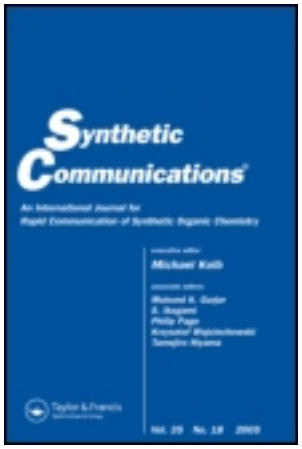

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Samarium Triflate as Mild and Efficient Catalyst for Aza-Diels-Alder Reaction: A Facile Synthesis of cis-Fused Pyrano- and Furanoquinolines

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SAMARIUM TRIFLATE AS MILD AND EFFICIENT CATALYST FOR AZA-DIELS–ALDER REACTION: A FACILE SYNTHESIS OF *CIS*-FUSED PYRANO- AND FURANOQUINOLINES

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Three-component coupling reactions of aldehydes, amines, and cyclic enol ethers have been carried out in the presence of samarium triflate to afford the corresponding pyrano and furanoquinolines in excellent yields with high* endo*-selectivity. The reaction conditions are mild and amenable to scale-up.

Keywords: Aldehydes; amines; hetero-Diels–Alder reaction; tetrahydroquinolines

The hetero-Diels–Alder reactions are becoming a mainstay for heterocycles and natural product synthesis.[1] Pyranoquinolines possess a wide spectrum of biological activities such as psychotropic, antiallergic, anti-inflammatory, and estrogenic activity.[2] Generally, they are prepared by means of imino-Diels–Alder reaction. The imines derived from aromatic amines act as heterodienes and undergo imino-Diels–Alder reaction with various dienophiles in the presence of acid catalysts.[3–5] However, many of these reactions cannot be carried out in a one-pot operation with carbonyl compound, amine, and enol ether because the amine and water that exist during imine formation can decompose or deactivate the Lewis acids. Even when the desired reactions proceed, more than stoichiometric amounts of the Lewis acids are required because the acids are trapped by nitrogen. Furthermore, most of the imines are hygroscopic, unstable at high temperatures, and difficult to purify by distillation or column chromatography. Subsequently, one-pot procedures have been developed for this transformation using various acid catalysts.[6–8] However, some of them require strongly acidic conditions, necessitate dry reaction conditions, and also involve tedious product-isolation procedures. Therefore, the development of mild, convenient, and efficient procedures would extend the scope of this methodology to synthesis of highly functionalized quinoline derivatives.

In view of the emerging importance of samarium triflate as a mild Lewis acid in organic synthesis, we herein report our results on samarium triflate–catalyzed

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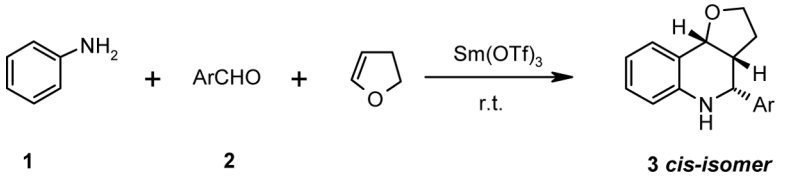


Scheme 1. Synthesis of furano tetrahydroquinoline.

synthesis of angularly fused pyrano and furanoquinolines via a three-component reaction. Accordingly, treatment of aniline (**1**) and benzaldehyde (**2**) with 2,3-dihydrofuran (**3**) in the presence of samarium triflate gave the corresponding furanoquinoline **3a** in 93% yield (Scheme 1).

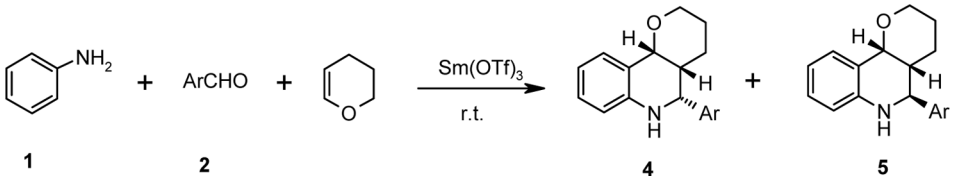
Similarly, several aldimines (formed in situ from aromatic aldehydes and anilines) reacted effectively with 2,3-dihydrofuran in presence of samarium triflate to afford the corresponding furano [3,2-*c*] quinolines in 87–93% yield (Table 1). In all the cases, the products were obtained exclusively as *endo*-isomers **3**. Like dihydrofuran (DHF), 3,4-dihydro-2*H*-pyran (DHP) also reacted effectively with imines under similar conditions to provide pyrano[3,2-*c*]-quinolines **4** and **5** in good yields (Scheme 2).

