

## SYNTHESIS OF FURO[2,3-*c*]QUINOLIN-4(5*H*)-ONES

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**Abstract** - A number of 1-aryloxymethyl-3*H*-pyrano[2,3-*c*]quinolin-5(6*H*)-ones (4*a-d*, 4*f-i*) on heating in *N,N*-diethylaniline for 8 h underwent an unusual ring contraction to give 1-aryloxymethyl-2-methylfuro[2,3-*c*]quinolin-4(5*H*)-ones (5*a-d*, 5*f-i*) in 66-79 % yields.

The occurrence of furo[3,2-*c*]quinolin-4(5*H*)-one and 2*H*-pyrano[3,2-*c*]quinolin-5(6*H*)-one derivatives in nature has been reported.<sup>1,2</sup> The synthesis of these heterocycles is also reported in literature.<sup>3-6</sup> Synthesis of the corresponding furo[2,3-*c*]quinolones has earlier been reported in low yields.<sup>7-9</sup> However, there was no report on the synthesis of pyrano[2,3-*c*]quinolones except our recent report of a simple synthesis for these heterocyclic ring systems.<sup>10</sup> The aryloxybutynyl ethers of 3-hydroxycoumarin were found to behave differently.<sup>11,12</sup> Therefore, we became interested to study the thermal rearrangement of 3-(4-aryloxybut-2-ynyloxy)-1-methylquinolin-2-ones<sup>13</sup> (3) which afforded 3*H*-pyrano[2,3-*c*]quinolones (4) and furo[2,3-*c*]quinolones (5). The 3*H*-pyrano[2,3-*c*]quinolones (4) contain allyl phenyl ether moiety which is a potential site for a further [3,3] sigmatropic rearrangement (Claisen). This prompted us to undertake a study on the thermal rearrangement of 3*H*-pyrano[2,3-*c*]quinolones (4) with a view to synthesise polyheterocycles (6). In this paper, we report<sup>14</sup> details of our investigation on the synthesis of furo[2,3-*c*]quinolin-4(5*H*)-ones.

The starting materials (4*a-k*) were prepared according to earlier published procedure<sup>13</sup> from the corresponding 3-(4-aryloxybut-2-ynyloxy)-1-methylquinolin-2-ones (3) (Scheme).

*N,N*-Diethylaniline is a solvent of choice for conducting thermal Claisen rearrangement of allyl phenyl and phenyl propargyl ethers. Therefore, the substrate (4*a*) was subjected to further rearrangement by refluxing in *N,N*-diethylaniline for 8 h to give a white crystalline solid, mp 180°C in 79 % yield. This was characterised from its elemental analysis and spectral data as 1-aryloxymethyl-2-methylfuro[2,3-*c*]quinolin-4(5*H*)-one (5*a*). Its mixed mp and superimposable IR spectrum with an authentic sample<sup>13</sup> also corroborated this. The possibility of an occurrence of further Claisen rearrangement was excluded by this



The regiochemical outcome of this unusual ring contraction to form furan derivatives (**5**) is remarkable. In refluxing *N,N*-diethylaniline the pyran ring underwent ring opening which is then followed by base-catalyzed cyclization. The reaction is shown to be a general one by the successful conversion of eight pyran derivatives to their corresponding furan derivatives. Such a ring contraction has not been reported earlier.

## EXPERIMENTAL

Melting points are uncorrected. UV absorption spectra were recorded on a Hitachi 200-20 spectrophotometer and Shimadzu UV-2201 spectrophotometer for ethanol. IR spectra were run for KBr discs on a Perkin-Elmer 1330 apparatus. <sup>1</sup>H NMR spectra were determined for solutions in deuteriochloroform with SiMe<sub>4</sub> as internal standard on Zeol FX-100 (100 MHz) at the Indian Institute of Chemical Biology, Calcutta, Bruker 250 MHz at the University of Konstanz, Germany and Bruker 200 MHz at IIT Kharagpur. Elemental analysis and recording of MS spectra were carried out by RSIC (CDRI), Lucknow and also by University of Konstanz, Germany. Silica gel (60-120 mesh) was obtained from Qualigen. Extracts were dried over anhydrous sodium sulphate.

