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Convenient, two-step synthesis of 2-styrylquinolines: an application of the CAN-catalyzed vinylogous type-II Povarov reaction

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ABSTRACT

A new, experimentally simple, synthesis of 2-styrylquinolines was developed using a two-step sequence based on a CAN-catalyzed three-component type-II vinylogous Povarov reaction from arylamines, cinnamaldehydes, and electron-rich cyclic and noncyclic vinyl ethers. The tetrahydroquinolines thus obtained were subsequently aromatized to styrylquinolines by DDQ-promoted dehydrogenation.

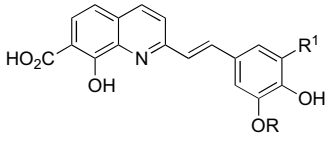
1. Introduction

The quinoline ring system[1] is an essential structural fragment of a large number of natural and unnatural compounds possessing a wide variety of pharmacological actions,[2,3] in addition to their application in materials science.[4,5] Amongst quinoline derivatives, there is much current interest in 2-styrylquinolines (SQLs), exemplified by FZ41 and KHD161 (Fig. 1). These compounds are normally devoid of significant cytotoxicity and provide a novel and promising strategy for AIDS therapy[6] due to their ability to act as HIV integrase inhibitors[7] by a previously unknown mechanism.[8]

The available methods for the synthesis of styrylquinolines are based on the synthesis of 2-methylquinolines followed by an acid or base catalyzed condensation with suitable aromatic aldehydes,[7a–d,9] in which the final step is not a facile one and gives moderate yields in many cases. Syntheses of the key intermediate 2-methylquinolines have been normally achieved by traditional methods like the Friedländer, Doebner–von Miller, Combes, and Pfitzinger reactions. In spite of their simplicity, these methods have considerable drawbacks such as low yields and the use of harsh reaction conditions and highly acidic reaction media, although some new procedures and improvements of the classical reactions have been reported.[10] Consequently, it is still important to develop a simple and efficient alternative synthetic route to the valuable styrylquinolines.

2. Results and discussion

In this context, we extend and generalize here the results in our recent preliminary communication on the synthesis of 2-functionalized tetrahydroquinolines[11] and also report our studies on their aromatization to styrylquinolines. This methodology is based on a novel three-component reaction between arylamines, vinyl ethers, and cinnamaldehyde catalyzed by cerium(IV) ammonium nitrate (CAN), which is a nontoxic, inexpensive, and water-tolerant reagent that has found widespread use in carbon–carbon and carbon–heteroatom bond forming reactions[12] but has received relatively little attention as a catalyst.[13] The first step in our protocol (Scheme 1) is a type-II vinylogous Povarov reaction[11] between an arylamine and cinnamaldehyde. This reaction involves the formation of an α,β-unsaturated imine as an intermediate, and this mechanism is the origin of the main potential drawback of our planned approach, namely the fact that cinnamaldehyde arylimines possess an exocyclic α,β-unsaturated imine system that may act as a diene in inverse electron demand Diels–Alder reactions with electron-rich dienophiles, leading to 1,4-dihydropyridines.[14] On the other hand, some nucleophilic 1,2-additions of ketene silyl ketals and thioketals to α,β-unsaturated arylimines have been described,[15] providing an encouraging, although remote, precedent because such an addition can be considered to be the first step of our proposed transformation (Scheme 1), as it is now generally accepted that the Povarov reaction normally proceeds stepwise.[13e,16,17]



FZ41 R = CH_3; R^1 = OH
KHD161 R = H; R^1 = H

Figure 1.

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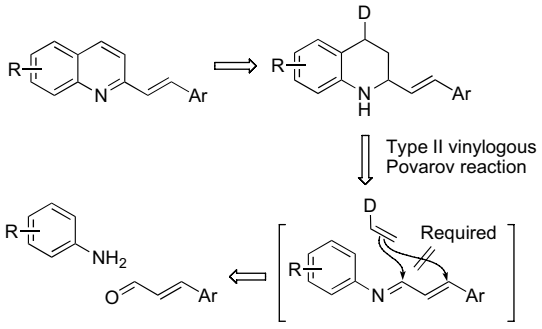


Scheme 1.

In the event, our starting hypothesis turned out to be correct and the desired vinylogous reaction could be carried out efficiently by mixing together anilines **1**, cinnamaldehyde **3** and 2,3-dihydrofuran **2** as a prototype cyclic ether in acetonitrile with a catalytic amount of CAN (5%), and led to 2,3,3a,4,5,9b-hexahydro-4-styrylfuro[3,2-*c*]quinoline derivatives (compounds **4** and **5**) in good to excellent yields, as almost equimolecular mixtures of diastereomers. The reactions proceeded well with both electron donating and withdrawing groups in the arylamine component (Scheme 2 and Table 1), although some substituents (specially alkoxy groups) disappointingly led to complex mixtures. These reactions have no significant stereoselectivity, as expected from literature precedent on straightforward Povarov reactions of cyclic vinyl ethers.[13b,18] The stereochemistry of the products was unambiguously determined by the combined use of coupling constant values and NOESY experiments.

In order to generalize the new synthesis of 2-styryl-1,2,3,4-tetrahydroquinolines, we explored the use of noncyclic vinyl ethers **6**, which so far has received little attention in Povarov chemistry (Scheme 3, Table 2). It is interesting to note that the reaction was completely diastereoselective and gave only 2-styryl-1,2,3,4-tetrahydroquinolines **7** with a cis arrangement between H-2 and H-4. The yields were lower than in the reactions involving cyclic vinyl ethers due to the formation of side product identified as 2-methyl-1,2,3,4-tetrahydroquinolines **8**, which can be explained by a CAN-catalyzed three-component reaction between arylamines and two molecules of vinyl ether.[10]

The complete diastereoselectivity found for the reactions starting from noncyclic vinyl ethers **6** can be explained by assuming a stepwise mechanism for the vinylogous Povarov reaction, where a cis arrangement between the alkoxy and styryl groups leads to minimum interactions between these bulky substituents and the axial protons in the chair-like transition state of the cyclization step leading to the tetrahydroquinoline system (Scheme 4).

In order to provide further support for this explanation, we considered it relevant to confirm whether our imino Diels–Alder reaction took place in a concerted or stepwise manner since, although the mechanism of the Povarov reaction is normally accepted to be stepwise,[16] there is also evidence pointing at concerted pathways in some cases.[19] For this reason, we wished to verify the generation of the putative intermediate oxonium species

Table 1
CAN-catalyzed synthesis of 3,3a,4,5,9b-hexahydro-4-styrylfuro[3,2-*c*]quinolines

Compd	R^1	R^2	R^3	R^4	Reaction time (h)	Yield (%)	**4**/**5** Ratio[a]
a	H	H	H	H	2	83	57:43
b	H	H	Cl	H	2	80	54:46
c	H	H	CH_3	H	4	68	60:40
d	H	H	Br	H	1.5	79	53:47
e	H	H	F	H	4	70	54:46
f	H	CH_3	H	CH_3	2	75	55:45
g	CH_3	H	CH_3	H	6	85	53:47

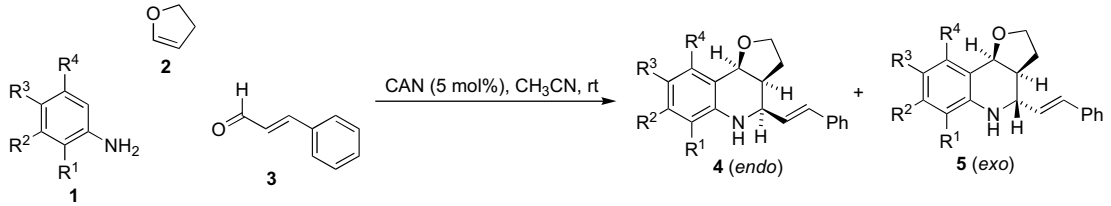
[a] This product ratio was calculated from the ^{1}H NMR spectrum of the crude reaction mixture and both products were subsequently separated by column chromatography.

postulated in the above mentioned stepwise mechanism. Indeed, when the reaction starting from *p*-chloroaniline, cinnamaldehyde, and butyl vinyl ether was carried out in ethanol, a nucleophilic solvent, tetrahydroquinoline **7f** was accompanied by an almost equimolecular amount of acetal **9**, arising from a four-component process involving trapping of the oxonium intermediate by a solvent molecule (Scheme 5). This behavior was similar to the one previously found by us for the non-vinylogous CAN-catalyzed Povarov reaction.[13b]

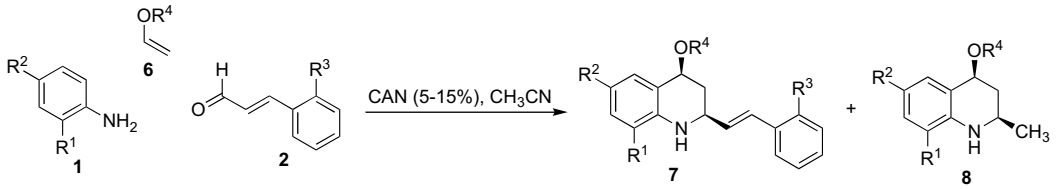
Finally, in an effort to clarify whether CAN exerts its role in our 2-styryl-1,2,3,4-tetrahydroquinoline synthesis through an oxidative pathway, as might be expected from a powerful one-electron oxidant, we performed the reaction between cinnamaldehyde, aniline, and ethyl vinyl ether (entry 1 in Table 2) in the presence of a large amount of 1,1-diphenylethylene, a well-known radical trap, finding no noticeable loss in yield. This result indicates that a radical mechanism is not in operation under our conditions and that therefore in this case CAN acts as a Lewis acid, a behavior that has some precedent in the literature.[13a–d,20]

With an efficient methodology for the synthesis of the intermediate tetrahydroquinolines in hand, we next examined their dehydrogenation into styrylquinolines. While the literature contains some examples of aromatization of 4-alkoxy-1,2,3,4-tetrahydroquinolines in acidic media, we had previously obtained product mixtures using this approach.[10] Therefore, anchored in our previous experience in the aromatization of 2-methyl-1,2,3,4-tetrahydroquinolines to the corresponding 2-methylquinolines,[10] we initially employed 10% activated Pd/C for the aromatization process. When some mixtures of compounds **4** and **5** were refluxed in methanol containing suspended 10% Pd/C, only the *endo* isomers **4** were converted into styrylquinolines **10**, with concomitant opening of the furan ring, whereas the *exo* isomers **5** remained unreacted (Scheme 6, Table 3). An increase of the Pd/C load and reaction time did not improve these results.