In the case of DHP, the products were obtained as a mixture of **4** *endo*- and **5** *exo*-isomers, favoring *endo*-diastereomers **4**, as has been observed by others also in most of the Povarov imino-Diels–Alder reactions. In all cases, the reactions proceeded smoothly at ambient temperature with excellent selectivity. However, in the absence of catalyst, the reaction did not yield the desired product even after

Table 1. $Sm(OTf)_3$-promoted synthesis of pyrano- and furanoquinolines[a]

Entry	R	Ar	Olefin	Reaction time (h)	Yield (%)[b]	*endo:exo*[c] trans[c]
a	H	C_6H_5		3.0	93	—
b	4-MeO	H	"	2.5	91	—
c	H	4-FC_6H_4	"	3.0	90	—
d	4-Me	4-ClC_6H_4	"	3.0	89	—
e	H	4-$MeOC_6H_4$	"	2.5	91	—
f	4-MeO	4-FC_6H_4	"	3.5	88	—
g	3,5-$(MeO)_2$	4-FC_6H_4	"	3.0	87	—
h	H	C_6H_5		2.5	90	92:8
i	H	4-FC_6H_4	"	3.0	88	88:12
j	2-Me	C_6H_5	"	2.5	90	85:15
k	4-MeO	C_6H_5	"	3.0	87	88:12
l	4-F	C_6H_5	"	3.0	85	86:14
m	1-Naphthyl	C_6H_5	"	3.5	84	82:18
n	1-Naphthyl	4-FC_6H_4	"	4.0	81	80:20

[a]All products were characterized by ^1H NMR, IR, and mass spectra.
[b]Isolated and unoptimized yields.
[c]*cis*/*trans* isomers were separated by column chromatography.



Scheme 2. Synthesis of pyrano tetrahydroquinoline.

an extended reaction time (15–20 h). Enhanced reaction rates, excellent yields, and high *cis*-selectivity are the features observed in this protocol.

All the products were characterized by ^{1}H NMR, infrared (IR), and mass spectrometry and also by comparison with authentic samples. The reactions of various aldehydes, amines, and cyclic enol ethers were examined under similar reaction conditions, and the results are presented in Table 1.

In summary, samarium triflate has proved to be an effective catalyst to perform imino-Diels–Alder reaction of aldehydes, aromatic amines, and enol ethers under mild conditions. The use of samarium triflate makes this method a simple, convenient, and attractive process for the preparation of highly functionalized tetrahydroquinoline derivatives.

EXPERIMENTAL

Melting points were recorded on a Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Fourier transform (FT)–IR 240-c spectrophotometer using KBr optics. ^{1}H NMR spectra were recorded on Gemini-200 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on a Finning MAT 1020 mass spectrometer operating at 70 eV. CHN analyses were recorded on a Vario EL analyzer.

General Procedure for the Synthesis of Pyrano- and Furanoquinolines

3,4-Dihydro-2*H*-pyran or 2,3-dihydrofuran (2 mmol) and samarium triflate (0.1 mmol) were added to a mixture of aldehyde (1 mmol) and aryl amine (1 mmol) in dichloromethane (5 mL). The resulting reaction mixture was stirred at ambient temperature for an appropriate time (Table 1). After completion of the reaction, as indicated by thin-layer chromatography (TLC), the reaction mixture was extracted with methylenedichloride (3×10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude products were purified by column chromatography using silica gel (60–120 mesh) and eluted with a mixture of ethyl acetate–*n*-hexane to afford pure products.

Spectral Data for Products

***cis*-4-Phenyl-2,3,3a,4,5,9b-hexahydrofuro-[3,2-c]-quinoline (3a).** Solid, mp 93–95 °C. IR (KBr): ν 3348, 3065, 2975, 2847, 1615, 1506, 1480, 1362, 1218, 1183,

1074, 1012, 968, 871, 732 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.52–1.57 (m, 1H), 2.20–2.30 (m, 1H), 2.70–2.80 (m, 1H), 3.75–3.85 (m, 3H), 4.72 (d, 1H, $J = 2.8$ Hz), 5.24 (d, 1H, $J = 8.0$ Hz), 6.56 (d, 1H, $J = 8.0$ Hz), 6.81 (t, 1H, $J = 8.0$ Hz), 7.03 (t, 1H, $J = 8.0$ Hz), 7.35–7.55 (m, 6H). EIMS m/z: 251 m,$^+$ 220, 206, 174, 130, 91, 77, 51.

