °C; FT-IR (KBr) ν_{max}: 1650, 1616, 1594, 1572, 1488, 1463, 1431, 1403, 1382, 1338, 1284, 1232, 1118, 1089, 944, 889 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 9.05 (s, 1H, Quino−H), 8.26 (d, *J*=8.4 Hz, 1H, ArH), 8.16 (d, *J*=8.4 Hz, 1H, ArH), 8.02 (d, *J*=8.1 Hz, 1H, ArH), 7.86 (ddd, *J*=8.4, 7.0, 1.2 Hz, 1H, ArH), 7.64–7.71 (m, 2H, ArH), 7.57–7.62 (m, 2H, ArH), 7.48 (d, *J*=12.5 Hz, 1H, Tropone−H), 7.28 (d, *J*=12.5 Hz, 1H, Tropone−H); MS (FAB) *m*/*z*: 113.0 (100), 258.0 ($[M+H]^+$, 70). Anal. Calcd for $C_{18}H_{11}NO$: C, 84.03; H, 4.31; N, 5.44%. Found: C, 83.81; H, 4.63; N, 5.37%.

*4.3.2. 10-Methyl-12H-benzo[4,5]cyclohepta[1,2-b]quinolin-12-one (**4b**).* White solid, mp 179–181 °C; FT-IR (KBr) ν_{max}: 1631, 1606, 1570, 1552, 1487, 1430, 1381, 1330, 1304, 1271, 1192, 1128, 1045, 937, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 9.06 (s, 1H, ArH), 8.26 (d, *J*=8.6 Hz, 1H, ArH), 8.17 (d, *J*=8.5 Hz, 1H, ArH), 8.03 (d, *J*=8.3 Hz, 1H, ArH), 7.84–7.90 (m, 1H, ArH), 7.65–7.70 (m, 1H, ArH), 7.57–7.62 (m, 2H, ArH), 7.48 (d, *J*=12.5 Hz, 1H, Tropone−H), 7.28 (d, *J*=12.5 Hz, 1H, Tropone−H), 1.59 (s, 3H, Me); MS (FAB) *m*/*z*: 272.1 ($[M+H]^+$, 100). Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16%. Found: C, 84.27; H, 4.99; N, 5.34%.

*4.3.3. 3-(4-Methoxyphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one (**4c**).* Pale yellow solid, mp 189–191 °C; FT-IR (KBr) ν_{max}: 3062, 3016, 2972, 1732, 1617, 1566, 1516, 1417, 1377, 1304, 1253, 1213, 1130, 1062, 1033, 847 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ 9.08 (s, 1H, Quino−H), 8.24 (d, *J*=7.8 Hz, 1H, Quino−H), 8.07 (d, *J*=8.4 Hz, 1H, Quino−H), 7.94 (t, *J*=8.4 Hz, 1H, Quino−H), 7.70 (dd, *J*=8.4, 7.8 Hz, 1H, Quino−H), 7.50 (d, *J*=8.7 Hz, 2H, Ph−H), 7.01 (d, *J*=8.7 Hz, 2H, Ph−H), 5.88 (dd, *J*=11.4, 3.0 Hz, 1H, CH), 3.80 (dd, *J*=16.8, 3.0 Hz, 1H, CH_2), 3.78 (s, 3H, Me), 3.42 (dd, *J*=16.8, 3.0 Hz, 1H, CH_2); MS (FAB) *m*/*z*: 306.1 ($[M+H]^+$, 100). Anal. Calcd for $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.59%. Found: C, 74.54; H, 5.01; N, 4.72%.

*4.3.4. 3-(4-Ethylphenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one (**4d**).* White solid, mp 171–173 °C; FT-IR (KBr) ν_{max}: 2966, 2931, 1724, 1619, 1567, 1498, 1417, 1379, 1216, 1194, 1053, 986, 834 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ 9.06 (s, 1H, Quino−H), 8.22 (d, *J*=8.1 Hz, 1H, Quino−H), 8.05 (d, *J*=8.4 Hz, 1H, Quino−H), 7.92 (t, *J*=7.8 Hz, 1H, Quino−H), 7.68 (t, *J*=8.1 Hz, 1H, Quino−H), 7.46 (d, *J*=7.8 Hz, 2H, Ph−H), 7.28 (d, *J*=8.1 Hz, 2H, Ph−H), 5.91 (dd, *J*=11.4, 3.0 Hz, 1H, CH), 3.75 (dd, *J*=16.5, 3.0 Hz, 1H, CH_2), 3.43 (dd, *J*=16.5, 3.0 Hz, 1H, CH_2), 2.62 (q, *J*=7.8 Hz, 2H, CH_2CH_3), 1.80 (t, *J*=7.8 Hz, 3H, CH_2CH_3); MS (FAB) *m*/*z*: 304.1 ($[M+H]^+$, 100). Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62%. Found: C, 79.41; H, 5.74; N, 4.54%.

