Synthesis of pyrano and furanoquinolines using silica chloride or amberlyst-15 as a heterogeneous catalyst

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The coupling of three components, anilines, benzaldehydes and 3,4-dihydro-2*H*- pyran or 2,3-dihydrofuran to prepare the corresponding pyrano or furanoquinolines has been achieved efficiently using silica chloride or Amberlyst-15 as a heterogeneous catalyst. Amberlyst-15 can be recovered and reused.

Keywords: pyrano and furanoquinolines, multicomponent coupling, silica chloride, Amberlyst-15, diasteroselectivity

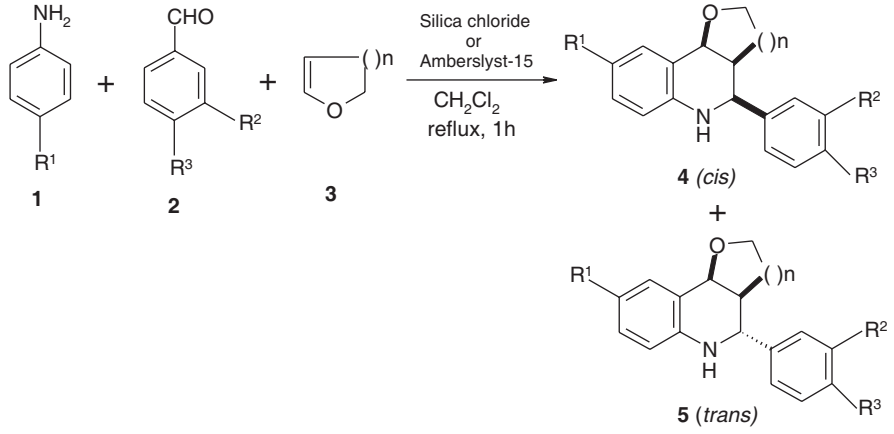
Compounds containing pyranoquinoline moiety are found to exhibit a wide range of biological properties including antiallergic, anti-inflammatory and estrogenic activities.[1] Many alkaloids possess this moiety.[2] The imino-Diels–Alder reaction is an important method for the preparation of pyranoquinolines.[3] Imines derived from aromatic amines act as heterodienes which undergo aza-Diels–Alder reaction with 3,4-dihydro-2*H*-pyran to produce such compounds. Different Lewis acids[3,4] are generally used to catalyse these reactions. However, many Lewis acids are deactivated or decomposed by nitrogen containing substrates and also by water formed in the intermediate imine formation stage if the coupling of anilines, benzaldehydes and 3,4-dihydro-2*H*-pyran is carried out in a single pot. Some of the Lewis acids are not easily available or inexpensive, give the mixture of products and catalyse the reactions with slow rate. Additionally, most of the used Lewis acids work under homogeneous conditions and so the recovery of these catalysts is always a problem. Many imines are also hydroscopic, unstable and difficult to purify and thus the preparation and purification of the imines followed by reactions of these compounds with dihydropyran or furan in steps lower the efficiency of the process.

In recent years multicomponent reactions are of increasing importance in organic synthesis. The speed, diversity and efficiency of multicomponent reactions offer significant advantages over conventional linear-types synthesis. We have currently discovered a facile synthetic route, involving a three-component coupling reaction of anilines **(1)**, benzaldehydes **(2)** and 3,4-dihydro-2*H*-pyran or 2,3-dihydrofuran **(3)** in the presence of a heterogenous catalyst, silica chloride or amberlyst-15 for the preparation of the corresponding pyrano or furanoquinolines in single step. Only a limited number of methods for one-pot coupling of these three components were known earlier.[4b,e,f]

Various anilines and benzaldehydes were used for the synthesis of differently substituted pyrano and furanoquinolines (Table 1). A mixture of these two substrates along with 3,4-dihydro-2*H*-pyran or 2,3-dihydrofuran in CH_2Cl_2 was refluxed for 1h in the presence of silica chloride or Amberlyst-15. The products **(4** and **5)** were formed in high yields and high diastereoselectivity. They were obtained as a mixture of *cis* and *trans* isomers which could be separated by column chromatography over silica gel. The ratio of the isomers formed in each reaction was determined by ^{1}H NMR spectrum of the crude product.