***cis*-8-Methoxy-4-phenyl-2,3,3a,4,5,9b-hexahydrofuro-[3,2-c]-quinoline (3b).** Solid, mp 132–133 °C. IR (KBr): ν 3305, 3071, 2965, 2849, 1605, 1578, 1516, 1473, 1396, 1225, 1153, 1051, 1006, 967, 912, 834, 749 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.52–1.58 (m, 1H), 2.21–2.30 (m, 1H), 2.74–2.81 (m, 1H), 3.63–3.72 (m, 3H), 3.78 (s, 3H), 4.63 (d, 1H, $J = 2.8$ Hz), 5.24 (d, 1H, $J = 8.0$ Hz), 6.52 (d, 1H, $J = 8.6$ Hz), 6.75 (dd, 1H, $J = 8.6$ & 2.8 Hz), 6.95 (d, 1H, $J = 2.8$ Hz), 7.25–7.43 (m, 5H). EIMS m/z: 281 m,$^+$ 236, 206, 160, 141, 115, 91, 76, 51, 41.

***cis*-4-(4-Fluorophenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (3c).** Solid, mp 173–175 °C. IR (KBr): ν 3315, 3052, 2976, 2880, 1606, 1567, 1508, 1472, 1329, 1223, 1105, 1059, 964, 841, 739 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.51–1.56 (m, 1H), 2.12–2.16 (m, 1H), 2.61–2.82 (m, 1H), 3.64–3.81 (m, 3H), 4.65 (d, 1H, $J = 2.5$ Hz), 5.21 (d, 1H, $J = 8.0$ Hz), 6.52 (d, 1H, $J = 8.0$ Hz), 6.77 (t, 1H, $J = 8.0$ Hz), 7.02–7.11 (m, 3H), 7.28–7.32 (m, 1H), 7.39–7.43 (m, 2H). EIMS m/z: 269 m,$^+$ 240, 224, 198, 174, 130, 117, 95, 76, 51, 43, 39.

***cis*-4-(4-Chlorophenyl)-8-methyl-2,3,3a,4,5,9b-hexahydrofuro-[3,2-c]-quinoline (3d).** Solid, mp. 148–149 °C. IR (KBr): ν 3345, 2991, 2878, 1610, 1493, 1145, 1031, 963, 845, 734 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.50–1.55 (m, 1H), 2.20–2.30 (m, 1H), 2.36 (s, 3H), 2.62–2.67 (m, 1H), 3.62 (brs, 1H, NH), 3.70–3.75 (m, 1H), 3.79–3.84 (m, 1H), 4.61 (d, 1H, $J = 2.1$ Hz), 5.21 (d, 1H, $J = 8.0$ Hz), 6.52 (d, 1H, $J = 8.0$ Hz), 6.84 (dd, 1H, $J = 8.0$ & 2.1 Hz), 7.12 (d, 1H, $J = 0.8$ Hz), 7.36 (d, 2H, $J = 8.0$ Hz), 7.41 (d, 2H, $J = 8.0$ Hz). EIMS m/z: 299 m,$^+$ 254, 188, 160, 144, 115, 77, 51.

***cis*-4-(4-Methoxyphenyl)-2,3,3a,4,5,9b-hexahydrofuro-[3,2-*c*]-quinoline (3e).** Solid, mp 155–156 °C. IR (KBr): ν 3340, 2990, 2870, 1605, 1520, 1135, 1105, 1063, 941, 813, 739 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.54–1.60 (m, 1H), 2.18–2.22 (m, 1H), 2.67–2.73 (m, 1H), 3.70–3.80 (m, 3H), 3.85 (s, 3H), 4.62 (d, 1H, $J = 2.2$ Hz), 5.22 (d, 1H, $J = 8.0$ Hz), 6.54 (d, 1H, $J = 8.0$ Hz), 6.78 (t, 1H, $J = 8.0$ Hz), 6.90 (t, 1H, $J = 8.0$ Hz), 7.05 (d, 2H, $J = 8.0$ Hz), 7.35–7.45 (m, 3H). EIMS m/z: 281 m,$^+$ 252, 236, 224, 167, 155, 141, 121, 91, 76, 69, 51, 43.