6-Bromo-3-hydroxy-1-methylquinolin-2(1*H*)-one (**1**, R = Br) was prepared according to published procedure.<sup>13</sup>

**6-Bromo-3-hydroxy-1-methylquinolin-2(1*H*)-one (1, R = Br)**, mp 202°C (chloroform) (40%); IR (ν, cm<sup>-1</sup>): 3266 and 1620; <sup>1</sup>H-NMR (δ, ppm) (100 MHz): 3.81 (s, 3H), 7.03 (s, 1H), 7.15 (s, 1H), 7.20-7.36 (d, J = 8 Hz, 1H), 7.43-7.64 (dd, J = 8, 2.5 Hz, 1H) and 7.68 (d, J = 3 Hz, 1H).

**General Procedure for the Preparation of 3-(4-Aryloxybut-2-ynyloxy)-1-methylquinolin-2-ones (3a-k)**. These were prepared according to earlier published procedure. Compounds (**3a-e**) are reported earlier.<sup>13</sup>

**6-Bromo-1-methyl-3-(4-phenoxybut-2-ynyloxy)quinolin-2-one (3f)**, mp 184°C (methanol) (86%); UV (λ, nm): 230 (log ε 4.28) and 326 (log ε 3.64); IR (ν, cm<sup>-1</sup>): 1670, 1580, 1520, 1450, 1325 and 1245; <sup>1</sup>H-NMR (δ, ppm) (100 MHz): 3.76 (s, 3H), 4.72 (t, J = 1.5 Hz, 2H), 4.88 (t, J = 1.5 Hz, 2H), 6.80-7.08 (m, 5H), 7.12-7.26 (m, 2H), 7.40-7.54 (dd, J = 8, 2.5 Hz, 1H) and 7.60 (d, J = 2.5 Hz, 1H); MS (m/z) 399 and 397 (M<sup>+</sup>). Anal. Calcd for C<sub>20</sub>H<sub>16</sub>NO<sub>3</sub>Br: C, 60.45; H, 4.03; N, 3.52. Found C, 60.46; H, 3.85; N, 3.42.

**6-Bromo-1-methyl-3-[4-(2'-methylphenoxy)but-2-ynyloxy]quinolin-2-one (3g)**, mp 159°C (methanol) (90%); UV (λ, nm): 276 (log ε 3.54), 287 (log ε 3.48) and 325 (log ε 3.57); IR (ν, cm<sup>-1</sup>): 1675, 1625, 1598, 1495, 1425, 1310 and 1230; <sup>1</sup>H-NMR (δ, ppm) (100 MHz): 2.20 (s, 3H), 3.77 (s, 3H), 4.76 (t, J = 1.5 Hz, 2H), 4.92 (t, J = 1.5 Hz, 2H), 6.76-7.14 (m, 5H), 7.22 (d, J = 8 Hz, 1H), 7.42-7.58 (dd, J = 8,

2.5 Hz, 1H) and 7.62 (d,  $J = 2.5$  Hz, 1H). Anal. Calcd for  $C_{21}H_{18}NO_3Br$ : C, 61.31; H, 4.38; N, 3.40. Found C, 61.09; H, 4.59; N, 3.66.

**6-Bromo-3-[4-(3',5'-dimethylphenoxy)but-2-ynyloxy]-1-methylquinolin-2-one (3h)**, mp 181°C (methanol) (91%); UV ( $\lambda$ , nm): 230 (log  $\epsilon$  4.57) and 277 (log  $\epsilon$  3.90); IR ( $\nu$ ,  $cm^{-1}$ ): 1675, 1625, 1600, 1510, 1425, 1325 and 1225;  $^1H$ -NMR ( $\delta$ , ppm) (100 MHz): 2.14 (s, 6H), 3.72 (s, 3H), 4.68 (t,  $J = 1.5$  Hz, 2H), 4.86 (t,  $J = 1.5$  Hz, 2H), 6.50 (s, 3H), 6.88 (s, 1H), 7.20 (d,  $J = 8$  Hz, 1H), 7.32-7.52 (dd,  $J = 8$ , 1.5 Hz, 1H) and 7.59 (d,  $J = 2.5$  Hz, 1H); MS ( $m/z$ ) 427 and 425 ( $M^+$ ). Anal. Calcd for  $C_{22}H_{20}NO_3Br$ : C, 62.12; H, 4.70; N, 3.29. Found C, 62.05; H, 4.78; N, 3.38.

