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SYNTHESIS AND OXIDATION OF 2-FURYL-4-R-SUBSTITUTED AND FURO[3,2-*c*]-CONDENSED 1,2,3,4-TETRAHYDRO-1,10-PHENANTHROLINES AND QUINOLINES*

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2-Furyl-4-substituted and furo[2,3-c]-condensed 1,2,3,4-tetrahydro-1,10-phenanthrolines were obtained for the first time from 8-aminoquinolines using the Povarov reaction. Various oxidizing agents were shown to effect the elimination of the substituent at C(4) with subsequent aromatization of the tetrahydroquinoline fragment.

Keywords: tetrahydroquinolines, 1,10-phenanthrolines, oxidation, Povarov reaction.

The Povarov reaction (the acid-catalyzed [4+2] cycloaddition of electron-rich alkenes to N-arylazomethines) is commonly used for the synthesis of substituted tetrahydroquinolines and, judging from the rising number of publications, is now experiencing a rebirth of interest [1-3]. Nevertheless, there have been only a few examples of the preparation of 2-furyl-1,2,3,4-tetrahydroquinolines by this method [4-6] and there is only one example of the use of an 8-aminoquinoline in the Povarov reaction [7]. This paucity is related primarily to the acidophobic nature of the furan fragment and, secondarily, to passivation of the acid catalysts. The behavior of 2-furyltetrahydroquinolines in the presence of oxidizing agents has also not been studied extensively and apparently is complex.

2-Furyltetrahydroquinolines **2a,b, 3,** and **4** used as the starting compounds in this work were obtained by the Povarov reaction from the corresponding furfurylideneanilines **1a**,**b** and electron-rich alkenes (dihydrofuran, 3,4-2H-dihydropyran, and N-vinyl-2-pyrrolidone) in the presence of boron trifluoride etherate as described in our previous work [8]. The hydrogenated quinolines **2-4** are *cis* addition adducts.

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* Dedicated to Professor Aleksei V. Varlamov of the Russian Peoples Friendship University on the occasion of his seventieth jubilee.

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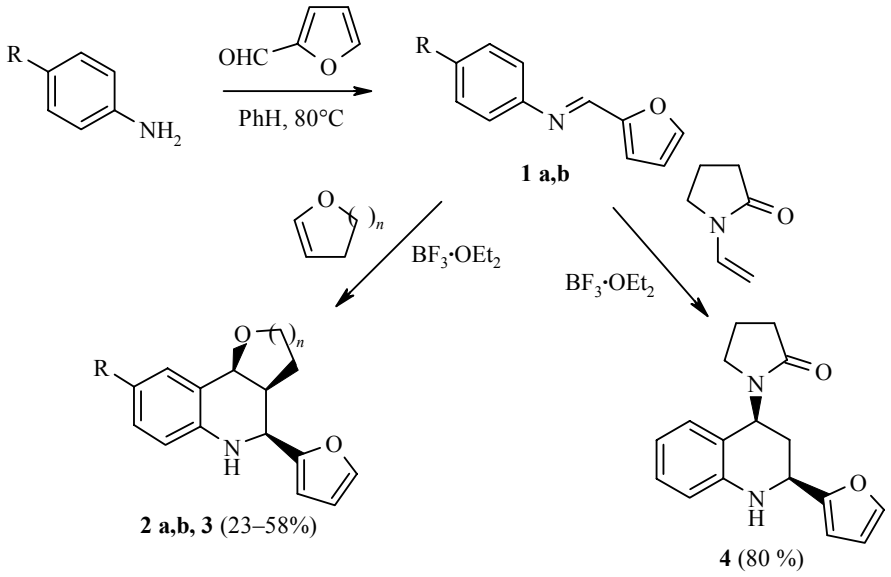
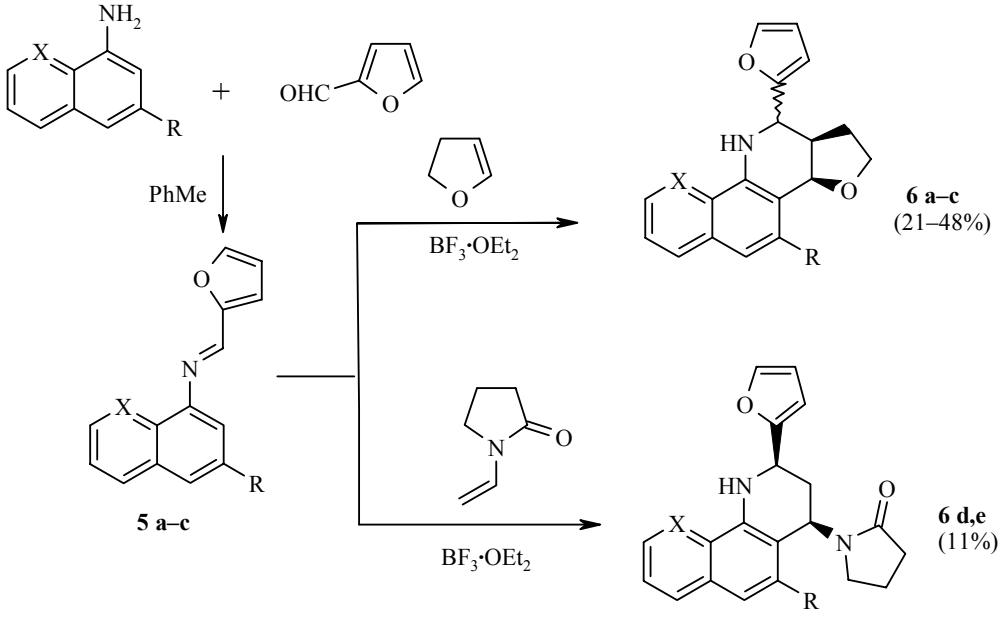
By analogy, azomethines **5a-c**, obtained by the condensation of furfural with α-naphthylamine and also with 8-amino-6-chloro- and 8-amino-6-bromoquinolines, are converted by cyclocondensation with 2,3-dihydrofuran into 1:1.1-1.5 mixtures of geometric isomers of furo[3,2-*c*]condensed hexahydro-1,10-phenanthrolines or the corresponding benzoquinolines **6a-c**.