***cis*-4-(4-Fluorophenyl)-8-methoxy-2,3,3a,4,5,9b-hexahydrofuro-[3,2-*c*]-quinoline (3f).** Solid, mp. 136–138 °C. IR (KBr): ν 3014, 1662, 1577, 1503, 1220, 1108, 1036, 1012, 986, 864, 812, 726 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.35–1.55 (m, 1H), 2.10–2.25 (m, 1H), 2.60–2.75 (m, 1H), 3.60–3.80 (m, 3H), 3.76 (s, 3H), 4.62 (d, 1H, $J = 2.8$ Hz), 5.20 (d, 1H, $J = 8.0$ Hz), 6.45 (d, 1H, $J = 8.4$ Hz), 6.68 (dd, 1H, $J = 8.4$ & 2.8 Hz), 6.92 (d, 1H, $J = 2.8$ Hz), 7.00–7.10 (m, 2H), 7.20–7.30 (m, 2H). EIMS m/z: 299 m,$^+$ 272, 255, 205, 150, 109, 77, 51, 43.

***cis*-4-(4-Fluorophenyl)-7,9-dimethoxy-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (3g).** Solid, mp 80–82 °C. IR (KBr): ν 3305, 2985, 2880, 1615, 1500, 1225, 1163, 1035, 910, 871, 769, 714 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.60–1.65 (m, 1H), 2.20–2.25 (m, 1H), 2.75–2.85 (m, 1H), 3.60–3.85 (m, 3H), 3.68 (s, 3H,

OCH_3), 3.80 (s, 3H, OCH_3), 4.78 (d, 1H, $J = 2.8$ Hz), 5.40 (d, 1H, $J = 8.0$ Hz), 6.16–6.23 (m, 1H), 6.57–6.62 (m, 1H), 7.02–7.10 (m, 2H), 7.38–7.42 (m, 2H). EIMS m/z: 329 m,$^+$ 314, 285, 254, 190, 149, 133, 109, 71, 51, 43.

***cis*-5-Phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano-[3,2-c]-quinoline (4h).** Solid, mp 129–130 °C. IR (KBr): ν 3340, 3052, 2970, 2850, 1610,1518, 1490, 1358, 1293, 1162, 1090, 1015, 961, 859, 735 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.22–1.27 (m, 1H), 1.50–1.70 (m, 3H), 2.15–2.20 (m, 1H), 3.40 (dt, 1H, $J = 11.3$ & 2.4 Hz), 3.55 (dd, 1H, $J = 11.3$ & 2.4 Hz), 3.80 (brs, 1H, NH), 4.70 (d, 1H, $J = 2.7$ Hz), 5.30 (d, 1H, $J = 5.6$ Hz), 6.55 (d, 1H, $J = 8.0$ Hz), 6.78 (t, 1H, $J = 8.0$ Hz), 7.05 (t, 1H, $J = 7.8$ Hz), 7.25–7.45 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 18.2, 25.7, 39.0, 59.3, 60.7, 72.8, 114.4, 118.0, 120.4, 126.9, 127.5, 127.7, 128.0, 128.4, 141.2, 145.2. EIMS m/z: 265 m,$^+$ 234, 220, 194, 129, 117, 91, 77, 76, 51.

***trans*-5-Phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano-[3,2-c]-quinoline (5h).** Viscous oil. IR (KBr): ν 3325, 3051, 2941, 2864, 1607, 1586, 1512, 1482, 1309, 1257, 1139, 1088, 1015, 981, 846, 736 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.25–1.60 (m, 3H), 1.80–1.90 (m, 1H), 2.00–2.10 (m, 1H), 3.75 (dt, 1H, $J = 11.5$ & 2.5 Hz), 4.00–4.10 (m, 2H), 4.40 (d, 1H, $J = 2.5$ Hz), 4.75 (d, 1H, $J = 10.8$ Hz), 6.50 (d, 1H, $J = 8.0$ Hz), 6.70 (t, 1H, $J = 7.5$ Hz), 7.10 (t, 1H, $J = 7.5$ Hz), 7.25 (d, 1H, $J = 8.0$ Hz), 7.40–7.55 (m, 5H).^{13}C NMR ($CDCl_3$): δ 22.3, 24.4, 39.3, 55.0, 69.2, 74.5, 114.2, 117.4, 120.5, 127.7, 127.9, 128.5, 129.4, 130.9, 142.2, 144.5.