**6-Bromo-3-[4-(2',4'-dimethylphenoxy)but-2-ynyloxy]-1-methylquinolin-2-one (3i)**, mp 134°C (methanol) (88%); UV ( $\lambda$ , nm): 230 (log  $\epsilon$  4.35), 277 (log  $\epsilon$  3.72) and 327 (log  $\epsilon$  3.69); IR ( $\nu$ ,  $cm^{-1}$ ): 1672, 1625, 1600, 1505, 1428, 1328 and 1230;  $^1H$ -NMR ( $\delta$ , ppm) (100 MHz): 2.15 (s, 3H), 2.20 (s, 3H), 3.75 (s, 3H), 4.71 (t,  $J = 1.5$  Hz, 2H), 4.87 (t,  $J = 1.5$  Hz, 2H), 6.76 (s, 2H), 6.91 (s, 1H), 7.19 (d,  $J = 8$  Hz, 1H), 7.28 (s, 1H), 7.40-7.55 (dd,  $J = 8$ , 2.5 Hz, 1H) and 7.61 (d,  $J = 2.5$  Hz, 1H); MS ( $m/z$ ) 427 and 425 ( $M^+$ ). Anal. Calcd for  $C_{22}H_{20}NO_3Br$ : C, 62.12; H, 4.70; N, 3.29. Found C, 62.07; H, 4.75; N, 3.36.

**6-Bromo-3-[4-(4'-methoxyphenoxy)but-2-ynyloxy]-1-methylquinolin-2-one (3j)**, mp 118°C (methanol) (84%); UV ( $\lambda$ , nm): 229 (log  $\epsilon$  4.59) and 326 (log  $\epsilon$  3.89); IR ( $\nu$ ,  $cm^{-1}$ ): 1768, 1620, 1510, 1463, 1425 and 1226;  $^1H$ -NMR ( $\delta$ , ppm) (250 MHz): 3.71 (s, 3H), 3.74 (s, 3H), 4.67 (t,  $J = 1.5$  Hz, 2H), 4.87 (t,  $J = 1.5$  Hz, 2H), 6.69-6.90 (m, 4H), 7.20 (d,  $J = 8$  Hz, 1H), 7.26 (s, 1H), 7.47-7.51 (dd,  $J = 8$ , 2.5 Hz, 1H) and 7.54 (d,  $J = 2.5$  Hz, 1H); MS ( $m/z$ ) 429 and 427 ( $M^+$ ). Anal. Calcd for  $C_{21}H_{18}NO_4Br$ : C, 59.02; H, 4.22; N, 3.28. Found C, 58.96; H, 4.16; N, 3.48.

**6-Bromo-3-[4-(2',4'-dichlorophenoxy)but-2-ynyloxy]-1-methylquinolin-2-one (3k)**, mp 169°C (methanol) (82%); UV ( $\lambda$ , nm): 223 (log  $\epsilon$  4.10) and 274 (log  $\epsilon$  3.60); IR ( $\nu$ ,  $cm^{-1}$ ): 1685, 1600, 1400, 1340, 1250 and 1165;  $^1H$ -NMR ( $\delta$ , ppm) (250 MHz): 3.75 (s, 3H), 4.79 (t,  $J = 1.5$  Hz, 2H), 4.86 (t,  $J = 1.5$  Hz, 2H), 6.80-6.92 (m, 3H), 7.19 (d,  $J = 8$  Hz, 1H), 7.26 (s, 1H), 7.46-7.54 (dd,  $J = 8$ , 2.5 Hz, 1H) and 7.57 (d,  $J = 2.5$  Hz, 1H). Anal. Calcd for  $C_{20}H_{14}NO_3BrCl_2$ : C, 51.61; H, 3.01; N, 3.01. Found C, 51.56; H, 3.20; N, 2.85.

