CHEMISTRY OF SUBSTITUTED QUINOLINONES IV. REGIOSELECTIVE NUCLEOPHILIC SUBSTITUTION OF DICHLOROBENZO[*f*]QUINOLINE

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Abstract

1,3-Dichlorobenzo[*f*]quinoline **2** was obtained from 1-hydroxybenzo[*f*]quinolin-3-one **1**. Nucleophilic substitution, hydrolysis, hydrazinolysis and azidation reactions of compound **2** have been studied and found to be regioselective. Also, 1-Aminobenzo[*f*]quinolinone **11** was obtained and transformed into benzoquinolinylthiourea derivative **12**, naphtho-naphthyridinedione **13**, benzoquinolinylhydrazone **15** and benzo[*f*]quinolinylenamine **17**.

Introduction

Within the framework of research related to chemistry of substituted quinolinones,[1-3] we decided to investigate the conversion of annelated quinolinones bearing an acidic hydroxy function to its corresponding basic amino derivatives, which of wide synthetic utilities. Since reduction of azide function using catalytic hydrogenation methods may lead to different reduced products, we utilized Staudinger reaction to reduce azidoquinolinone to the desired basic aminoquinolinone derivative.

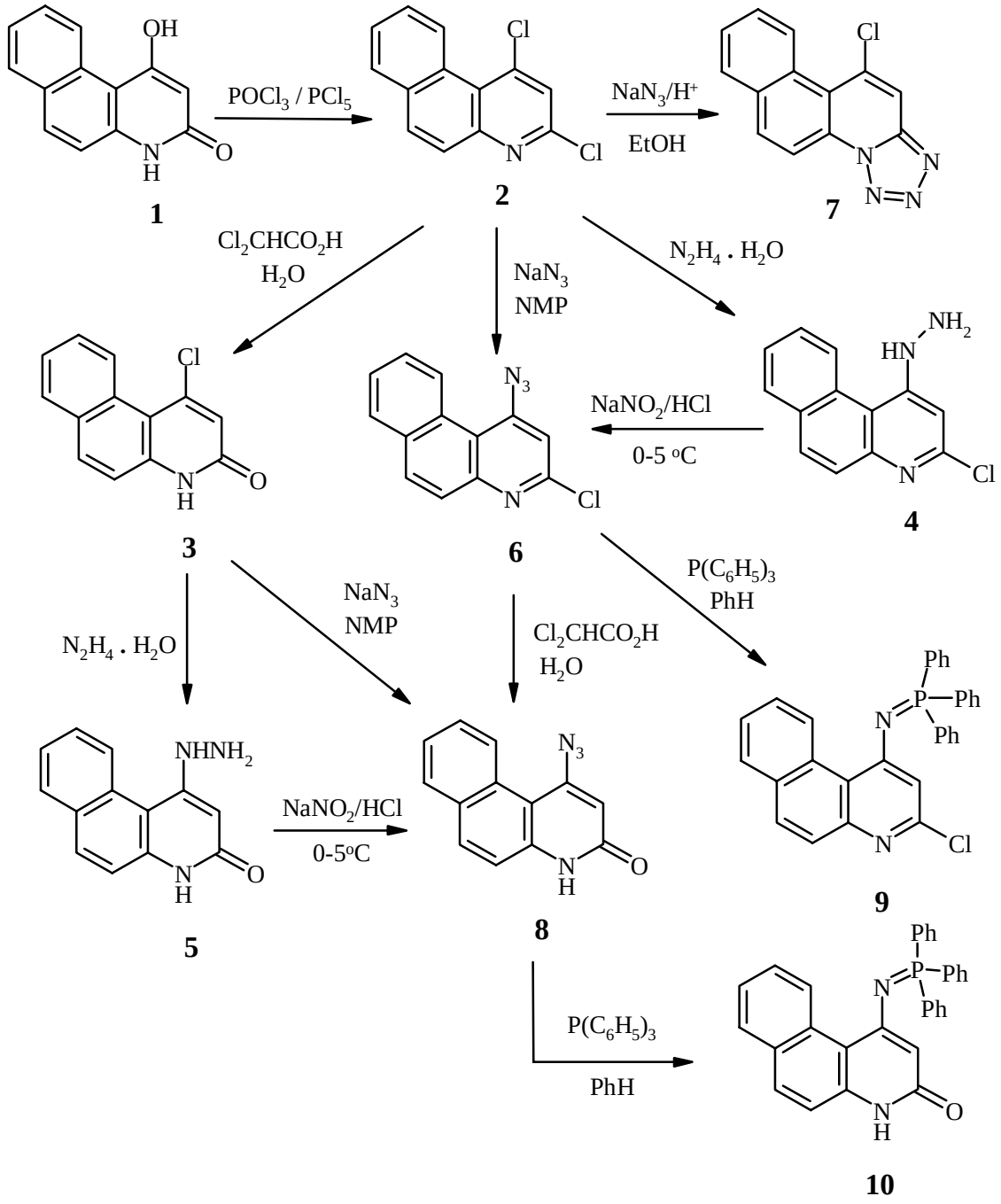
The necessity of this study arises from what we well know that literature lacks to such study of the chemical behavior on annelated quinolinones, in particular benzo derivatives, which are of great biological importance.[4,5]