***cis*-5-(4-Fluorophenyl)-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano-[3,2-*c*]-quinoline (4i).** Solid, mp 174–175 °C. IR (KBr): ν 3325, 2945, 2860, 1608, 1490, 1252, 1081 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.30 (m, 1H), 1.45–1.60 (m, 3H), 2.12 (m, 1H), 3.40 (dt, 1H, $J = 11.5$ & 2.5 Hz), 3.56 (dd, 1H, $J = 11.5$ & 2.5 Hz), 3.75 (brs, 1H, NH), 4.65 (d, 1H, $J = 2.7$ Hz), 5.28 (d, 1H, $J = 5.7$ Hz), 6.52 (d, 1H, $J = 8.0$ Hz), 6.75 (dd, 1H, $J = 8.0$ & 2.5 Hz), 7.05 (m, 3H), 7.40 (m, 3H). EIMS m/z: 283 m,$^+$ 239, 225, 198, 150, 148, 91, 76, 51.

***trans*-5-(4-Fluorophenyl)-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano-[3,2-*c*]-quinoline (5i).** Solid, mp 174–175 °C. IR (KBr). ν 3327, 2950, 2870, 1610, 1495, 1250, 1089 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.30–1.35 (m, 1H), 1.40–1.45 (m, 1H), 1.60–1.70 (m, 1H), 1.75–1.85 (m, 1H), 2.05 (m, 1H), 3.70 (dt, $J = 11.5$ and $J = 2.5$ Hz, 1H), 3.95 (brs, 1H, NH), 4.10 (d, $J = 2.5$ Hz, 1H), 4.35 (d, $J = 2.7$ Hz, 1H), 4.70 (d, $J = 10.8$ Hz, 1H),), 6.48 (d, $J = 8.0$ Hz, 1H), 6.68 (dd, $J = 8.0$ and 2.5 Hz, 1H), 7.05 (m, 3H), 7.18 (m, 1H), 7.38 (m, 2H).

***cis*-7-Methyl-5-phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano-[3,2-c]-quinoline (4j).** Solid, mp 142–143 °C. IR (KBr): ν 3345, 2970, 2845, 1610, 1509, 1030 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.25 (m, 1H), 1.35–1.50 (m, 4H), 2.10 (s, 3H), 3.34 (dt, 1H, $J = 11.3$ and 2.4 Hz), 3.50 (dd, 1H, $J = 11.3$ and 2.4 Hz), 3.55 (brs, 1H, NH), 4.62 (d, $J = 2.5$ Hz, 1H), 5.30 (d, $J = 5.2$ Hz, 1H), 6.70 (t, $J = 7.8$ Hz, 1H), 6.90 (dd, $J = 7.8$ and 0.7 Hz, 1H), 7.20–7.40 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 17.4, 18.0, 25.3, 38.6, 59.3, 60.6, 73.4, 117.8, 119.0, 121.6, 125.3, 126.9, 127.5, 128.9, 129.2, 141.0, 143.5. EIMS: m/z: 279 m,$^+$ 260, 220, 184, 155, 144, 104, 91, 76, 65, 51.

***trans*-7-Methyl-5-phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano-[3,2-c]-quinoline (5j).** Solid, mp 130–131 °C. IR (KBr): ν 3340, 2975, 2840, 1615, 1504, 1085 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.25–1.35 (m, 3H), 1.60–1.65 (m, 1H), 1.80–1.85 (m, 1H), 2.10 (s, 3H), 3.70, (dt, 1H, $J = 11.5$ & 2.5 Hz), 3.90 (brs, 1H, NH), 4.10 (m, 1H), 4.40 (d, 1H, $J = 2.8$ Hz), 4.78 (d, 1H, $J = 10.5$ Hz), 6.64 (t, 1H, $J = 8.0$ Hz), 7.00 (dd, 1H, $J = 8.0$ & 0.8 Hz,), 7.10 (dd, 1H, $J = 8.0$ & 1.5 Hz), 7.30–7.40 (m, 3H), 7.44 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 17.2, 22.1, 24.3, 38.7, 55.3, 68.7, 74.5, 117.0, 120.0, 121.3, 127.8, 128.0, 128.5, 128.9, 130.5, 142.5, 142.9.

