Inverse Electron Demand Diels–Alder Reactions of Heterodienes Catalyzed by Potassium Hydrogen Sulfate: Diastereoselective, One-Pot Synthesis of Pyranobenzopyrans, Furanobenzopyrans and Tetrahydroquinolines Derivatives

R. Senthil Kumar, Rajagopal Nagarajan, Paramasivan T. Perumal*

Organic Chemistry Division, Central Leather Research Institute, Adyar, Chennai – 600 020, India
Fax +91(44)24911589; E-mail: ptperumal@hotmail.com

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Abstract: Potassium hydrogen sulfate catalyzes the one-pot three components coupling of aldehydes, anilines, and electron rich dienophiles such as dihydropyran, dihydrofuran, ethyl vinylether, and cyclopentadiene. With *o*-hydroxybenzaldehyde, the reaction probably proceeds through the formation of *o*-quinonemethide intermediate, which subsequently undergoes cycloaddition with cyclic and acyclic enol ethers leading to the formation of respective chromanes. However, in case of benzaldehydes with no *o*-hydroxy group, the imine formed acts as the heterodiene and leads to the formation of tetrahydroquinolines.

***Keywords*:** heterodienes, potassium hydrogen sulfate, pyranobenzopyrans, furanobenzopyrans, tetrahydroquinolines

Nitrogen and oxygen containing heterocycles are ubiquitous in nature and display a wide variety of interesting biological properties. Among the numerous oxygen heterocycles, chromenes (2*H*-1 benzopyrans), chromans (3,4-dihydro-2*H*-1-benzopyrans) and their pyran, furan fused analogs seems attractive targets for synthetic chemists due to the useful biological properties that their naturally occurring representatives[1,2] display. For example, 4-aminobenzopyran and its derivatives are found to act as modulators of potassium channels and influence the activity of heart and blood pressure levels.[3]

Tetrahydroquinolines and their derivatives form a major part of nitrogen containing heterocycles that occurs in nature. Discohabdin C, a polycyclic system based on tetrahydroquinoline is a marine alkaloid.[4–6] Dynemycin, a natural antitumor antibiotic has a complex structure built on a tetrahydroquinoline system.[7,8] Some tetrahydroquinolines are potent inhibitors of (H^+ and K^+) adenosine triphosphatase[9] and angiotension I converting enzyme,[10] they also are cardiovascular [11] and anticonvulsant agents.[12] Besides pharmaceutical applications they are also useful as pesticides,[13] antioxidants,[14] and corrosion inhibitors.[15] Pyranotetrahydroquinolines are found in several alkaloids such as flindersine, oricine, and veprisine.[16] Derivatives of these alkaloids are found to have useful biological activities such as psychotropic,[17] antiallergic,[18] anti-inflammatory[19] and estrogenic properties.[20] The furoquinoline moiety is seen in the alkaloids skimmianine and balfouridine[21] and the phenanthridine skeleton[22] is present in lycorine, haemanthamine, and chelidonine alkaloids.

The classical Diels–Alder reaction, a [4+2] cycloaddition of a diene and dienophile to generate a six membered carbocyclic system, in its modified form can be used to generate nitrogen or oxygen containing six-membered system by the use of appropriate heterodiene or heterodienophile. However, instead of starting with preformed diene the in situ formation of diene is preferred. This one-pot procedure is especially useful when the diene is unstable and is difficult to purify either by distillation or chromatography.[23] Lewis acids such as lanthanide triflates, $Yb(OTf)_3$, $Sc(OTf)_3$, $BF_3 \cdot OEt_2$, and $GdCl_3$ were found to catalyze this reaction. However most of these reactions suffer from various disadvantages such as, more than stoichimetric amount of Lewis acid is needed due to strong co-ordination of it with the heteroatoms, longer reaction time, high cost and use of only aprotic solvents under anhydrous conditions. Also these reactions cannot be performed in one-pot because the amines and water that are present during imine formation can decompose or deactivate these Lewis acids. However to the best of our knowledge there is no report of the use of $KHSO_4$ as catalyst for this type of reactions. The catalyst is inexpensive, mild, and does not require the maintenance of anhydrous conditions.

Treatment of salicylaldehyde, amine, and dihydropyran in the presence of $KHSO_4$ in methanol at room temperature gave an inseparable mixture of linearly *cis* fused pyranochromanes **3** and **4** with high diasteroselectivity in favor of **3** (Scheme 1). The stereochemistry of the product **3** was assigned based on the coupling constant values and NOE studies. The *cis* fusion of the tetrahydropyran ring in compound **3** was determined from the coupling constant of 2.5 Hz between H_4 and H_5. Along with a coupling constant between H_4 and H_6 of 1.8 Hz and the presence of NOE between H_6 and H_5 and H_5 and H_4 proved that H_6 is *cis* to H_4. From the coupling constant value and absence of NOE between H_6 and H_5 and H_5 and H_4 in compound **4** it is concluded that H_6 is *trans* to H_4. Reactions were also performed with substituted anilines and the results are given in Table 1.

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Table 1 Synthesis of Pyrano and Furobenzopyrans

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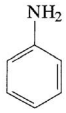
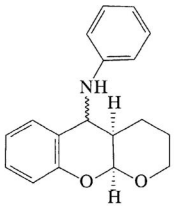
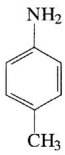
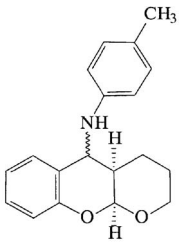
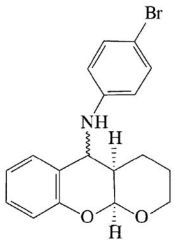
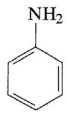
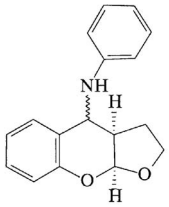
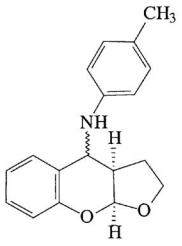
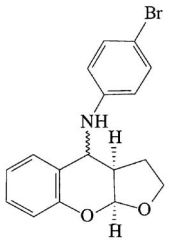
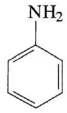
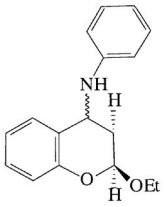
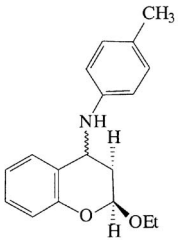
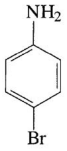
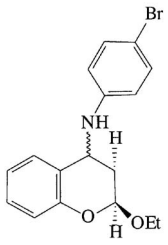
a			 **3a,4a**	50	61	98:2[d]
b			 **3b,4b**	50	50	97:3[d]
c			 **3c,4c**	50	71	98:2[d]
d			 **3d,4d**	30	60	77:23
e			 **3e,4e**	30	50	77:23
f			 **3f,4f**	30	80	75:25

Table 1 Synthesis of Pyrano and Furobenzopyrans (continued)

