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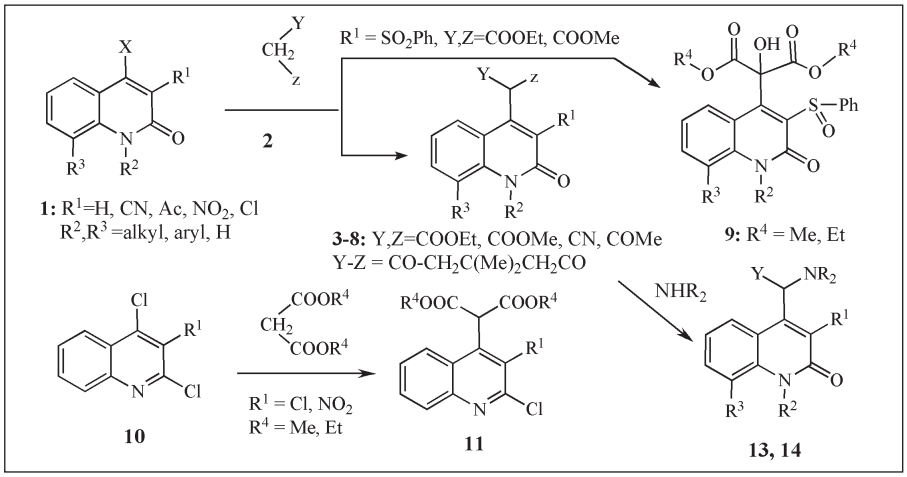

4-Chloro- or 4-tosyloxyquinolines **1** and **10** react with CH-acidic compounds such as malonates **2a,b**, ethyl cyanoacetate (**2c**), malononitrile (**2d**), ethyl acetoacetate (**2e**), acetylacetone (**2f**) or dimedone (**2g**) under mild conditions and good yields to quinolin-4-yl substituted derivatives **3-8** and **11**. With 3-phenylsulfonylquinolones **1i-k** a redox reaction to 2-hydroxy-2-quinolin-4-yl-malonates **9** was observed. Amination of 3-nitroquinolinyl malonate **3f** leads to malonester-amides **13** and **14**.

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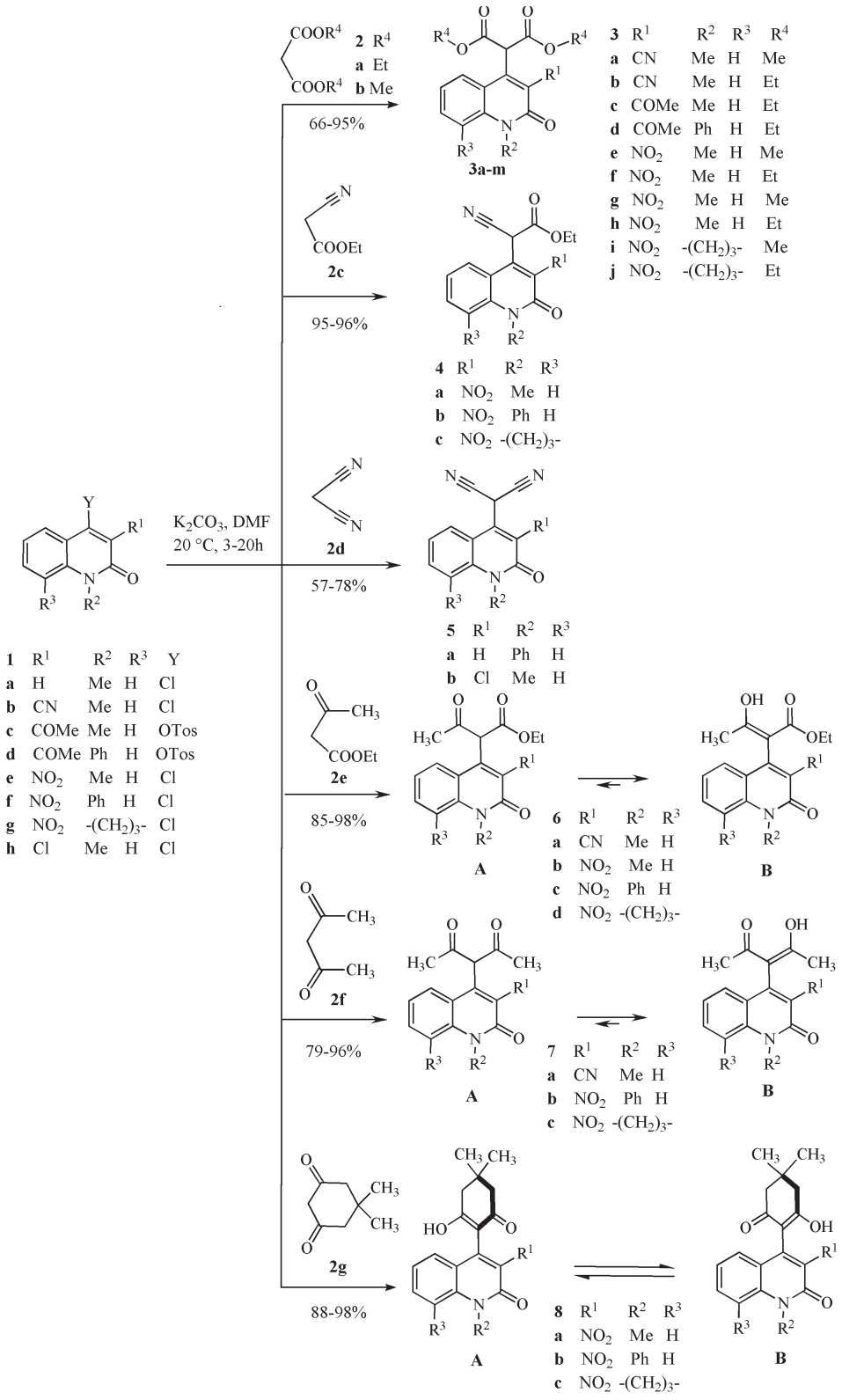
Recently we could show that 3-nitroquinolin-4-yl-malonates, obtained from 4-chloro-3-nitroquinolones and malonates, give in thermal reactions either quinolinylacetates or a ringclosure reaction to isoxazolo[3,4-*c*]quinolines [1]. A literature survey revealed that the synthesis of quinolinyl substituted malonates, cyanoacetates and related CH-acidic compounds has found great interest either due to their biological properties or their use as synthons for further reactions [2-6]. The synthetic pathways include ring transformations [6], cine-substitution [3,4], metallation [2] and substitution with halo-hetaryl compounds, however the latter one with poor results [2]. In this work we report on a study about the introduction of 4-quinolinyl substituents at the CH-acidic carbon of various CH-acidic compounds. Moreover, the influence of substituents in position 3 of the quinoline nucleus on this reaction was studied.