The *in situ* generated imines formed by condensation of anilines and benzaldehydes reacted with the electron-rich dinophile, 3,4-dihydro-2*H*-pyran or 2,3-dihydrofuran in the presence of the catalyst, silica chloride or Amberlyst-15. When the reaction was carried out in absence of a catalyst it did not afford the quinolines. However, the imines (prepared separately) on treatment with the pyran or furan derivative using a catalyst produced the desired compounds in high yields.

The catalyst, silica chloride and Amberlyst-15 work under heterogenous conditions. The heterogeneous catalysts have recently been gaining more attraction due to environmental and economic considerations. The presently used two catalysts can conveniently be handled and removed from the reaction mixture by simple filtration. Silica chloride can easily be prepared[5] from the readily available ingredients, thionyl chloride and silica gel. Its activity is somewhat better than that of the other catalyst in terms of the yields of the products. However, Amberlyst-15 can be recovered, activated and reused.



Scheme 1

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Table 1 Preparation of pyrano and furanoquinolines using silica chloride and amberlyst-15[a]

Entry	Aniline (1) R^1	Benzaldehyde (2) R^2	Benzaldehyde (2) R^3	Olefin (3) *n*	Catalyst[b]	Isolated yield /%	Product ratio[c] (4:5)	Ref.	M.p./°C (lit.) (4, 5)
a	H	H	H	2	i	84	18:82	4b	134–137, 140–143
					ii	78	20:80		(130–132)[4b], 142[4b]
b	H	H	Br	2	i	88	15:85	4e	124–126, 127–129
					ii	80	17:83		
c	H	H	Cl	2	i	90	25:75	4c	155, 147–149
					ii	86	20:80		
d	H	H	OMe	2	i	85	17:83	4c	157, 144–147
					ii	81	15:85		(154)[4c], (146)[4c]
e	H	Cl	Cl	2	i	94	12:88	4c	198–200, 203–206
					ii	87	14:86		
f	H	OCH_2O		2	i	92	10:90	4f	159–160, 152–153
					ii	85	10:90		
g	Me	H	H	2	i	86	20:80	4e	133–134, 140–141
					ii	78	25:75		
h	Cl	H	H	2	i	83	16:84	4b	124–127, 171–174
					ii	80	18:82		(125) [4b], (170) [4b]
i	Me	H	Cl	2	i	82	14:86	4f	98–100, 120–121
					ii	76	15:85		
j	H	H	H	1	i	83	17:83	4b	109–111, 118–123
					ii	76	16:84		(110) [4b], (117) [4b]
k	H	H	Cl	1	i	85	23:77	4f	152–153, 148–149
					ii	79	21:79		(152) [4f], (148) [4f]
l	H	H	OMe	1	i	91	16:84	4f	94–97, 112–114
					ii	84	14:86		
m	H	Cl	Cl	1	i	90	11:89	4f	117–118, 123–126
					ii	81	13:87		
n	Me	H	H	1	i	84	8:92	4d	92–94, 102–103
					ii	77	10:90		
o	Me	H	Cl	1	i	88	15:85	4c	131–132, 143–145
					ii	82	12:88		

[a]All the products were characterised from their spectral (^{1}H NMR and MS) data.
[b]Catalyst i : silica chloride; ii. Amberlyst-15.
[c]Product ratio was determined from the ^{1}H NMR spectrum of the crude product.