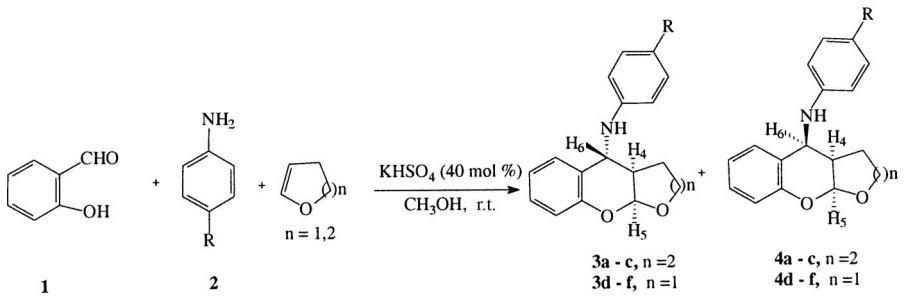
Entry	Amine	Dienophile	Product[a]	Time (min)	Yield[b] (%)	Product Ratio[c] 3:4
g			 **3g,4g**	70	45	42:58
h			 **3h,4h**	60	50	40:60
i			 **3i,4i**	60	50	39:61

[a] All the products were characterized by IR, NMR, and mass spectroscopy and elemental analysis.
[b] The yield is based on isolation by column chromatography.
[c] The product ratio is based on isolation by column chromatography.
[d] The product ratio is based on ^1H NMR of product mixture.

Similarly when dihydrofuran was treated with salicylaldehyde and amine in the presence of $KHSO_4$ in methanol at room temperature, a mixture of linearly *cis* fused furanobenzopyrans was obtained in good yield (Scheme 1). The diastereoselectivity, however in this case was moderate and the isomers were separated by column chromatography. From the coupling constant value and a similar NOE study as was done for pyranochromanes, the *cis* fusion of the furan ring was proven.

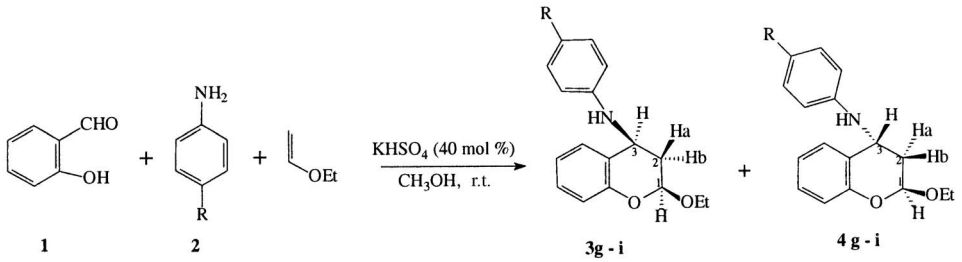
When the acyclic dienophile, ethylvinylether was used in the above procedure the corresponding adducts 2-ethoxy-4-*N*-arylaminobenzopyrans **3g–i** and **4g–i** were obtained as a separable mixture of diastereomers (Scheme 2). The diastereomers were isolated by column chromatography and the stereochemistry of the products was arrived at from the ^1H NMR spectroscopy based on the chemical shift and coupling constant values.

One pot cycloaddition of 2,3-dihydropyran with imines generated in situ from aldehydes having no *o*-hydroxy group was performed in the presence of $KHSO_4$ (Scheme 4). A diastereomeric mixture of the corresponding pyranoquinolines was obtained. The pyran ring is *cis*

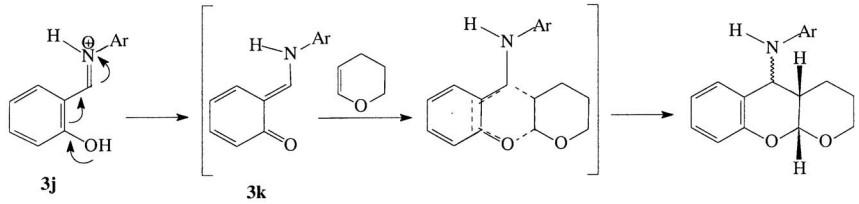


1 2

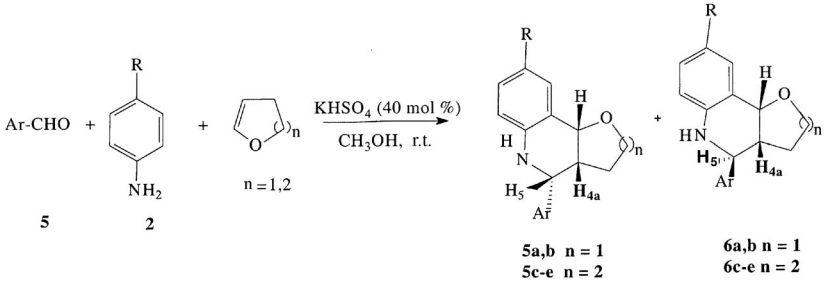
Scheme 1



Scheme 2



Scheme 3



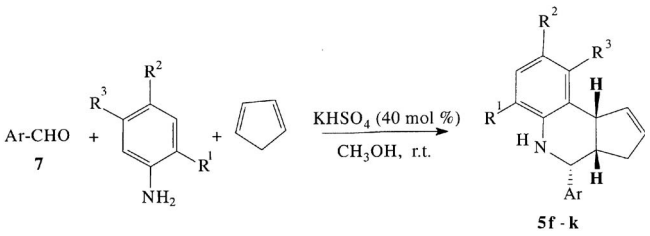
Scheme 4

fused and the stereochemistry of the products was established based on the coupling constant values. In isomer **5c** $J(H_{4a}\text{-}H_5)$ is 4.5 Hz and is significantly smaller and typical for a gauche conformation. This orientation is present in both conformers of the configuration having a *cis* orientation of the pyran ring and phenyl group. The $J(H_{4a}\text{-}H_5)$ value of 10.6 Hz in isomer **6c** is appropriate and indicative of *anti* reciprocal orientation of protons H_5 and $H_{4a.}$ Similarly with 2,3-dihydrofuran the corresponding furoquinolines were obtained as a mixture of diastereomers with *cis* fused ring junction.

Cyclopentaquinolines were synthesized by three component coupling reaction of aldehyde, aniline with cyclopentadiene (Scheme 5, Table 2). Imines derived from phenylglyoxal are generally unstable at higher temperatures and are difficult to purify either by distillation or by column chromatography so the one-pot coupling of phenylglyoxal, aniline and cyclopentadiene was attempted successfully (Table 2).

In the case of *o*-hydroxy benzaldehyde the reaction probably proceeds through the intermediate formation of *o*-quinonemethides[24] from the in situ generated imine **3j**. A plausible mechanism for the formation of *o*-quinonemethide, **3k** is given in Scheme 3. The *o*-quinonemethide formed acts as oxadiene and subsequently adds to 2,3-dihydropyran or 2,3-dihydrofuran giving the pyrano or furano benzopyrans. However with aldehydes having no *ortho* hydroxy group, reaction takes alternative path in which case the imine formed acts as a azadiene giving the pyrano and furoquinolines.

In summary, we have shown for the first time that the salt, $KHSO_4$ can catalyze the one-pot coupling of various aldehydes, amines, and dieneophiles (both cyclic and acyclic) giving the cycloadducts. The catalyst is mild, inexpensive, and easily available and also offers several advantages including shorter reaction times, cleaner reactions as well as simple experimental and isolation procedures, which makes it useful and attractive for the synthesis of chromanes and tetrahydroquinolines.