**Thermal rearrangement of ethers (3a-k) in refluxing chlorobenzene.** This was carried out according to earlier published procedure.<sup>13</sup> Thermal rearrangement of **3a-e** is reported earlier.<sup>13</sup>

**9-Bromo-6-methyl-1-phenoxyethyl-3H-pyrano[2,3-c]quinolin-5(6H)-one (4f)**, mp 178°C (methanol) (94%); UV ( $\lambda$ , nm): 230 (log  $\epsilon$  4.28) and 326 (log  $\epsilon$  3.64); IR ( $\nu$ ,  $cm^{-1}$ ): 1660, 1635, 1600, 1570, 1422, 1330 and 1235;  $^1H$ -NMR ( $\delta$ , ppm) (100 MHz): 3.76 (s, 3H), 4.79 (d,  $J = 4$  Hz, 2H), 4.87 (s,

2H), 6.27 (t,  $J = 4$  Hz, 1H), 6.88-7.34 (m, 6H), 7.44-7.60 (dd,  $J = 8, 2.5$  Hz, 1H) and 8.06 (d,  $J = 2.5$  Hz, 1H); MS ( $m/z$ ) 399 and 397 ( $M^+$ ). Anal. Calcd for  $C_{20}H_{16}NO_3Br$ : C, 60.45; H, 4.03; N, 3.52. Found C, 60.30; H, 3.99; N, 3.63.

**9-Bromo-6-methyl-1-(2'-methylphenoxyethyl)-3H-pyrano[2,3-c]quinolin-5(6H)-one (4g)**, mp  $128^{\circ}C$  (methanol) (86%); UV ( $\lambda$ , nm): 230 ( $\log \epsilon$  4.54), 277 ( $\log \epsilon$  3.63) and 289 ( $\log \epsilon$  3.58); IR ( $\nu$ ,  $cm^{-1}$ ): 1659, 1640, 1580, 1500, 1460, 1422 and 1238;  $^1H$ -NMR ( $\delta$ , ppm) (100 MHz): 2.20 (s, 3H), 3.76 (s, 3H), 4.80 (d,  $J = 4$  Hz, 2H), 4.89 (s, 2H), 6.26 (t,  $J = 4$  Hz, 1H), 6.76-7.28 (m, 5H), 7.46-7.62 (dd,  $J = 8, 2.5$  Hz, 1H) and 8.09 (d,  $J = 2.5$  Hz, 1H); MS ( $m/z$ ) 413 and 411 ( $M^+$ ). Anal. Calcd for  $C_{21}H_{18}NO_3Br$ : C, 61.31; H, 4.38; N, 3.40. Found C, 61.12; H, 4.46; N, 3.21.

**9-Bromo-1-(3',5'-dimethylphenoxyethyl)-6-methyl-3H-pyrano[2,3-c]quinolin-5(6H)-one (4h)**, mp  $206^{\circ}C$  (methanol) (85%); UV ( $\lambda$ , nm): 232 ( $\log \epsilon$  4.60) and 332 ( $\log \epsilon$  3.84); IR ( $\nu$ ,  $cm^{-1}$ ): 1660, 1640, 1592, 1500, 1425, 1330 and 1225;  $^1H$ -NMR ( $\delta$ , ppm) (100 MHz): 2.28 (s, 6H), 3.75 (s, 3H), 4.78 (d,  $J = 4$  Hz, 2H), 4.82 (s, 2H), 6.26 (t,  $J = 4$  Hz, 1H), 6.56-6.72 (m, 3H), 7.24 (d,  $J = 8$  Hz, 1H), 7.48-7.62 (dd,  $J = 8, 2.5$  Hz, 1H) and 8.11 (d,  $J = 2.5$  Hz, 1H); MS ( $m/z$ ) 427 and 425 ( $M^+$ ). Anal. Calcd for  $C_{22}H_{20}NO_3Br$ : C, 61.12; H, 4.70; N, 3.29. Found C, 61.90; H, 4.85; N, 3.46.