The stereoselective dehydrogenation of the *endo* isomer **4** can be explained by admitting that coordination to palladium takes place preferentially on the less hindered H-3a and H-4 hydrogens and that this coordination is expected to be more favorable in **4** than **5**, where both hydrogens have a trans relationship. A subsequent elimination reaction involving the oxygen atom of the tetrahydrofuran ring as a leaving group explains the isolation of compounds **10** (Scheme 7).



Scheme 2.

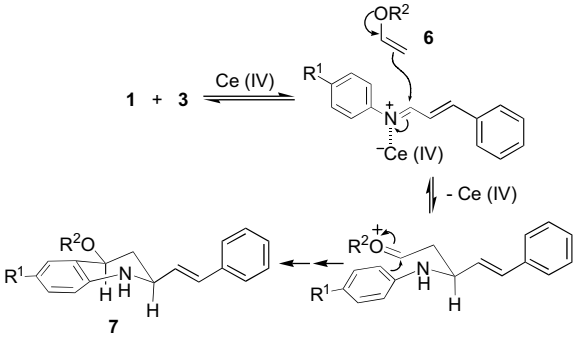


Scheme 3.

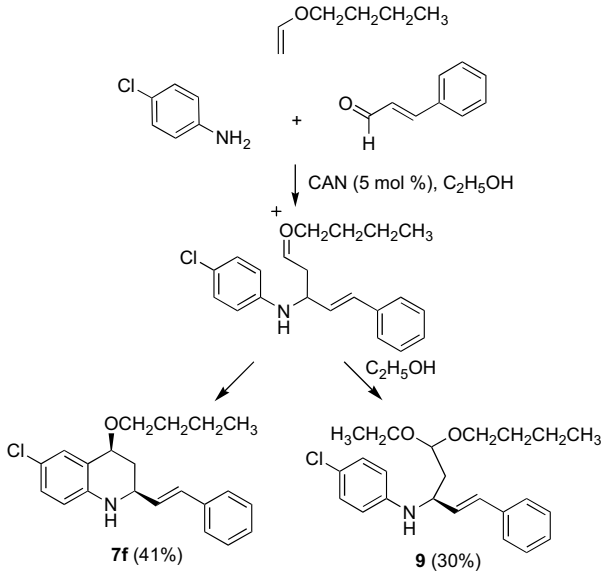
Table 2
Type-II vinylogous Pavarov reaction with noncyclic vinyl ethers

Comp	R^1	R^2	R^3	R^4	CAN (mol %)	Time (h)	Yield (%)	
							7	**8**
a	H	H	H	Et	5	3	60	6
b	H	H	H	Pr	5	3	63	5
c	H	H	H	Bu	5	3	65	3
d	H	Cl	H	Et	5	2	48	13
e	H	Cl	H	Pr	5	2	55	13
f	H	Cl	H	Bu	5	2	49	15
g	H	F	H	Et	15	2	40	16
h	H	F	H	Bu	15	2	41	18
i	H	Br	H	Et	5	1.5	46	16
j	H	CH_3	H	Et	15	5	60	3[a]
k	OCH_3	H	H	Et	15	1	53	32
l	H	H	NO_2	Et	5	1	41	5

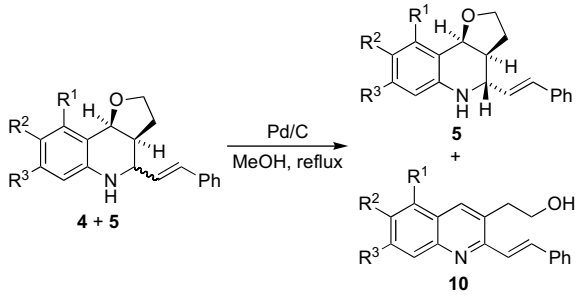
[a] Together with 15% of the corresponding aromatized styrylquinoline.



Scheme 4. Stepwise mechanism proposed for the type-II vinylogous Povarov reaction.



Scheme 5. CAN-catalyzed one-pot reaction of 4-chloroaniline, cinnamaldehyde, and butyl vinyl ether in ethanol.

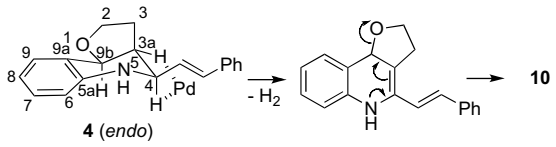


Scheme 6. Aromatization of *endo*/*exo* mixtures of furo[3,2-*c*]quinolines **4** and **5** in the presence of Pd/C.

Table 3
Results obtained in the aromatization of mixtures of **4** and **5** in the presence of Pd/C

Compd	R^1	R^2	R^3	Initial **4**/**5** ratio	Reaction time (h)	Final **5**/**10** ratio[a]
a	H	H	H	57:43	6	46:54
c	H	CH_3	H	60:40	6	36:64
f	CH_3	H	CH_3	55:45	6	43:57

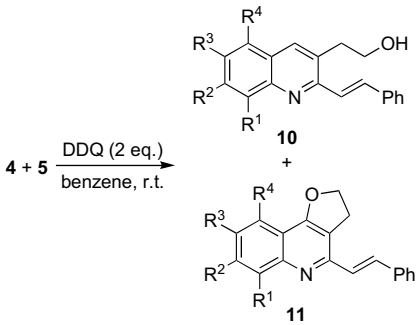
[a] Product ratio was determined from the crude ^{1}H NMR spectrum of the reaction mixture.



Scheme 7. Explanation for the stereospecific dehydrogenation of the endo isomer of compound **4**.

In an effort to improve these results, we investigated the aromatization reaction in the presence of the well-known oxidizing agent DDQ (Scheme 8, Table 4). Treatment of diastereomeric mixtures of **4** and **5** in benzene with 2 equiv of DDQ under mild conditions (room temperature) afforded mixtures of isomeric styrylquinolines **10** and **11** in excellent overall yields and in ca. 2:1 ratios, in a reaction that proceeded very well irrespectively of the nature of the substituents.

DDQ was also employed for the aromatization of tetrahydroquinolines **7**. As expected, the reaction proceeded smoothly to give styrylquinolines **12** in excellent yields and under mild



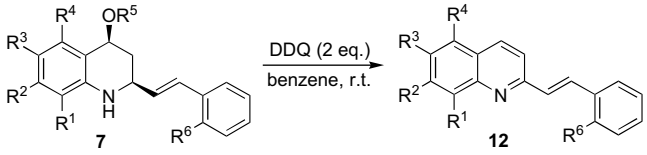
Scheme 8. Aromatization of mixtures of compounds **4** and **5** in the presence of DDQ.

Table 4
DDQ-mediated aromatization of mixtures of compounds **4** and **5**

Compd	R^1	R^2	R^3	R^4	Yield (%)	**10**/**11** Ratio[a]
a	H	H	H	H	97	68:32
b	H	H	Cl	H	96	66:34
c	H	H	CH_3	H	94	68:32
d	H	H	Br	H	96	61:39
e	H	H	F	H	97	68:32
f	H	CH_3	H	CH_3	95	70:30

[a] Product ratio was calculated from the ^{1}H NMR spectrum of the crude reaction mixture and products were separated by column chromatography.

conditions (Scheme 9, Table 5). In two cases (entries 9 and 10) we used the crude tetrahydroquinolines, obtained in the previous reaction, for the second aromatization step. Products were isolated without any significant loss of yield with regard to the cases where pure tetrahydroquinolines were used as starting materials.



Scheme 9. Aromatization of tetrahydroquinolines **7** in the presence of DDQ.

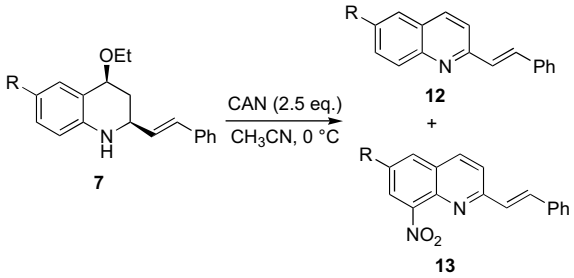
Table 5
Results obtained in the DDQ-mediated aromatization of **7**

Entry	R^1	R^2	R^3	R^4	R^5	R^6	Yield (%)	Product
1	H	H	H	H	Et	H	96	**12a**
2	H	H	H	H	Pr	H	95	**12a**
3	H	H	H	H	Bu	H	94	**12a**
4	H	H	Cl	H	Et	H	97	**12b**
5	H	H	Br	H	Et	H	95	**12c**
6	H	H	F	H	Et	H	94	**12d**
7	H	H	CH_3	H	Et	H	90	**12e**
8	H	H	H	H	Et	NO_2	94	**12f**
9[a]	H	CH_3	H	CH_3	Et	H	87[b]	**12g**
10[a]	CH_3	H	CH_3	H	Et	H	84[b]	**12h**

[a] Tetrahydroquinoline **7** was not separated. The crude obtained in the previous reaction, containing a mixture of quinoline and tetrahydroquinoline, was directly treated with 1 equiv of DDQ.
[b] Overall yield from the corresponding anilines.

Finally, and due to the existence of a literature precedent for a CAN-mediated aromatization of tetrahydroquinolines,[21] we set out to study the use of this reagent to achieve the aromatization step because, if successful, this reaction would pave the way for a one-pot synthesis of 2-styrylquinolines from simple acyclic precursors. We carried out some exploratory experiments involving treatment of 2-styryltetrahydroquinolines with 2.5 equiv of CAN in acetonitrile at 0 °C, and found that compounds containing electron-withdrawing groups (**7d** and **7g**) afforded the expected styrylquinolines (**12b** and **12d**) in excellent yields. However, compounds with an electron-donating group (**7j**) gave a 1:2 mixture of the expected styrylquinoline **12** and its 8-nitro derivative (**13**) (Scheme 10, Table 6). Interestingly, since both the aza Diels–Alder and the aromatization reactions are promoted by CAN, they can be performed in a one-pot procedure without any noticeable loss of yield (entry 2 of Table 6).