Scheme 5

Table 2 Synthesis of Tetrahydroquinolines

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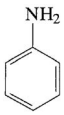
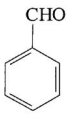
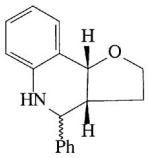
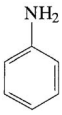
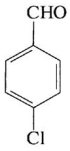
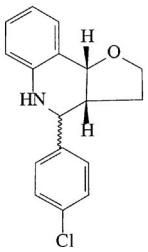
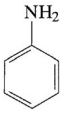
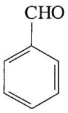
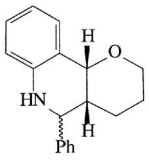
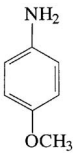
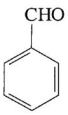
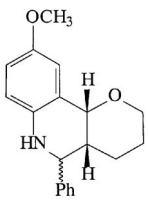
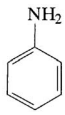
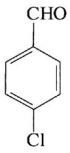
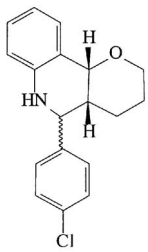
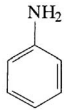
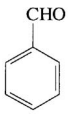
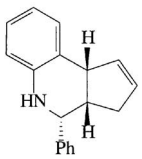
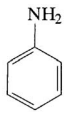
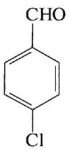
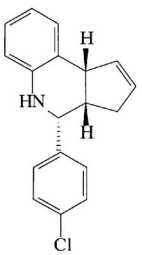
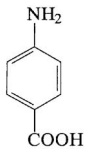
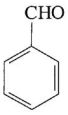
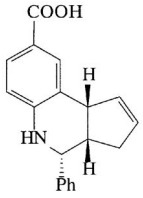
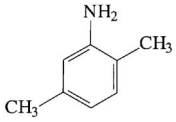
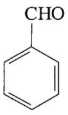
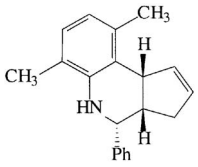
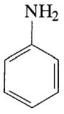
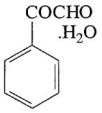
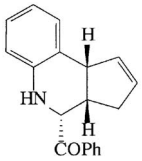
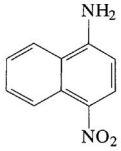
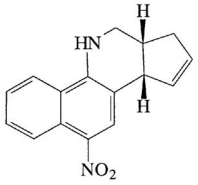
a					45	60	38:62
b					40	57	35:65
c					60	64	65:35
d					60	52	26:73
e					60	40	35:65
f					75	44	–
g					75	40	–

Table 2 Synthesis of Tetrahydroquinolines (continued)

No	Amine	Aldehyde	Dienophile	Product[a]	Time (min)	Yield[b] (%)	Product Ratio[c] 5: 6
h					75	42	–
i					75	41	–
j					75	52	–
k		HCHO(aq)			60	42	–

[a] All the products were characterized by IR, NMR, and mass spectroscopy and elemental analysis.
[b] The yield is based on isolation by column chromatography.
[c] The product ratio is applicable for pyrano and furoquinolines only. In the case of cyclopentaquinolines only one isomer was observed.

Mass spectra were recorded on Varian VG 70-70H mass spectrometer. Analytical TLC was performed on precoated sheets of silica gel G of 0.25 mm thickness containing PF 254 indicator (Merck, Darmstadt). Column chromatography was performed with silica gel (60–120 mesh, S.d Fine, Boisar). IR spectra were recorded as solids in KBr pellets on a Perkin-Elmer FTIR spectrometer. ^{1}H NMR spectra were recorded on a Bruker spectrometer using TMS as internal standard. ^{13}C NMR spectra were recorded on 300, 400, and 500 MHz spectrometer in $CDCl_3$ and chemical shifts are given relative to the solvent peak. The enol ether used was brought from Lancaster. The procedure does not require dry solvent or an inert atmosphere. All the products obtained were purified by column chromatography using silica gel (Merck, 100–200 mesh).

Preparation of Pyrano and Furanobenzopyran; General Procedure

A mixture of *o*-hydroxybenzaldehyde (4 mmol), aniline (4.8 mmol), dihydropyran or dihydrofuran (10 mmol) and $KHSO_4$ (0.21g, 40 mol%) in MeOH (10 mL) was stirred at ambient temperature for the appropriate time. After completion of the reaction, as indicated by TLC monitoring, the excess MeOH was distilled off and the reaction mixture was diluted with water (20 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuum and the resulting product was purified by column chromatography (EtOAc–and petroleum ether, 1:9) to afford pure *cis*-fused pyrano and furanochromanes obtained as mixture of **3a–c** and **4a–c** or pure **3d–f** or **4d–f**.

Phenyl(3,4,4a,10a-Tetrahydro-2*H*,5H-pyrano[2,3-*b*]chromen-5-yl)amine (3a and 4a)

Yield: 0.80g (60%).

3a

IR (KBr): 3347 (NH), 3029, 1485 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.57–1.67 (m, 2 H, H3), 1.87–1.96 (m, 2 H, H2), 3.08-3.15 (m, 1 H, H4), 3.82–3.95 (m, 3 H, H1, including NH), 4.98 (d, 1 H, H6, *J* = 4.9 Hz), 5.89 (d, 1 H, H5, *J* = 5.4 Hz), 6.74, (d, 2 H, *J* = 7.8 Hz), 6.79 (t, 1 H, *J* = 7.6 Hz), 6.92–6.98 (m, 2 H), 7.19–7.27 (m, 2 H), 7.36 (d, 2 H, *J* = 7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$, proton decoupled): δ = 17.1, 24.2, 34.8, 50.9, 60.9, 96.4, 112.6, 113.2, 116.4, 118.1, 121.1, 126.7, 128.9, 129.5, 146.8, 153.1.

MS: *m*/*z* = 281 (M^+).

Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.68; H, 6.94; N, 4.76.

4a

^{1}H NMR: δ = 4.62 (d, 1 H, H6, *J* = 2.3 Hz), 5.65 (d, 1 H, H5, *J* = 5.4 Hz).

^{13}C NMR: δ = 21.7, 24.3, 36.6, 53.3, 61.7, 94.6, 112.6, 117.0, 117.8, 118.0, 121.2, 121.8, 129.5, 130.4, 146.2, 153.0.

(4-Methylphenyl)3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromen-5-ylamine (3b and 4b)

Yield: 0.60g, (50%).