1a, **2a, 3**, **4** R = H; **1b**, **2b** R = F; **2a, b** *n* = 1; **3** *n* = 2

Only *cis* diastereomers **6d**,**e** are obtained in low yield in the reaction of aldimines **5a**,**c** (see Experimental). The predominant *cis* isomers of adducts **6a-c** were isolated as pure products by fractional recrystallization.



5a, 6a, d X = N, R = Cl; **5b, 6b** X = N, R = Br; **5c, 6c, e** X = CH, R = H

TABLE 1. Physicochemical Characteristics of Compounds **6-10** and **13**

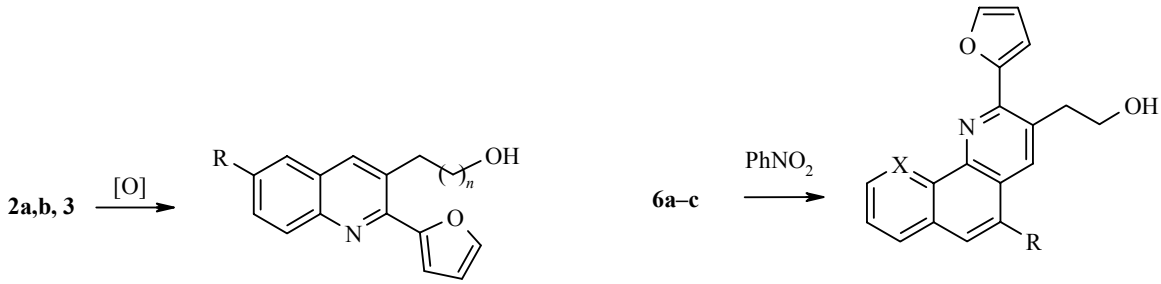
Compound	Empirical formula	Found, % / Calculated, %			mp, ºC	R_f*	IR spectrum, ν, cm^{-1}
		C	H	N			
6a	$C_{18}H_{15}ClN_2O_2$	66.28 / 66.16	4.52 / 4.63	8.64 / 8.57	159-160	0.63	3355 (NH)
6b	$C_{18}H_{15}BrN_2O_2$	58.31 / 58.24	4.10 / 4.07	7.59 / 7.55	139-140	0.67	3347 (NH)
6c	$C_{19}H_{17}NO_2$	78.52 / 78.33	5.76 / 5.88	4.69 / 4.81	98-102	0.53	3310 (NH)
6d	$C_{20}H_{18}ClN_3O_2$	65.72 / 65.31	4.47 / 4.93	11.11 / 11.42	178-180	0.43	3380 (NH), 1674 (NCO)
6e	$C_{21}H_{20}N_2O_2$	75.72 / 75.88	6.47 / 6.06	8.11 / 8.43	161-163	0.52	3409 (NH), 1673 (NCO)
7a	$C_{15}H_{13}NO_2$	75.41 / 75.30	5.59 / 5.48	5.53 / 5.85	58-60	0.32	3396 (OH)
7b	$C_{15}H_{12}FNO_2$	70.22 / 70.03	4.98 / 4.70	5.35 / 5.44	58-59	0.54	3230 (OH)
7c	$C_{16}H_{15}NO_2$	75.67 / 75.87	6.07 / 5.97	5.32 / 5.53	—	0.21	3420 (OH)
8a	$C_{18}H_{13}ClN_2O_2$	66.81 / 66.57	3.65 / 4.03	8.16 / 8.63	202-205	0.59	3381 (OH)
8b	$C_{18}H_{13}BrN_2O_2$	59.01 / 58.56	3.65 / 3.55	7.16 / 7.59	146-148	0.48	3225 (OH)
8c	$C_{18}H_{13}BrN_2O_2$	80.17 / 78.87	5.15 / 5.23	5.01 / 4.84	135-136	0.70	3372 (OH)
9	$C_{13}H_9NO$	80.08 / 79.98	4.62 / 4.65	7.26 / 7.17	58-59	0.62	1595 (C=C)
10	$C_{16}H_9ClN_2O$	68.32 / 68.46	3.19 / 3.23	10.27 / 9.98	156-158	0.41	—
13	$C_{16}H_{17}NO_4$	66.79 / 66.89	5.54 / 5.96	4.95 / 4.88	195-197	—	3433 (OH), 1682 (CO_2H)

*Solvents: ethyl acetate–hexane, 1:6 (**6a, 9**), 1:4 (**6b**) 1:8 (**6c**), 1:2 (**6d, 7a,b**), 1:1 (**7c, 8c**); ethyl acetate (**6e**), ethyl acetate–ethanol, 8:1 (**8a,b, 10**).