While CAN is a relatively well-known reagent for the nitration of electron-rich aromatic substrates,[22] very often in acidic media or on solid supports,[23] this regioselective nitration of a quinoline derivative at its C-8 position is remarkable, and can be probably attributed to coordination of Ce(IV) to the quinoline nitrogen. We are currently studying the scope of this reaction as a new method for



Scheme 10. Exploratory study of the CAN-mediated aromatization of compounds **7**.

Table 6
Results obtained in the CAN-mediated aromatization of **7**

Entry	Starting compd	R	Yield of **12** (%)	Yield of **13** (%)
1	**7d**	Cl	95	0
2	**7d**	C	45	0[a]
3	**7g**	F	94	0
4	**7j**	CH_3	35	59

[a] This reaction was performed in a one-pot procedure from 4-chloroaniline, cinnamaldehyde, and ethyl vinyl ether.

the preparation of 8-nitroquinolines, which are important intermediates in the preparation of several families of bioactive quinoline systems.[24]

3. Conclusion

In conclusion, we have developed an efficient two-reaction sequence that provides synthetic entry into biologically relevant 2-styrylquinolines based on a new CAN-catalyzed type-II vinylogous Povarov reaction and a DDQ-mediated aromatization. This methodology requires mild conditions and employs very simple starting materials and inexpensive and easily handled catalysts.

4. Experimental

4.1. General

All reagents (Aldrich, Fluka, SDS, Probus) and solvents (SDS, Scharlau) were of commercial quality and were used as received. Reactions were monitored by TLC on aluminum plates coated with silica gel with fluorescent indicator (SDS CCM221254). Separations by flash chromatography were performed on silica gel (SDS 60 ACC 40–63 mm). Melting points were measured on a Reichert 723 hot stage microscope and are uncorrected. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrophotometer with all compounds examined as thin films on NaCl disks. NMR spectra were obtained on a Bruker Avance 250 spectrometer operating at 250 and 62.9 MHz for ^{1}H and ^{13}C NMR spectra, respectively (CAI de Resonancia Magnética Nuclear, Universidad Complutense), with the signal of the residual non-deuterated solvent as an internal standard. Combustion elemental analyses were determined by the CAI de Microanálisis Elemental, Universidad Complutense, using a Leco 932 CHNS microanalyzer.

4.2. General procedure for the CAN-catalyzed synthesis of 2,3,3a,4,5,9b-hexahydro-4-styrylfuro[3,2-*c*]quinolines (4, 5)

An equimolar (3 mmol) mixture of arylamine (**1**) and cinnamaldehyde (**2**) was dissolved in acetonitrile (20 mL) and stirred at room temperature. To this stirred solution, dihydrofuran, **3** (4.5 mmol), and 5 mol% of CAN were added, and stirring was continued for the time period specified in Table 1. After completion

of the reaction, as indicated by TLC, the mixture was extracted with dichloromethane (2×20 mL), dried (anhydrous Na_2SO_4), and evaporated. The ratio of *endo* and *exo* 2,3,3a,4,5,9b-hexahydro-2-styrylfuro[3,2-*c*]quinolines (**4**, **5**) was calculated from the ^{1}H NMR spectrum of the crude reaction mixture, and the products were separated through silica column using petroleum ether/ethyl acetate mixture (98:2 to 95:5, v/v).

4.2.1. *endo-2,3,3a,4,5,9b-Hexahydro-4-styrylfuro[3,2-c]quinoline* **4a**

Viscous liquid. IR (neat) 3327.2, 3024.0, 2875.2, 1609.3, 1484.2, 1364.6, 1259.6, 1063.4 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.03–2.22 (m, 2H), 2.73–2.84 (m, 1H), 3.82–3.88 (m, 3H), 4.19 (dd, J=7.8, 3.5 Hz, 1H), 5.13 (d, J=7.3 Hz, 1H), 6.35 (dd, J=15.8, 7.8 Hz, 1H), 6.61–6.71 (m, 2H), 6.85 (td, J=7.5, 0.9 Hz, 1H), 7.14 (td, J=7.5, 0.9 Hz, 1H), 7.27–7.47 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 26.1, 43.1, 56.2, 66.9, 75.9, 115.4, 119.4, 122.3, 126.9, 128.3, 129.0, 129.2, 130.2, 130.8, 131.8, 137.1, 144.7. Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 81.92; H, 6.78; N, 5.00.

4.2.2. *exo-2,3,3a,4,5,9b-Hexahydro-4-styrylfuro[3,2-c]quinoline* **5a**

Viscous liquid. IR (neat) 3333.8, 3024.6, 2861.3, 1611.3, 1482.8, 1363.1, 1264.0, 1127.0, 1042.2 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.91–2.01 (m, 1H), 2.20–2.35 (m, 2H), 3.48 (dd, J=9.7, 8.9 Hz, 1H), 3.84–3.94 (m, 1H), 4.01–4.11 (m, 2H), 4.64 (d, J=4.8 Hz, 1H), 6.24 (dd, J=15.8, 8.5 Hz, 1H), 6.67–6.73 (m, 2H), 6.84 (td, J=7.4, 0.8 Hz, 1H), 7.17 (td, J=7.4, 0.8 Hz, 1H), 7.28–7.49 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 29.4, 41.9, 56.3, 65.7, 76.2, 115.4, 118.9, 120.6, 127.0, 128.5, 129.2, 129.5, 130.2, 131.7, 133.9, 136.8, 145.2. Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.01; H, 6.81; N, 4.96.

4.2.3. *endo-8-Chloro-2,3,3a,4,5,9b-hexahydro-4-styrylfuro[3,2-c]-quinoline* **4b**

Viscous liquid. IR (neat) 3327.9, 3023.3, 2877.6, 1603.8, 1489.3, 1295.5, 1259.4, 1063.9 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.01–2.21 (m, 2H), 2.69–2.80 (m, 1H), 3.81–3.87 (m, 3H), 4.17 (dd, J=7.9, 3.6 Hz, 1H), 5.04 (d, J=7.3 Hz, 1H), 6.30 (dd, J=15.8, 7.9 Hz, 1H), 6.53 (d, J=8.6 Hz, 1H), 6.67 (d, J=15.8 Hz, 1H), 7.06 (dd, J=8.6, 2.4 Hz, 1H), 7.26–7.45 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 25.8, 42.8, 56.0, 67.0, 75.4, 116.5, 123.7, 123.8, 126.9, 128.4, 128.9, 129.1, 129.6, 130.3, 132.2, 136.8, 143.1. Anal. Calcd for $C_{19}H_{18}ClNO$: C, 73.19; H, 5.82; N, 4.49. Found: C, 73.02; H, 5.67; N, 4.30.

4.2.4. *exo-8-Chloro-2,3,3a,4,5,9b-hexahydro-4-styrylfuro[3,2-c]-quinoline* **5b**

Viscous liquid. IR (neat) 3330.3, 3025.3, 2875.7, 1606.9, 1491.1, 1351.9, 1264.9, 1127.8, 1043.2 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.95–2.02 (m, 1H), 2.16–2.32 (m, 2H), 3.43 (dd, J=9.5, 9.0 Hz, 1H), 3.81–3.92 (m, 1H), 3.99–4.15 (m, 1H), 4.18 (br s, 1H), 4.56 (d, J=4.8 Hz, 1H), 6.21 (dd, J=15.8, 8.5 Hz, 1H), 6.60 (d, J=8.6 Hz, 1H), 6.69 (d, J=15.8 Hz, 1H), 7.11 (dd, J=8.6, 2.4 Hz, 1H), 7.29–7.49 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 29.3, 41.8, 56.4, 65.7, 75.7, 116.5, 122.1, 123.2, 126.9, 128.6, 129.2, 129.4, 129.7, 131.2, 134.2, 136.7, 143.7. Anal. Calcd for $C_{19}H_{18}ClNO$: C, 73.19; H, 5.82; N, 4.49. Found: C, 72.88; H, 5.64; N, 4.40.

4.2.5. *endo-2,3,3a,4,5,9b-Hexahydro-8-methyl-4-styrylfuro[3,2-c]-quinoline* **4c**

Viscous liquid. IR (neat) 3324.0, 3022.9, 2869.4, 1619.1, 1506.5, 1308.3, 1255.9, 1159.8, 1063.4 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.06–2.28 (m, 2H), 2.33 (s, 3H), 2.74–2.85 (m, 1H), 3.77 (br s, 1H), 3.81–3.90 (m, 2H), 4.15 (dd, J=7.8, 3.5 Hz, 1H), 5.12 (d, J=7.4 Hz, 1H), 6.37 (dd, J=15.8, 7.9 Hz, 1H), 6.57 (d, J=8.1 Hz, 1H), 6.68 (d, J=15.8 Hz, 1H), 6.98 (dd, J=8.1, 1.8 Hz, 1H), 7.25 (d, J=1.8 Hz, 1H), 7.28–7.49 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 21.0, 26.2, 43.2, 56.5, 67.0, 75.9, 115.5, 122.4, 126.9, 128.2, 128.7, 129.1, 129.8, 130.3, 131.1, 131.7, 137.1, 142.4. Anal. Calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.19; H, 7.11; N, 4.70.

4.2.6. *exo-2,3,3a,4,5,9b-Hexahydro-8-methyl-4-styrylfuro-[3,2-c]quinoline* **5c**

Viscous liquid. IR (neat) 3334.4, 3016.9, 2862.0, 1621.2, 1508.0, 1353.4, 1264.4, 1128.1, 1042.6 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.95–2.00 (m, 1H), 2.13–2.29 (m, 2H), 2.34 (s, 3H), 3.44 (dd, J=10.0, 8.7 Hz, 1H), 3.85–4.06 (m, 3H), 4.60 (d, J=5.0 Hz, 1H), 6.24 (dd, J=15.8, 8.5 Hz, 1H), 6.61 (d, J=8.1 Hz, 1H), 6.69 (d, J=15.8 Hz, 1H), 6.98 (dd, J=8.1, 1.8 Hz, 1H), 7.23 (d, J=1.8 Hz, 1H), 7.29–7.49 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 20.9, 29.4, 42.2, 56.7, 65.7, 76.2, 115.3, 120.7, 126.9, 128.2, 128.4, 129.1, 130.2, 130.3, 131.7, 133.8, 136.8, 142.7. Anal. Calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.28; H, 7.25; N, 4.75.