In conclusion, we have demonstrated that silica chloride and Amberlyst-15 are two efficient heterogenous catalysts for coupling of the three components, anilines, benzaldehydes and 3,4-dihydro-2*H*-pyran or 2,3-dihydrofuran to construct pyrano or furanoquinolines. The simple experimental procedure, mild reaction conditions, shorter reaction times, high yields and high diastereoselectivity of the products and reusability of one of the catalysts are the advantages of the described protocol. We feel the present procedure is a useful attractive method for the synthesis of quinoline derivatives.

Experimental

The spectra were recorded with the following instruments: ^{1}H NMR: Varian Gemini 200 MHz and EIMS: VG Micromass 7070H (70 eV).

General procedure: To a solution of aniline (1 mmol), benzaldehyde (1 mmol) and 3,4-dihydro-2*H*-pyran or 2,3-dihydrofuran (0.1ml) in CH_2Cl_2 (10 ml) silica chloride ($SOCl_2$:SiO_2, 6.56:1) (100 mg) or Amberlyst-15 (100 mg) was added. This mixture was refluxed for 1h. This was cooled to room temperature and filtered. The filtrate was concentrated and the viscous mass was subjected to column chromatography over silica gel. The column was eluted with hexane-EtoAc (20:1) to obtain pyrano or furanoquinolines.

Amberlyst –15 was recovered from the residue of filtration of the reaction mixture. This was washed with EtOAc (3 × 5 ml), activated and reused.

All the products were characterised from their spectroscopic (IR, ^{1}H NMR and MS) properties. The spectral values which were not reported are given below.

Compound **4b** (*cis-5-(4-bromophenyl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline*): Light yellow solid, m.p. 124–126 °C; IR (KBr): 3362, 1485, 1467 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.45–7.13 (6H, m), 6.72 (1H, t, *J* = 8.0 Hz), 6.57 (1H, d, *J* = 8.0 Hz), 5.28 (1H, d, *J* = 6.0 Hz), 4.65 (1H, d, *J* = 3.0 Hz), 3.68–3.57 (2H, m), 3.47 (1H, brs), 2.21 (1H, m), 1.60–1.41 (4H,m); EIMS: *m/z* 345, 343 ($M^{+\cdot}$). Anal. Calcd for $C_{18}H_{18}BrNO$: C, 62.79; H, 5.23; N, 4.07; Found: C, 62.84; H, 5.18; N, 4.12%.

Compound **5b** (*trans-5-(4-bromophenyl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline)*: Light yellow solid, m.p. 127–129 °C; IR (KBr): 3384, 1490, 1454 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.38–7.11 (6H, m), 6.74 (1H, t, *J* = 8.0 Hz), 6.55 (1H, d, *J* = 8.0 Hz), 4.61 (1H, d, *J* = 10.0 Hz), 4.35 (1H, d, *J* = 4.0 Hz), 4.12–3.74 (3H, m), 2.07 (1H, m), 1.87–1.18 (4H, m), 1.60–1.41 (4H,m); EIMS: *m/z* 345, 343 ($M^{+\cdot}$). Anal. Calcd for $C_{18}H_{18}BrNO$: C, 62.79; H, 5.23; N, 4.07; Found: C, 62.72; H, 5.19; N, 4.14%.

Compound **4c** (*cis-5-(4-chlorophenyl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline)*: Light yellow solid, m.p. 155 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.45–7.33 (5H, m), 7.14 (1H, t, *J* = 8.0 Hz), 6.81 (1H, t, *J* = 8.0 Hz), 6.62 (1H, d, *J* = 8.0 Hz), 5.26 (1H, d, *J* = 6.0 Hz), 4.68 (1H, d, *J* = 3.0 Hz), 3.73 (1H, brs), 3.61 (1H, m), 3.42 (1H, m), 2.12 (1H, m), 1.62–1.21 (4H,m); EIMS: *m/z* 301, 299 ($M^{+\cdot}$).