Results and Discussion

1-Hydroxy-3,4-dihydrobenzo[*f*]quinolin-3-one (**1**)[6] was prepared and chlorinated using a mixture of phosphoryl chloride and phosphorus pentachloride to give 1,3-dichlorobenzo[*f*]quinoline (**2**).[7] Hydrolysis of the dichloro derivative **2** using 6M hydrochloric acid,[8] caused production of a tarry material which, after several crystallizations, gave very low yield of 1-chloro-3,4-dihydrobenzo[*f*]quinolin-3-one (**3**).

We found that softer aliphatic carboxylic acids gave better yields. The best one in our case was dichloroacetic acid. Upon hydrazinolysis of 1,3-dichlorobenzoquinolinone **2** with hydrazine hydrate was found regioselective, in which we have obtained only 3-chloro-1-hydrazinobenzo[*f*]quinoline (**4**). Similarly, nucleophilic substitution of 1-chloro atom of compound **3** led to 1-hydrazino-3,4-dihydrobenzo[*f*]quinolin-3-one (**5**). We noticed that hydrolysis of 1,3-dichlorobenzoquinoline **2** occurs at position-3 while hydrazinolysis takes place at position-1. This versatile behavior directed our attention to investigate the azidation of **2** reaction at different reaction conditions. Thus, when compound **2** was treated with sodium azide in *N*-methylpyrrolidin-2-one (NMP), only 1-azido-3-chlorobenzo[*f*]quinoline (**6**) was separated even on use of excess sodium azide. The same compound **6** was also afforded on treatment of compound **4** with nitrous acid. The presence of the stretching absorption band at 2110 cm^{-1} specific for azide function proved with no doubt that both azidation and hydrazinolysis processes take place selectively at position-1, whereas the encounter replacement at position-3 should finally gave 11-chlorobenzo[*f*]tetrazolo[1,5-*a*]quinoline (**7**). However compound **7** was obtained by carrying out azidation reaction of compound **2** in the presence of trifluoroacetic acid as a catalyst. This regioselectivity of dichlorobenzoquinoline **2** towards hydrolysis, hydrazinolysis and azidation reactions is highlighted by the findings in literature in which kinetic studies indicate that γ-chloro atom of dichloroquinolines is about two times more reactive towards nucleophiles and predominantly an addition-elimination process occurs.[9,10] Nucleophilic substitution of chlorine atom of compound **3** using sodium azide led to 1-azido-3,4-dihydrobenzo[*f*]quinolin-3-one (**8**). The same compound was obtained from acid hydrolysis of azide **6** and/or conversion of the hydrazino group of compound **5** to the azido one by action of nitrous acid. These three paths to get compound **8** strongly support our postulation about regioselectivity of compound **2** towards nucleophilic replacement. Azides **6** and **8** have been subjected to Staudinger reaction,[11,12] with triphenylphosphine (TPP), to give their corresponding phosphazenes **9** and **10**, respectively (Scheme 1).