The presence of a pyridine nitrogen atom in starting Schiff bases **5a**,**b** was found, on the whole, not to affect the conditions for the cycloaddition, which was carried out in toluene at 20°C over 24 h with ~10 mole % $BF_3 \cdot Et_2O$, but sharply lowered the yield of products **6** in comparison with quinolines **2-4**. Combinations of other solvents such as acetonitrile, ether, and benzene and other catalysts such as aluminum chloride, tin chloride, titanium chloride, and *p*-TsOH and an increased Schiff base-catalyst ratio were also tested in the reaction. The yield of phenanthrolines **6** could not be increased over 30% in any case and an increased mole fraction of the Lewis acid only increased the amount of polymer impurities.

In the second part of this work, we studied the behavior of the tetrahydroquinoline ring in adducts **2-6** in the presence of various oxidizing agents.

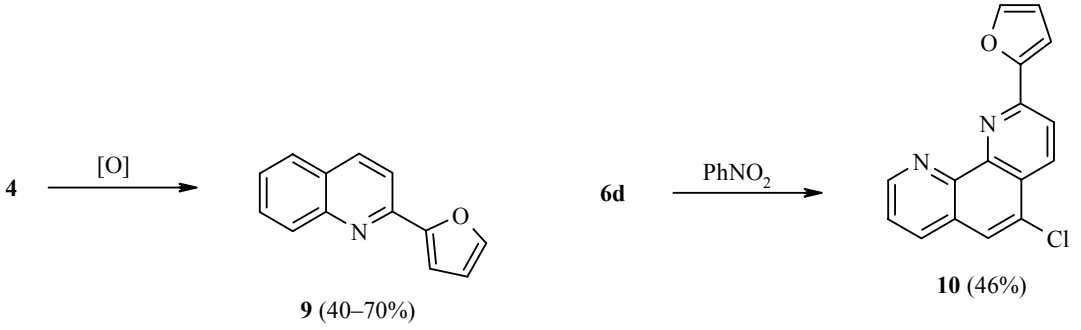
Condensed tetrahydrofuran and tetrahydropyran fragments in **2a,b, 3,** and **6a-c** proved unstable upon the action of various reagents. 2-Furyl-3-hydroxyalkylquinolines **7a-c**, 2-furyl-1,10-phenanthrolines **8a**,**b**, and 2-furylbenzoquinoline **8c** were formed upon heating quinolines **2a, 3,** and **6a-c** at reflux in nitrobenzene as the result of opening of the fused oxo fragment at the C(4)–O bond and aromatization of the tetrahydropyridine ring. Quinolines **7a-c** were also obtained upon heating furoquinolines **2a,b,** and **3** with sulfur in DMF at reflux, in the reaction of furo- and pyranoquinolines **2a** and **3** with 2 N hydrochloric acid in acetonitrile at 50°C, and in the potassium permanganate oxidation of **2a** in the presence of DB18C6 crown ether. The primary hydroxyl group and 2-furyl substituent in quinolines **7a-c** and phenanthrolines **8a-c** were not affected in the oxidation.



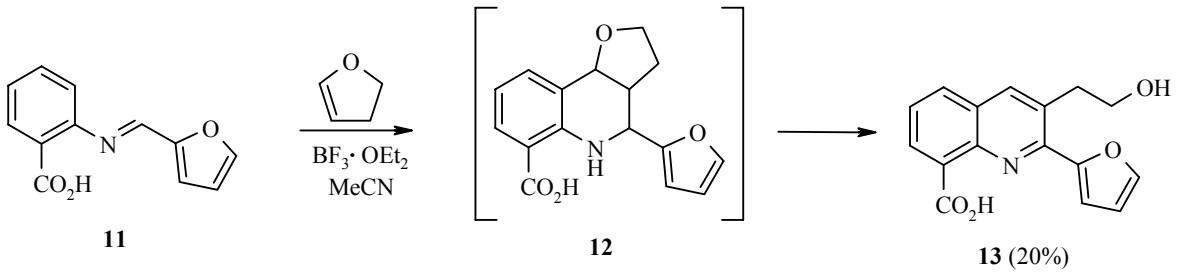
7 a R = H, *n* = 1; **b** R = F, *n* = 1; **c** R = H, *n* = 2; **8 a** R = Cl, X = N, **b** R = Br, X = N, **c** R = H, X = CH

The oxidation of 4-pyrrolidonyltetrahydroquinolines **4** by sulfur in DMF at reflux, by potassium permanganate under phase-transfer catalysis conditions, or by nitrobenzene at reflux is accompanied by the elimination of the pyrrolidone fragment such that 2-furylquinoline (**9**) is formed in 40-70% yield. Analogously, 4-pyrrolidonyltetrahydrophenanthroline **6d** is converted upon heating in nitrobenzene at reflux into 2-furyl-1,10-phenanthroline **10**.

We note that products of the elimination of 4-N- and 4-O-alkyl substituents with subsequent aromatization of the tetrahydroquinoline fragment analogous to quinolines **7** and **9** are often observed as by-products in the Povarov reaction [9-11] but have not been obtained in preparative reactions. The synthesis of functional derivatives of 1,10-phenanthrolines such as **8a,b,** and **10** has not been studied extensively [12, 13] although their 9-amino and 9-pyridyl derivatives display useful photoluminescence properties [14] and are ligands in chromogenic receptors [15, 16].



Adduct **12** formed in the cycloaddition of aldimine **11** to dihydrofuran in the presence of $BF_3 \cdot OEt_2$ could not be isolated since this compound spontaneously is converted to furylquinolinecarboxylic acid **13** as the result of opening of the tetrahydrofuran fragment.