4.2.7. *endo-8-Bromo-2,3,3a,4,5,9b-hexahydro-4-styrylfuro-[3,2-c]quinoline* **4d**

Viscous liquid. IR (neat) 3328.0, 3024.8, 2873.8, 1597.8, 1486.4, 1333.6, 1295.5, 1259.0, 1178.8, 1063.4 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.04–2.21 (m, 2H), 2.72–2.76 (m, 1H), 3.81–3.87 (m, 2H), 4.16 (dd, J=7.8, 3.5 Hz, 1H), 5.04 (d, J=7.3 Hz, 1H), 6.29 (dd, J=15.8, 7.9 Hz, 1H), 6.48 (d, J=8.6 Hz, 1H), 6.66 (d, J=15.8 Hz, 1H), 7.19 (dd, J=8.6, 2.3 Hz, 1H), 7.27–7.49 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 25.8, 42.8, 55.9, 67.0, 75.3, 110.9, 116.9, 124.3, 126.9, 128.4, 129.1, 129.5, 131.7, 132.2, 133.2, 136.8, 143.6. Anal. Calcd for $C_{19}H_{18}BrNO$: C, 64.06; H, 5.09; N, 3.93. Found: C, 63.78; H, 5.00; N, 3.81.

4.2.8. *exo-8-Bromo-2,3,3a,4,5,9b-hexahydro-4-styrylfuro-[3,2-c]quinoline* **5d**

Viscous liquid. IR (neat) 3384.8, 3024.8, 2875.7, 1601.2, 1488.4, 1351.8, 1265.4, 1128.0, 1043.0 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.92–1.99 (m, 1H), 2.13–2.32 (m, 2H), 3.44 (dd, J=9.4, 9.1 Hz, 1H), 3.81–4.10 (m, 3H), 4.56 (d, J=4.8 Hz, 1H), 6.20 (dd, J=15.8, 8.5 Hz, 1H), 6.55 (d, J=8.6 Hz, 1H), 6.69 (d, J=15.8 Hz, 1H), 7.22 (dd, J=8.6, 2.3 Hz, 1H), 7.28–7.51 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 29.3, 41.7, 56.3, 65.7, 75.6, 110.3, 116.9, 122.6, 126.9, 128.5, 129.2, 129.6, 132.2, 134.1, 134.3, 136.6, 144.1. Anal. Calcd for $C_{19}H_{18}BrNO$: C, 64.06; H, 5.09; N, 3.93. Found: C, 63.90; H, 5.01; N, 3.88.

4.2.9. *endo-8-Fluoro-2,3,3a,4,5,9b-hexahydro-4-styrylfuro-[3,2-c]quinoline* **4e**

Viscous liquid. IR (neat) 3332.1, 3027.3, 2876.1, 1598.5, 1499.5, 1315.3, 1247.6, 1151.7, 1062.9 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.01–2.23 (m, 2H), 2.70–2.81 (m, 1H), 3.77–3.88 (m, 3H), 4.16 (dd, J=7.8, 3.5 Hz, 1H), 5.07 (d, J=7.4 Hz, 1H), 6.32 (dd, J=15.8, 7.8 Hz, 1H), 6.55 (dd, J=8.8, 4.7 Hz, 1H), 6.68 (d, J=15.8 Hz, 1H), 6.85 (td, J=8.6, 2.9 Hz, 1H), 7.10 (dd, J=9.1, 2.9 Hz, 1H), 7.27–7.46 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 25.5, 42.7, 56.1, 66.8, 75.4 (d, J=1.0 Hz), 115.7 (d, J=19.1 Hz), 116.0 (d, J=3.6 Hz), 116.3 (d, J=21.7 Hz), 123.3 (d, J=6.3 Hz), 126.6, 128.1, 128.9, 129.6, 131.7, 136.7, 140.6 (d, J=1.8 Hz), 156.1 (d, J=236.5 Hz). Anal. Calcd for $C_{19}H_{18}FNO$: C, 77.27; H, 6.14; N, 4.74. Found: C, 77.01; H, 6.03; N, 4.62.

4.2.10. *exo-8-Fluoro-2,3,3a,4,5,9b-hexahydro-4-styrylfuro-[3,2-c]quinoline* **5e**

Viscous liquid. IR (neat) 3329.4, 3029.7, 2872.1, 1598.5, 1501.7, 1352.8, 1256.0, 1149.9, 1043.8 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.92–2.00 (m, 1H), 2.16–2.35 (m, 2H), 3.42 (dd, J=9.9, 8.7 Hz, 1H), 3.81–4.08 (m, 3H), 4.58 (d, J=5.1 Hz, 1H), 6.22 (dd, J=15.8, 8.4 Hz, 1H), 6.62 (dd, J=8.8, 4.7 Hz, 1H), 6.69 (d, J=15.8 Hz, 1H), 6.89 (td, J=8.5, 2.9 Hz, 1H), 7.13 (dd, J=9.0, 2.9 Hz, 1H), 7.29–7.48 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 29.3, 41.9, 56.8, 65.8, 75.9 (d, J=1.0 Hz), 116.2 (d, J=7.6 Hz), 116.4 (d, J=22.9 Hz), 117.3 (d, J=21.7 Hz), 121.9 (d, J=6.8 Hz), 126.9, 128.5, 129.2, 129.9, 134.1, 136.7, 141.4 (d, J=1.8 Hz),

156.5 (d, J=236.6 Hz). Anal. Calcd for $C_{19}H_{18}FNO$: C, 77.27; H, 6.14; N, 4.74. Found: C, 76.96; H, 5.99; N, 4.69.

4.2.11. endo-2,3,3a,4,5,9b-Hexahydro-7,9-dimethyl-4-styrylfuro[3,2-c]quinoline **4f**

Viscous liquid. IR (neat) 3360.8, 3025.4, 2869.6, 1614.5, 1586.1, 1468.9, 1356.0, 1299.3, 1164.7, 1037.0 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.08–2.23 (m, 2H), 2.28 (s, 3H), 2.46 (s, 3H), 2.76–2.85 (m, 1H), 3.80–3.94 (m, 3H), 4.05 (dd, J=8.2, 4.0 Hz, 1H), 5.09 (d, J=7.1 Hz, 1H), 6.34 (d, J=1.4 Hz, 1H), 6.39 (dd, J=15.8, 8.2 Hz, 1H), 6.55 (d, J=1.4 Hz, 1H), 6.63 (d, J=15.8 Hz, 1H), 7.27–7.52 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 19.7, 21.6, 27.2, 42.8, 56.9, 66.6, 74.1, 113.9, 117.8, 122.5, 126.9, 128.1, 129.1, 130.2, 131.7, 137.2, 138.7, 140.3, 145.0. Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.32; H, 7.42; N, 4.45.

4.2.12. exo-2,3,3a,4,5,9b-Hexahydro-7,9-dimethyl-4-styrylfuro-[3,2-c]quinoline **5f**

Viscous liquid. IR (neat) 3358.2, 3025.5, 2856.2, 1615.1, 1587.8, 1469.4, 1358.3, 1290.7, 1136.2, 1036.3 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.94–2.01 (m, 1H), 2.15–2.25 (m, 2H), 2.27 (s, 3H), 2.43 (s, 3H), 3.45 (dd, J=10.0, 8.7 Hz, 1H), 3.81–4.09 (m, 3H), 4.64 (d, J=4.3 Hz, 1H), 6.24 (dd, J=15.8, 8.5 Hz, 1H), 6.36 (d, J=1.5 Hz, 1H), 6.52 (d, J=1.5 Hz, 1H), 6.71 (d, J=15.8 Hz, 1H), 7.33–7.51 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 19.2, 21.7, 28.9, 42.1, 55.8, 65.2, 74.3, 113.5, 116.2, 121.9, 126.9, 128.4, 129.1, 130.5, 133.9, 136.9, 139.0, 140.3, 145.2. Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.34; H, 7.45; N, 4.51.

4.2.13. endo-2,3,3a,4,5,9b-Hexahydro-6,8-dimethyl-4-styrylfuro[3,2-c]quinoline **4g**

Viscous liquid. IR (neat) 3391.8, 3021.6, 2867.5, 1617.3, 1488.4, 1311.3, 1250.0, 1163.3, 1051.4 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.07–2.21 (m, 2H), 2.24 (s, 3H), 2.31 (s, 3H), 2.74–2.84 (m, 1H), 3.64 (br s, 1H), 3.84–3.90 (m, 2H), 4.18 (dd, J=7.9, 3.6 Hz, 1H), 5.14 (d, J=7.4 Hz, 1H), 6.41 (dd, J=15.8, 8.0 Hz, 1H), 6.71 (d, J=15.8 Hz, 1H), 6.90 (d, J=1.5 Hz, 1H), 7.13 (d, J=1.5 Hz, 1H), 7.29–7.50 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 17.7, 20.9, 26.1, 43.1, 56.6, 66.9, 76.2, 121.8, 122.4, 126.9, 127.9, 128.3, 128.7, 129.1, 130.4, 131.0, 131.8, 137.1, 140.5. Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.35; H, 7.48; N, 4.48.

4.2.14. exo-2,3,3a,4,5,9b-Hexahydro-6,8-dimethyl-4-styrylfuro-[3,2-c]quinoline **5g**

Viscous liquid. IR (neat) 3398.0, 3025.1, 2858.4, 1619.0, 1491.8, 1316.6, 1257.9, 1161.7, 1055.1 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.97–2.04 (m, 1H), 2.19 (s, 3H), 2.16–2.26 (m, 2H), 2.32 (s, 3H), 3.49 (dd, J=10.2, 8.7 Hz, 1H), 3.84–3.95 (m, 3H), 4.03–4.12 (m, 1H), 4.64 (d, J=4.8 Hz, 1H), 6.33 (dd, J=15.8, 8.6 Hz, 1H), 6.75 (d, J=15.8 Hz, 1H), 6.94 (d, J=1.5 Hz, 1H), 7.16 (d, J=1.5 Hz, 1H), 7.32–7.55 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 17.7, 20.9, 29.5, 41.9, 56.8, 65.6, 76.6, 120.1, 122.4, 127.0, 127.5, 128.5, 129.2, 129.6, 130.5, 131.4, 133.9, 136.8, 140.8. Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.29; H, 7.42; N, 4.43.