Compound **5c** (*trans-5-(4-chlorophenyl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline)*: Light yellow solid, m.p. 147–149 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.43–7.31 (4H, m), 7.22 (1H, d, *J* = 8.0Hz), 7.12 (1H, t, *J* = 8.0 Hz), 6.75 (1H, t, *J* = 8.0 Hz), 6.56 (1H, d, *J* = 8.0 Hz) 4.65 (1H, d, *J* = 10.0 Hz), 4.36 (1H, d, *J* = 3.0 Hz), 4.12–3.72 (3H, m), 2.05 (1H, m), 1.88–1.24 (4H,m); EIMS: *m/z* 301, 299 ($M^{+\cdot}$).

Compound **4f** (*cis-5-(1,3-benzodioxol-5-yl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline)*: IR (KBr): 3370, 1482, 1470 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.38 (1H, d, *J* = 8.0Hz), 7.04 (1H, t, *J* = 8.0Hz), 6.92–6.76 (4H,m), 6.56 (1H, d, *J* = 8.0Hz), 5.96 (2H,s), 5.24 (1H, d, *J* = 6.0Hz), 4.60 (1H, d, *J* = 3.0Hz), 3.78 (1H, brs), 3.60–3.38 (2H,m), 2.05 (1H,m), 1.60–1.38 (4H,m); EIMS: *m/z* 309(M^+). Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.77; H, 7.07; Found: C, 73.68; H, 7.12%.

Compound **5f** (*trans-5-(1,3-benzodioxol-5-yl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline)*: IR (KBr): 3384, 1490, 1464 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200MHz): δ 7.18 (1H, d, *J* = 8.0Hz), 7.04 (1H, t, *J* = 8.0Hz), 6.92 (1H, d, *J* = 2.0Hz), 6.84–6.62 (3H,m), 6.46 (1H,

d, *J* = 8.0Hz), 5.96 (2H,s), 4.62 (1H, d, *J* = 10.0Hz), 4.36 (1H, d, *J* = 4.0Hz), 4.10 (1H,m), 3.98 (1H,brs), 3.70 (1H,m), 2.02 (1H,m), 1.85–1.22 (4H,m), EIMS: *m/z* 309 ($M^{+\cdot}$), Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.77; H, 7.07; Found: C, 73.62; H, 7.01%.

Compound **4g** (*cis-9-methyl-5-phenyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline)*: Light yellow solid, m.p. 133–134 °C; IR (KBr): 3347, 1610, 1492 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.44–7.23 (6H, m), 6.82 (1H, dd, *J* = 8.0, 2.0 Hz), 6.51 (1H, d, *J* = 8.0 Hz), 5.26 (1H, d, *J* = 6.0 Hz), 4.61 (1H, d, *J* = 3.0 Hz), 3.62–3.51 (3H, m), 2.31 (3H, s), 2.15 (1H, m), 1.62–1.19 (4H,m); EIMS: *m/z* 279 ($M^{+\cdot}$). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.72; H, 7.53; N, 6.02; Found: C, 81.68; H, 7.46; N, 6.11%.

Compound **5g** (*trans-9-methyl-5-phenyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline)*: Light yellow solid, m.p. 140–141 °C; IR (KBr): 3352, 1610, 1481 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.45–7.18 (6H, m), 6.91 (1H, dd, *J* = 8.0, 2.0 Hz), 6.44 (1H, d, *J* = 8.0 Hz), 4.62 (1H, d, *J* = 10.0 Hz), 4.36 (1H, d, *J* = 3.0 Hz), 4.13–3.72 (2H, m), 3.55 (1H, brs), 2.30 (3H, s), 2.08 (1H, m), 1.92–1.21 (4H,m); EIMS: *m/z* 279 ($M^{+\cdot}$). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.72; H, 7.53; N, 6.02; Found: C, 81.83; H, 7.58; N, 5.99%.