*4.3.5. 10-Fluoro-12H-benzo[4,5]cyclohepta[1,2-b]quinolin-12-one (**4e**).* White solid, mp 186–188 °C; FT-IR (KBr) ν_{max}: 1650, 1604, 1573, 1515, 1496, 1395, 1329, 1227, 1213, 1158, 1064, 993, 840 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 9.08 (s, 1H, Quino−H), 8.17 (d, *J*=8.6 Hz, 1H, ArH), 7.96–8.01 (m, 2H, ArH), 7.85–7.90 (m, 1H, ArH), 7.57–7.66 (m, 2H, ArH), 7.45 (d, *J*=12.6 Hz, 1H, Tropone−H), 7.38–7.41 (m, 1H, ArH), 7.24 (d, *J*=12.6 Hz, 1H, Tropone−H); MS (FAB) *m*/*z*: 276.0 ($[M+H]^+$, 100). Anal. Calcd for $C_{18}H_{10}FNO$: C, 78.54; H, 3.66; N, 5.09%. Found: C, 78.75; H, 3.73; N, 4.84%.

*4.3.6. 8-Chloro-12H-benzo[4,5]cyclohepta[1,2-b]quinolin-12-one (**4f**).* Pale yellow solid, mp 218–219 °C; FT-IR (KBr) ν_{max}: 1655, 1616, 1584, 1557, 1488, 1464, 1425, 1382, 1337, 1299, 1268, 1191, 1133, 1098, 964, 936, 866, 830 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.87 (s, 1H, Quino−H), 8.17 (d, *J*=8.5 Hz, 1H, ArH), 7.87 (ddd, *J*=8.5, 6.9,

1.2 Hz, 1H, ArH), 7.99–8.03 (m, 2H, ArH), 7.73 (dd, *J*=7.9, 1.1 Hz, 1H, ArH), 7.79 (d, *J*=12.9 Hz, 1H, Tropone–H), 7.62 (t, *J*=7.2 Hz, 1H, ArH), 7.54 (d, *J*=12.9 Hz, 1H, Tropone–H), 7.47 (t, *J*=7.9 Hz, 1H, ArH); MS (FAB) *m*/*z*: 113.0 (16), 292.0 ([M+H]$^+$, 100), 294.0 (37). Anal. Calcd for $C_{18}H_{10}ClNO$: C, 74.11; H, 3.46; N, 4.80%. Found: C, 73.95; H, 3.60; N, 4.93%.

*4.3.7. 9-Chloro-12H-benzo[4,5]cyclohepta[1,2-b]quinolin-12-one (**4g**).* Yellow solid, mp 221–222 °C; FT-IR (KBr) ν_{max}: 1645, 1618, 1585, 1553, 1487, 1377, 1321, 1281, 1221, 1171, 1111, 944, 893, 821 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.07 (s, 1H, ArH), 8.22 (d, *J*=8.4 Hz, 1H, ArH), 8.17 (d, *J*=8.6 Hz, 1H, ArH), 8.03 (d, *J*=8.0 Hz, 1H, ArH), 7.88 (ddd, *J*=8.4, 6.9, 1.3 Hz, 1H, ArH), 7.64 (dd, *J*=7.9, 7.1 Hz, 1H, ArH), 7.52–7.57 (m, 2H, ArH and Tropone–H), 7.50 (d, *J*=6.9 Hz, 1H, ArH), 7.17 (d, *J*=12.6 Hz, 1H, Tropone–H); MS (FAB) *m*/*z*: 200.1 (8), 292.0 ([M+H]$^+$, 100), 294.0 (35). Anal. Calcd for $C_{18}H_{10}ClNO$: C, 74.11; H, 3.46; N, 4.80%. Found: C, 73.89; H, 3.63; N, 4.98%.

*4.3.8. 10-Chloro-12H-benzo[4,5]cyclohepta[1,2-b]quinolin-12-one (**4h**).* Pale yellow solid, mp 209–210 °C; FT-IR (KBr) ν_{max}: 1655, 1617, 1577, 1551, 1482, 1432, 1384, 1306, 1304, 1260, 1228, 1213, 1127, 967, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.06 (s, 1H, Quino–H), 8.25 (d, *J*=2.2 Hz, 1H, Ph–H), 8.17 (d, *J*=8.5 Hz, 1H, ArH), 8.04 (d, *J*=8.1 Hz, 1H, ArH), 7.88 (ddd, *J*=8.4, 7.0, 1.4 Hz, 1H, ArH), 7.62–7.67 (m, 2H, ArH), 7.53 (d, *J*=8.4 Hz, 1H, ArH), 7.49 (d, *J*=12.6 Hz, 1H, Tropone–H), 7.23 (d, *J*=12.6 Hz, 1H, Tropone–H); MS (FAB) *m*/*z*: 292.0 ([M+H]$^+$, 100), 294.0 (32). Anal. Calcd for $C_{18}H_{10}ClNO$: C, 74.11; H, 3.46; N, 4.80%. Found: C, 74.29; H, 3.31; N, 4.92%.