The reaction of ethyl- or methyl malonates **2a,b** as CH-acidic compounds with various 4-chloro- or 4-tosyloxy-2-quinolones **1b-g** in dimethylformamide and potassium carbonate as the base, was investigated and found to give good to excellent yields of 4-quinolinyl substituted malonates **3a-j**. It was reported recently that similar 3-nitroquinolones give such malonates of type **3** only in poor yields (8-37%) at reaction temperatures of about 100 °C using sodium hydride as the base [2]. It is likely that these reaction conditions favor already the decomposition reactions we have described earlier in a few examples [1]; however, with our mild reaction conditions 3-nitroquinolinyl-malonates **3e-j** were obtained in yields of 66-95%. Quinolones **1** having other electron-withdrawing groups in 3-position reacted too in excellent yields to the corresponding malonates **3**: in this manner, 4-chloro-3-cyanoquinolone **1b** gave with malonates **2a,b** in 85-86% yield the corresponding quinolinyl-malonates **3a,b**; 3-acetylquinolones **1c,d** with 4-tosyloxy substituents as leaving group gave with diethyl malonate (**2a**) in 66-69% yield the corresponding quinolinyl-malonates **3c,d**.

When ethyl cyanoacetate (**2c**) was used as CH-acidic compound the 3-nitroquinolones **1e-g** gave in excellent yields and short reaction times (3 hours compared with up to 20 hours in the malonate series [1]) the quinolinyl-cyanoacetates **4a-c**. Malononitrile (**2d**) reacted with 3-nitroquinolone **1e** to give a very labile compound that decomposed on work-up. Attempts to purify and identify the follow-up product were unsuccessful, but it seems from spectral data (*e.g.* mass of 239) that a reaction of one cyano group with the 3-nitro group of the quinolone has taken place. When the 3,4-dichloroquinolone **1h** was reacted with malononitrile (**2d**), the expected quinolinyl-

malononitrile **5b** was obtained in good yield. In the malononitrile series we were also successful with the reaction of the 3-unsubstituted quinolone **1a** using a slightly changed reaction protocol: the reaction was carried out in

Scheme 1



refluxing dimethylformamide (instead of room temperature) and use of sodium acetate as the base (instead of potassium carbonate). In this manner, we obtained in 57% yield the expected quinolinyl-malononitrile **5a**.

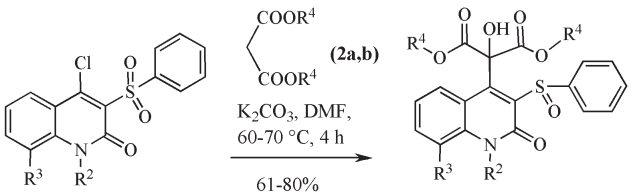
The reaction of ethyl acetoacetate (**2e**) with 3-cyanoquinolone **1b** or 3-nitroquinolones **1e-g** gave in excellent yields quinolinyl-acetoacetates **6a-d**. The ^{1}H nmr and ^{13}C nmr spectra spectral data show that these compounds exist predominantly in the enolized form **B** because CH signals disappeared and OH signals can be observed. Both the ^{1}H and ^{13}C NMR spectra of **6** showed two sets of peaks for all protons and carbons, which is indicative of *E/Z* isomers at the enolic double bond. Interestingly, the OH signals at 10.50 (broad singlet) and 13.2 ppm (sharp singlet) show the different environment of the isomers, enabling in the *Z*-form hydrogen bonding to the ester carbonyl group. Mass spectra reveal the correct mass signals; infrared spectra show an ester signal shifted to lower frequencies of 1660-1670 cm^{-1}, together with a weak OH signal, which indicates again hydrogen bonding of the enol structure **B**.

Acetylacetone (**2f**) gave similarly with 3-cyanoquinolone **1b** or 3-nitroquinolones **1f,g** the quinolinyl-substituted acetylacetones **7a-c**. Again the spectral data revealed that not the diketone structure **A** but the tautomeric enol structure **B** is favored: The ^{1}H nmr spectra do not show the CH signal; the ^{13}C shift of this carbon confirms the enolic structure **B**. In contrast to the acetoacetates **6**, no indication for *E/Z* isomers could be found. Infrared spectra show the carbonyl signals at lower frequencies of 1660-1670 similar to **6**. Mass spectra and elemental analysis confirmed the structures of **7**.