Acetonitrile was used as the solvent in the latter case in light of the low solubility of aldimine **11** in toluene.

TABLE 2. ^{1}H NMR Spectra of Compounds **6-10** and **13**

Com-pound	Chemical shifts, δ, ppm (*J*, Hz)
1	2
6a*	1.65 (br. s, NH); 1.94 (1H, m, H-1B); 2.37 (1H, m, H-1A); 3.18 (1H, ddq, *J* = 3.2, *J* = 8.5, *J* = 1.7, H-11a); 3.85-3.73 (2H, m, H-2A+H-2B); 4.77 (1H, d, *J* = 3.2, H-11); 6.45-6.39 (2H, m, H-3'+H-4'); 6.50 (1H, d, *J* = 8.5, H-3a); 7.24 (1H, s, H-5); 7.39 (1H, dd, *J* = 4.2, *J* = 8.3, H-7); 7.43 (1H, dd, *J* = 0.8, *J* = 1.7, H-5'); 7.96 (1H, dd, *J* = 8.3, *J* = 1.6, H-6); 8.71 (1H, dd, *J* = 4.2, *J* = 1.6, H-8)
6b*	1.95 (1H, m, H-1B); 2.37 (1H, dq, *J* = 12.4, *J* = 8.3, H-1A); 3.18 (1H, ddq, *J* = 3.4, *J* = 8.3, *J* = 2.0, H-11a); 3.75 (1H, dt, *J* = 8.1, *J* = 8.3, H-2B); 3.83 (1H, q, *J* = 8.0, H-2A); 4.77 (1H, br. s, *J* = 3.4, H-11); 6.45-6.39 (2H, m, H-3'+H-4'); 5.55 (1H, d, *J* = 8.4, H-3a); 7.47 (1H, s, H-5); 7.39 (1H, dd, *J* = 4.2, *J* = 8.3, H-7); 7.43 (1H, dd, *J* = 0.8, *J* = 1.6, H-5'); 7.96 (1H, dd, *J* = 8.3, *J* = 1.6, H-6); 8.73 (1H, dd, *J* = 4.2, *J* = 1.6, H-8)
6c*	1.93 (1H, m, H-1B); 2.29 (1H, dq, *J* = 12.5, *J* = 8.5, H-1A); 3.06 (1H, dq, *J* = 2.9, *J* = 8.3, H-11a); 3.71 (1H, dt, *J* = 8.5, *J* = 4.7, H-2B); 3.84 (1H, q, *J* = 8.0, H-2A); 4.66 (br. s, NH); 4.84 (1H, d, *J* = 2.9, H-11); 5.44 (1H, d, *J* = 7.8, H-3a); 6.40 (1H, br. dd, *J* = 0.7, *J* = 3.1, H-3'); 6.44 (1H, dd, *J* = 1.8, *J* = 3.1, H-4'); 7.34 (1H, d, *J* = 8.4, H-9); 7.44-7.48 (2H, m, H-4+H-5); 7.48 (1H, dd, *J* = 0.7, *J* = 1.8, H-5'); 7.76-7.80 (3H, m, H arom)
6d	1.56 (1H, m, H-4"B); 1.74 (1H, m, H-4"A); 2.37-2.23 (2H, m, H-3"); 2.42 (1H, ddd, *J* = 1.0, *J* = 5.7, *J* = 14.0, H-3B); 2.62 (1H, m, H-5"B); 2.73 (1H, m, H-5"A); 2.86 (1H, ddd, *J* = 0.7, *J* = 5.7, *J* = 14.0, H-3A); 4.84 (1H, m, H-2); 5.57 (1H, t, *J* = 5.7, H-4); 6.24 (1H, dd, *J* = 0.6, *J* = 3.2, H-3'); 6.31 (1H, dd, *J* = 1.8, *J* = 3.2, H-4'); 7.11 (1H, s, H-6); 6.86 (br. s, NH); 7.38 (1H, dd, *J* = 0.6, *J* = 1.8, H-5'); 7.41 (1H, dd, *J* = 8.4, *J* = 4.3, H-8); 7.95 (1H, dd, *J* = 1.6, *J* = 8.4, H-7); 8.72 (1H, dd, *J* = 1.6, *J* = 4.3, H-9)
6e	2.07-1.99 (2H, m, H-4"); 2.39 (1H, dt, *J* = 11.0, *J* = 12.2, H-3*ax*); 2.41 (1H, ddd, *J* = 3.3, *J* = 7.0, *J* = 12.2, H-3*eq*); 2.63-2.48 (2H, m, H-3"); 3.09 (1H, dt, *J* = 9.7, H-5"B); 3.26 (1H, dt, *J* = 9.7, H-5"A); 4.74 (br. s, NH); 4.79 (1H, dd, *J* = 3.3, *J* = 11.0, H-2); 5.89 (1H, dd, *J* = 7.0, *J* = 11.0, H-4); 6.39 (1H, dd, *J* = 3.2, *J* = 0.6, H-3'); 6.43 (1H, dd, *J* = 1.8, *J* = 3.2, H-4'); 7.05 (1H, d, *J* = 8.4, H-6); 7.28 (1H, d, *J* = 8.4, H-5), 7.45 (1H, dd, *J* =0.6, *J* = 1.8, H-5'); 7.48-7.45 (2H, m, H-7+H-10); 7.79-7.75 (2H, m, H-8+H-9)