*4.3.9. 8,9-Dichloro-12H-benzo[4,5]cyclohepta[1,2-b]quinolin-12-one (**4i**).* White solid, mp 241–242 °C; FT-IR (KBr) ν_{max}: 1652, 1617, 1575, 1549, 1488, 1457, 1431, 1382, 1355, 1332, 1294, 1265, 1225, 1169, 1099, 961, 812 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.86 (s, 1H, Quino–H), 8.17 (d, *J*=8.6 Hz, 1H, ArH), 8.01 (d, *J*=8.1 Hz, 1H, ArH), 7.95 (d, *J*=8.6 Hz, 1H, ArH), 7.85–7.90 (m, 1H, ArH), 7.80 (d, *J*=12.9 Hz, 1H, Tropone–H), 7.62–7.66 (m, 2H, ArH), 7.56 (d, *J*=12.9 Hz, 1H, Tropone–H); MS (FAB) *m*/*z*: 113.0 (15), 326.0 ([M+H]$^+$, 100), 327.9 (75), 330.0 (15). Anal. Calcd for $C_{18}H_9Cl_2NO$: C, 66.28; H, 2.78; N, 4.29%. Found: C, 66.07; H, 2.89; N, 4.38%.

*4.3.10. 9,11-Dichloro-12H-benzo[4,5]cyclohepta[1,2-b]quinolin-12-one (**4j**).* White solid, mp 225–226 °C; FT-IR (KBr) ν_{max}: 1673, 1616, 1577, 1542, 1488, 1458, 1369, 1328, 1226, 1248, 1164, 1118, 958, 929, 891, 862, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.66 (s, 1H, Quino–H), 8.16 (d, *J*=8.7 Hz, 1H, Quino–H), 8.01 (d, *J*=8.1 Hz, 1H, Quino–H), 7.84–7.89 (m, 1H, Quino–H), 7.62–7.67 (m, 1H, Quino–H), 7.58 (d, *J*=1.9 Hz, 1H, Ph–H), 7.45 (d, *J*=12.6 Hz, 1H, Tropone–H), 7.43 (d, *J*=1.5 Hz, 1H, Ph–H), 7.14 (d, *J*=12.5 Hz, 1H, Tropone–H); MS (FAB) *m*/*z*: 326.0 ([M+H]$^+$, 100), 328.0 (65), 330.0 (10). Anal. Calcd for $C_{18}H_9Cl_2NO$: C, 66.28; H, 2.78; N, 4.29%. Found: C, 66.47; H, 2.83; N, 4.11%.

*4.3.11. 8-Bromo-12H-benzo[4,5]cyclohepta[1,2-b]quinolin-12-one (**4k**).* White solid, mp 210–211 °C; FT-IR (KBr) ν_{max}: 1656, 1616, 1581, 1558, 1489, 1463, 1382, 1338, 1298, 1267, 1191, 1127, 1093, 961, 863, 828 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.85 (s, 1H, Quino–H), 8.17 (d, *J*=8.5 Hz, 1H, ArH), 8.04 (d, *J*=7.8 Hz, 1H, ArH), 8.00 (d, *J*=8.3 Hz, 1H, ArH), 7.94 (d, *J*=7.8 Hz, 1H, ArH), 7.87 (dd, *J*=8.0, 7.2 Hz, 1H, ArH), 7.75 (d, *J*=12.9 Hz, 1H, Tropone–H), 7.63 (t, *J*=7.4 Hz, 1H, ArH), 7.52 (d, *J*=12.9 Hz, 1H, Tropone–H), 7.39 (t, *J*=7.9 Hz, 1H, ArH); MS (FAB) *m*/*z*: 116.1 (20), 149.1 (18), 336.0 ([M+H]$^+$, 100), 338.0 (93). Anal. Calcd for $C_{18}H_{10}BrNO$: C, 64.31; H, 3.00; N, 4.17%. Found: C, 64.16; H, 2.90; N, 4.31%.