Compound **4i** (*cis-5-(4-chlorophenyl)-9-methyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline)*: Light yellow solid, m.p. 98–100 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.41 (2H, d, *J* = 8.0 Hz), 7.34 (2H, d, *J* = 8.0 Hz), 7.18 (1H, d, *J* = 2.0 Hz), 6.85 (1H, dd, *J* = 8.0, 2.0 Hz), 6.52 (1H, d, *J* = 8.0 Hz), 5.24 (1H, d, *J* = 6.0 Hz), 4.60 (1H, d, *J* = 3.0 Hz), 3.76 (1H, brs), 3.62–3.37 (2H, m), 2.31 (3H, s), 2.05 (1H, m), 1.63-1.39 (4H, m); EIMS: *m/z* 315, 313 ($M^{+\cdot}$).

Compound **5i** (*trans-5-(4-chlorophenyl)-9-methyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline)*: Light yellow solid, m.p. 120–121 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.40 (2H, d, *J* = 8.0 Hz), 7.32 (2H, d, *J* = 8.0 Hz), 7.22 (1H, d, *J* = 2.0 Hz), 6.81 (1H, dd, *J* = 8.0, 2.0 Hz), 6.54 (1H, d, *J* = 8.0 Hz), 4.61 (1H, d, *J* = 10.0 Hz), 4.35 (1H, d, *J* = 4.0 Hz), 4.12 (1H. m), 3.84 (1H, brs), 3.75 (1H, m), 2.31 (3H, s), 2.02 (1H, m), 1.82–1.20 (4H, m); EIMS: *m/z* 315, 313 ($M^{+\cdot}$).

Compound **4l** (*cis-4-(4-methoxyphenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline)*: Light yellow solid, m.p. 98–100 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.42–7.15 (4H, m), 7.03 (1H, d, *J* = 8.0 Hz), 6.92 (1H, t, *J* = 8.0 Hz), 6.77 (1H, t, *J* = 8.0 Hz), 6.52 (1H, d, *J* = 8.0 Hz), 5.20 (1H, d, *J* = 8.0 Hz), 4.61 (1H, d, *J* = 3.0 Hz), 3.87 (3H, s), 3.82–3.68 (3H, m), 2.72 (1H, m), 2.21 (1H, m), 1.55 (1H,m); EIMS: *m/z* 281 ($M^{+\cdot}$).

Compound **5l** (*trans-4-(4-methoxyphenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline)*: Light yellow solid, m.p. 112–114 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.53–7.21 (4H, m), 7.05 (1H, d, *J* = 8.0 Hz), 6.91 (1H, t, *J* = 8.0 Hz), 6.80 (1H, t, *J* = 8.0 Hz), 6.54 (1H, d, *J* = 8.0 Hz), 4.62 (1H, d, *J* = 10.0 Hz), 4.32 (1H, d, *J* = 3.0 Hz), 3.88 (3H, s), 3.86–3.62 (3H, m), 2.43 (1H, m), 2.01 (1H, m), 1.73 (1H,m); EIMS: *m/z* 281 ($M^{+\cdot}$).

Compound **4m** (*cis-4-(3,4-dichlorophenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline)*: Light yellow solid, m.p. 117–118 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.58 (1H, m), 7.42 (1H, m), 7.22–7.18 (2H, m), 7.06 (1H, t, *J* = 8.0 Hz), 6.81 (1H, t, *J* = 8.0 Hz), 6.60 (1H, d, *J* = 8.0 Hz), 5.21 (1H, d, *J* = 6.0 Hz), 4.62 (1H, d, *J* = 3.0 Hz), 3.85–3.72 (2H, m), 3.64 (1H, brs), 2.65 (1H, m), 2.22 (1H, m), 1.51 (1H,m); EIMS: *m/z* 323, 321, 319 ($M^{+\cdot}$).