5,5-Dimethylcyclohexane-1,3-dione (dimedone, **2g**) as cyclic CH-acidic compound was found to react in the same manner as the open-chain compounds **2a-f** with 4-chloroquinolines **1e-g** to give in good yields the quinolinyl-substituted cyclohexanediones **8a-c**. The ^{1}H nmr spectra, ^{13}C DEPT 135 and 2D HMBC experiments again confirm the enolized form **B** of **8**. In the ^{13}C spectrum of **8a** two methyl signals were detected, but the CH_2 groups only gave rise to a broad ^{13}C signal around 46 ppm and the enolized cyclohexane carbonyl groups were broadenend beyond detection. These data can be explained by either a hindered rotation of the cyclohexene ring caused by the 3-nitro group of quinoline or a slowed conformational change of the cyclohexene ring around the C4-C5-C6 bonds of the cyclohexene. The broadening of ^{13}C signals points to flexibility on the NMR time scale (conformational exchange rates are in the range of shift differences *i.e.* several 100 s^{-1}). Mass spectra of **8a-c** confirm the structures, but only **8a** gave correct elemental analysis, whereas analyses of **8b, c** gave deviations of 0.7-0.9%, although decomposition studies by differential scanning calorimetry indicated thermal stability up to 270 °C.

Malonates **2a,b** reacted in good yields with 4-chloro-3-phenylsulfonylquinolones **1i-k** at 60-70 °C to pure, uniform products **9a-d**. The mass spectra and elemental analyses of these products were in accordance with structures corresponding to **3**. The ^{1}H nmr spectra, however, did not show any CH-signal of the CH-acidic group. A ^{13}C DEPT-135 nmr experiment confirmed the aliphatic CH_2 and CH_3 carbon atoms. One aliphatic carbon of the 1D ^{13}C nmr spectrum at 69.9 ppm was missing and can thereby be clarified as a quarternary carbon without hydrogen atoms. According to the shift it has to be bonded to a hetero atom, most likely an oxygen. All data are in agreement with the structure of 2-(3-phenylsulfinylquinolin-4-yl)-2-hydroxymalonates of structure **9a-d** formed by an intra- or intermolecular redox-reaction of the phenylsulfonyl compounds. In the literature the oxidation of heterocyclic substituted malonates to 2-hydroxymalonates has been described by reaction with bromine or hydrogen peroxide [7]. Separated signals deriving from diastereotopic sulfones could not be detected.

Scheme 2



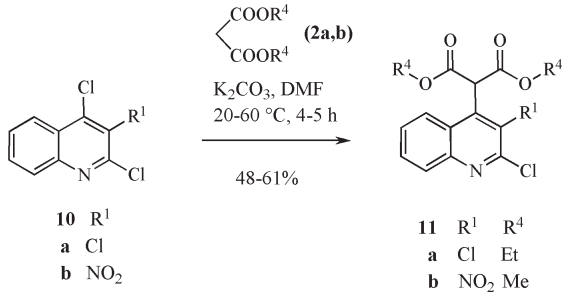
1 R^2 R^3
i Me H
j Ph H
k $-(CH_2)_3-$

9 R^2 R^3 R^4
a Me H Et
b Ph H Et
c $-(CH_2)_3-$ Me
d $-(CH_2)_3-$ Et

When malonates **2a,b** were brought to reaction with 2,4-dichloroquinolines **10**, the reaction took place to give only monosubstituted quinolinyl-malonates **11a,b**. As expected from former findings in regioselective nucleophilic displacements of 2,4-dichloroquinolines [8], the substitution in 4-position was assumed. These findings were confirmed by ^{13}C nmr spectra: the C-4 signal of the 3-chloro derivative **10a** at 142.6 ppm is shifted in **11a** to 140.6 ppm, whereas the C-2- signal remains nearly unchanged. Similar findings were obtained with the 3-nitro derivative **10b** and **11b**: the C-4 signal is shifted from 137.8 to 140.2 ppm. The reaction conditions were different depending on the substituent in 3-position of the quinoline: with 3-nitroquinolines **10b**, already at room temperature the reaction proceeded smoothly, whereas with 3-chloroquinolines **10a**, 60-70 °C was necessary as reaction temperature.

Recently we have studied the thermal behaviour of diethyl- and dimethyl malonates **3e-j** having 3-nitroquinolinyl substituents [1]. These findings show that depending

Scheme 3



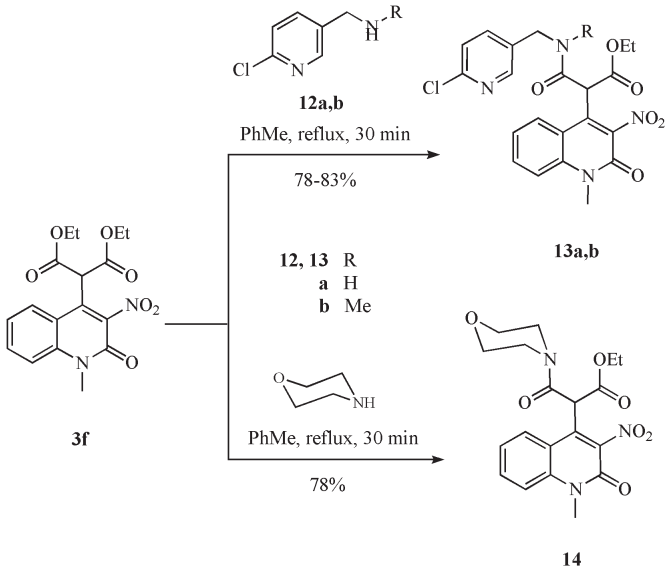
10 R^1
a Cl
b NO_2

11 R^1 R^4
a Cl Et
b NO_2 Me

on the ester substituent, either a ring closure reaction to isoxazolo[3,4-*c*]quinolones took place or quinolinyl-acetates were formed by decarboxylation. In this report we studied some amination reactions, which should give malondiamides. However, when diethyl quinolinylmalonate **3f** was reacted with primary or secondary amines such as pyridylmethanamines **12a,b** or morpholine, even with excess amines and long reaction times, only malonestermonoamides **13a,b** and **14** were formed.