7a	1.87 (1H, br. s, OH); 3.28 (2H, t, *J* = 6.4, H-1"); 3.93 (2H, t, *J* = 6.4, H-2"); 6.54 (1H, dd, *J* = 1.7, *J* = 3.2, H-4'); 7.11 (1H, d, *J* = 3.2, H-3'); 7.43 (1H, dd, *J* = 7.5, *J* = 8.2, H-7); 7.57 (1H, dd, *J* = 0.8, *J* = 1.7, H-5'); 7.62 (1H, br. t, *J* = 7.5, H-6); 7.63 (1H, d, *J* = 7.5, H-5); 7.96 (1H, s, H-4); 8.04 (1H, d, *J* = 8.2, H-8)
7b	2.01 (1H, br. s, OH); 3.32 (2H, t, *J* = 6.4, H-1"); 3.96 (2H, t, *J* = 6.4, H-2"); 6.58 (1H, dd, *J* = 1.8, *J* = 3.4, H-4'); 7.12 (1H, dd, *J* = 0.8, *J* = 3.4, H-3'); 7.30 (1H, dd, *J* = 2.8, *J* = 8.8, H-5); 7.42 (1H, ddd, *J* = 9.2, *J* = 2.8, *J* = 8.4, H-7); 7.61 (1H, dd, *J* = 0.8, *J* = 1.8, H-5'); 7.95 (1H, s, H-4); 8.04 (1H, dd, *J* = 5.4, *J* = 9.2, H-8)
7c	1.62 (1H, br. s, OH); 1.94 (2H, m, H-2"); 3.18 (2H, t, *J* = 7.7, H-3"); 3.75 (2H, t, *J* = 6.2, H-1"); 6.59 (1H, dd, *J* = 1.7, *J* = 3.2, H-4'); 7.16 (1H, dd, *J* = 0.8, *J* = 3.2, H-3'); 7.49 (1H, ddd, *J* = 1.1, *J* = 6.9, *J* = 8.2, H-7); 7.63 (1H, dd, *J* = 0.8, *J* = 1.7, H-5'); 7.66 (1H, ddd, *J* = 1.0, *J* = 6.9, *J* = 8.3, H-6); 7.74 (1H, dd, *J* =1.1, *J* =8.3, H-5); 8.00 (1H, s, H-4); 8.11 (1H, dd, *J* = 1.0, *J* = 8.2, H-8)
8a	3.35 (1H, t, *J* = 5.2, H-1"B); 3.79 (2H, q, *J* = 5.2, H-2"); 4.85 (1H, t, *J* = 5.2, H-1"A); 6.78 (1H, dd, *J* = 3.2, *J* = 1.7, H-4'); 7.37 (1H, dd, *J* = 0.8, *J* = 3.2, H-3'); 7.78 (1H, dd, *J* = 8.1, *J* = 4.2, H-8); 8.01 (1H, dd, *J* = 0.8, *J* = 1.7, H-5'); 8.20 (1H, s, H-6); 8.44 (1H, dd, *J* = 1.6, *J* = 8.1, H-7); 8.53 (1H, s, H-4); 9.12 (1H, dd, *J* = 1.6, *J* = 4.2, H-9)
8b	1.88 (1H, br. s, OH); 3.45 (2H, t, *J* = 6.4, H-1"); 4.11 (2H, t, *J* = 6.4, H-2"); 6.61 (1H, dd, *J* = 3.3, *J* = 1.7, H-4'); 7.43 (1H, br. s, *J* = 3.3, H-3'); 7.62 (1H, dd, *J* = 8.1, *J* = 4.3, H-8); 7.63 (1H, br. s, *J* = 1.7, H-5'); 7.93 (1H, s, H-6); 8.12 (1H, dd, *J* = 1.5, *J* = 8.1, H-7); 8.33 (1H, s, H-4); 9.17 (1H, dd, *J* = 1.5, *J* = 4.3, H-9)
8c	1.49 (1H, br. s, OH); 3.46 (2H, t, *J* = 6.5, H-2"); 4.01 (2H, dd, *J* = 4.8, *J* = 6.5, H-2"); 6.63 (1H, dd, *J* = 3.1, *J* = 1.9, H-4'); 7.41 (1H, br. s, *J* = 3.1, H-3'); 7.62 (1H, d, *J* = 8.7, H-5); 7.63 (1H, br. s, *J* = 1.9, H-5'); 7.66 (1H, dt, *J* = 1.2, *J* = 6.9, H-8); 7.71 (1H, dt, *J* = 1.0, *J* = 6.9, H-9); 7.75 (1H, d, *J* = 8.7, H-6); 8.04 (1H, s, H-4); 9.32 (1H, d, *J* = 7.5, H-10)