**9-Bromo-1-(2',4'-dimethylphenoxyethyl)-6-methyl-3H-pyrano[2,3-c]quinolin-5(6H)-one (4i)**, mp  $160^{\circ}C$  (methanol) (26%); UV ( $\lambda$ , nm): 233 ( $\log \epsilon$  4.61) and 266 ( $\log \epsilon$  4.42); IR ( $\nu$ ,  $cm^{-1}$ ): 1780, 1750, 1720, 1560, 1460, 1310 and 1210;  $^1H$ -NMR ( $\delta$ , ppm) (100 MHz): 2.17 (s, 3H), 2.27 (s, 3H), 3.77 (s, 3H), 4.79 (d,  $J = 4$  Hz, 2H), 4.87 (s, 2H), 6.25 (t,  $J = 4$  Hz, 1H), 6.64-7.03 (m, 3H), 7.23 (d,  $J = 8$  Hz, 1H), 7.43-7.63 (dd,  $J = 8, 2.5$  Hz, 1H) and 8.12 (d,  $J = 2.5$  Hz, 1H); MS ( $m/z$ ) 427 and 425 ( $M^+$ ). Anal. Calcd for  $C_{22}H_{20}NO_3Br$ : C, 61.12; H, 4.70; N, 3.29. Found C, 62.15; H, 4.86; N, 3.12.

**9-Bromo-1-(4'-methoxyphenoxyethyl)-6-methyl-3H-pyrano[2,3-c]quinolin-5(6H)-one (4j)**, mp  $156^{\circ}C$  (methanol) (65%); UV ( $\lambda$ , nm): 230 ( $\log \epsilon$  4.55) and 277 ( $\log \epsilon$  3.65); IR ( $\nu$ ,  $cm^{-1}$ ): 1705, 1635, 1505, 1460, 1420 and 1245;  $^1H$ -NMR ( $\delta$ , ppm) (250 MHz): 3.76 (s, 3H), 3.79 (s, 3H), 4.78 (d,  $J = 5.2$  Hz, 2H), 4.80 (s, 2H), 6.25 (t,  $J = 4.6$  Hz, 1H), 6.80-6.99 (m, 4H), 7.25 (d,  $J = 8$  Hz, 1H), 7.48-7.58 (dd,  $J = 8, 2.5$  Hz, 1H) and 8.10 (d,  $J = 2.5$  Hz, 1H); MS ( $m/z$ ) 429 and 427 ( $M^+$ ). Anal. Calcd for  $C_{21}H_{18}NO_4Br$ : C, 59.02; H, 4.22; N, 3.28. Found C, 58.84; H, 4.45; N, 3.15.

**8-Bromo-2,5-dimethyl-1-(4'-methoxyphenoxyethyl)furo[2,3-c]quinolin-4(5H)-one (5j)**, mp  $182^{\circ}C$  (methanol) (35%); UV ( $\lambda$ , nm): 231 ( $\log \epsilon$  4.45) and 321 ( $\log \epsilon$  3.56); IR ( $\nu$ ,  $cm^{-1}$ ): 1680, 1622, 1570, 1514, 1445, 1410, 1300 and 1225;  $^1H$ -NMR ( $\delta$ , ppm) (250 MHz): 2.55 (s, 6H), 3.80 (s, 3H), 5.17 (s, 2H), 6.82-7.00 (m, 4H), 7.34 (d,  $J = 8$  Hz, 1H), 7.60-7.64 (dd,  $J = 8, 2.5$  Hz, 1H) and 8.21 (d,  $J = 2.5$  Hz, 1H); MS ( $m/z$ ) 429 and 427 ( $M^+$ ). Anal. Calcd for  $C_{21}H_{18}NO_4Br$ : C, 59.02; H, 4.22; N, 3.28. Found C, 58.92; H, 4.02; N, 3.42.

**9-Bromo-1-(2',4'-dichlorophenoxy)methyl-6-methyl-3H-pyrano[2,3-c]quinolin-5(6H)-one (4k)**, mp 176°C (methanol) (93%); UV ( $\lambda$ , nm): 225 (log  $\epsilon$  4.51) and 326 (log  $\epsilon$  3.76); IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1660, 1632, 1605, 1470, 1292, 1245 and 1200;  $^1\text{H-NMR}$  ( $\delta$ , ppm) (100 MHz): 3.76 (s, 3H), 4.80 (d,  $J = 4$  Hz, 2H), 4.94 (s, 2H), 6.30 (t,  $J = 4$  Hz, 1H), 6.80-7.08 (m, 2H), 7.38-7.66 (m, 3H), and 8.02 (d,  $J = 2.5$  Hz, 1H). Anal. Calcd for  $\text{C}_{20}\text{H}_{14}\text{NO}_3\text{BrCl}_2$ : C, 51.61; H, 3.01; N, 3.01. Found C, 51.28; H, 3.28; N, 2.89.