Because diethyl- and dimethyl malonates **3e-j** have shown interesting thermal reactions [1], a series of the compounds obtained in this paper was investigated by thermoanalytical methods such as differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) in order to obtain hints for possible thermolytical reactions. DSC diagrams of 3-nitroquinolinyl-cyclohexenones **8a-c** showed sharp, single decomposition peaks between 268-278 °C with reaction enthalpies between –570 and – 840 mcal/mg without further decomposition signals. The thermal gravimetrical analysis indicates a mass loss of 11%, but the further diagram does not show a plateau, but a slope. Preparative experments by heating the compounds **8a-c** in diphenylether to 270-280 °C did not furnish a consistent product, but a mixture of many compounds. DSC diagrams of 3-nitroquinolinyl-acetoacetate **6b** and 3-nitroquinolinyl-acetylacetone **7b** showed a broad decomposition range at 157 and 229 °C, respectively and were not further investigated. Similarly, 2-(3-phenylsulfinylquinolin-4-yl)-2-hydroxymalonates **9b,c** gave broad decomposition signals in DSC measurements. Quinolinyl-malonate **11a** showed a decomposition signal at 312 °C in the DSC diagram which is too high for reasonable thermolytic reactions. Methyl 3-nitroquinolinyl-malonate **11b**, with a structure similar to 3-nitroquinolinyl-malonates **3f,h,j**, showed two exothermic peaks at 178 and 249 °C, the first one with a rather high reaction enthalpy of –380 mJ/mg. A preparative experiment, however, by heating **11a** to 170-180 °C in diphenylether, yielded a mixture of many compounds.

Scheme 4



EXPERIMENTAL

Melting points were determined on a Gallenkamp Melting Point Apparatus, Mod. MFB-595 in open capillary tubes. Calorimetric data were obtained on a Rheometric Scientific DSC-Plus instrument with the differential scanning calorimetry software Orchestrator V6.5.8. The differential scanning calorimetry (DSC) plots were recorded between 25 - 700 °C, with a heating rate of 2-10 °C/min, and 1.5-3 mg compound in sealed aluminium crucibles (11 bar). The thermogravimetric analyses (TGA) were recorded with a Perkin Elmer thermogravimetric analyzer TGA7

between 30-450 °C with a heating rate of 10°C/min, and 5-12 mg compound in platinum crucibles, using nitrogen as protective gas. The ^{1}H nmr spectra were recorded on a Bruker AMX 360 instrument (360 MHz ^{1}H frequency) or on a Bruker Avance DRX 500 instrument (500 MHz ^{1}H frequency). The ^{13}C nmr-spectra were recorded on a Bruker AMX 360 instrument (90 MHz ^{13}C frequency) or on a Bruker Avance DRX 500 instrument (125 MHz ^{13}C frequency). Chemical shifts are reported in ppm from internal tetramethylsilane standard and are given in δ-units. Evaluation of ^{1}H nmr spectra was performed using the software Mestrec 4. Infrared spectra were taken on a Mattson Galaxy Series FTIR 7020 instrument in potassium bromide pellets unless otherwise stated. Elemental analyses were performed on a Fisons elemental analyzer Mod. EA 1108, and are within ±0.4 of the theoretical percentages. Mass spectra were taken on a HP 1100 LC/MSD mass spectral instrument (positive or negative APCI: 50-200 eV, nitrogen). All reactions were monitored by thin layer chromatography, carried out on 0.2 mm silica gel 60 F-254 (Merck) plates using uv light (254 and 366 nm) for detection. Column chromatography was carried out on silica gel (Merck silica gel 60 H).

Common reagent-grade chemicals are either commercially available and were used without further purification or prepared by standard literature procedures.

4-Chloro-1-methyl-3-phenyl-2(1*H*)-quinolone (**1a**).

This compound was prepared from 4-hydroxy-1-methyl-3-phenyl-2(1*H*)-quinolone according to ref. [9].

4-Chlor-1-methyl-2-oxo-1,2-dihydroquinolin-3-carbonitril (**1b**).

A solution of 4-hydroxy-1-methyl-2-oxo-1,2-dihydroquinolin-3-carbonitrile [10] (14.0 g, 70 mmol) in abs. triethylamine (10 mL) and phosphoroxychloride (100 mL) was heated under reflux for 72 hours. Excess phosphoroxychloride was removed *in vacuo* and the residue poured on crushed ice (200 g). The mixture was neutralized with 6 *N* sodium hydroxyide solution and the precipitated product filtered by suction and washed with water until acid-free. The yield was 10.30 g (67 %) light-brown prisms, mp 198-200 °C (ethanol); ir: 2220 s, 1640 s, 1610s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 3.65 (s, NMe), 7.49 (t, J = 7.3 Hz, 1 ArH), 7.73 (d, J = 8.6 Hz, 8-H), 7.91 (t, J = 7.2 Hz, 1 ArH), 8.07 (d, J = 7.4 Hz, 5-H).

Anal. Calcd. for $C_{11}H_7ClN_2O$: C, 60.43; H, 3.23; N, 12.81. Found: C, 60.12; H, 3.46; N, 12.56.

3-Acetyl-1-methyl-4-tosyloxy-2(1*H*)-quinolone (**1c**) and 3-Acetyl-1-phenyl-4-tosyloxy-2(1*H*)-quinolone (**1d**).

These compounds were prepared from 3-acetyl-4-hydroxy-2(1*H*)-quinolones and tosylchloride according to ref. [11].

4-Chloro-1-methyl-3-nitro-2(1*H*)-quinolone (**1e**), 4-Chloro-1-phenyl-3-nitro-2(1*H*)-quinolone (**1f**) and 1-Chloro-2-nitro-6,7-dihydro-benzo[*ij*]quinolizin-3-one (**1g**).