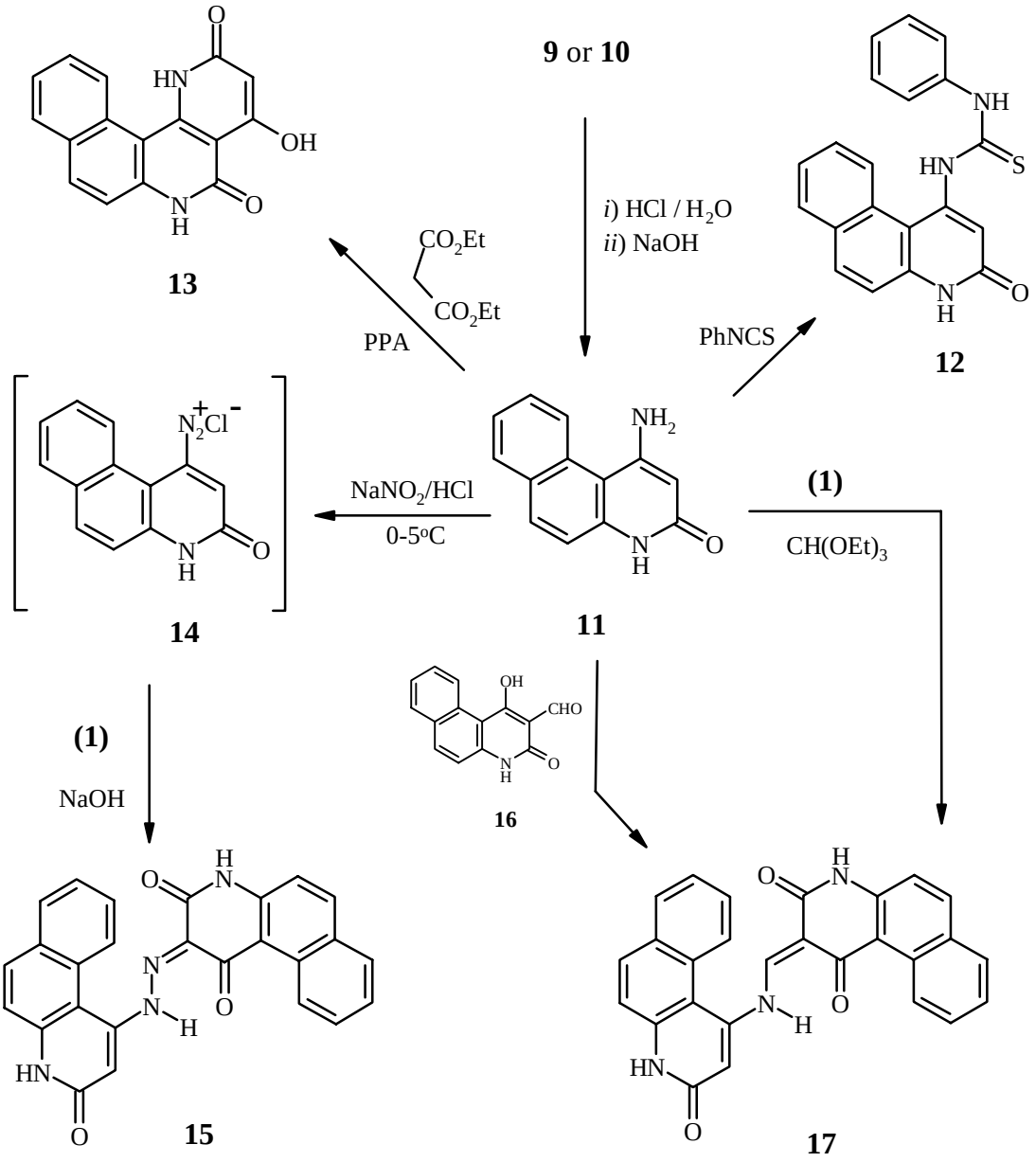
Scheme 1



Acid hydrolysis of either compound **9** or **10** afforded the targeted 1-amino-3,4-dihydrobenzo[*f*]quinolin-3-one (**11**). It is expected that getting compound **11** directly from derivative **9** may intermediary form the quinolinone **10** which then would be ready for smooth hydrolysis of the phosphoranylideneamino group to furnish the amine **11** along with triphenylphosphine oxide which is insoluble in the aqueous acidic medium.