TABLE 2 (continued)

1	2
9	6.59 (1H, dd, *J* = 1.8, *J* = 3.4, H-4'); 7.22 (1H, dd, *J* = 0.8, *J* = 3.4, H-3'); 7.50 (1H, ddd, *J* = 1.2, *J* = 6.9, *J* = 8.0, H-7); 7.64 (1H, dd, *J* = 0.8, *J* = 1.8, H-5'); 7.71 (1H, ddd, *J* = 1.6, *J* = 6.9, *J* = 8.2, H-6); 7.78 (1H, dd, *J* = 1.2, *J* = 8.2, H-5); 7.82 (1H, d, *J* = 8.6, H-3), 8.13 (1H, ddd, *J* = 1.1, *J* = 1.6, *J* = 8.0, H-8); 8.16 (1H, br. s, *J* = 8.6, H-4)
10	6.63 (1H, dd, *J* = 3.4, *J* = 1.8, H-4'); 7.52 (1H, br. s, *J* = 3.4, H-3'); 7.64 (1H, dd, $J_{7,8}$ = 8.1, *J* = 4.3, H-8); 7.67 (1H, dd, *J* = 0.6, *J* = 1.8, H-5'); 7.85 (1H, s, H-6); 8.14 (1H, d, *J* = 8.7, H-3); 8.16 (1H, dd, *J* = 8.1, *J* = 1.6, H-7); 8.69 (1H, d, *J* = 8.7, H-4); 9.20 (1H, dd, *J* = 1.6, *J* = 4.3, H-9)
13	1.87 (1H, br. s, OH); 3.44 (2H, t, *J* = 6.0, H-1"); 4.11 (2H, t, *J* = 6.0, H-2"); 6.67 (1H, dd, *J* = 1.7, *J* = 3.4, H-4'); 7.24 (1H, br. s, *J* = 3.4, H-3'); 7.57 (1H, dd, *J* = 8.2, *J* = 7.1, H-6); 7.71 (1H, dd, *J* = 1.7, *J* = 0.7, H-5'); 7.99 (1H, dd, *J* = 1.2, *J* = 8.2, H-5); 8.32 (1H, s, H-4); 8.54 (1H, dd, *J* = 1.2, *J* = 7.1, H-7)

* Data are given for the predominant *cis* isomers of **6a-c** isolated as pure compounds.

TABLE 3. Mass Spectra of Compounds **6-10** and **13**

Com-pound	*m/z* (I_{rel}, %)
6a	326 $[M]^+$ (for ^{35}Cl) (62), 281 (61), 255 (11), 229 (12), 215 (52), 202 (14), 191 (12), 140 (14), 126 (12), 114 (11), 91 (14), 81 (100), 77 (26), 62 (16), 51 (29), 39 (77)
6b	372 $[M]^+$ (for ^{79}Br) (34), 327 (36), 261 (33), 247 (12), 218 (11), 180 (13), 166 (12), 140 (12), 128 (13), 115 (12), 102 (12), 91 (18), 81 (100), 65 (14), 51 (13), 39 (83)
6c	291 $[M]^+$ (100), 260 (11), 246 (59), 217 (12), 180 (19), 167 (15), 139 (7), 115 (14), 91 (13), 77 (18), 55 (7), 39 (20)
6d	367 $[M]^+$ (for ^{35}Cl) (2), 281 (100), 253 (6), 218 (9), 191 (2), 140 (2), 126 (3), 81 (3), 41 (2)
6e	332 $[M]^+$ (11), 246 (100), 217 (11), 180 (8), 167 (4), 151 (4), 127 (3), 81 (5), 41 (2)
7a	239 $[M]^+$ (80), 222 (25), 208 (42), 180 (100), 152 (20), 89 (13), 77 (11), 63 (13), 51 (9), 39 (15)
7b	257 $[M]^+$ (84), 240 (28), 226 (33), 212 (13), 198 (100), 186 (11), 170 (17), 151 (7), 99 (8), 57 (8), 39 (12)
7c	235 $[M–H_2O]^+$ (33), 218 (100), 206 (72), 192 (24), 181 (22), 152 (8), 136 (5), 115 (6), 102 (7), 39 (3)
8a	324 $[M]^+$ (for ^{35}Cl) (83), 307 (14), 293 (31), 279 (14), 265 (100), 253 (14), 229 (34), 203 (13), 164 (7), 101 (5), 31 (4)
8b	368 $[M]^+$ (69), 351 (17), 339 (36), 311 (73), 297 (15), 229 (100), 203 (23), 164 (14), 101 (9), 31 (7)
8c	289 $[M]^+$ (87), 258 (49), 230 (100), 202 (26), 165 (7), 114 (10), 88 (9), 51 (9)
9	195 $[M]^+$ (100), 167 (30), 139 (16), 128 (7), 101 (4), 75 (5), 63 (6), 51 (5), 39 (7)
10	280 $[M]^+$ (for ^{35}Cl) (100), 252 (39), 216 (18),189 (7), 140 (8), 126 (6), 95 (5)
13	283 $[M]^+$ (7), 239 (100), 207 (12), 192 (7), 180 (16), 152 (7), 127 (3), 44 (8)

Thus, promising intermediates for the preparation of polydentate ligands, namely, 2-furyl-1,10-phenanthrolines, were synthesized for the first time by the Povarov reaction in this work. The reaction of furfurylidene-8-aminoquinolines with electron-rich alkenes was shown to proceed in the presence of catalytic amounts of a Lewis acid. The oxidation of 4-N- and 4-O-alkyl-substituted and furocondensed 2-furyl-1,2,3,4-tetrahydroquinolines and phenanthrolines by nitrobenzene and elemental sulfur was found to give high yields of the products of aromatization with prior elimination of the N-alkyl or O-alkyl substituent.