These compounds were prepared from 4-hydroxy-3-nitro-2(1*H*)-quinolones and phosphoryl chloride according to ref. [12].

3,4-Dichloro-1-methyl-2(1*H*)-quinolone (**1h**).

This compound was prepared from 3-chloro-4-hydroxy-2(1*H*)-quinolone and phosphoryl chloride according to ref. [8].

4-Chloro-1-methyl-3-phenylsulfonyl-2(1*H*)-quinolone (**1i**), 4-Chloro-1-phenyl-3-phenylsulfonyl-2(1*H*)-quinolone (**1j**) and 1-Chloro-2-phenylsulfonyl-6,7-dihydro-benzo[*ij*]quinolizin-3-one (**1k**).

These compounds were prepared from 3-phenylsulfonyl-4-hydroxy-2(1*H*)-quinolones and phosphorylchloride according to ref. [13].

Dimethyl (3-Cyano-1-methyl-2-oxo-1,2-dihydroquinolin-4-yl)-malonate (**3a**).

To a solution of 4-chloro-3-cyanoquinolone **1b** (2.18 g, 10 mmol) and dimethyl malonate (**2b**) (2.64 g, 20 mmol) in dimethylformamide (40 mL), anhydrous potassium carbonate (2.8 g, 20 mmol) was added at 20 °C. The mixture was stirred at room temperature for 3 hours, then poured into ice/water (100 mL) and acidified with conc. hydrochloric acid to pH = 1. After standing for 12 hours at room temperature, the formed precipitate was filtered by suction, washed with water until acid-free and dried. The yield was 2.70 g (86 %) fine brown needles, mp 195 °C (ethanol); ir: 2950 w, 2220 s, 1760 s, 1740 s, 1650 s, cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 3.78 (s, NMe), 3.81 (s, 2 OMe), 5.48 (s, CH), 7.33 and 7.74 (2 t, J = 7.1 Hz, 6-H, 7-H), 7.45 (d, J = 7.5 Hz, 8-H), 7.85 (d, J = 6 Hz, 5-H).

Anal. Calcd. for $C_{16}H_{14}N_2O_5$: C, 61.14; H, 4.49; N, 8.91. Found: C, 61.17; H, 4.36; N, 8.81.

Diethyl (3-Cyano-1-methyl-2-oxo-1,2-dihydroquinolin-4-yl)-malonate (**3b**).

This compound was prepared from 4-chloro-3-cyanoquinolone **1b** (2.18 g, 10 mmol) and diethyl malonate (**2a**) (3.20 g, 20 mmol) according to the procedure described for **3a**; the yield was 2.90 g (85 %) fine pale-yellow needles, mp 151 °C (ethanol); ir: 3000 m, 2220 s, 1750 s, 1720 m, 1650 s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 1.10 (t, J = 7.0 Hz, 2 ethyl-CH_3), 3.80 (s, NMe), 4.30 (q, J = 6.0 Hz, 2 ethyl-CH_2), 5.50 (s, CH), 7.30 and 7.70 (2 t, J = 7.1 Hz, 6-H, 7-H), 7.50 (d, J = 7.2 Hz, 8-H), 7.90 (d, J = 7 Hz, 5-H); ms: *m/z* (%) 343 (20, M+1), 342 (100, M), 270 (57, M – COOEt), 198 (66, M – 2 COOEt).

Anal. Calcd. for $C_{18}H_{18}N_2O_5$: C, 63.15; H, 5.30; N, 8.18. Found: C, 63.11; H, 5.24; N, 8.17.

Diethyl (3-Acetyl-1-methyl-2-oxo-1,2-dihydroquinolin-4-yl)-malonate (**3c**).

This compound was prepared from 3-acetyl-4-tosyloxyquinolone **1c** (3.71 g, 10 mmol) and diethyl malonate (**2a**) (3.20 g, 20 mmol) according to the procedure described for **3a** (20 hours reaction time); the yield was 2.27 g (69 %) colorless microprisms, mp 128 °C (ethanol); ir: 3000 m, 1760 s, 1730 s, 1700 s, 1650 m cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 1.20 (t, J = 7.0 Hz, 2 ethyl-CH_3), 2.60 (s, Me), 3.70 (s, NMe), 4.18-4.26 (m, 2 ethyl-CH_2), 5.00 (s, CH), 7.25 and 7.60 (2 t, J = 7.1 Hz, 6-H, 7-H), 7.40 (d, J = 8.5 Hz, 8-H), 7.86 (d, J = 8.0 Hz, 5-H).

Anal. Calcd. for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.12; H, 5.89; N, 4.13.

Diethyl (3-Acetyl-2-oxo-1-phenyl-1,2-dihydroquinolin-4-yl)-malonate (**3d**).

This compound was prepared from 3-acetyl-4-tosyloxyquinolone **1d** (2.30 g, 5 mmol) and diethyl malonate (**2a**) (1.60 g, 10 mmol) according to the procedure described for **3a** (13 hours reaction time); the yield was 1.40 g (66 %) light yellow needles, mp 134.8 °C (ethanol); ir: 2940 m, 1760 s, 1740 s, 1650 m cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 1.25 (t, J = 7.0 Hz, 2 ethyl-CH_2), 2.65 (s, Me), 4.20-435 (m, 2 ethyl-CH_2), 5.20 (s, CH), 6.70 (d, J = 7.5 Hz, 8-H), 7.20-7.40 (m, 4 ArH), 7.55-7.70 (m, 3 ArH), 7.90

(d, J = 8.1 Hz, 5-H); ms: *m/z* (%) 422 (34, M+1), 421 (100, M), 376 (16), 304 (20).

Anal. Calcd. for $C_{24}H_{23}NO_6$: C, 68.40; H, 5.50; N, 3.32. Found: C, 68.64; H, 5.79; N, 3.23.