Addition of the amine **11** to phenyl isothiocyanate resulted the corresponding thiourea derivative **12**. 4-Hydroxy-1,2,5,6-tetrahydronaphtho[2,1-*h*][1,6]naphthyridine-2,5-dione (**13**) was obtained when compound **11** was fused with diethyl malonate in the presence of polyphosphoric acid (PPA) [6]. Due to the well known wide spectrum industrial use of arylazoquinolinones as dyestuffs,[13,14] compound **11** was subjected to diazotization reaction by action of nitrous acid to give the diazonium chloride **14**, which was treated in situ with an aq. alkaline solution of compound **1**. The brick red material isolated from the latter reaction was characterized as 2-[(3-oxo-3,4-dihydro-benzo[*f*]quinolin-1-yl)hydrazono]-1,2,3,4-tetrahydrobenzo[*f*]quinoline-1,3-dione (**15**). The hydrazone structure of compound **15** was based on both IR and ^{1}H NMR spectral data, showing strong stretching absorption vibration at ν: 1688 cm^{-1} due to C=O group at C-1 beside a broad band at ν: 3168–2688 cm^{-1} due hydrogen bonded N–H. ^{1}H NMR spectrum of which reveals that the hydrazone form is the predominating structure where the characteristic peak of γ-hydroxy group is not observable. Finally, condensation of compound **11** with 2-formyl-1-hydroxy-3,4-dihydrobenzo[*f*]quinolin-3-one (**16**)[15] furnished the dibenzoquinolinyl-enamine **17**. The same product was also obtained when compounds **1** and **11** were subjected to thermal condensation with triethyl orthoformate.[16] The enamine form of the compound **17** was checked by its spectral data, which supported the keto-enamine structure on the cost of enol-amine structure by observation of a doublet peak at δ: 8.6 ppm (J = 13 Hz) characteristic for C–H of α-enamino cyclic ketones.[17] This result is similar to that obtained by Hansen et al.[18] which proved using isotopic studies that these compounds have to be present as keto-enamine form (Scheme 2). The structure of all the new compounds was elucidated by spectral and microanalytical results.

Scheme 2



Experimental

Melting points are uncorrected and were determined on a digital Gallen-Kamp MFB-595. IR spectra were taken on a Perkin-Elmer FT-IR 1650 instrument (ν, cm^{-1}), using samples in KBr disks. ^1H NMR spectra were recorded on a Jeol FX-90 (90 MHz) spectrometer (δ, ppm), using DMSO-d_6 as a solvent and TMS as internal standard. Elemental microanalyses were performed on a Perkin-Elmer CHN-2400 analyzer.

1-Hydroxy-3,4-dihydrobenzo[*f*]quinolin-3-one (1). A mixture of malonic acid (15.75 g, 0.15 mol), phosphoryl chloride (28 ml, 0.3 mol) and 2-aminonaphthalene (15 g, 0.1 mol) was refluxed, on a boiling water-bath, for 1 h. Then the reaction mixture was poured onto crushed ice and the precipitate that obtained was collected by filtration, washed with water and crystallized to give compound **1**, yield: 18.7 g (88 %), m.p. > 300 ^{o}C (acetic acid).[6]

1,3-Dichlorobenzo[*f*]quinoline (2). Phosphoryl chloride (93 ml, 1 mol) was added to a mixture of phosphorus penta-chloride (32 g, 0.15 mol) and hydroxyquinolone **1** (10.55 g, 0.05 mol) and then heated under reflux for 2 h. The excess phosphoryl chloride was removed *in vacuo* and the residue was poured onto crushed ice. The solution so obtained was neutralized using cold 2M sodium hydroxide solution to give a solid precipitate, which was collected by filtration and crystallized to give compound **2**, yield: 7.94 g (64 %), m.p. 130-131 ^{o}C (methanol).[7]

1-Chloro-3,4-dihydrobenzo[*f*]quinolin-3-one (3). A suspension of dichloro-quinoline **2** (2.48 g, 0.01 mol) in dilute dichloroacetic acid (50 ml, 50 %) was heated under reflux for 4 h. The solution was diluted with cold water and the solid precipitate so formed was collected by filtration and crystallized to produce compound **3**, yield: 1.7 g (74 %), m.p. 220-221 ^{o}C (DMF). IR, ν: 3214 (N–H), 2853, 1667 (C=O), 1603, 1566 and 762 (C–Cl). ^{1}H NMR, δ: 6.95 (s, 1H, 2–H), 7.24-8.05 (m, 6H, H_{arom} + 10–H) and 11.73 (b, 1H, N–H). Anal. calculated for $C_{13}H_8ClNO$ (229.66): C, 67.99; H, 3.51; N 6.10. Found: C, 68.10; H, 3.50; N, 6.00.