3b
IR (KBr): 3360 (NH), 3022, 1485 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.18–1.62 (m, 4 H, H2, H2′, H3, H3′), 2.18 (s, 3 H, CH_3), 2.38–2.44 (m, 1 H, H4), 3.62 (br s overlapped, NH, 1 H), 3.62–3.69 (m, 1 H, H1), 3.89–3.96 (m, 1 H, H1′), 4.88 (d, 1 H, H6, *J* = 1.8 Hz), 5.47 (d, 1 H, H5, *J* = 2.5 Hz), 6.45 (d, 1 H, *J* = 8.3 Hz), 6.55 (d, 2 H, *J* = 8.3 Hz), 6.81–6.94 (m, 1 H), 6.95 (d, 2 H, *J* = 7.8 Hz), 7.11–7.17 (m, 1 H), 7.36 (d, 1 H, *J* = 7.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled): δ = 17.0, 20.4, 24.1, 34.7, 51.1, 60.9, 96.3, 112.7, 113.3, 116.2, 120.7, 126.7, 127.0, 128.9, 130.0, 144.5, 153.0.

MS: *m*/*z* = 295 (M^+).

Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.41; H, 7.32; N, 4.53.

4b
^1H NMR: δ = 4.17 (d, 1 H, H6, *J* = 2.4 Hz), 5.37 (d, 1 H, H5, *J* = 2.5 Hz).

^{13}C NMR: δ = 16.8, 21.7, 24.3, 36.6, 53.4, 61.7, 94.6, 116.9, 121.1, 121.2, 122.0, 127.2, 129.3, 129.9, 130.3, 144.1, 152.9.

(4-Bromophenyl)3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromen-5-ylamine (3c and 4c)
Yield: 1.00 g (71%).

3c
IR (KBr): 3398 (NH), 3037, 1494 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.28–1.69 (m, 4 H, H2, H3), 2.42–2.46 (m, 1 H, H4), 3.71–3.85 (m, 1 H, H1), 3.94–4.03 (m, 1 H, H1′), 3.83 (br s, 1 H, NH), 4.93 (d, 1 H, H6, *J* = 4.5 Hz), 5.52 (d, 1 H, H5, *J* = 2.3 Hz), 6.45 (d, 1 H, *J* = 8.7 Hz), 6.57 (d, 2 H, *J* = 8.7 Hz), 6.89 (t, 1 H, *J* = 6.3 Hz), 7.21–7.33 (m, 2 H), 7.26 (d, 2 H, *J* = 6.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$, proton decoupled): δ = 17.1, 19.7, 24.1, 34.7, 51.1, 60.93, 96.2, 109.5, 114.8, 116.5, 121.3, 126.6, 129.1, 132.2, 145.6, 152.3.

MS: *m*/*z* = 360 (M^+).

Anal. Calcd for $C_{18}H_{18}BrNO_2$: C, 60.01; H, 5.04; N, 3.89. Found: C, 60.18; H, 5.24; N, 3.72.

4c
^1H NMR: δ = 3.99 (br s, 1 H, H6), 5.45 (br s, 1 H, H5).

^{13}C NMR: δ = 19.7, 21.8, 25.4, 30.7, 36.5, 53.2, 62.9, 94.5, 109.1, 114.2, 117.1, 121.3, 123.4, 129.6, 145.2, 152.1.

Phenyl(2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-yl)amine (3d)
Yield: 0.5 g (77%); colorless solid; mp 110–112 °C.

IR (KBr): 3366 (NH), 3024, 1481 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.49–1.68 (m, 1 H, H2), 1.75–1.95 (m, 1 H, H2′), 3.05–3.15 (m, 1 H, H3), 3.77–3.95 (m, 3 H, H1, including NH), 4.96 (br s, 1 H, H5), 5.88 (br s, 1 H, H4), 6.70–7.20 (m, 8 H), 7.34 (d, 1 H, *J* = 6.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$, proton decoupled): δ = 23.9, 43.3, 48.8, 68.0, 102.4, 113.4, 117.2, 118.4, 121.9, 124.6, 126.2, 128.8, 129.6, 147.0, 152.9.

MS: *m*/*z* = 267 (M^+).

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24; Found: C, 76.62; H, 6.23; N, 5.36.

Phenyl(2, 3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-yl)amine (4d)
Yield: 0.15 g (23%); colorless solid; mp 90–92 °C.

IR (KBr): 3363 (NH), 3022, 1454 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.23–1.70 (m, 1 H, H2), 2.12–2.19 (m, 1 H, H2′), 2.89–2.96 (m, 1 H, H3), 3.90 (br s, 1 H, NH overlapped), 3.91–3.98 (m, 1 H, H1), 4.01–4.08 (m, 1 H, H′1), 4.51 (br s, 1 H, H5,), 5.66 (d, 1 H, H4, *J* = 4.7 Hz), 6.63 (d, 2 H, *J* = 8.0 Hz), 6.76 (t, 1 H, *J* = 7.3 Hz), 6.91–6.95 (m, 2 H), 7.16–7.24 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$, proton decoupled): δ = 26.9, 43.3, 50.5, 67.8, 99.9, 113.0, 117.6, 118.1, 121.6, 121.7, 124.2, 129.5, 129.8, 146.3, 152.5.

MS: *m*/*z* 267 (M^+).

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24; Found: C, 76.69; H, 6.15; N, 5.19.

(4-Methylphenyl)2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-ylamine (3e)
Yield: 0.5 g (77%); colorless solid; mp 80–82 °C.

IR (KBr) 3386 (NH), 2976, 1482 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.56–1.64 (m, 1 H, H2), 1.87–1.94 (m, 1 H, H2′), 2.27 (s, 3 H, CH_3), 3.08–3.14 (m, 1 H, H3), 3.70 (br s, 1 H, NH), 3.84 (q, 1 H, H1, *J* = 8.6 Hz), 3.92 (dt, 1 H, H1′ *J* = 4, 8.9 Hz), 4.95 (d, 1 H, H5, *J* = 4.6 Hz), 5.88 (d, 1 H, H4, *J* = 5.7 Hz), 6.67 (d, 2 H, *J* = 8.5 Hz), 6.91–6.99 (m, 2 H), 7.04 (d, 2 H, *J* = 8.0 Hz), 7.20–7.29 (m, 1 H), 7.38 (d, 1 H, *J* = 7.4 Hz).

^{13}C NMR (125 MHz, $CDCl_3$, proton decoupled): δ = 20.5, 24.0, 43.3, 49.1, 68.1, 102.4, 113.7, 117.2, 122.9, 124.8, 126.3, 127.7, 128.8, 130.1, 144.7, 153.0.

MS: *m*/*z* = 281 (M^+).

Anal. calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98; Found: C, 76.64; H, 6.53; N, 4.76.

(4-Methylphenyl)2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-ylamine (4e)
Yield: 0.15 g (23%); colorless solid; mp 108–110 °C.

IR (KBr): 3384 (NH), 3022, 2948, 1486 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.65–1.73 (m, 1 H, H2), 2.13–2.10 (m, 1 H, H2′), 2.27 (s, 3 H, CH_3), 2.91–2.96 (m, 1 H, H3), 3.79 (br s, 1 H, NH), 3.96 (q, 1 H, H1, *J* = 8.0 Hz), 4.07 (dt, 1 H, H1′, *J* = 4, 8.6 Hz), 4.50 (d, 1 H, H5, *J* = 2.2 Hz), 5.68 (d, 1 H, H4, *J* = 5.1 Hz), 6.59 (d, 2 H, *J* = 8.0 Hz), 6.91–6.98 (m, 2 H), 7.04 (d, 2 H, *J* = 8.0 Hz), 7.24–7.26 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$, proton decoupled): δ = 20.5, 27.0, 43.3, 50.8, 67.9, 100.0, 113.3, 117.6, 121.7, 121.9, 127.4, 129.8, 129.9, 130.1, 144.1, 152.5.