Dimethyl (1-Methyl-3-nitro-2-oxo-1,2-dihydroquinolin-4-yl)malonate (**3e**), Diethyl (1-Methyl-3-nitro-2-oxo-1,2-dihydroquinolin-4-yl)malonate (**3f**), Dimethyl (3-Nitro-2-oxo-1-phenyl-1,2-dihydroquinolin-4-yl)malonate (**3g**), Diethyl (3-Nitro-2-oxo-1-phenyl-1,2-dihydroquinolin-4-yl)malonate (**3h**), Dimethyl (2-Nitro-3-oxo-6,7-dihydro-3*H*,5*H*-benzo[*ij*]quinolizin-4-yl)malonate (**3i**) and Diethyl (2-Nitro-3-oxo-6,7-dihydro-3*H,*5*H*-benzo[*ij*]quinolizin-4-yl)malonate (**3j**).

These compounds were prepared from 4-chloro-3-nitroquinolones **1e,f** and 1-chloro-2-nitro-benzoquinolizinone (**1g**) with malonates **2a,b** according to ref. [1].

Ethyl Cyano-(1-methyl-3-nitro-2-oxo-1,2-dihydroquinolin-4-yl)acetate (**4a**).

This compound was prepared from 4-chloro-3-nitroquinolone **1e** (2.39 g, 10 mmol) and ethyl cyanoacetate (**2c**) (2.26 g, 20 mmol) according to the procedure described for **3a** (3 hours reaction time); the yield was 3.02 g (95 %) orange microprisms, mp 161 °C (ethanol); ir: 2900 m, 2260 m, 1750 s, 1660 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.30 (t, J = 7 Hz, ethyl-CH_3), 3.81 (s, NMe), 4.2-4.4 (m, ethyl-CH_2), 5.10 (s, CH), 7.42-7.63 (m, 2 ArH), 7.81 (d, J = 7.1 Hz, 8-H), 8.02 (d, J = 7.0 Hz, 5-H); ms: *m/z* (%) 316 (21, M+1), 315 (M, 100), 246 (19), 188 (28), 174 (67).

Anal. Calcd. for $C_{15}H_{13}N_3O_5$: C, 57.14; H, 4.16; N, 13.33. Found: C, 56.26; H, 4.18; N, 12.86.

Ethyl Cyano-(3-nitro-2-oxo-1-phenyl-1,2-dihydroquinolin-4-yl)acetate (**4b**).

This compound was prepared from 4-chloro-3-nitroquinolone **1f** (3.00 g, 10 mmol) and ethyl cyanoacetate (**2c**) (2.26 g, 20 mmol) according to the procedure described for **3a** (4 hours reaction time); the yield was 3.60 g (95 %) yellow microprisms, mp 143 °C (ethanol); ir: 2900 m, 2260 m, 1760 s, 1680 s cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.32 (t, J = 7.1 Hz, ethyl-CH_3), 4.25-4.40 (m, ethyl-CH_2), 5.21 (s, CH), 6.91 (d, J = 7.2 Hz, 8-H), 7.32-7.61 (m, 7 ArH), 8.02 (d, J = 7.1 Hz, 5-H).

Anal. Calcd. for $C_{20}H_{15}N_3O_5$: C, 63.66; H, 4.01; N, 11.14. Found: C, 63.56; H, 4.02; N, 10.93.

Ethyl Cyano-(2-nitro-3-oxo-6,7-dihydro-3*H*,5*H*-benzo[*ij*]quinolizin-1-yl)-acetate (**4c**).

This compound was prepared from 1-chloro-2-nitrobenzoquinolizinone **1g** (2.65 g, 10 mmol) and ethyl cyanoacetate (**2c**) (2.26 g, 20 mmol) according to the procedure described for **3a** (4 hours reaction time); the yield was 3.26 g (96 %) brown microprisms, mp 145 °C (ethanol); ir: 2900 m, 2260 m, 1750 s, 1650 s cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.10 (t, J = 7.0 Hz, ethyl-CH_3), 2.00-2.15 (m, CH_2), 3.00 (t, J = 7.1 Hz, Ar-CH_2), 4.10-4.30 (m, ethyl-CH_2 and NCH_2), 6.50 (s, CH), 7.35-7.51 (m, 9-H), 7.60 (d, J = 7.2 Hz, 8-H), 7.85 (d, J = 7 Hz, 10-H).

Anal. Calcd. for $C_{17}H_{15}N_3O_5$: C, 59.82; H, 4.43; N, 12.31. Found: C, 59.77; H, 4.50; N, 12.01.

(2-Oxo-1-phenyl-1,2-dihydroquinolin-4-yl)malononitrile (**5a**).

To a solution of 1-chloroquinolone **1a** (2.55 g, 10 mmol) and malonodinitrile (**2d**) (0.66 g, 10 mmol) in dimethylformamide (40 mL), anhydrous sodium acetate (1.64 g, 20 mmol) was added at 20 °C. The mixture was heated under reflux for 12 hours and then poured into ice/water (100 mL). After standing for 12 hours at room temperature, the formed precipitate was filtered by suction, washed with water and dried. The yield was 1.62 g (57%) brownish prisms, mp 252 °C (ethanol); ir: 3065-2592 s, 2207 s, 2180 s, 1605 s, 1591 s cm^{-1}; ^1H nmr (DMSO-d_6): δ 6.34 (s, CH), 6.67 (d, J = 8.4 Hz, 1 ArH), 7.34-7.40 (m, 3 ArH), 7.50 -7.62 (m, 5 PhH), 8.82 (d, J = 8.0 Hz, 5-H); ms: *m/z* (%) 286 (8, M+1), 285 (100, M), 278 (24), 260 (37, M–25).