4.3. General procedure for the CAN-catalyzed synthesis of 1,2,3,4-tetrahydro-2-styrylquinolines (7)

An equimolar (3 mmol) mixture of the suitable arylamine (**1**) and cinnamaldehyde (**2**) was dissolved in acetonitrile (20 mL) and stirred at room temperature. To this stirred solution, the suitable alkyl vinyl ether **6** (4.5 mmol) and 5–15 mol % of CAN were added, and stirring was continued for the time period specified in Table 2. After completion of the reaction, as indicated by TLC, the mixture was extracted with dichloromethane (2×20 mL), dried (anhydrous Na_2SO_4), and evaporated. 1,2,3,4-Tetrahydro-2-styrylquinolines **7** and 1,2,3,4-tetrahydro-2-methylquinolines **8** were separated through silica column using petroleum ether/ethyl acetate mixture (96:4, v/v). When the reaction starting from *p*-chloroaniline, cinnamaldehyde, and butyl vinyl ether was performed in ethanol, a mixture of compounds **7f** and **9** was obtained. Data for compounds **7** and **9** follow. Compounds **8** had been previously described.[10]

4.3.1. 4-Ethoxy-1,2,3,4-tetrahydro-2-styrylquinoline **7a**

Viscous liquid. IR (neat) 3384.4, 2972.7, 2859.2, 1608.3, 1482.3, 1311.1, 1254.3, 1094.5 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.33 (t, J=6.9 Hz, 3H), 1.95–2.08 (m, 1H), 2.38 (ddd, J=12.5, 5.2, 3.3 Hz, 1H), 3.59–3.80 (m, 2H), 3.93 (br s, 1H), 4.11–4.19 (m, 1H), 4.73 (dd, J=9.2, 5.2 Hz, 1H), 6.40 (dd, J=15.8, 7.8 Hz, 1H), 6.56 (d, J=8.0 Hz, 1H), 6.63 (d, J=15.8 Hz, 1H), 6.77 (td, J=8.2, 0.9 Hz, 1H), 7.10 (td, J=8.2, 1.2 Hz, 1H), 7.26–7.46 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 16.2, 34.6, 54.1, 63.9, 73.7, 114.6, 118.1, 122.7, 126.8, 128.1, 128.2, 128.9, 129.1, 130.8, 132.3, 137.1, 144.2. Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.44; H, 7.49; N, 4.92.

4.3.2. 1,2,3,4-Tetrahydro-4-propoxy-2-styrylquinoline **7b**

Viscous liquid. IR (neat) 3378.8, 2960.2, 2874.4, 1608.1, 1493.7, 1311.3, 1255.0, 1093.1 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.03 (t, J=7.5 Hz, 3H), 1.65–1.76 (m, 2H), 1.94–2.06 (m, 1H), 2.39 (ddd, J=12.6, 5.3, 3.3 Hz, 1H), 3.48–3.72 (m, 2H), 3.93 (br s, 1H), 4.11–4.19 (m, 1H), 4.71 (dd, J=9.3, 5.3 Hz, 1H), 6.40 (dd, J=15.8, 7.8 Hz, 1H), 6.56 (dd, J=8.0, 1.0 Hz, 1H), 6.63 (d, J=15.8 Hz, 1H), 6.77 (td, J=8.2, 1.0 Hz, 1H), 7.10 (td, J=8.0, 1.0 Hz, 1H), 7.26–7.46 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 11.3, 23.9, 34.6, 54.1, 70.5, 73.8, 114.6, 118.1, 122.8, 126.8, 128.1, 128.2, 128.8, 129.1, 130.8, 132.3, 137.1, 144.2. Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.60; H, 7.88; N, 4.70.

4.3.3. 4-Butoxy-1,2,3,4-tetrahydro-2-styrylquinoline **7c**

Viscous liquid. IR (neat) 3387.1, 2956.4, 2859.2, 1608.6, 1481.6, 1310.8, 1254.2, 1093.8 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 0.97 (t, J=7.2 Hz, 3H), 1.43–1.52 (m, 2H), 1.62–1.71 (m, 2H), 1.93–2.06 (m, 1H), 2.38 (ddd, J=12.6, 5.2, 3.3 Hz, 1H), 3.51–3.75 (m, 2H), 3.93 (br s, 1H), 4.11–4.19 (m, 1H), 4.70 (dd, J=9.2, 5.3 Hz, 1H), 6.40 (dd, J=15.8, 7.8 Hz, 1H), 6.55 (dd, J=8.0, 1.0 Hz, 1H), 6.63 (d, J=15.8 Hz, 1H), 6.76 (td, J=8.0, 1.0 Hz, 1H), 7.09 (td, J=8.0, 1.0 Hz, 1H), 7.28–7.45 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.4, 19.9, 32.7, 34.6, 54.1, 68.5, 73.8, 114.6, 118.1, 122.8, 126.8, 128.1, 128.2, 128.8, 129.0, 130.8, 132.3, 137.1, 144.2. Anal. Calcd for $C_{21}H_{25}NO$: C, 82.06; H, 8.11; N, 4.80. Found: C, 81.81; H, 8.00; N, 4.71.

4.3.4. 6-Chloro-4-ethoxy-1,2,3,4-tetrahydro-2-styrylquinoline **7d**

Viscous liquid. IR (neat) 3386.9, 2972.4, 2866.9, 1602.9, 1488.0, 1300.8, 1249.1, 1100.1 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.34 (t, J=7.0 Hz, 3H), 1.87–2.00 (m, 1H), 2.37 (ddd, J=12.6, 5.2, 3.3 Hz, 1H), 3.56–3.84 (m, 2H), 3.94 (br s, 1H), 4.08–4.16 (m, 1H), 4.64 (dd, J=9.5, 5.2 Hz, 1H), 6.35 (dd, J=15.8, 8.0 Hz, 1H), 6.46 (d, J=8.6 Hz, 1H), 6.64 (d, J=15.8 Hz, 1H), 7.03 (dd, J=8.5, 2.4 Hz, 1H), 7.29–7.45 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 16.1, 34.3, 53.9, 64.4, 73.4, 115.7, 122.6, 124.2, 126.9, 127.8, 128.3, 128.7, 129.1, 131.2, 131.7, 136.9, 142.7. Anal. Calcd for $C_{19}H_{20}ClNO$: C, 72.72; H, 6.42; N, 4.46. Found: C, 72.45; H, 6.33; N, 4.30.

4.3.5. 6-Chloro-1,2,3,4-tetrahydro-4-propoxy-2-styrylquinoline **7e**

Viscous liquid. IR (neat) 3401.9, 2960.1, 2873.0, 1602.4, 1488.0, 1300.2, 1250.4, 1098.8 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.03 (t, J=7.4 Hz, 3H), 1.65–1.77 (m, 2H), 1.86–1.99 (m, 1H), 2.38 (ddd, J=12.5, 5.2, 3.3 Hz, 1H), 3.47–3.72 (m, 2H), 3.92 (br s, 1H), 4.08–4.17 (m, 1H), 4.63 (dd, J=9.5, 5.2 Hz, 1H), 6.34 (dd, J=15.8, 7.9 Hz, 1H), 6.46 (d, J=8.5 Hz, 1H), 6.63 (d, J=15.8 Hz, 1H), 7.02 (dd, J=8.5, 2.4 Hz, 1H), 7.26–7.45 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 11.3, 23.8, 34.3,

54.0, 70.8, 73.6, 115.6, 122.6, 124.3, 126.8, 127.7, 128.2, 128.6, 129.0, 131.3, 131.7, 136.9, 142.7. Anal. Calcd for $C_{20}H_{22}ClNO$: C, 73.27; H, 6.76; N, 4.27. Found: C, 72.92; H, 6.66; N, 4.27.

4.3.6. 4-Butoxy-6-chloro-1,2,3,4-tetrahydro-2-styrylquinoline ***7f***

Viscous liquid. IR (neat) 3386.1, 2956.3, 2862.0, 1601.5, 1488.2, 1300.6, 1246.9, 1098.9 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 0.99 (t, J=7.2 Hz, 3H), 1.45–1.54 (m, 2H), 1.64–1.73 (m, 2H), 1.86–1.99 (m, 1H), 2.38 (ddd, J=12.5, 5.2, 3.3 Hz, 1H), 3.52–3.77 (m, 2H), 3.94 (br s, 1H), 4.08–4.17 (m, 1H), 4.62 (dd, J=9.5, 5.2 Hz, 1H), 6.35 (dd, J=15.8, 7.8 Hz, 1H), 6.46 (d, J=8.5 Hz, 1H), 6.63 (d, J=15.8 Hz, 1H), 7.04 (dd, J=8.5, 2.4 Hz, 1H), 7.29–7.46 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.3, 19.9, 32.7, 34.3, 53.9, 68.9, 73.5, 115.7, 122.6, 124.3, 126.9, 127.8, 128.2, 128.6, 129.1, 131.2, 131.8, 136.9, 142.7. Anal. Calcd for $C_{21}H_{24}ClNO$: C, 73.78; H, 7.08; N, 4.10. Found: C, 73.65; H, 7.00; N, 4.01.