MS: *m*/*z* = 281 (M^+).

Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.75; H, 6.46; N, 4.89.

(4-Bromophenyl)2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-ylamine (3f)
Yield: 0.76g, (75%); colorless solid; mp 107–109 °C.

IR (KBr): 3383 (NH), 3038, 1493 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.54–1.83 (m, 1 H, H2), 1.90–1.94 (m, 1 H, H2′), 3.08–3.14 (m, 1 H, H3), 3.84–3.96 (m, 3 H, H1, including NH), 4.93 (br s, 1 H, H5), 5.90 (d, 1 H, H4, *J* = 5.4 Hz), 6.63 (d, 2 H, *J* = 8.8 Hz), 6.94–7.00 (m, 2 H), 7.22–7.27 (m, 2 H), 7.31 (d, 2 H, *J* = 8.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled): δ = 24.2, 43.5, 49.2, 68.2, 102.5, 110.0, 115.2, 117.6, 122.2, 124.4, 126.3, 129.2, 132.5, 146.3, 153.2.

MS: *m*/*z* = 346 (M^+).

Anal. Calcd for $C_{17}H_{16}BrNO_2$: C, 58.98; H, 4.66; N, 4.05. Found: C, 58.67; H, 4.43; N, 4.25.

(4-Bromophenyl)2,3,3a,9a-tetrahydro-4*H*-furo[2,3-*b*]chromen-4-ylamine(4f)
Yield: 0.26g, (25%); colourless solid; mp 124–126 °C.

IR (KBr): 3392 (NH), 3042, 1493 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53–1.63 (m, 1 H, H2), 2.06–2.08 (m, 1 H, H2′), 2.74–2.84 (m, 1 H, H3), 3.86–3.96 (m, 3 H, H1, including NH), 4.39 (br s, 1 H, H5), 5.57 (d, 1 H, H4, *J* = 4.9 Hz), 6.44 (d, 2 H, *J* = 8.8 Hz), 6.84–7.16 (m, 4 H), 7.20 (d, 2 H, *J* = 8.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled): δ = 27.2, 43.4, 50.8, 67.9, 100.1, 109.8, 114.8, 117.9, 121.6, 122.0, 129.9, 130.2, 132.4, 145.6, 152.7.

MS: *m*/*z* = 346 (M^+).

Anal. Calcd for $C_{17}H_{16}BrNO_2$: C, 58.98; H, 4.66; N, 4.05. Found: C, 58.56; H, 4.57; N, 4.43.

Preparation of 2-Ethoxy-4-*N*-aryl Amino Benzopyran; General Procedure
Ethyl vinyl ether (10 mmol) was added slowly at 0 °C to a mixture of *o*-hydroxybenzaldehyde (4 mmol), aniline (4.8 mmol), and $KHSO_4$ (0.21g, 40 mol%). The resulting reaction mixture was stirred at ambient temperature for an appropriate time. After completion of the reaction, as indicated by TLC, the reaction mixture was quenched with water (20 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined extracts were dried over anhyd Na_2SO_4, filtered, concentrated in vacuo and purified by column chromatography on silica gel (Merck, 100–200 mesh; EtOAc–hexane, 5:95) to afford pure *cis*-fused acetal **3g–i** and **4g–i**.

2-(Ethoxy-3, 4-dihydro-2*H*-chromen-4-yl)phenylamine (3g)
Yield: 0.29g (58%); colorless liquid.

IR (neat): 3390 (NH), 3048, 1498 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (t, 3 H, *J* = 6.84 Hz), 2.1–2.19 (m, 1 H), 2.34–2.38 (m, 1 H), 3.51–3.59 (m, 1 H), 3.84–3.91 (m, 1 H), 4.57 (br s, 1 H, NH), 4.67 (br s, 1 H), 5.35 (t, 1 H, *J* = 2.9 Hz), 6.71–6.76 (m, 3 H), 6.89 (d, 1 H, *J* = 8.3 Hz), 6.94 (t, 1 H, *J* = 8.0 Hz), 7.18–7.24 (m, 3 H), 7.37 (d, 1 H, *J* = 7.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled): δ = 15.2, 31.5, 45.5, 64.2, 97.2, 114.2, 117.4, 117.9, 121.3, 124.1, 128.9, 129.3, 130.1, 147.4, 151.1.

MS: *m*/*z* = 269 (M^+).

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.63; H, 7.26; N, 5.03.

(2-Ethoxy-3,4-dihydro-2*H*-chromen-4-yl)phenylamine (4g)
Yield: 0.21g, (42%); colorless liquid.

IR (neat): 3395 (NH), 3050, 1494 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, 3 H, *J* = 6.8 Hz), 1.97 (m, 1 H), 2.36 (dt, 1 H, *J* = 6.7, 12.8 Hz), 3.65 (dq, 1 H, *J* = 6.8, 9.2 Hz), 3.78 (br s, 1 H, NH), 3.94 (dq, 1 H, *J* = 6.8, 9.2 Hz), 4.91 (dd, 1 H, *J* = 5.4, 9.3 Hz), 5.28 (dd, 1 H, *J* = 2.4, 9.3 Hz), 6.70–6.76 (m, 3 H), 6.87 (d, 1 H, *J* = 8.3 Hz), 6.92 (t, 1 H, *J* = 7.4 Hz), 7.18–7.25 (m, 3 H), 7.42 (d, 1 H, *J* = 7.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled): δ = 15.1, 33.4, 45.1, 64.2, 97.5, 113.0, 117.0, 117.7, 121.1, 124.9, 127.6, 128.8, 129.5, 147.2, 152.2.

MS: *m*/*z* = 269 (M^+).

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.92; H, 7.09; N, 5.32.

(2-Ethoxy-3,4-dihydro-2*H*-chromen-4-yl)(4-methylphenyl)amine (3h)
Yield: 0.344 g (60%); colorless liquid.

IR (neat): 3385 (NH), 3045, 1492 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (t, 3 H, *J* = 6.5 Hz), 2.15–2.23 (m, 1 H), 2.26 (s, 3 H, CH_3), 2.37–2.41 (m, 1 H), 3.53–3.58 (m, 1 H), 3.81–3.89 (m, 1 H), 4.32 (br s, 1 H, NH), 4.69 (br s, 1 H), 5.37 (t, 1 H, *J* = 2.8 Hz), 6.72 (d, 2 H, *J* = 8.4 Hz), 6.70–6.78 (m, 2 H), 7.08 (d, 2 H, *J* = 8.5 Hz), 7.25-7.29 (m, 1 H), 7.43 (d, 1 H, *J* = 7.9 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled): δ = 15.4, 20.2, 31.4, 45.3, 64.3, 97.3, 114.3, 117.5, 118.9, 121.5, 124.1, 128.9, 129.4, 130.1, 147.5, 151.2.

MS: *m*/*z* 283 (M^+).

Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.52; H, 7.23; N, 4.73.