3-Chloro-1-hydrazinobenzo[*f*]quinoline (4). A mixture of dichloroquinoline **2** (0.5 g, 0.002 mol) and hydrazine hydrate (0.5 ml, 0.01 mol), in ethylene glycol (5 ml), was heated under reflux for 2 h and the solid product so afforded was collected by filtration. The residue was washed with methanol and recrystallized to give compound **4**, yield: 0.21 g (43 %), m.p. 178-180 ^{o}C (ethanol). IR, ν: 3422, 3330, 3265 (NH_2, N–H), 1620

(C=N), 1582 and 1548. ^{1}H NMR, δ: 4.20 (s, 2H, NH_2), 6.86 (s, 1H, 2–H), 7.28-8.03 (m, 6H, H_{arom} + 10–H) and 8.20 (b, 1H, N–H). Anal. calculated for $C_{13}H_{10}ClN_3$ (243.70): C, 64.07; H, 4.14; N, 17.24. Found: C, 63.80; H, 4.00; N, 17.10.

1-Hydrazino-3,4-dihydrobenzo[*f*]quinolin-3-one (5). To a solution of chloroquinolone **3** (2.3 g, 0.01 mol), in DMF (20 ml), hydrazine hydrate (2.5 ml, 0.05 mol) was added and then heated under reflux for 5 h. The reaction mixture was left to cool and poured onto cold water. The formed deposits collected by filtration and crystallized to give compound **5**, yield: 1.4 g (62 %), m.p. > 300 °C (n-butanol). IR, ν: 3435, 3369 (NH_2), 3293, 3196 (N–H), 1651 (C=O), 1582, 1544 and 1508. ^{1}H NMR, δ: 4.22 (s, 2H, NH_2), 6.15 (s, 1H, 2–H), 7.24-7.95 (m, 6H, H_{arom} + 10–H), 8.25 (b, 1H, N–H) and 11.28 (b, 1H, CON–H). Anal. calculated for $C_{13}H_{11}N_3O$ (225.25): C, 69.32; H, 4.92; N, 18.66. Found: C, 69.20; H, 4.80; N, 18.50.

1-Azido-3-chlorobenzo[*f*]quinoline (6). Procedure A. To a solution of dichloroquinoline **2** (2.48 g, 0.01 mol), in N-methylpyrrolidone (25 ml), sodium azide (1 g, 0.015 mol) was added and then stirred at 60-70 °C for 6 h. Then, the reaction mixture was poured onto cold water and the precipitate so formed was collected by filtration and crystallized to give azidoquinoline **6**, yield: 2.2 g (86 %), m.p. 167-168 °C (acetone). IR, ν: 3049, 2110 (N_3), 1612 (C=N), 1557, 1518, 1486 and 746 (C–Cl). ^{1}H NMR, δ: 7.01 (s, 1H, 2–H), 7.46-7.85 (m, 5H, H_{arom}) and 8.15 (d, 1H, 10–H). Anal. calculated for $C_{13}H_7ClN_4$ (254.67): C, 61.31; H, 2.77; N, 22.00. Found: C, 61.20; H, 2.60; N, 21.80.

Procedure B. To a solution of hydrazinoquinoline **4** (1.22 g, 0.005 mol), in hydrochloric acid (10 ml, 1M), sodium nitrite (5 ml, 1M) was added dropwise, with continuos stirring at 0-5 °C over a period of 15 min. Then the reaction mixture was stirred at room temperature for additional 30 min and the precipitate so obtained was collected by filtration and crystallized give compound **6**, yield: 0.96 g (75 %), (identified by mixed m.p. and spectra).