Anal. Calcd. for $C_{18}H_{11}N_3O$: C, 75.78; H, 3.89; N, 14.73. Found: C, 75.39; H, 3.28; N, 14.34.

(1-Methyl-3-chloro-2-oxo-1,2-dihydroquinolin-4-yl)malononitrile (**5b**).

This compound was prepared from 1-chloroquinolone **1h** (1.14 g, 5 mmol) and malonodinitrile (**2d**) (0.66 g, 10 mmol) according to the procedure described for **3a** (5 hours reaction time); the yield was 1.00 g (78%) light-brown prisms, mp 180 °C (ethanol); ir: 3461m, 2939 s, 2207 s, 1657 s, 1609 s, 1595 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 3.87 (s, Me), 6.14 (s, CH), 7.55 (q, J = 8.0 Hz, 2 ArH), 7.79 (t, J = 7.6 Hz, 1 ArH), 8.06 (d, J = 7.8 Hz, 5-H); ms: *m/z* (%) 259 (40, M+2), 257 (100, M).

Anal. Calcd. for $C_{13}H_8N_4O_3$: C, 60.60; H, 3.13; N, 16.31. Found: C, 60.61 H, 3.02; N, 16.15.

Ethyl 2-(3-Cyano-1-methyl-2-oxo-1,2-dihydroquinolin-4-yl)-3-oxobutanoate (**6a**).

This compound was prepared from 4-chloro-3-cyanoquinolone **1b** (2.18 g, 10 mmol) and ethyl acetoacetate (**2e**) (2.60 g, 20 mmol) according to the procedure described for **3a** (3 hours reaction time); the yield was 2.69 g (86 %) lightbrown needles, mp 170 °C (ethanol); ir: 3000 m, 2220 s, 1650 s, 1620 m 1550 s cm^{-1}; ^1H nmr (DMSO-d_6): δ 0.96 and 1.03 (2 t, J = 7.1 Hz, ethyl-CH_3), 1.82 and 2.56 (2 s, Me), 3.68 and 3.69 (s, NMe), 4.01 and 4.11 (2 q, J = 7.2 Hz, ethyl-CH_2), 7.34 and 7.36 (2 t, J = 7.0 Hz, 7-H), 7.60 and 7.62 (2 t, J = 7.0 Hz, 6-H), 7.66 and 7.68 (2 d, J = 7.0 Hz, 8-H), 7.79 and 7.81 (2 d, J = 7.1 Hz, 5-H), 11.20 and 13.16 (2 s, OH); ^{13}C nmr (DMSO-d_6): δ 14.4 and 14.6 (ethyl-CH_3), 20.1 and 20.2 (Me), 30.3 and 30.5 (NMe), 59.8 and 61.6 (OCH_2), 97.4 and 99.9 (C-2 of acetoacetate), 115.9-157.0 (ArC and CN), 158.8 (amide-CO), 165.5 and 170.0 (ester-CO), 171.3 and 176.2 (enol-C).

Anal. Calcd. for $C_{17}H_{16}N_2O_4$: C, 65.38; H, 5.16; N, 8.97. Found: C, 65.31; H, 5.07; N, 8.89.

Ethyl 2-(1-Methyl-3-nitro-2-oxo-1,2-dihydroquinolin-4-yl)-3-oxobutanoate (**6b**).

This compound was prepared from 4-chloro-3-nitroquinolone **1e** (2.38 g, 10 mmol) and ethyl acetoacetate (**2e**) (2.60 g, 20 mmol) in dimethylsulfoxide (40 mL) according to the procedure described for **3a** (5 hours reaction time); the yield was 3.04 g (90 %) yellow microprisms, mp 148-150 °C (ethanol); calorimetric data for thermolysis: mp onset 147.7 °C, peak maximum 150.0 °C, ΔH = 16 mcal/mg; decomposition onset 157.4 °C, peak maximum 163.1 °C, ΔH = –13 mcal/mg; ir: 3000 m, 1670 s, 1600 m, 1540 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.10 and 1.12 (2 t, J = 6.1 Hz, ethyl-CH_3), 1.90 and 2.60 (2 s, Me), 3.90 and 3.92 (2 s, NMe), 4.00-4.35 (m, ethyl-CH_2), 7.40 and 7.42 (2 t, J = 6.3 Hz, 1 ArH), 7.45 and 7.47 (2 d, J = 7.0 Hz, 8-H), 7.60-7.80 (m, 2 ArH), 11.50 and 13.25 (2 s, OH); ^{13}C nmr (DMSO-d_6): δ 14.3 and 14.6 (ethyl-CH_3), 20.1 and 20.2 (Me), 30.5 and 30.7 (NMe), 59.7 and 61.6 (OCH_2), 97.5 and 100.0

(C-2 of acetoacetate), 116.1-149.0 (ArC and CN), 159.0 (amide-CO), 165.0 and 170.0 (ester-CO), 171.0 and 176.0 (enol-C).

Anal. Calcd. for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.99, H, 4.87; N, 8.40.

Ethyl 2-(3-Nitro-2-oxo-1-phenyl-1,2-dihydroquinolin-4-yl)-3-oxobutanoate (**6c**).

This compound was prepared from 4-chloro-3-nitroquinolone **1f** (3.01 g, 10 mmol) and ethyl acetoacetate (**2e**) (2.60 g, 20 mmol) in dimethylsulfoxide (40 mL) according to the procedure described for **3a** (5 hours reaction time); the yield was 3.86 g (98 %) lightbrown needles, mp 176 °C (ethanol); ir: 3000 w, 1670 s, 1640 s, 1530 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.10 and 1.12 (2 t, J = 6.0 Hz, ethyl-CH_3), 1.95 and 2.60 (2 s, Me), 4.05 and 4.15 (2 m, ethyl-CH_2), 6.80 and 6.82 (d, J = 6.1 Hz, 1 ArH), 7.30-7.70 (m, 8 ArH), 11.50 and 13.30 (2 s, OH); ms: *m/z* (%) 395 (15, M+1), 394 (100%, M), 334 (14), 237 (37).