EXPERIMENTAL

Reagents obtained from Acros Organics were used without further purification. Freshly distilled solvents were used for the syntheses. The melting points of the products were measured on an SMP 10 instrument and not corrected. The IR spectra were taken on an Infralum FT-801 IR Fourier spectrometer in KBr pellets. The ^{1}H NMR spectra were taken on a Bruker WH-400 spectrometer at 400 MHz at 26°C for ~3% solutions in $CDCl_3$ with residual $CHCl_3$ as the internal standard. Some of the electron impact mass spectra were obtained on a Thermo Focus DSQ II GC/MS at 70 eV with direct inlet. The ion source temperature was 200°C. A Varian FactorFour VF-5ms chromatographic column was used. Other electron impact mass spectra were taken on a Thermo Trace DSQ mass spectrometer at 70 eV with direct inlet. The ion source temperature was 200°C. Plates coated with Sorbfil PTSKh-AF-A-UF-254 were used for the thin-layer chromatography with development by iodine vapor. The purification of the final products was carried out on activated neutral 50-200 mesh alumina or by recrystallization from hexane–ethyl acetate. The isomer ratio in the reaction products was found from the ^{1}H NMR spectra as the ratio of the integral intensities of monotypic proton signals.

The physicochemical characteristics and elemental analysis data of all the new compounds are given in Table 1, while the ^{1}H NMR spectral data are given in Table 2 and the mass spectra are given in Table 3.

5-Chloro-1,2,3a,10,11,11a-hexahydro- (6a) and 6-Bromo-1,2,3a,10,11,11a-hexahydro-11-(2-furyl)furo-[3,2-*c*]-1,10-phenanthrolines (6b), 11-(2'-Furyl)-1,2,3a,10,11,11a-hexahydrobenzo[H]furo[3,2-*c*]quinoline (6c), 5-Chloro-2-(2-furyl)-4-(N-2-oxopyrrolidinyl)-(2*S,4*S**)-1,2,3,4-tetrahydro-1,10-phenanthroline (6d), 2-(2-Furyl)-4-(N-2-oxopyrrolidinyl)benzo-(2*S**,4*S**)-1,2,3,4-tetrahydro[H]quinoline (6e) (General Method)**. A sample of $BF_3 \cdot OEt_2$ (0.11 ml, 0.84 mmol) and then dihydrofuran (for **6a-c**) (2.8 ml, 40 mmol) or N-vinyl-2-pyrrolidone (for **6d,e**) (4.3 ml, 40 mmol) were added to a stirred solution of azomethine **5a-c** (30 mmol) in dry toluene (50 ml) at 25°C and stirred for 24 h at 20°C with monitoring by thin-layer chromatography. Then, 3-4 ml 25% aqueous ammonia was added and the solvent was removed in vacuum. The viscous brown oily residue was purified by column chromatography using 1:5 ethyl acetate–hexane as the eluent. Phenanthrolines and benzoquinolines **6a-e** were obtained as white crystals.

The recrystallization solvents were toluene for **6a,b,d,** and **6e** and benzene for **6c**. The yields and *trans/cis* diastereomer ratios were: **6a** – 28%, 40:60; **6b** – 21%, 45:55; **6c** – 48%, 50:50; the yields of *cis*-**6d** and *cis*-**6d** were 100%.

2'-[2-(2-Furyl)-3-quinolinyl]-1'-ethanol (7a) and 2'-[6-Fluoro-2-(2-furyl)-3-quinolinyl]-1'-ethanol (7b). A. Dibenzo-18-crown-6 (0.072 g, 0.2 mmol) and potassium permanganate (1.30 g, 8.3 mmol) were added to a solution of tetrahydroquinoline **2a** (1.00 g, 4.15 mmol) in dichloromethane (100 ml) and stirred for 4 h at ~20°C with monitoring by thin-layer chromatography. The manganese(IV) oxide formed was filtered off and washed with two dichloromethane portions (30 ml). The solution was evaporated to dryness. Then, 10 ml ether was added to the residue and the crown ether residue was filtered off. The yellow oily residue was subjected to chromatography on a 45×1 cm column, which was eluted consecutively with 1:10, 1:5, and 1:1 ethyl acetate–hexane to give 0.47 g (49%) quinoline **7a** as light-brown crystals, mp 58-60°C.

B. Tetrahydroquinoline **2a** (1.0 g, 4.15 mmol) in nitrobenzene (15 ml) was heated at reflux for 10 h. The solvent was removed in vacuum. The black oily residue was subjected to chromatography on a 25×4 cm column using 1:10 ethyl acetate–hexane as the eluent to give 0.81 g (82%) quinoline **7a**, mp 59-61°C. This product mixed with a sample obtained by Method A did not give a depressed melting point.

C. A mixture of sulfur powder (1.60 g, 49 mmol) and amine **2a** or **2b** (16.5 mmol) was heated at reflux for 4 h until hydrogen sulfide was no longer evolved. The reaction mixture was poured into water (50 ml) and extracted with three chloroform portions (50 ml). The combined organic extracts were dried over magnesium sulfate. After removal of the solvent, the dark-brown oil was subjected to chromatography on a 25×4 cm column using ether as the eluent to give 2.00 g (50%) quinoline **7a** as brown crystals, mp 60-62°C or 1.27 g (30%) quinoline **7b** as light-beige crystals.

D. 2 N Hydrochloric acid (2 ml) was added to a solution of tetrahydroquinoline **2a** (0.22 g, 0.9 mmol) in acetonitrile (20 ml). The reaction mixture was maintained for 2 h at 50°C with monitoring by thin-layer chromatography. The solution was poured into water (20 ml), neutralized by adding 25% ammonium hydroxide, and extracted with three portions of ethyl acetate (25 ml). The combined organic extracts were dried over magnesium sulfate. Removal of the solvent gave 0.18 g (84%) quinoline **7a** as light-yellow crystals, mp 60-61°C.