11-Chlorobenzo[*f*]tetrazolo[1,5-*a*]quinoline (7). A mixture of dichloroquinoline **2** (2.48 g, 0.01 mol), sodium azide (0.65 g, 0.01 mol) and trifluoroacetic acid (0.2 ml), in ethanol (30 ml), was stirred at 80-90 °C for 4 h. Then, the mixture was poured onto cold water and the deposits so formed was collected by filtration and crystallized to give compound **7**, yield: 1.21 g (43 %), m.p. 148-149 °C (methanol). IR, ν: 3052, 1623 (C=N), 1556, 1211, 1153 and 1101 (tetrazole ring). ^{1}H NMR, δ: 6.99 (s, 1H, 12–H), 7.30-7.78 (m, 3H, 7–H, 8–H, 9–H), 8.25 (d, 1H, 10–H), 8.40 (d, 1H, 6–H) and 8.85 (d, 1H, 5–H). Anal. calculated for $C_{13}H_7ClN_4$ (254.67): C, 61.31; H, 2.77; N, 22.00. Found: C, 61.10; H, 2.50; N, 21.90.

1-Azido-3,4-dihydrobenzo[*f*]quinolin-3-one (8). Procedure A. A mixture of chloroquinolone **3** (1.15 g, 0.005 mol) and sodium azide (0.65 g, 0.01 mol), in N-methylpyrrolidone (25 ml), was stirred at 60-80 °C for 6 h. Then, the mixture was poured onto cold water and the precipitate material so formed was collected by filtration and crystallized to give compound **8**, yield: 0.5 g (42 %), m.p. 268-270 °C (DMF). IR, ν: 3047, 2115 (N_3), 1667 (C=O), 1613, 1566, 1528 and 1488. ^{1}H NMR, δ: 6.69 (s, 1H, 2–H), 7.22-7.86 (m, 6H, H_{arom}) and 10.66 (b, 1H, CON–H). Anal. calculated for $C_{13}H_8N_4O$ (236.23): C, 66.10; H, 3.41; N, 23.72. Found: C, 66.00; H, 3.40; N, 23.50.

Procedure B. A suspension of azidoquinoline **6** (0.64 g, 0.0025 mol) in dilute dichloro-acetic acid (30 ml, 50 %) was refluxed for 8 h. Then solution was poured onto crushed ice and the precipitate so formed was collected by filtration and crystallized to produce compound **8**, yield: 0.3 g (50 %) (identified by mixed m.p. and spectra).

Procedure C. To a solution of hydrazinoquinolone **5** (1.13 g, 0.005 mol), in hydrochloric acid (10 ml, 1 M), sodium nitrite (5 ml, 1 M) was added dropwise, with continuos stirring at 0-5 °C over a period of 15 min. Then the reaction mixture was stirred for further 30 min. and the deposit so formed was collected by filtration and crystallized to give compound **8**, yield: 0.65 g (55 %) (identified by mixed m.p. and spectra).

3-Chloro-1-[(triphenylphosphoranylidene)amino]benzo[*f*]quinoline (9). A solution of azidoquinoline **6** (2.54 g, 0.01 mol), in dry benzene (25 ml), was treated with triphenylphosphine (4.55 g, 0.02 mol) and refluxed for 4 h. Then benzene was evaporated *in vacuo* and the residue was triturated with diethyl ether (50 ml), collected by filtration and recrystallized to give compound **9**, yield: 3.3 g (67 %), m.p. 172-173 °C (pet. ether 40-60 °C). IR, ν: 3050, 1620 (C=N), 1588, 1555, 1510, 1486 and 1433 (P=N). ^{1}H NMR, δ: 7.05 (s, 1H, 2–H), 7.21-7.78 (m, 20H, H_{arom}) and 8.31 (d, 1H, 10–H). Anal. calculated for $C_{31}H_{22}N_2ClP$ (488.95): C, 76.15; H, 4.54; N, 5.73. Found: C, 76.20; H, 4.54; N, 5.60.