**General procedure for the conversion of pyran derivative (4a-d, 4f-i) to furan derivatives.** Compound (4a-k) (0.05 g) was refluxed in *N,N*-diethylaniline (2 mL) for 8 h. TLC indicated complete conversion of the starting material (4). The reaction mixture was cooled and poured into ice-cold 6*N* hydrochloric acid. Crude solid was separated and this was extracted with chloroform. The extract was washed with 3*N* hydrochloric acid, brine, water and dried ( $\text{Na}_2\text{SO}_4$ ). Evaporation of the solvent gave the crude product which was chromatographed over silica gel. Elution of the column with benzene gave exclusively 5a-d, 5f-i. The butynes(3a-d, 3f-i) on similar treatment and similar work up gave products (5a-d, 5f-i) (direct route).

**2,5-Dimethyl-1-phenoxyethylfuro[2,3-c]quinolin-4(5H)-one (5a)**, mp 180°C (methanol) (79%, direct 70%); UV ( $\lambda$ , nm): 224 (log  $\epsilon$  4.45) and 312 (log  $\epsilon$  3.57); IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1665, 1570, 1450, 1315 and 1220;  $^1\text{H-NMR}$  ( $\delta$ , ppm) (200 MHz): 2.57 (s, 3H), 3.84 (s, 3H), 5.24 (s, 2H), 7.01-7.08 (m, 3H), 7.21-7.39 (m, 3H), 7.45-7.58 (m, 2H) and 8.00 (d,  $J = 2.5$  Hz, 1H); MS ( $m/z$ ) 319 ( $M^+$ ). Anal. Calcd for  $\text{C}_{20}\text{H}_{17}\text{NO}_3$ : C, 75.24; H, 5.33; N, 4.39. Found C, 75.08; H, 5.22; N, 4.20.

**2,5-Dimethyl-1-(2'-methylphenoxy)methylfuro[2,3-c]quinolin-4(5H)-one (5b)**, mp 178°C (methanol) (69%, direct 80%); UV ( $\lambda$ , nm): 224 (log  $\epsilon$  4.68) and 312 (log  $\epsilon$  3.80); IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1655, 1595, 1560, 1485, 1430 and 1225;  $^1\text{H-NMR}$  ( $\delta$ , ppm) (100 MHz): 2.09 (s, 3H), 2.56 (s, 3H), 3.84 (s, 3H), 5.24 (s, 2H), 6.86-7.24 (m, 4H), 7.32-7.64 (m, 3H) and 8.08 (d,  $J = 8$  Hz, 1H); MS ( $m/z$ ) 333 ( $M^+$ ). Anal. Calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}_3$ : C, 75.68; H, 5.71; N, 4.20. Found C, 75.72; H, 5.86; N, 4.32.

**2,5-Dimethyl-1-(3',5'-dimethylphenoxy)methylfuro[2,3-c]quinolin-4(5H)-one (5c)**, mp 200°C (methanol) (79%, direct 80%), showed no depression of mp and gave superimposable IR spectra with an authentic sample<sup>13</sup> (lit. mp 200°C).

**1-(4'-Chlorophenoxy)methyl-2,5-dimethylfuro[2,3-c]quinolin-4(5H)-one (5d)**, mp 174°C (methanol) (75%, direct 73%), showed no depression of mp and superimposable IR spectra with an authentic sample<sup>13</sup> (lit. mp 174°C).

**8-Bromo-2,5-dimethyl-1-phenoxyethylfuro[2,3-c]quinolin-4(5H)-one (5f)**, mp 192°C (methanol) (76%, direct 70%); UV ( $\lambda$ , nm): 230 (log  $\epsilon$  4.66) and 320 (log  $\epsilon$  3.77); IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1656, 1590, 1550, 1485, 1430 and 1225;  $^1\text{H-NMR}$  ( $\delta$ , ppm) (200 MHz): 2.58 (s, 3H), 3.80 (s, 3H), 5.23 (s, 2H), 7.01-7.08 (m, 3H), 7.30-7.39 (m, 3H), 7.58-7.64 (dd,  $J = 8, 2.5$  Hz, 1H) and 8.17 (d,  $J = 2.5$  Hz, 1H); MS ( $m/z$ )

399 and 397 ( $M^+$ ). Anal. Calcd for  $C_{20}H_{16}NO_3Br$ : C, 60.45; H, 4.03; N, 3.52. Found C, 60.36; H, 3.91; N, 3.70.