4.3.7. 4-Ethoxy-6-fluoro-1,2,3,4-tetrahydro-2-styrylquinoline ***7g***

Viscous liquid. IR (neat) 3384.2, 2971.4, 2857.0, 1600.2, 1496.5, 1304.3, 1252.6, 1094.4 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.33 (t, J=7.0 Hz, 3H), 1.87–2.00 (m, 1H), 2.39 (ddd, J=12.5, 5.3, 3.0 Hz, 1H), 3.58–3.84 (m, 2H), 3.81 (br s, 1H), 4.07–4.15 (m, 1H), 4.68 (dd, J=9.4, 5.5 Hz, 1H), 6.35 (dd, J=15.8, 7.8 Hz, 1H), 6.48 (dd, J=8.8, 4.7 Hz, 1H), 6.64 (d, J=15.8 Hz, 1H), 6.81 (td, J=8.7, 3.0 Hz, 1H), 7.13 (ddd, J=9.5, 2.9, 0.7 Hz, 1H), 7.26–7.45 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 13.8, 32.3, 51.9, 61.9, 71.3, 111.9 (d, J=22.7 Hz), 113.1 (d, J=7.3 Hz), 113.2 (d, J=22.9 Hz), 121.9 (d, J=6.3 Hz), 124.6, 125.9, 126.8, 128.8, 129.6, 134.7, 138.1 (d, J=1.8 Hz), 154.3 (d, J=232.7 Hz). Anal. Calcd for $C_{19}H_{20}FNO$: C, 76.74; H, 6.78; N, 4.71. Found: C, 76.30; H, 6.70; N, 4.59.

4.3.8. 4-Butoxy-6-fluoro-1,2,3,4-tetrahydro-2-styrylquinoline ***7h***

Viscous liquid. IR (neat) 3388.3, 2957.6, 2869.1, 1599.6, 1497.1, 1304.3, 1252.4, 1098.0 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.00 (t, J=7.2 Hz, 3H), 1.46–1.58 (m, 2H), 1.64–1.75 (m, 2H), 1.86–1.99 (m, 1H), 2.40 (ddd, J=12.3, 5.1, 3.0 Hz, 1H), 3.52–3.78 (m, 2H), 3.82 (br s, 1H), 4.07–4.16 (m, 1H), 4.67 (dd, J=9.6, 5.3 Hz, 1H), 6.36 (dd, J=15.8, 7.8 Hz, 1H), 6.49 (dd, J=8.7, 4.7 Hz, 1H), 6.64 (d, J=15.8 Hz, 1H), 6.82 (td, J=8.4, 2.8 Hz, 1H), 7.15 (dd, J=9.5, 2.7 Hz, 1H), 7.29–7.46 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 14.4, 19.9, 32.7, 34.5, 54.2, 68.7, 73.7, 114.2 (d, J=22.8 Hz), 115.4 (d, J=7.6 Hz), 115.5 (d, J=21.5 Hz), 124.3 (d, J=6.3 Hz), 126.9, 128.2, 129.1, 131.1, 131.9, 137.0, 140.4 (d, J=1.7 Hz), 156.4 (d, J=234.9 Hz). Anal. Calcd for $C_{21}H_{24}FNO$: C, 77.51; H, 7.43; N, 4.30. Found: C, 77.22; H, 7.32; N, 4.25.

4.3.9. 6-Bromo-4-ethoxy-1,2,3,4-tetrahydro-2-styrylquinoline ***7i***

Viscous liquid. IR (neat) 3406.0, 2972.0, 2858.0, 1598.8, 1485.0, 1300.5, 1247.0, 1098.1 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.34 (t, J=7.0 Hz, 3H), 1.91–1.99 (m, 1H), 2.36 (ddd, J=12.4, 4.8, 3.5 Hz, 1H), 3.58–3.80 (m, 2H), 3.94 (br s, 1H), 4.08–4.16 (m, 1H), 4.63 (dd, J=9.3, 5.1 Hz, 1H), 6.34 (dd, J=15.8, 7.8 Hz, 1H), 6.42 (d, J=8.6 Hz, 1H), 6.62 (d, J=15.8 Hz, 1H), 7.15 (dd, J=8.6, 2.2 Hz, 1H), 7.26–7.48 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 16.0, 34.2, 53.9, 64.4, 73.3, 109.7, 116.1, 124.6, 126.8, 128.2, 129.1, 130.6, 131.3, 131.5, 131.7, 136.9, 143.1. Anal. Calcd for $C_{19}H_{20}BrNO$: C, 63.70; H, 5.63; N, 3.91. Found: C, 63.45; H, 5.60; N, 3.88.

4.3.10. 4-Ethoxy-1,2,3,4-tetrahydro-6-methyl-2-styrylquinoline ***7j***

Viscous liquid. IR (neat) 3373.6, 2972.5, 2864.9, 1619.2, 1504.8, 1301.2, 1251.2, 1095.9 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.35 (t, J=7.0 Hz, 3H), 1.95–2.08 (m, 1H), 2.31 (s, 3H), 2.39 (ddd, J=12.6, 5.3, 3.2 Hz, 1H), 3.58–3.85 (m, 2H), 3.83 (br s, 1H), 4.08–4.16 (m, 1H), 4.71 (dd, J=9.1, 5.3 Hz, 1H), 6.42 (dd, J=15.8, 7.8 Hz, 1H), 6.51 (d, J=8.1 Hz, 1H), 6.63 (d, J=15.8 Hz, 1H), 6.93 (dd, J=8.1, 2.0 Hz, 1H), 7.22–7.45 (m, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 16.2, 21.1, 34.8, 54.2, 64.0, 73.8, 114.9, 122.7, 126.8, 127.4, 128.1, 128.6, 129.1, 129.5, 130.7, 132.5, 137.2, 141.9. Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.67; H, 7.82; N, 4.71.

4.3.11. 4-Ethoxy-1,2,3,4-tetrahydro-8-methoxy-2-styrylquinoline ***7k***

Viscous liquid. IR (neat) 3419.3, 2970.4, 2865.6, 1588.4, 1493.2, 1324.7, 1249.6, 1082.9 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.32 (t, J=7.0 Hz, 3H), 2.00–2.12 (m, 1H), 2.38 (ddd, J=12.5, 5.2, 3.2 Hz, 1H), 3.56–3.82 (m, 2H), 3.87 (s, 3H), 4.12–4.21 (m, 1H), 4.42 (br s, 1H), 4.78 (dd, J=9.1, 5.4 Hz, 1H), 6.46 (dd, J=15.8, 7.8 Hz, 1H), 6.65 (d, J=15.8 Hz, 1H), 6.73–6.78 (m, 2H), 7.04–7.08 (m, 1H), 7.25–7.49 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 16.2, 34.5, 53.8, 55.9, 63.9, 73.7, 109.0, 116.9, 120.2, 122.6, 126.8, 128.0, 129.0, 130.7, 132.5, 134.2, 137.2, 146.5. Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.55; H, 7.33; N, 4.44.

4.3.12. 2-(2-Nitrostyryl)-4-ethoxy-1,2,3,4-tetrahydroquinoline ***7l***

Viscous liquid. IR (KBr) 3336.0, 2963.1, 2861.2, 1608.3, 1519.8, 1485.2, 1304.2, 1255.0, 1082.3, 1032.1 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 1.29 (t, J=7.0 Hz, 3H), 2.04–2.15 (m, 1H), 2.36 (ddd, J=12.8, 4.7, 4.1 Hz, 1H), 3.59–3.77 (m, 2H), 4.19–4.27 (m, 1H), 4.66 (dd, J=7.7, 4.9 Hz, 1H), 6.47 (dd, J=15.6, 8.0 Hz, 1H), 6.57 (dd, J=8.0, 0.8 Hz, 1H), 6.75 (td, J=7.5, 1.0 Hz, 1H), 7.04–7.15 (m, 2H), 7.32–7.44 (m, 2H), 7.54–7.67 (m, 2H), 7.96 (dd, J=8.1, 1.3 Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 16.1, 34.0, 53.5, 64.1, 73.3, 114.8, 118.1, 122.2, 125.0, 125.4, 128.5, 128.8, 129.0, 129.1, 133.0, 133.5, 138.2, 143.7, 148.2. Anal. Calcd for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.21; N, 8.64. Found: C, 70.01; H, 6.09; N, 8.58.

4.3.13. N-[(E)-5-Butoxy-5-ethoxy-1-phenylpent-1-en-3-yl]-4-chloroaniline ***9***

Viscous liquid. IR (neat) 3395.9, 3025.5, 2958.7, 2871.7, 1599.7, 1498.2, 1315.9, 1122.0, 1063.8 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ 1.00 (t, J=7.0 Hz, 3H), 1.31 (t, J=7.1 Hz, 3H), 1.43–1.53 (m, 2H), 1.60–1.69 (m, 2H), 2.06–2.11 (m, 2H), 3.47–3.80 (m, 4H), 4.17 (br q, J=5.8 Hz, 1H), 4.61 (br s, 1H), 4.76 (t, J=5.5 Hz, 1H), 6.21 (dd, J=16.0, 6.0 Hz, 1H), 6.60–6.67 (m, 3H), 7.15 (d, J=9.0 Hz, 2H), 7.27–7.43 (m, 5H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 14.4, 15.9, 19.9, 32.5, 40.0, 53.4, 62.1, 66.5, 101.7, 114.8, 122.1, 126.8, 128.0, 129.0, 129.4, 130.8, 131.4, 137.1, 146.7. Anal. Calcd for $C_{23}H_{30}ClNO_2$: C, 71.21; H, 7.79; N, 3.61. Found C, 71.17; H, 7.56; N, 3.86.

4.4. General procedure for the DDQ-mediated aromatization of mixtures of compounds (4) and (5): synthesis of 2-styrylquinolines (10) and 2,3-dihydro-4-styrylfuro[3,2-*c*]-quinolines (11)

To a stirred solution of a mixture of *endo* and *exo* 2,3,3a,4,5,9b-hexahydro-4-styrylfuro[3,2-*c*]quinolines (**4** and **5**, 1 mmol) in benzene (15 mL), DDQ (2 mmol) was added slowly and stirring was continued for 2 h. After completion of the reaction, CH_2Cl_2 and water were added, and shaken well with saturated $NaHCO_3$ solution to get clear layers. Organic layer was separated, aqueous layer was again extracted with CH_2Cl_2, the combined organic layer was dried (anhydrous Na_2SO_4), and evaporated. The reaction products, namely 2-styrylquinolines **10** and 2,3-dihydro-4-styrylfuro[3,2-*c*]quinolines **11** were separated through silica gel column using petroleum ether/ethyl acetate mixture (80:20, v/v).