1-[(Triphenylphosphoranylidene)amino]-3,4-dihydrobenzo[*f*]quinolin-3-one (10). Using the same procedure to prepare compound **9**, the phosphazene **10** was obtained from azidoquinolone **8** (2.36 g, 0.01 mol) and triphenylphosphine (4.55 g, 0.02 mol). The product was crystallized to give phosphazene **10**, yield: 3.0 g (64 %), m.p. 222-224 °C (dioxane). IR, ν: 3195 (CON–H), 1650 (C=O), 1587, 1554, 1485 and 1435 (P=N). ^{1}H NMR, δ: 6.95 (s, 1H, 2–H), 7.13-7.92 (m, 20H, H_{arom}), 8.28 (d, 1H, 10–H) and 10.80 (s, 1H, CON–H). Anal. calculated for $C_{31}H_{23}N_2OP$ (470.50): C, 79.14; H, 4.93; N, 5.95. Found: C, 79.10; H, 4.80; N, 5.70.

1-Amino-3,4-dihydrobenzo[*f*]quinolin-3-one (11). A suspension of 0.002 mol of either phosphazene **9** (0.98 g) or **10** (0.94g), in hydrochloric acid (25 ml, 2 M), was heated under reflux for 2 h, then left to cool in a ice bath for 1 h. Triphenylphosphine oxide precipitate was filtered off and the clear filtrate was neutralized using aq. sodium carbonate solution till pH 8 was reached. The white solid that formed was collected by filtration and crystallized to give compound **11**, yield: 0.15 g (36 %, starting with **9**) and 0.18 g (43 %, starting with **10**), m.p. > 300 °C (DMF). IR, ν: 3429, 3304 (NH_2), 3195 (CON–H), 1638 (C=O), 1563, 1554, 1527 and 1490. ^{1}H NMR, δ: 6.20 (s, 2H, NH_2), 6.85 (s, 1H, 2–H), 7.22-7.89 (m, 6H, H_{arom} + 10–H) and 11.48 (s, 1H, CON–H). Anal. calculated for $C_{13}H_{10}N_2O$ (210.23): C, 74.27; H, 4.97; N, 13.33. Found: C, 74.10; H, 4.70; N, 13.20.

1-(3,4-Dihydro-3-oxobenzo[*f*]quinolin-1-yl)-3-phenyl-2-thiourea (12). To a suspension of aminoquinolone **11** (0.21 g, 0.001 mol), in dioxane (5 ml), phenyl isothiocyanate (0.15 ml, 0.00125 mol) was added and the mixture was heated under reflux for 30 min. Then, the reaction mixture was filtered while hot, giving a solid residue which was crystallized to give thiourea **12**, yield: 0.2 g (58 %), m.p. > 300 °C (DMF). IR, ν: 3301, 3176 (N–H), 1638 (C=O), 1587, 1565, 1358 and 1240 (NHC=S). ^{1}H NMR, δ: 6.55 (s, 1H, 2–H), 7.00-8.12 (m, 11H, H_{arom}), 9.43-9.52 (b, 2H, 2 x N–$H_{thiourea}$) and 10.95 (b, 1H, N–$H_{quinolone}$). Anal. calculated for $C_{20}H_{15}N_3OS$ (345.42): C, 69.54; H, 4.38; N, 12.16. Found: C, 69.50; H, 4.40; N, 11.90.

4-Hydroxy-1,2,5,6-tetrahydronaphtho[2,1-*h*][1,6]naphthyridine-2,5-dione (13). A mixture of aminoquinolone **11** (1.05 g, 0.005 mol), diethyl malonate (2 ml, 0.0125 mol) and polyphosphoric acid (3 g) was heated at 160-170 °C for 1 h and then the temperature was raised gradually to 220 °C over 30 min. The mixture was cool-ed and poured onto crushed ice. The precipitate so obtained was filtered off and dissolv-ed in aq. sodium hydroxide (10 ml, 2 M) and filtered. The clear solution was acidified with hydrochloric acid till complete precipitation and the solid so formed was collected by filtration and crystallized to give naphthyridine **13**, yield: 0.9 g (65 %), m.p.: > 300 °C (acetic acid). IR, ν: 3229-2676 (N–H + O–H), 1682 (C=O), 1651 (C=O), 1605, 1585, 1547 and 1521. ^{1}H NMR, δ: 6.82 (s, 1H, 3–H), 7.25-8.15 (m, 6H, H_{arom}), 10.90-11.20 (b, 2H, 2 x N–H) and 10.95 (b, 1H, O–H). Anal. calculated for $C_{16}H_{10}N_2O_3$ (278.27): C, 69.06; H, 3.62; N, 10.07. Found: C, 68.90; H, 3.50; N, 9.80.