*4.3.12. 9-Bromo-12H-benzo[4,5]cyclohepta[1,2-b]quinolin-12-one (**4l**).* White solid, mp 219–220 °C; FT-IR (KBr) ν_{max}: 1645, 1617, 1580, 1551, 1486, 1430, 1372, 1319, 1282, 1226, 1129, 1100, 943, 894, 817 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.05 (s, 1H, Quino–H), 8.17 (d, *J*=8.7 Hz, 1H, ArH), 8.12 (d, *J*=8.5 Hz, 1H, ArH), 8.02 (d, *J*=8.2 Hz, 1H, ArH), 7.88 (ddd, *J*=8.5, 6.9, 1.4 Hz, 1H, ArH), 7.73 (d, *J*=1.8 Hz, 1H, Ph–H), 7.68 (dd, *J*=8.6, 1.9 Hz, 1H, Ph–H), 7.61–7.66 (m, 1H, ArH), 7.50 (d, *J*=12.5 Hz, 1H, Tropone–H), 7.15 (d, *J*=12.6 Hz, 1H, Tropone–H); MS (FAB) *m*/*z*: 336.0 ([M+H]$^+$, 100), 338.0 (95). Anal. Calcd for $C_{18}H_{10}BrNO$: C, 64.31; H, 3.00; N, 4.17%. Found: C, 64.41; H, 3.07; N, 4.06%.

*4.3.13. 10-Bromo-12H-benzo[4,5]cyclohepta[1,2-b]quinolin-12-one (**4m**).* White solid, mp 213–214 °C; FT-IR (KBr) ν_{max}: 1655, 1616, 1576, 1557, 1488, 1431, 1382, 1306, 1261, 1125, 1094, 964, 900, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.05 (s, 1H, Quino–H), 8.40 (d, *J*=1.8 Hz, 1H, Ph–H), 8.17 (d, *J*=8.5 Hz, 1H, ArH), 8.03 (d, *J*=8.2 Hz, 1H, ArH), 7.88 (dd, *J*=8.1, 7.2 Hz, 1H, ArH), 7.78 (dd, *J*=8.3, 2.0 Hz, 1H, Ph–H), 7.64 (t, *J*=7.4 Hz, 1H, ArH), 7.50 (d, *J*=12.5 Hz, 1H, Tropone–H), 7.45 (d, *J*=8.3 Hz, 1H, ArH), 7.21 (d, *J*=12.5 Hz, 1H, Tropone–H); MS (FAB) *m*/*z*: 335.9 ([M+H]$^+$, 100), 338.0 (94). Anal. Calcd for $C_{18}H_{10}BrNO$: C, 64.31; H, 3.00; N, 4.17%. Found: C, 64.43; H, 3.08; N, 4.02%.

*4.3.14. 3-(3-Nitrophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one (**4o**).* Yellow solid, mp 184–185 °C; FT-IR (KBr) ν_{max}: 1722, 1619, 1599, 1489, 1447, 1405, 1349, 1258, 1225, 1153, 1102, 1035, 924; ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 9.12 (s, 1H, Quino–H), 8.48 (s, 1H, Ph–H), 8.22–8.29 (m, 3H, ArH), 7.91–7.97 (m, 2H, ArH), 7.79 (t, *J*=8.0 Hz, 1H, ArH), 7.71 (t, *J*=8.1 Hz, 1H, ArH), 6.15 (dd, *J*=11.8, 2.8 Hz, 1H, CH), 3.82 (dd, *J*=16.4, 3.0 Hz, 1H, CH_2), 3.56 (dd, *J*=16.4, 3.0 Hz, 1H, CH_2); MS (FAB) *m*/*z*: 321.0 ([M+H]$^+$, 100). Anal. Calcd for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.75%. Found: C, 67.75; H, 4.08; N, 8.83%.

*4.3.15. 3-(4-Nitrophenyl)-3,4-dihydro-1H-pyrano[4,3-b]quinolin-1-one (**4p**).* Yellow solid, mp 192–193 °C; FT-IR (KBr) ν_{max}: 1730, 1617, 1567, 1525, 1494, 1464, 1413, 1377, 1347, 1320, 1292, 1262, 1195, 1064, 1003, 964, 937, 844 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.03 (s, 1H, Quino–H), 8.32 (d, *J*=8.8 Hz, 2H, Ph–H), 8.12 (d, *J*=8.4 Hz, 1H, Quino–H), 8.01 (d, *J*=8.3 Hz, 1H, Quino–H), 7.89–7.94 (m, 1H, Quino–H), 7.74 (d, *J*=8.7 Hz, 2H, Ph–H), 7.67 (dd, *J*=8.0, 7.3 Hz, 1H, Quino–H), 5.87 (dd, *J*=10.1, 4.8 Hz, 1H, CH), 3.62–3.66 (m, 2H, CH_2); MS (FAB) *m*/*z*: 294.1 (10), 321.1 ([M+H]$^+$, 100). Anal. Calcd for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.75%. Found: C, 67.77; H, 3.61; N, 8.94%.

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Supplementary data

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