(2-Ethoxy-3,4-dihydro-2*H*-chromen-4-yl)(4-methylphenyl)amine (4h)
Yield: 0.236 g (40%); colorless liquid.

IR (neat): 3392 (NH), 3042, 1495 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, 3 H, *J* = 6.7 Hz), 1.98 (m, 1 H), 2.21 (s, 3 H, CH_3), 2.35 (dt, 1 H, *J* = 6.5, 12.5 Hz), 3.64 (dq, 1 H, *J* = 6.6, 9.4 Hz), 3.79 (br s, 1 H, NH), 3.95 (dq, 1 H, *J* = 6.7, 9.4 Hz), 4.92 (dd, 1 H, *J* = 5.6, 9.4 Hz), 5.26 (dd, 1 H, *J* = 2.4, 9.4 Hz), 6.62 (d, 2 H, *J* = 8.5 Hz), 6.72–6.79 (m, 2 H), 7.09 (d, 2 H, *J* = 8.5 Hz), 7.24–7.27 (m, 1 H), 7.45 (d, 1 H, *J* = 7.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled): δ = 15.7, 20.5, 31.8, 45.6, 64.1, 97.2, 114.6, 117.9, 118.4, 121.2, 124.4, 128.3, 129.7, 130.4, 147.6, 151.4.

MS: *m*/*z* = 283 (M^+).

Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.46; H, 7.58; N, 4.82.

(2-Ethoxy-3,4-dihydro-2*H*-chromen-4-yl)(4-bromophenyl)amine (3i)
Yield: 0.380g (58%); colorless solid; mp 119–121 °C.

IR (KBr): 3394 (NH), 3026, 1491 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (t, 3 H, *J* = 6.5 Hz), 1.93 (m, 1 H), 2.36–2.43 (m, 1 H), 3.52–3.56 (m, 1 H), 3.82–3.87 (m, 1 H), 4.30 (br s, 1 H, NH), 4.73 (br s, 1 H), 5.58 (t, 1 H, *J* = 2.9 Hz), 6.64 (d, 2 H, *J* = 8.9 Hz), 6.93–7.01 (m, 2 H), 7.21–7.29 (m, 2 H), 7.32 (d, 2 H, *J* = 8.9 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled): δ = 15.4, 32.5, 45.7, 64.5, 97.2, 114.4, 117.7, 117.9, 122.3, 124.5, 126.3, 129.4, 132.5, 146.4, 153.4.

MS: *m*/*z* = 348 (M^+).

Anal. Calcd for $C_{17}H_{18}BrNO_2$: C, 58.63; H, 5.21; N, 4.02. Found: C, 58.24; H, 5.10; N, 4.24.

(2-Ethoxy-3, 4-dihydro-2*H*-chromen-4-yl)(4-bromophenyl)amine (4i)
Yield: 0.270g (42%); colorless solid; mp 109–111 °C.

IR (KBr): 3390 (NH), 3040, 1493 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, 3 H, *J* = 6.8 Hz), 1.92 (m, 1 H), 2.34 (dt, 1 H, *J* = 6.8, 12.3 Hz), 3.63 (dq, 1 H, *J* = 6.8, 9.3 Hz), 3.76 (br s, 1 H, NH), 3.92 (dq, 1 H, *J* = 6.8, 9.3 Hz), 4.91 (dd, 1 H, *J* = 5.5, 9.4 Hz), 5.29 (dd, 1 H, *J* = 2.5, 9.4 Hz), 6.45 (d, 2 H, *J* = 8.9 Hz), 6.85-7.19 (m, 4 H), 7.21 (d, 2 H, *J* = 8.9 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled): δ = 15.3, 33.6, 45.2, 64.3, 97.9, 113.6, 117.2, 117.4, 121.7, 122.3, 129.8, 130.4, 132.6. 145.7, 152.5.

MS: *m*/*z* = 348 (M^+).

Anal. Calcd for $C_{17}H_{18}BrNO_2$: C, 58.63; H, 5.21; N, 4.02. Found: C, 58.81; H, 5.07; N, 4.14.

Synthesis of Tetrahydroquinolines; General Procedure

$KHSO_4$ (0.256g, 40 mol%) was added to a mixture of aldehyde (4.7 mmol), aromatic amine (5.1 mmol), and dienophile [cyclopentadiene (11.7 mmol) or 3,4-dihydropyran (11.7 mmol) dihydrofuran (11.7 mmol)] in MeOH (10 mL) and stirred at room temperature for the appropriate time. To the reaction mixture water was added (25 mL), the product was extracted with CH_2Cl_2 (3 × 10 mL), the combined organic phase was washed with brine, dried over anhyd Na_2SO_4, filtered, and the solvent evaporated. The residue was purified by column chromatography (petroleum ether–EtOAc) to afford the cycloadducts.

4-Phenyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (5a)

Yield: 0.510g (60%); colorless solid; mp115–117°C (Lit.[25] 117–118 °C).

IR (KBr): 3345, 1484 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.25 (m, 6 H), 7.10 (td, 1 H, *J* = 8.0, 1.1 Hz), 6.80 (t, 1 H, *J* = 7.4 Hz), 6.60 (d, 1 H, *J* = 8.0 Hz), 5.28 (d, 1 H, *J* = 7.4 Hz), 4.60 (d, 1 H, *J* = 2.8 Hz), 3.76 (m, 3 H,), 2.78 (m, 1 H), 2.21 (m, 1 H), 1.52 (m, 1 H).

^{13}C (75 MHz, $CDCl_3$): δ = 145.0, 142.2, 130.2, 128.7, 128.4, 127.7, 126.6, 122.7,119.2, 115.0, 76.0, 66.9, 57.6, 45.8, 24.7.

MS: *m*/*z* = 251 (M^+).

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.28; H, 6.77; N, 5.58. Found: C, 80.90; H, 6.68; N, 5.30.

4-Phenyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (6a)

Yield: 0.340g (40%); viscous oil.

IR (KBr): 3324, 1483 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.25 (m, 6 H), 7.12 (td, 1 H, *J* = 7.4, 1.1 Hz), 6.80 (t, 1 H, J = 7.4 Hz), 6.62 (d, 1 H, *J* = 8.0 Hz), 4.60 (d, 1 H, *J* = 5.1 Hz), 4.15 (br s, 1 H), 4.05–4.01(m, 1 H), 3.86–3.78 (m, 2 H), 2.50–2.43 (m, 1 H), 2.06–1.97 (m, 1 H), 1.74–1.69 (m, 1 H).

^{13}C (75 MHz, $CDCl_3$): δ = 145.5, 141.7, 131.3, 129.0, 128.7, 128.3, 128.2, 120.1, 118.4, 114.8, 76.3, 65.3, 57.8, 43.4, 28.9.

MS: *m*/*z* = 251 (M^+).

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.28; H, 6.77; N, 5.58. Found: C, 80.92; H, 6.66; N, 5.31.

4-(4-Chlorophenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (5b)

Yield: 0.450g (65%); colorless solid; mp 129–130 °C.