4.4.1. 2-(2-Styrylquinolin-3-yl)ethanol ***10a***

IR (KBr) 3299.5, 3026.2, 2920.4, 1595.9, 1493.8, 1417.7, 1321.5, 1211.3, 1066.1 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 3.06 (t, J=6.2 Hz, 2H), 4.01 (t, J=6.2 Hz, 2H), 4.01 (br s, 1H), 7.28–7.45 (m, 6H), 7.55–7.62 (m, 3H), 7.70 (s, 1H), 7.85 (d, J=15.6 Hz, 1H), 7.95 (d, J=8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 36.6, 62.6, 124.5, 126.4, 127.4, 127.6, 127.9, 128.7, 129.0, 129.2, 129.4, 130.6, 136.5, 137.1, 137.8, 146.9, 154.9. Anal. Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.60; H, 6.08; N, 5.00.

4.4.2. 2-(6-Chloro-2-styrylquinolin-3-yl)ethanol ***10b***

IR (KBr) 3240.3, 3021.5, 2949.5, 1634.4, 1595.7, 1480.3, 1403.2, 1343.8, 1207.7, 1051.0 cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz) δ 3.12 (t, J=6.6 Hz, 2H), 3.72 (q, J=6.6 Hz, 2H), 4.92 (t, J=5.3 Hz, 1H), 7.36–7.47 (m, 3H), 7.64–7.78 (m, 4H), 7.90–8.10 (m, 4H). ^{13}C NMR (DMSO-d_6, 62.9 MHz) δ 35.8, 61.6, 124.3, 126.2, 127.9, 128.3, 129.1, 129.2, 129.9, 130.6, 130.9, 132.8, 135.5, 136.3, 136.7, 145.0, 154.9. Anal. Calcd for $C_{19}H_{16}ClNO$: C, 73.66; H, 5.21; N, 4.52. Found: C, 73.38; H, 5.08; N, 4.41.

4.4.3. 2-(6-Methyl-2-styrylquinolin-3-yl)ethanol ***10c***

IR (KBr) 3231.3, 3021.0, 2947.3, 1636.5, 1598.3, 1494.1, 1347.9, 1219.5, 1051.4 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.42 (s, 3H), 2.96 (t, J=6.0 Hz, 2H), 3.98 (t, J=6.0 Hz, 2H), 4.66 (br s, 1H), 6.98 (s, 1H), 7.29–7.37 (m, 5H), 7.48–7.56 (m, 3H), 7.73 (d, J=15.8 Hz, 1H), 7.78 (d, J=8.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz)* δ 22.1, 36.7, 62.5, 124.6, 126.2, 127.5, 127.8, 128.1, 128.9, 129.2, 130.7, 131.5, 135.9, 137.2, 145.2, 153.9. Anal. Calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.71; H, 6.52; N, 4.77. *Two carbon signals are merged with others.

4.4.4. 2-(6-Bromo-2-styrylquinolin-3-yl)ethanol ***10d***

IR (KBr) 3242.6, 3021.8, 2948.2, 1633.9, 1592.3, 1478.3, 1401.7, 1342.3, 1208.8, 1050.2 cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz) δ 3.12 (t, J=6.5 Hz, 2H), 3.72 (q, J=6.5 Hz, 2H), 4.92 (t, J=5.3 Hz, 1H), 7.33–7.47 (m, 3H), 7.63–7.78 (m, 4H), 7.90–7.97 (m, 2H), 8.09–8.12 (m, 2H). ^{13}C NMR (DMSO-d_6, 62.9 MHz) δ 35.8, 61.2, 119.2, 124.3, 127.9, 128.9, 129.1, 129.2, 129.5, 130.9, 132.5, 132.8, 135.6, 136.3, 136.7, 145.2, 155.0. Anal. Calcd for $C_{19}H_{16}BrNO$: C, 64.42; H, 4.55; N, 3.95. Found: C, 64.22; H, 4.43; N, 3.80.

4.4.5. 2-(6-Fluoro-2-styrylquinolin-3-yl)ethanol ***10e***

IR (KBr) 3181.2, 3030.7, 2929.5, 1605.8, 1561.1, 1494.7, 1355.2, 1223.6, 1138.2, 1062.8 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 3.12 (t, J=6.3 Hz, 2H), 4.02 (t, J=6.3 Hz, 2H), 7.12 (dd, J=8.9, 2.8 Hz, 1H), 7.35–7.46 (m, 5H), 7.58–7.62 (m, 2H), 7.75 (s, 1H), 7.87 (d, J=15.8 Hz, 1H), 7.97 (dd, J=9.3, 5.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 36.4, 62.6, 110.3 (d, J=21.8 Hz), 119.7 (d, J=25.8 Hz), 124.0, 127.9, 128.2 (d, J=10.0 Hz), 129.1, 129.2, 131.3, 131.4 (d, J=9.1 Hz), 136.5, 137.0 (d, J=5.3 Hz), 137.1, 144.2, 154.4 (d, J=2.9 Hz), 160.6 (d, J=244.7 Hz). Anal. Calcd for $C_{19}H_{16}FNO$: C, 77.80; H, 5.50; N, 4.77. Found: C, 77.55; H, 5.38; N, 4.61.

4.4.6. 2-(5,7-Dimethyl-2-styrylquinolin-3-yl)ethanol ***10f***

IR (KBr) 3354.0, 3021.9, 2933.5, 1596.8, 1493.5, 1447.6, 1370.5, 1182.5, 1050.3 cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz) δ 2.46 (s, 3H), 2.59 (s, 3H), 3.14 (t, J=6.8 Hz, 2H), 3.71 (q, J=6.8 Hz, 2H), 4.89 (t, J=5.4 Hz, 1H), 7.19 (s, 1H), 7.36–7.47 (m, 3H), 7.63–7.79 (m, 4H), 7.92 (d, J=15.6 Hz, 1H), 8.16 (s, 1H). ^{13}C NMR (DMSO-d_6, 62.9 MHz) δ 18.9, 22.2, 36.6, 62.6, 125.2, 125.5, 126.5, 128.3, 129.4, 129.5, 129.7, 130.8, 134.3, 134.4, 134.9, 137.4, 139.1, 147.7, 154.1. Anal. Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 82.92; H, 6.86; N, 4.51.

4.4.7. 2,3-Dihydro-4-styrylfuro[3,2-c]quinoline ***11a***

IR (neat) 3058.3, 2911.4, 1623.6, 1592.0, 1505.7, 1410.5, 1314.3, 1068.1 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 3.53 (t, J=8.9 Hz, 2H), 4.90 (t, J=8.9 Hz, 2H), 7.28 (d, J=16.1 Hz, 1H), 7.34–7.46 (m, 4H), 7.63–7.70 (m, 3H), 7.83 (d, J=16.1 Hz, 1H), 7.91 (dd, J=8.3, 1.0 Hz, 1H), 8.07 (d, J=8.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 29.2, 73.5, 115.9, 116.5, 121.8, 125.5, 126.8, 127.7, 129.0, 129.2, 129.3, 130.1, 135.3, 137.1, 149.7, 152.8, 164.2. Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.23; H, 5.38; N, 5.00.

4.4.8. 8-Chloro-2,3-dihydro-4-styrylfuro[3,2-c]quinoline ***11b***

IR (neat) 3028.2, 2916.9, 1618.5, 1591.3, 1496.2, 1329.6, 1086.8 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 3.49 (t, J=9.0 Hz, 2H), 4.88 (t, J=9.0 Hz, 2H), 7.19 (d, J=16.1 Hz, 1H), 7.34–7.44 (m, 3H), 7.56 (dd, J=9.1, 2.4 Hz, 1H), 7.62–7.65 (m, 2H), 7.80 (d, J=16.1 Hz, 1H), 7.83 (d, J=2.4 Hz, 1H), 7.96 (d, J=9.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz)* δ 29.1, 73.6, 116.8, 116.9, 120.8, 126.2, 127.8, 129.2, 130.8, 130.9, 131.0, 135.6, 136.9, 147.9, 152.9, 163.4. Anal. Calcd for $C_{19}H_{14}ClNO$: C, 74.15; H, 4.58; N, 4.55. Found: C, 74.00; H, 4.47; N, 4.50. *One carbon signal is merged with others.

4.4.9. 2,3-Dihydro-8-methyl-4-styrylfuro[3,2-c]quinoline ***11c***

IR (neat) 3024.7, 2917.6, 1597.9, 1552.9, 1500.5, 1447.6, 1332.2, 1193.7, 1061.2 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.51 (s, 3H), 3.50 (t, J=8.9 Hz, 2H), 4.87 (t, J=8.9 Hz, 2H), 7.26 (d, J=16.1 Hz, 1H), 7.33–7.44 (m, 3H), 7.49 (dd, J=8.7, 2.0 Hz, 1H), 7.63–7.66 (m, 3H), 7.78 (d, J=16.1 Hz, 1H), 7.97 (d, J=8.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 22.0, 29.2, 73.3, 115.9, 116.4, 120.5, 126.9, 127.7, 128.8, 128.9, 129.1, 132.4, 134.8, 135.4, 137.2, 148.2, 151.9, 163.6. Anal. Calcd for $C_{20}H_{17}NO$: C, 83.59; H, 5.96; N, 4.87. Found: C, 83.32; H, 5.88; N, 4.81.

4.4.10. 8-Bromo-2,3-dihydro-4-styrylfuro[3,2-c]quinoline ***11d***

IR (neat) 3026.2, 2911.4, 1616.0, 1587.0, 1492.6, 1328.9, 1276.2, 1076.3 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 3.46 (t, J=9.0 Hz, 2H), 4.86 (t, J=9.0 Hz, 2H), 7.17 (d, J=16.0 Hz, 1H), 7.34–7.44 (m, 3H), 7.61–7.70 (m, 3H), 7.80 (d, J=16.0 Hz, 1H), 7.88 (d, J=9.1 Hz, 1H), 8.00 (d, J=2.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz)* δ 29.1, 73.6, 116.8, 117.5, 119.1, 124.2, 126.2, 127.8, 129.2, 130.9, 133.4, 135.7, 136.9, 148.1, 153.0, 163.2. Anal. Calcd for $C_{19}H_{14}BrNO$: C, 64.79; H, 4.01; N, 3.98. Found: C, 64.48; H, 3.82; N, 3.90. *One carbon signal is merged with others.