**8-Bromo-2,5-dimethyl-1-(2'-methylphenoxy)methylfuro[2,3-c]quinolin-4(5H)-one (5g)**, mp 163°C (methanol) (70%, direct 80%); UV ( $\lambda$ , nm): 230 (log  $\epsilon$  4.59), 289 (log  $\epsilon$  3.72) and 321 (log  $\epsilon$  3.73); IR ( $\nu$ ,  $cm^{-1}$ ): 1670, 1565, 1500, 1448, 1315 and 1238;  $^1H$ -NMR ( $\delta$ , ppm) (100 MHz): 2.16 (s, 3H), 2.59 (s, 3H), 3.81 (s, 3H), 5.26 (s, 2H), 6.88-7.28 (m, 4H), 7.36 (d,  $J$  = 8 Hz, 1H), 7.57-7.72 (dd,  $J$  = 8, 2.5 Hz, 1H) and 8.26 (d,  $J$  = 2.5 Hz, 1H); MS ( $m/z$ ) 413 and 411 ( $M^+$ ). Anal. Calcd for  $C_{21}H_{18}NO_3Br$ : C, 61.31; H, 4.38; N, 3.40. Found C, 61.20; H, 4.57; N, 3.49.

**8-Bromo-2,5-dimethyl-1-(3',5'-dimethylphenoxy)methylfuro[2,3-c]quinolin-4(5H)-one (5h)**, mp 206°C (methanol) (73%, direct 71%); UV ( $\lambda$ , nm): 224 (log  $\epsilon$  4.23), 277 (log  $\epsilon$  3.58) and 319 (log  $\epsilon$  3.64); IR ( $\nu$ ,  $cm^{-1}$ ): 1680, 1615, 1600, 1568, 1445, 1410 and 1240;  $^1H$ -NMR ( $\delta$ , ppm) (100 MHz): 2.30 (s, 6H), 2.57 (s, 3H), 3.80 (s, 3H), 5.19 (s, 2H), 6.69 (s, 3H), 7.32 (d,  $J$  = 8 Hz, 1H), 7.54-7.72 (dd,  $J$  = 8, 2.5 Hz, 1H) and 8.22 (d,  $J$  = 2.5 Hz, 1H); MS ( $m/z$ ) 427 and 425 ( $M^+$ ). Anal. Calcd for  $C_{22}H_{20}NO_3Br$ : C, 62.12; H, 4.70; N, 3.29. Found C, 61.92; H, 4.56; N, 3.16.

**8-Bromo-2,5-dimethyl-1-(2',4'-dimethylphenoxy)methylfuro[2,3-c]quinolin-4(5H)-one (5i)**, mp 202°C (methanol) (66%, direct 65%); UV ( $\lambda$ , nm): 230 (log  $\epsilon$  4.60), 277 (log  $\epsilon$  3.78) and 322 (log  $\epsilon$  3.71); IR ( $\nu$ ,  $cm^{-1}$ ): 1740, 1600, 1570, 1435, 1400 and 1280;  $^1H$ -NMR ( $\delta$ , ppm) (100 MHz): 2.12 (s, 3H), 2.27 (s, 3H), 2.56 (s, 3H), 3.79 (s, 3H), 5.21 (s, 2H), 6.81-7.11 (m, 3H), 7.35 (d,  $J$  = 8 Hz, 1H), 7.55-7.71 (dd,  $J$  = 8, 2.5 Hz, 1H) and 8.27 (d,  $J$  = 2.5 Hz, 1H); MS ( $m/z$ ) 427 and 425 ( $M^+$ ). Anal. Calcd for  $C_{22}H_{20}NO_3Br$ : C, 62.12; H, 4.70; N, 3.29. Found C, 61.96; H, 4.52; N, 3.32.

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