IR (KBr): 3321, 1486 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.32 (m, 5 H), 7.09 (t, 1 H, *J* = 8.5 Hz), 6.82 (t, 1 H, *J* = 7.4 Hz), 6.60 (d, 1 H, *J* = 8.0 Hz), 5.26 (d, 1 H, J = 8.0 Hz), 4.67 (d, 1 H, *J* = 2.9 Hz), 4.01(m, 1 H), 3.82–3.69 (m, 3 H), 2.76–2.71 (m, 1 H), 2.19–2.10 (m, 1 H), 1.53–1.46 (m, 1 H).

^{13}C (75MHz, $CDCl_3$): δ = 144.7, 140.7, 133.3, 130.2, 128.9, 128.5, 127.9, 122.7, 119.5, 115.1, 75.8, 66.8, 57.0, 45.7, 24.6.

MS: *m*/*z* = 287 (M^+ + 2), 285 (M^+).

Anal. Calcd for $C_{17}H_{16}ClNO$: C, 71.48; H, 5.60; N, 4.90; Found: C, 71.40; H, 5.57; N, 5.10.

4-(4-Chlorophenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (6b)

Yield: 0.250g (65%); colorless solid; mp 98–100 °C.

IR (KBr): 3392, 1481 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.33 (m, 5 H), 7.12 (t, 1 H, *J* = 7.2 Hz), 6.80 (td, 1 H, *J* = 7.4, 1.0 Hz), 6.63 (d, 1 H, *J* = 8.2 Hz), 4.58 (d, 1 H, *J* = 5.1 Hz), 4.10 (br s, 1 H), 4.04–3.70 (m, 3 H), 2.43–2.37 (m, 1 H), 2.04–1.97 (m, 1 H), 1.69–1.62 (m, 1 H).

^{13}C (75 MHz, $CDCl_3$): δ = 145.2, 140.3, 133.9, 131.3, 129.6, 129.1, 128.9, 120.7, 118.7, 114.8, 76.1, 65.2, 57.2, 43.5, 28.8.

MS: *m*/*z* = 287 (M^+ + 2), 285 (M^+).

Anal. Calcd for $C_{17}H_{16}ClNO$: C, 71.48; H, 5.60; N, 4.90. Found: C, 71.42; H, 5.56; N, 5.09.

5-Phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-*c*]quinoline (5c)

Yield: 0.515 g (65%); colorless solid; mp 129–131 °C (Lit.[25] 132 °C).

IR (KBr): 3378, 3316, 2936, 1605, 1485, 1071 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.24 (m, 6 H), 7.13–7.06 (m, 1 H), 6.83–6.76 (m, 1 H), 6.62 (d, 1 H, *J* = 7.6 Hz), 5.34 (d, 1 H, *J* = 4.5 Hz), 4.68 (s, 1 H), 3.89 (br s, 1 H, NH), 3.61 (d, 1 H, *J* = 11.2 Hz), 3.44–3.26 (m, 1 H), 2.17–1.99 (m, 1 H), 1.75–1.31 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.2, 141.1, 128.3, 128.0, 127.6, 127.5, 126.8, 119.8, 118.3, 114.4, 72.8, 60.6, 59.3, 38.9, 25.4, 18.0.

MS: *m*/*z* = 265 (M^+).

Anal. calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.07; H, 7.25; N, 5.30.

5-Phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-*c*]quinoline (6c)

Yield: 0.275 g (35%); viscous oil.

IR (KBr): 3374, 2928, 1610, 1489, 1077 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.34 (m, 5 H), 7.26 (d, 1 H, *J* = 7.0 Hz), 7.13–7.03 (m, 1 H), 6.75–6.59 (m, 1 H), 6.54 (d, 1 H, *J* = 7.8 Hz), 4.74 (d, 1 H, *J* = 10.6 Hz), 4.41 (br s, 1 H, NH), 4.10–4.02 (m, 2 H), 3.78–3.69 (m, 1 H), 2.08–2.02 (m, 1 H), 1.89–1.31 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.1, 141.7, 130.2, 128.7, 128.0, 127.2, 127.1, 120.0, 116.8, 113.5, 73.9, 68.0, 54.1, 38.2, 23.5, 21.4.

MS: *m*/*z* = 265 (M^+).

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.09; H, 7.24; N, 5.25.

9-Methoxy-5-phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-*c*]quinoline (5d)

Yield: 0.740 g (73%); mp146–147 °C (Lit.[25] 144–146 °C).

IR (KBr): 3295, 2942, 1502, 1262, 1065 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.29 (m, 5 H), 7.03 (s, 1 H), 6.73 (d, 1 H, *J* = 8.2 Hz), 6.57 (d, 1 H, *J* = 8.2 Hz), 5.31 (d, 1 H,

J = 5.4 Hz), 4.61 (s, 1 H), 3.73 (s, 3 H), 3.67 (br s, 1 H, NH), 3.61–3.36 (m, 2 H), 2.15 (m, 1 H), 1.54–1.26 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.8, 141.3, 139.1, 128.3, 127.4, 126.8, 121.1, 115.7, 115.0, 111.8, 72.9, 60.8, 59.5, 55.8, 39.1, 25.3, 17.9.

MS: *m*/*z* = 295 (M^+).

Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74; Found: C, 77.65; H, 7.20; N, 4.77.

9-Methoxy-5-phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-*c*]quinoline (6d)
Yield: 0.280 g (27%); viscous liquid.

IR (neat): 3361, 2938, 1504, 1255, 1032 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.27 (m, 5 H), 6.82 (s, 1 H), 6.75 (d, 1 H, *J* = 9.1 Hz), 6.49 (d, 1 H, *J* = 8.5 Hz), 4.62 (d, 1 H, *J* = 10.5 Hz), 4.38 (s, 1 H), 4.10 (m, 1 H), 3.75 (m, 5 H), 2.10 (m, 1 H), 1.84–1.30 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.9, 142.2, 138.7, 128.1, 127.7, 121.3, 116.7, 115.5, 114.7, 74.5, 68.3, 55.7, 55.1, 38.8, 24.0, 21.9.

MS: *m*/*z* = 295 (M^+).

5-(4-Chlorophenyl)-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-*c*]quinoline (5e)
Yield: 0.300 g (64%); colorless solid; mp 168–169 °C.

IR (KBr): 3379, 2928, 1492, 1261 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.26 (m, 5 H), 7.21 (s, 1 H), 6.76–6.62 (m, 1 H), 6.54 (d, 1 H, *J* = 8.1 Hz), 5.23 (d, 1 H, *J* = 5.4 Hz), 4.84 (s, 1 H), 3.91 (br s, 1 H, NH), 3.71 (d, 1 H, *J* = 11.3 Hz), 3.64–3.43 (m, 1 H), 1.98–1.81 (m, 1 H), 1.79–1.54 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$) 144.1, 140.6, 133.0, 130.4, 129.1, 128.8, 128.5, 120.6, 117.4, 113.9, 74.5, 68.6, 53.9, 38.8, 24.0, 21.9.

MS: *m*/*z* = 299 (M^+); 301 (M + 2).

Anal. Calcd for $C_{18}H_{18}ClNO$: C, 72.11; H, 6.05; N, 4.67. Found: C, 72.38; H, 5.98; N, 4.65.

5-(4-Chlorophenyl)-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano[3,2-*c*]quinoline (6e)
Yield: 0.170 g (35%); colorless solid; mp 139–140°C.