***cis*-9-Methoxy-5-phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano-[3,2-c]-quinoline (4k).** Solid, mp 145–146 °C. IR (KBr): ν 3340, 2970, 2855, 1610, 1520, 1065 cm^{-1}. ^1H NMR ($CDCl_3$). δ 1.30–1.60 (m, 4H), 2.15 (m, 1H), 3.42 (m, 1H), 3.58 (m, 1H), 3.60 (brs, 1H, NH), 3.80 (s, 3H), 4.62 (d, 1H, $J = 2.0$ Hz), 5.25 (d, 1H, $J = 5.2$ Hz), 6.50 (d, 1H, $J = 8.0$ Hz), 6.70 (dd, $J = 8.2$, 2.7 Hz, 1H), 7.05 (d, 1H, $J = 2.7$ Hz), 7.30–7.45 (m, 5H). EIMS: m/z: 295 $m,^+$ 237, 225, 160, 91.

***trans*-9-Methoxy-5-phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano-[3,2-c]-quinoline (5k).** Solid, mp 98–99 °C. IR (KBr): ν 3325, 3059, 2961, 2868, 1605, 1515, 1457, 1324, 1279, 1163, 1070, 928, 861, 741 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.20–1.26 (m, 1H), 1.30–1.45 (m, 1H), 1.52–1.62 (m, 1H), 1.68–1.78 (m, 1H), 1.95–2.05 (m, 1H), 3.40–3.50 (m, 1H), 3.60 (s, 3H, OCH_3), 3.90–4.10 (m, 1H), 4.30 (d, 1H, $J = 2.7$ Hz), 4.55 (d, 1H, $J = 10.5$ Hz), 6.38 (d, 1H, $J = 8.0$ Hz), 6.60 (dd, 1H, $J = 8.1$, 2.7 Hz), 6.65 (d, 1H, $J = 2.7$ Hz), 7.20–7.30 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 22.0, 24.5, 39.0, 55.4, 55.9, 68.5, 74.5, 114.9, 115.5, 116.7, 121.4, 127.9, 128.5, 139.0, 142.4, 152.3.

***cis*-9-Fluoro-5-phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano-[3,2-*c*]-quinoline (4l).** Solid, mp 174–175 °C. IR (KBr). ν 3326, 3063, 2945, 2847, 1618, 1582, 1505, 1492, 1356, 1251, 1163, 1089, 1006, 931, 847, 739 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.24–1.32 (m, 1H), 1.38–1.60 (m, 3H), 2.05–2.15 (m, 1H), 3.40 (dt, 1H, $J = 11.5$, 2.5 Hz), 3.58 (dd, 1H, $J = 11.5$, 2.5 Hz), 3.68 (brs, 1H, NH), 4.60 (d, 1H, $J = 2.7$ Hz), 5.20 (d, 1H, $J = 5.7$ Hz), 6.44 (d, 1H, $J = 8.4$ Hz), 6.78 (dd, 1H, $J = 8.4$, 2.8 Hz), 7.10 (d, 1H, $J = 2.8$ Hz), 7.25–7.40 (m, 5H). EIMS m/z: 283 $m,^+$ 239, 225, 198, 150, 148, 91.

***trans*-9-Fluoro-5-phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-pyrano-[3,2-*c*]-quinoline (5l).** Viscous oil. IR (KBr): ν 3325, 3062, 2945, 2853, 1612, 1589, 1495, 1367, 1250, 1153, 1080, 927, 831, 743 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.30–1.40 (m, 1H), 1.45–1.52 (m, 1H), 1.55–1.65 (m, 1H), 1.75–1.90 (m, 1H), 2.05–2.15 (m, 1H), 3.68 (dt, 1H, $J = 11.5$, 2.8 Hz), 3.90 (brs, 1H, NH), 4.10 (d, 1H, $J = 2.8$ Hz), 4.32 (d, 1H, $J = 2.8$ Hz), 4.65 (d, 1H, $J = 10.5$ Hz), 6.45 (d, 1H, $J = 8.4$ Hz), 6.80 (dd, 1H, $J = 8.4$, 2.8 Hz), 6.95 (d, 1H, $J = 2.8$ Hz), 7.30–7.40 (m, 5H).