Compound **5m** (*trans-4-(3,4-dichlorophenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline)*: Light yellow solid, m.p. 123–126 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.56 (1H, m), 7.41 (1H, m), 7.25–7.17 (2H, m), 7.04 (1H, t, *J* = 8.0 Hz), 6.78 (1H, t, *J* = 8.0 Hz), 6.62 (1H, d, *J* = 8.0 Hz), 4.60 (1H, d, *J* = 10.0 Hz), 4.32 (1H, d, *J* = 4.0 Hz), 3.82 (1H, m), 3.72 (1H, m), 3.64 (1H, brs), 2.48 (1H, m), 2.11 (1H, m), 1.70 (1H,m); EIMS: *m/z* 323, 321, 319 ($M^{+\cdot}$).

Compound **4n** (*cis-9-methyl-4-phenyl-2,3,3a,4,5,9b-hexahydrofuro [3,2-c]quinoline)*: Light yellow solid, m.p. 92–94 °C; IR (KBr): 3344, 1612, 1474 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.55–7.22 (6H, m), 7.02 (1H, d, *J* = 8.0 Hz), 6.71 (1H, t, *J* = 8.0 Hz), 5.31 (1H, d, *J* = 8.0 Hz), 4.62 (1H, d, *J* = 3.0 Hz), 3.82 (2H, m), 3.71 (1H, m), 3.61 (1H, brs), 2.72 (1H, m), 2.32 (3H, s), 2.13 (1H, m), 1.47 (1H,m); EIMS: *m/z* 265 ($M^{+\cdot}$). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.51; H, 7.17; N, 5.28; Found: C, 81.59; H, 7.21; N, 5.22%.

Compound **5n** (*trans-9-methyl-4-phenyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline)*: Light yellow solid, m.p. 102–103 °C; IR (KBr): 3352, 1610, 1482 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.46–7.18 (6H, m), 7.05 (1H, d, *J* = 8.0 Hz), 6.68 (1H, t, *J* = 8.0 Hz), 4.62 (1H, d, *J* = 10.0 Hz), 4.32 (1H, d, *J* = 4.0 Hz), 3.84 (1H, m), 3.68 (1H, brs), 3.64 (1H, brs), 2.42 (1H, m), 2.31 (3H, s), 2.04 (1H, m), 1.71 (1H,m); EIMS: *m/z* 265 ($M^{+\cdot}$). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.51; H, 7.17; N, 5.28; Found: C, 81.46; H, 7.22; N, 5.20%.

Compound **4o** (*cis-4-(4-chlorophenyl)-9-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline)*: Light yellow solid, m.p. 131–132 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.62 (2H, d, *J* = 8.0 Hz), 7.36 (2H, d, *J* = 8.0 Hz), 7.12 (1H, d, *J* = 2.0 Hz), 6.87 (1H, dd, *J* = 8.0, 2.0 Hz), 6.54 (1H, d, *J* = 8.0 Hz), 5.22 (1H, d, *J* = 8.0 Hz), 4.61 (1H, d, *J* = 3.0 Hz), 3.84 (1H, m), 3.63 (1H, brs), 3.61 (1H, m), 2.65 (1H, m), 2.34 (3H, s), 2.20 (1H, m), 1.50 (1H,m); EIMS: *m/z* 301, 299 ($M^{+\cdot}$).

Compound **5o** (*trans-4-(4-chlorophenyl)-9-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline)*: Light yellow solid, m.p. 143–145 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.46 (1H, d, *J* = 8.0 Hz), 7.35 (1H, d, *J* = 8.0 Hz), 7.16 (1H, d, *J* = 2.0 Hz), 6.90 (1H, dd, *J* = 8.0, 2.0 Hz), 6.55 (1H, d, *J* = 8.0 Hz), 6.42 (1H, d, *J* = 8.0 Hz), 4.58 (1H, d, *J* = 4.0 Hz), 3.92 (1H, brs), 3.85–3.42 (2H, m), 2.48 (2H, m), 2.32 (3H, s), 2.01 (2H, m), 1.72 (1H,m); EIMS: *m/z* 301, 299 ($M^{+\cdot}$).

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