IR (KBr): 3345, 2931, 1492, 1265 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.06 (m, 6 H), 6.73–6.68 (m, 1 H), 6.53 (d, 1 H, *J* = 8.0 Hz), 4.70 (d, 1 H, *J* = 10.8 Hz), 4.37 (d, 1 H, *J* = 2.5 Hz), 4.11–4.06 (m, 1 H), 4.02 (br s, 1 H, NH), 3.75–3.67 (m, 1 H), 2.05–2.00 (m, 1 H), 1.83–1.60 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.5, 140.8, 133.5, 130.9, 129.4, 129.1, 128.8, 120.6, 117.7, 114.2, 74.3, 68.6, 54.2, 38.9, 24.0, 22.0.

MS: *m*/*z* = 299 (M^+); 301 (M + 2).

Anal. Calcd for $C_{18}H_{18}ClNO$: C, 72.11; H, 6.05; N, 4.67. Found: C, 72.01; H, 5.98; N, 4.75.

4-Phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (5f)
Yield: 0.510g (44%); colorless solid; mp 120–121 °C (Lit.[26] 120 °C).

IR (KBr): 3353, 1478 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (m, 5 H), 7.06 (m, 2 H), 6.78 (m, 1 H), 6.64 (d, 1 H, *J* = 7.9 Hz), 5.90 (m, 1 H), 5.71 (m, 1 H), 4.67 (d, 1 H, *J* = 2.9 Hz), 4.15 (d, 1 H, *J* = 8.6 Hz), 3.78 (br s, 1 H), 3.05 (m, 1 H), 2.71 (m, 1 H), 1.85 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ =145.6, 142.8, 134.0, 130.3, 129.0, 128.4, 127.2, 126.4, 126.3, 126.0, 119.1, 115.9, 58.0, 46.4, 46.0, 31.5.

MS: *m*/*z* = 247 (M^+).

Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 86.88; H, 6.95; N, 5.68.

4-(4-Chlorophenyl)-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (5g)
Yield: 0.398g (40%); colorless solid; mp 141–142 °C.

IR (KBr): 3363, 1478 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (m, 4 H), 7.36–6.98 (m, 2 H), 6.80–6.75 (m, 1 H), 6.65 (d, 1 H, *J* = 7.7 Hz), 5.87–5.85 (m, 1 H), 5.66 (s, 1 H), 4.62 (d, 1 H, *J* = 3.0 Hz), 4.13 (d, 1 H, *J* = 8.5 Hz), 3.69 (br s, 1 H, NH), 3.03–2.93 (m, 1 H), 2.65–2.56 (m, 1 H), 1.85–1.76 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.2, 141.3, 133.9, 132.8, 130.2, 128.9, 127.9, 126.3, 125.9, 119.4, 115.9, 57.4, 46.2, 45.9, 31.3.

MS: *m*/*z* = 281 (M^+), 283 (M + 2).

Anal. Calcd for $C_{18}H_{16}ClN$: C, 76.72; H, 5.72; N, 4.97. Found: C, 76.56; H, 5.53; N, 4.91.

4-Phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline-8-carboxylic acid (5h)
Yield: 0.580g (42%); colorless solid; mp 206–207 °C.

IR (KBr): 3349, 1608, 1491 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, 1 H, *J* = 8.0 Hz), 7.38 (m, 5 H), 6.64 (m, 2 H), 5.81 (m, 1 H), 5.65 (m, 1 H), 4.75 (d, 1 H, *J* = 2.7 Hz), 4.48 (s, 1 H), 4.13 (d, 1 H, *J* = 8.4 Hz), 3.02 (m, 1 H), 2.58 (m, 1 H), 1.82 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ =173.3, 150.2, 142.1, 135.5, 134.9, 130.6, 130.0, 128.6, 128.2, 127.1, 127.0, 126.8, 126.1, 116.2, 111.8, 56.4, 45.8, 45.3, 31.7.

MS: *m*/*z* = 291(M^+).

Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 77.99; H, 5.86; N, 4.82.

6,7-Dimethyl-4-phenyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (5i)
Yield: 0.530 g (41%); colorless solid; mp 114–115 °C.

IR (KBr): 3384, 1469 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.40 (m, 5 H), 6.97 (d, 1 H, *J* = 7.5 Hz), 6.71 (d, 1 H, *J* = 7.5 Hz), 5.98 (m, 1 H), 5.79 (s, 1 H), 4.65 (d, 1 H, *J* = 2.7 Hz), 4.42 (d, 1 H, *J* = 8.1 Hz), 3.80 (br s, 1 H, NH), 3.33–3.25 (m, 1 H), 2.96–2.87 (m, 1 H), 2.48 (s, 3 H), 2.26 (s, 3 H), 2.04–1.96 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.8, 142.9, 134.2, 130.6, 128.4, 127.6, 126.4, 124.4, 120.5, 119.7, 58.5, 46.1, 45.6, 32.0, 19.5, 17.0.

MS: *m*/*z* = 275.

Anal. Calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.36; H, 7.01; N, 4.99.

4-Benzoyl-3a,4,5,9b-tetrahydro-3*H*-cyclopenta[*c*]quinoline (5j)
Yield: 0.480 g (50%); colorless solid; mp 157–158 °C.

IR (KBr): 3384, 1681 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93–7.85 (m, 2 H), 7.60–7.47 (m, 3 H), 7.06–6.98 (m, 2 H), 6.76–6.67 (m, 2 H), 5.73 (t, 1 H), 5.56 (s, 1 H), 5.05 (d, 1 H, *J* = 3.1 Hz), 4.42 (br s, 1 H), 4.21 (d, 1 H, *J* = 8.9 Hz), 3.37–3.27 (m, 1 H), 2.47–2.38 (m, 1 H), 1.94–1.86 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.1, 143.9, 135.5, 133.9, 133.2, 129.5, 128.7, 128.0, 126.5, 125.8, 118.9, 115.8, 59.7, 46.9, 42.5, 31.4.

MS: *m*/z = 275 (M^+).

Anal. Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.08. Found: C, 83.69; H, 6.19; N, 5.16.

10-Nitro-3a,4,5,11b-tetrahydro-3*H*-benzo[*h*]cyclopenta[*c*]quinoline (5k)

Yield: 0.300 g (42%); brown solid; mp 198.7–199 °C.

IR (KBr): 3398, 1495 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.99 (d, 1 H, *J* = 8.8 Hz), 8.41 (s, 1 H), 7.72–7.60 (m, 2 H), 7.49–7.44 (m, 1 H), 5.90 (m, 1 H), 5.74–5.72 (m, 1 H), 5.54 (br s, 1 H, NH), 3.99 (s, 1 H), 3.43–3.37 (m, 1 H), 3.06 (t, 1 H), 2.77–2.73 (m, 2 H), 2.20–2.15 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.5, 135.5, 130.1, 129.1, 126.3, 121.9, 119.8, 115.6, 46.2, 43.5, 37.0, 34.7.

MS: *m*/z = 266 (M^+).

Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.17; H, 5.30; N, 10.52. Found: C, 71.32; H, 5.49; N, 9.88.

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