***cis*-12-Phenyl-2,3,4a,11,12,12a-hexahydro-1*H*-benzo[H]pyrano-[3,2-c]-quinoline (4m).** Solid, mp 163–163 °C. IR (KBr): ν 3375, 3054, 2941, 2861, 1667, 1574, 1510, 1465, 1371, 1081, 1012, 962, 873, 741 cm^{-1}. ^1H NMR ($CDCl_3$): 1.35–1.45 (m, 3H), 1.60–1.70 (m, 1H), 2.25–2.35 (m, 1H), 3.40 (dt, 1H, $J = 11.5$, 2.5 Hz), 3.62 (dd, 1H, $J = 11.5$, 2.5 Hz), 4.50 (brs, 1H, NH), 4.88 (d, 1H, $J = 2.7$ Hz), 5.50 (d, 1H, $J = 5.7$ Hz), 7.22–7.31 (m, 2H), 7.35–7.50 (m, 4H), 7.58–7.68 (m, 3H), 7.75–7.85 (m, 2H). EIMS m/z: 316 $m,^+$ 256, 206, 180, 155, 141, 115, 69, 43.

***trans*-12-Phenyl-2,3,4a,11,12,12a-hexahydro-1*H*-benzo[H]pyrano-[3,2-c]-quinoline (5 m).** Solid, mp 144–145 °C. IR (KBr): ν 3378, 3079, 2961, 2852, 1625, 1575, 1506, 1468, 1352, 1275, 1105, 1042, 938, 861, 750 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.33–1.42 (m, 1H), 1.50–1.60 (m, 1H), 1.65–1.73 (m, 1H), 1.78–1.83 (m, 1H), 2.10–2.20 (m, 1H), 3.75 (dt, 1H, $J = 11.8$, 2.8 Hz), 4.10 (d, 1H, $J = 2.8$ Hz), 4.45 (d, 1H, $J = 2.8$ Hz), 4.70 (brs, 1H, NH), 4.80 (d, 1H, $J = 10.5$ Hz), 7.20–7.25 (m, 2H), 7.30–7.45 (m, 4H), 7.45–7.55 (m, 3H), 7.65–7.75 (m, 2H).

***cis*-12-(4-Fluorophenyl)-2,3,4a,11,12,12a-hexahydro-1*H*-benzo[h]pyrano-[3,2-c]-quinoline (4n).** Solid, mp 138–140 °C. IR (KBr): ν 3370, 3063, 2945, 2860, 1615 1570, 1506, 1465, 1347, 1215, 1173, 1045, 951, 867, 742 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.20–1.35 (m, 2H), 1.40–1.50 (m, 2H), 2.05–2.15 (m, 1H), 3.25 (dt, 1H, $J = 11.5$, 2.5 Hz), 3.50 (dd, 1H, $J = 11.5$, 2.5 Hz), 4.00 (brs, 1H, NH), 4.70 (d, 1H, $J = 2.7$ Hz), 5.40 (d, 1H, $J = 5.7$ Hz), 7.01–7.08 (m, 2H), 7.12–7.19 (m, 1H), 7.30–7.40 (m, 2H), 7.40–7.50 (m, 3H), 7.60–7.70 (m, 2H). EIMS m/z: 333 $m,^+$ 274, 238, 220, 180, 155, 141, 119, 69, 57, 43.

***trans*-12-(4-Fluorophenyl)-2,3,4a,11,12,12a-hexahydro-1*H*-benzo[H]-pyrano-[3,2-c]-quinoline (5n).** Solid, mp 179–181 °C. IR (KBr): ν 3378, 3073, 2948, 2860, 1648, 1572, 1468, 1362, 1274, 1108, 1079, 952, 846, 732 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.30–1.45 (m, 2H), 1.60–1.80 (m, 2H), 2.05–2.15 (m, 1H), 3.75 (dt, 1H, $J = 11.5$, 2.7 Hz), 4.10 (d, 1H, $J = 2.7$ Hz), 4.42 (d, 1H, $J = 2.7$ Hz), 4.65 (brs, 1H, NH), 4.80 (d, 1H, $J = 10.5$ Hz), 7.05–7.15 (m, 2H), 7.20–7.40 (m, 4H), 7.45–7.50 (m, 3H), 7.70–7.80 (m, 2H).

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