4.4.11. 8-Fluoro-2,3-dihydro-4-styrylfuro[3,2-c]quinoline ***11e***

IR (neat) 3024.7, 2919.5, 1604.7, 1509.1, 1401.8, 1333.0, 1227.7, 1184.5, 1052.4 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 3.53 (t, J=9.0 Hz, 2H), 4.90 (t, J=9.0 Hz, 2H), 7.23 (d, J=16.1 Hz, 1H), 7.34–7.50 (m, 5H), 7.62–7.67 (m, 2H), 7.80 (d, J=16.1 Hz, 1H), 8.04 (dd, J=9.2, 5.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 29.2, 73.5, 105.3 (d, J=23.0 Hz), 116.5, 116.7 (d, J=10.1 Hz), 120.3 (d, J=25.8 Hz), 126.4, 127.7, 129.1, 129.2, 131.8 (d, J=9.0 Hz), 135.3, 136.9, 146.8, 152.1 (d, J=2.6 Hz), 160.0 (d, J=246.9 Hz), 163.9 (d, J=5.4 Hz). Anal. Calcd for $C_{19}H_{14}FNO$: C, 78.33; H, 4.84; N, 4.81. Found: C, 78.00; H, 4.72; N, 4.71.

4.4.12. 2,3-Dihydro-7,9-dimethyl-4-styrylfuro[3,2-c]quinoline ***11f***

IR (neat) 3020.1, 2915.7, 1620.0, 1593.7, 1507.4, 1448.1, 1323.0, 1274.0, 1167.6, 1067.7 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.48 (s, 3H), 2.76 (s, 3H), 3.42 (t, J=9.1 Hz, 2H), 4.80 (t, J=9.1 Hz, 2H), 6.98 (s, 1H), 7.22 (d, J=16.1 Hz, 1H), 7.33–7.41 (m, 3H), 7.63–7.68 (m, 3H), 7.81 (d, J=16.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 20.7, 21.3, 27.1, 71.5, 113.4, 114.5, 124.9, 125.2, 126.3, 127.5, 127.7, 127.8, 132.8, 133.4, 135.8, 138.2, 149.9, 150.6, 164.0. Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.44; H, 6.21; N, 4.55.

4.5. General procedure for the DDQ-mediated aromatization of 1,2,3,4-tetrahydro-2-styrylquinolines (7): synthesis of 2-styrylquinolines (12)

A solution of the suitable 1,2,3,4-tetrahydro-2-styrylquinoline **7** (1 mmol) in benzene (15 mL) was stirred at room temperature. DDQ (2 mmol) was added slowly, and stirring was continued for 2 h. After completion of the reaction, CH_2Cl_2 and water were added, and shaken well with saturated $NaHCO_3$ solution to get clear layers. The organic layer was separated, aqueous layer was again extracted with CH_2Cl_2, and the combined organic layer was dried (anhydrous Na_2SO_4), and evaporated. The crude product was purified through silica column using petroleum ether/ethyl acetate mixture (90:10, v/v).

4.5.1. 2-Styrylquinoline ***12a***

IR (neat) 3056.3, 3030.8, 1611.5, 1595.5, 1503.8, 1445.8, 1316.1, 1204.0, 1118.4 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 7.32–7.55 (m, 5H), 7.65–7.82 (m, 6H), 8.13 (d, J=8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 119.7, 126.6, 127.7, 127.8, 127.9, 129.1, 129.2, 129.4, 129.6, 130.2, 134.8, 136.8, 136.9, 148.7, 156.4. Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 87.95; H, 5.58; N, 6.00.

4.5.2. 6-Chloro-2-styrylquinoline ***12b***

IR (neat) 3042.1, 2998.9, 1630.6, 1592.9, 1491.8, 1447.3, 1390.2, 1327.8, 1186.3, 1073.7 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 7.33–7.47 (m, 4H), 7.63–7.78 (m, 6H), 8.01–8.06 (m, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 120.6, 126.6, 127.7, 128.3, 128.9, 129.2, 129.3, 131.0, 131.2, 132.2, 135.3, 135.8, 136.7, 147.0, 156.9. Anal. Calcd for $C_{17}H_{12}ClN$: C, 76.84; H, 4.55; N, 5.27. Found: C, 76.55; H, 4.40; N, 5.21.

4.5.3. 6-Bromo-2-styrylquinoline ***12c***

IR (KBr) 3039.7, 2996.6, 1630.1, 1589.0, 1544.6, 1489.6, 1386.5, 1313.3, 1189.2 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 7.34–7.46 (m, 4H), 7.64–7.80 (m, 5H), 7.93–7.97 (m, 2H), 8.01 (d, J=8.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz)* δ 120.3, 120.6, 127.7, 128.8, 128.9, 129.3, 129.9, 131.3, 133.6, 135.4, 135.7, 136.7, 147.2, 156.7. Anal. Calcd for $C_{17}H_{12}BrN$: C, 65.83; H, 3.90; N, 4.52. Found: C, 65.71; H, 3.81; N, 4.47. *One carbon signal is merged with others.

4.5.4. 6-Fluoro-2-styrylquinoline ***12d***

IR (KBr) 3030.7, 2920.8, 1634.4, 1601.4, 1554.4, 1503.0, 1449.8, 1347.5, 1218.9, 1138.4, 1108.1 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 7.36–7.54 (m, 6H), 7.65–7.73 (m, 4H), 8.07–8.12 (m, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 111.1 (d, J=21.7 Hz), 120.2 (d, J=23.6 Hz), 120.5, 127.7, 128.2 (d, J=9.8 Hz), 129.0, 129.1, 129.2, 132.0 (d, J=9.1 Hz), 134.8, 136.1 (d, J=5.2 Hz), 136.8, 145.7, 155.8 (d, J=2.9 Hz), 160.7 (d, J=252.8 Hz). Anal. Calcd for $C_{17}H_{12}FN$: C, 81.91; H, 4.85; N, 5.62. Found: C, 81.67; H, 4.76; N, 5.52.

4.5.5. 6-Methyl-2-styrylquinoline ***12e***

IR (KBr) 3028.0, 2909.4, 1634.1, 1589.9, 1495.9, 1445.2, 1371.4, 1122.0 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.56 (s, 3H), 7.34–7.45 (m, 4H), 7.54–7.58 (m, 2H), 7.64–7.71 (m, 4H), 8.01 (d, J=9.2 Hz, 1H), 8.06 (d, J=8.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 22.0, 119.7, 126.9, 127.6, 127.8, 128.9, 129.2, 129.3, 129.5, 132.4, 134.3, 136.1, 136.5, 137.0, 147.2, 155.6. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 87.96; H, 6.08; N, 5.60.

4.5.6. 2-(2-Nitrostyryl)quinoline ***12f***

IR (neat) 3057.7, 1594.3, 1519.6, 1426.9, 1342.7, 1304.6, 1140.0, 1119.5 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 7.41 (d, J=16.1 Hz, 1H), 7.47–7.57 (m, 2H), 7.63–7.91 (m, 5H), 8.01–8.08 (m, 2H), 8.12–8.19 (m, 2H). ^{13}C NMR ($CDCl_3$, 62.9 MHz)* δ 119.4, 125.3, 127.1, 127.9, 128.9, 129.3, 129.6, 129.8, 130.3, 132.7, 133.7, 134.6, 137.0, 148.5, 148.6, 155.6. Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.61; H, 4.28; N, 10.05. *One carbon signal is merged with others.

4.5.7. 5,7-Dimethyl-2-styrylquinoline ***12g***

IR (neat) 3031.8, 2919.9, 1620.1, 1596.0, 1508.7, 1447.8, 1404.8, 1379.6, 1202.6, 1175.0, 1031.9 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.54 (s, 3H), 2.64 (s, 3H), 7.18 (s, 1H), 7.34–7.45 (m, 4H), 7.59–7.76 (m, 5H), 8.21 (d, J=8.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 18.9, 22.3, 118.4, 125.1, 126.9, 127.6, 128.9, 129.2, 129.5, 129.6, 132.9, 134.3, 134.4, 137.0, 139.9, 149.2, 155.8. Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.77; H, 6.58; N, 5.32.

4.5.8. 6,8-Dimethyl-2-styrylquinoline ***12h***

IR (neat) 3031.7, 2917.9, 1598.1, 1560.8, 1496.9, 1446.8, 1370.4, 1176.8, 1075.6 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.52 (s, 3H), 2.88 (s, 3H), 7.35–7.47 (m, 6H), 7.60–7.79 (m, 4H), 8.02 (d, J=8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 18.2, 22.0, 119.7, 124.8, 127.6, 127.8, 128.7, 129.1, 130.0, 132.5, 133.6, 136.0, 136.2, 137.2, 137.3, 146.3, 154.2. Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.65; H, 6.54; N, 5.56.

4.6. General procedure for the CAN-mediated aromatization of 1,2,3,4-tetrahydro-2-styrylquinolines (7)

To a stirred solution of the suitable 1,2,3,4-tetrahydro-2-styrylquinoline **7** (1 mmol) in acetonitrile (10 mL) at 0 °C was added dropwise a solution of CAN (2.5 mmol) in acetonitrile (15 mL). Stirring was continued for further 30 min at the same temperature, and water (50 mL) was added. The solution thus obtained was extracted with CH_2Cl_2 (3×20 mL), dried (anhydrous Na_2SO_4), and evaporated. The crude products were separated through silica column using petroleum ether/ethyl acetate mixture (90:10, v/v).

4.6.1. 6-Methyl-8-nitro-2-styrylquinoline ***13***

IR (neat) 3033.6, 2913.3, 1631.9, 1598.9, 1497.0, 1444.9, 1325.6, 1201.3, 1071.3 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.67 (s, 3H), 7.14 (d, J=16.1 Hz, 1H), 7.22–7.35 (m, 4H), 7.40–7.43 (m, 2H), 7.57 (d, J=8.5 Hz, 1H), 7.68 (d, J=2.0 Hz, 1H), 7.92 (d, J=2.0 Hz, 1H), 8.15 (d, J=8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 22.3, 119.8, 126.7, 127.5, 128.1, 128.5, 128.9, 129.8, 133.7, 135.4, 135.6, 136.1, 137.3, 138.4, 146.0, 154.4. Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.17; H, 4.80; N, 9.55.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.12.077.

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