3'-[2-(2-Furyl)-3-quinolinyl]-1'-propanol (7c). A. Dibenzo-18-crown-6 (0.21 g, 0.6 mmol) and potassium permanganate (2.46 g, 15.6 mmol) were added to a solution of tetrahydroquinoline **3** (1.00 g, 3.9 mmol) in dichloromethane (100 ml) and stirred for 24 h at ~20°C with monitoring by thin-layer chromatography. The manganese(IV) oxide formed was filtered off and washed with two 30 ml dichloromethane portions. The solution was evaporated to dryness. The residue was subjected to chromatography on a 45×1 cm column with 1:10 ethyl acetate–hexane as the eluent to give 0.36 g (37%) quinoline **7c** as a yellow oil, which darkens upon standing in the air.

B. A mixture of sulfur powder (0.38 g, 12 mmol) and amine **3** (1.00 g, 3.9 mmol) in DMF (20 ml) was heated at reflux until no further hydrogen sulfide evolved with monitoring by thin-layer chromatography. The reaction mixture was poured into water (30 ml) and extracted with three 30-ml chloroform portions. The combined organic extracts were dried over magnesium sulfate. After removal of the solvent, the dark-brown oily residue was purified on a 25×4 cm column using 1:10 ethyl acetate–hexane as the eluent to give 0.60 g (61%) quinoline **7c**.

C. 2 N Hydrochloric acid (4.4 ml) was added to a solution of tetrahydroquinoline **3** (1.0 g, 3.9 mmol) in acetonitrile (40 ml) and maintained for 2 h at 50°C with monitoring by thin-layer chromatography. The solution was poured into 40 ml water, neutralized with 25% ammonium hydroxide, and extracted with three portions of ethyl acetate (30 ml). The combined organic extracts were dried over magnesium sulfate. After removal of the solvent, the dark oil was purified on a 25×4 cm column using 1:10 ethyl acetate–hexane as the eluent to give 0.32 g (32%) quinoline **7c** as a light-yellow oil.

2'-[2-(2-Furyl)-1,10-phenanthrolin-3-yl]-1'-ethanols 8a,b and 2'-[2-(2-Furyl)benzoquinolin-3-yl]-1'-ethanol 8c (General Method). A mixture of corresponding phenanthroline **6a-c** (4.82 mmol) and nitrobenzene (27 ml, 260 mmol) was heated at reflux for 6 h with monitoring by thin-layer chromatography. Nitrobenzene was distilled off and the remaining black oil was subjected to chromatography on a 30×5 cm column with gradient elution from hexane to 1:10 and 1:5 ethyl acetate–hexane and, finally, ethyl acetate to give alcohols **8a** (in 66% yield), **8b** (in 62% yield), and **8c** (in 69% yield) as white crystals.

2-(2-Furyl)quinoline (9). A. A solution of tetrahydroquinoline **4** (54 mmol) and sulfur (5.12 g, 160 mmol) in DMF (50 ml) was heated at reflux until no further hydrogen sulfide evolved with monitoring by thin-layer chromatography. The reaction mixture was poured into water (50 ml) and extracted with three portions of ethyl acetate (50 ml). The combined organic extracts were dried over magnesium sulfate. The solvent was evaporated in vacuum and the dark oily residue was purified by column chromatography using 1:10 ethyl acetate–hexane as the eluent to give 7.39 g (70%) quinoline **9**.

B. Potassium permanganate (1.12 g, 7.08 mmol) was added to a solution of tetrahydroquinoline **4** (3.54 mmol) and dibenzo-18-crown-6 (0.06 g, 0.18 mmol) in chloroform (50 ml) and stirred at room temperature for 4 h with monitoring by thin-layer chromatography. The manganese (IV) oxide formed was filtered off and washed with two 30 ml chloroform portions. The solvent was evaporated at reduced pressure and the brown oily residue was purified by column chromatography using ether as the eluent to give 0.13 g (19%) quinoline **9.**

C. A solution of tetrahydroquinoline **4** (3.54 mmol) in nitrobenzene (15 ml) was heated at reflux for 7 h with monitoring by thin-layer chromatography. Nitrobenzene was distilled off in vacuum and the remaining black oil was subjected to column chromatography using 1:10 ethyl acetate–hexane as the eluent to give 0.14 g (20%) quinoline **9**.

5-Chloro-2-(2-furyl)-1,10-phenanthroline (10). A mixture of 2-(2-furyl)phenanthroline **6d** (1.00 g, 2.7 mmol) and nitrobenzene (15 ml, 150 mmol) was heated at reflux for 6 h with monitoring by thin-layer chromatography. Nitrobenzene was distilled off in vacuum. The dark oily residue was subjected to chromatography on a 25×2 cm column with gradient elution starting with hexane, then 1:10, 1:5, 1:2 ethyl acetate–hexane, and finally ethyl acetate to give 0.35 g (46%) phenanthroline **10** as light-brown crystals.

3-(2-Hydroxyethyl)-2-(2-furyl)quinoline-8-carboxylic acid (13). A sample of $BF_3 \cdot OEt_2$ (0.3 ml, 25 mmol) and then dihydrofuran (7.6 ml, 100 mmol) were added to a stirred solution of azomethine **11** (100 mmol) in dichloromethane (100 ml). The reaction mixture was stirred for 24 h at room temperature. At the end of the reaction, three or four drops of 25% ammonium hydroxide were added and the solvent was evaporated off in vacuum. The residue was recrystallized from ethyl acetate–hexane to give 2.92 g (20%) furylquinoline **13** as white prisms.

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