2-[(3,4-Dihydro-3-oxobenzo[*f*]quinolin-1-yl)hydrazono]-1,2,3,4-tetrahydro-benzo[*f*]quinoline-1,3-dione (15). To a stirred solution of aminoquinolone **11** (0.42 g, 0.002 mol), in dilute hydrochloric acid (50 ml, 0.1 M), aq. sodium nitrite solution (20 ml, 0.1 M) was added drop-wise at 0-5 °C. The formed diazonium salt **14** was transferred portionwise to a stirred solution of 1-hydroxybenzo[*f*]quinolin-3-one **1** (0.42 g, 0.002 mol) in aq. sodium hydroxide (15 ml, 0.2 M). The separated brick red precipitate was

filtered off and crystallized to give hydrazone **15**, yield: 0.45 g (52 %), m.p. > 300 °C (DMF). IR, ν: 3186-2688 (H-bonded N–H), 1688 (C=O $_{\gamma\text{-pyridone}}$), 1650-1637 (C=O $_{\alpha\text{-pyridone}}$), 1620 (C=N), 1582 and 1527. ^{1}H NMR, δ: 6.95 (s, 1H, 2–H), 7.20-8.14 (m, 13H, H_{arom} + N–H $_{hydrazone}$) and 10.54-11.02 (b, 2H, 2 x N–H $_{quinolone}$). Anal. calculated for $C_{26}H_{16}N_4O_3$ (432.44): C, 72.21; H, 3.73; N, 12.96. Found: C, 72.00; H, 3.50; N, 12.80.

2-[(3,4-Dihydro-3-oxobenzo[*f*]quinolin-1-yl)aminomethylene]-1,2,3,4-tetrahydro-benzo[*f*]quinoline-1,3-dione (17). Procedure A. A mixture of amino-quinolone **11** (0.42 g, 0.002 mol) and 2-formylquinolone **16**[15] (0.48 g, 0.002 mol), in DMF (25 ml) was heated under reflux for 2 h. The crystalline material that separated during the course of reaction was filtered while hot, washed with ethanol (20 ml) and recrystallized to give compound **17**, yield: 0.7 g (81 %), m.p. > 300 °C (DMSO). IR, ν: 3173-2880 (H-bonded N–H), 1682 (C=O $_{\gamma\text{-pyridone}}$), 1652-1638 (C=O $_{\alpha\text{-pyridone}}$), 1608, 1557 and 1518. ^{1}H NMR, δ: 6.96 (s, 1H, 2–H), 7.22-8.12 (m, 12H, H_{arom}), 8.60 (d, *J* = 13Hz, 1H, C–$H_{methylene}$), 11.14-11.60 (bs, 2H, 2 x N–$H_{quinolone}$) and 12.24 (b, 1H, N–$H_{enamine}$). Anal. calculated for $C_{27}H_{17}N_3O_3$ (431.45): C, 75.16; H, 3.97; N, 9.74. Found: C, 75.00; H, 3.80; N, 9.50.

Procedure B. A mixture of equimolar amounts (0.0025 mol) of aminoquinolone **11** (0.53 g), hydroxyquinolone **1** (0.53 g) and triethyl orthoformate (0.43 ml) in ethylene glycol (10 ml) was heated using short air condenser at 100-120 °C for 20 min. The temperature was then raised gradually to 190 °C for an additional hour. The solid that separated during the course of reaction was triturated with ethanol (25 ml), filtered and crystallized to give compound **17**, yield: 0.71 g (65 %) (identified by m.p. and spectra).

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Povzetek

1,3-Diklorobenzo[*f*]kinolin **2** smo pripravili iz 1-hidroksibenzo[*f*]kinolin-3-ona **1**. Ugotovili smo, da nukleofilne substitucije, hidroliza, hidrazinoliza in reakcija z azidom s spojino **2** potečejo regioselektivno. Pripravili smo tudi 1-aminobenzo[*f*]kinolinon **11** in ga pretvorili v derivat benzokinoliniltiosečnmine **12**, nafto-nafthiridindion **13**, benzokinolinilhidrazon **15** in benzo[*f*]kinolinilenamin **17**.