Anal. Calcd. for $C_{21}H_{18}N_2O_6$: C, 63.96; H, 4.60; N, 7.10. Found: C, 64.00; H, 4.58; N, 7.10.

Ethyl 2-(2-Nitro-3-oxo-6,7-dihydro-3*H*,5*H*-benzo[*ij*]quinolizin-1-yl)-3-oxobutanoate (**6d**).

This compound was prepared from 1-chloro-2-nitro-benzoquinolizinone **1g** (2.65 g, 10 mmol) and ethyl acetoacetate (**2e**) (2.60 g, 20 mmol) in dimethylsulfoxide (40 mL) according to the procedure described for **3a** (3 hours reaction time); the yield was 3.04 g (85 %) light yellow needles, mp 132 °C (ethanol/water); ir: 2800-3000 w, 1660 s, 1600 s cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.02 and 1.04 (2 t, J = 7.2 Hz, 2 ethyl-CH_3), 1.70 and 2.60 (2 s, Me), 2.10-2.20 (m, CH_2), 3.00-3.10 (m, $ArCH_2$), 4.05-4.20 (m, ethyl-CH_2 and NCH_2), 7.25-7.35 (m, 1 ArH), 7.45-7.60 (m, 2 ArH), 11.50 and 13.10 (2 s, OH).

Anal. Calcd. for $C_{18}H_{18}N_2O_6$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.34; H, 5.16; N, 7.70.

4-(2,4-Dioxopent-3-yl)-1-methyl-2-oxo-1,2-dihydroquinolin-3-carbonitrile (**7a**).

This compound was prepared from 4-chloro-2-cyanoquinolone **1b** (2.18 g, 10 mmol) and acetylacetone (**2f**) (2.05 g, 20 mmol) according to the procedure described for **3a** (3 hours reaction time); the yield was 2.24 g (79 %) fine light yellow needles, mp 167 °C (ethanol); ir: 3000 w, 2220 s, 1650 s, 1610 m 1550 m, cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.93 (s, 2 Me), 3.83 (s, NMe), 7.37 (t, J = 7.1 Hz, 1 ArH), 7.51 (d, J = 7.0 Hz, 8-H), 7.66 (t, J = 7.1 Hz, ArH), 7.80 (d, J = 7.2 Hz, 5-H); ^{13}C nmr (DMSO-d_6): δ 23.9 (Me), 30.5 (NMe), 108.3 (C-3 of acetylacetone), 109.5-154.5 (ArC and CN), 158.6 (amide-CO), 190.9 (enol-C); ms: *m/z* (%) 283 (20, M+1), 282 (100, M), 241 (26), 198 (38).

Anal. Calcd. for $C_{16}H_{14}N_2O_3$: C, 68.08; H, 5.00; N, 9.92. Found: C, 67.81; H, 5.01; N, 9.92.

3-(3-Nitro-2-oxo-1-phenyl-1,2-dihydroquinolin-4-yl)pentan-2,4-dione (**7b**).

This compound was prepared from 4-chloro-3-nitroquinolone **1f** (0.90 g, 3 mmol) and acetylacetone (**2f**) (0.70 g, 7 mmol) according to the procedure described for **3a** (3 hours reaction time); the yield was 0.83 g (96 %), greenish microprisms, mp 202 °C (ethanol); calorimetric data for thermolysis: mp onset 197.5 °C, peak maximum 202.0 °C, ΔH = 88 mJ/mg; decomposition onset 229.0 °C, peak maximum 259.6 °C, ΔH = –723 mJ/mg; ir: 1670 s, 1600 s, 1540 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.03 (s, 2 Me), 6.85 (d, J = 8.5 Hz, 1 ArH), 7.35-7.39 (m, 3 ArH), 7.53 (t, J = 7.3 Hz, 1 ArH), 7.58-7.69 (m, 4 ArH); ^{13}C nmr (DMSO-d_6): δ 24.2 (Me), 104.1 (C-3 of acetylacetone), 117.0-143.6 (ArC), 154.2 (amide-CO), 191.1 (enol-C).

Anal. Calcd. for $C_{20}H_{16}N_2O_5$: C, 65.93; H, 4.43; N, 7.69. Found: C, 65.75; H, 4.46; N, 7.56.

3-(2-Nitro-3-oxo-6,7-dihydro-3*H*,5*H*-benzo[*ij*]quinolizin-1-yl)pentan-2,4-dione (**7c**).

This compound was prepared from 1-chloro-2-nitrobenzo-quinolizinone **1g** (2.65 g, 10 mmol) and acetylacetone (**2f**) (2.05 g, 20 mmol) according to the procedure described for **3a** (4 hours reaction time); the yield was 2.68 g (82 %), yellow microprisms, mp 171 °C (ethanol); ir: 2900 w, 1660 s, 1600 s, 1540 s cm^{-1}; ^1H nmr ($CDCl_3$): δ = 1.90 (s, 2 Me), 2.05-2.20 (m, CH_2), 3.00-3.10 (m, $ArCH_2$), 4.15-4.25 (m, NCH_2), 7.35 (t, J = 6.0 Hz, 1 ArH), 7.55-7.70 (m, 2 ArH).

Anal. Calcd. for $C_{17}H_{16}N_2O_5$: C, 62.19; H, 4.91; N, 8.53. Found: C, 62.34; H, 4.92; N, 8.49.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-1-methyl-3-nitroquinolin-2(1*H*)-one (**8a**).

This compound was prepared from 4-chloro-3-nitroquinolone **1e** (2.38 g, 10 mmol) and dimedone (**2g**) (2.10 g, 15 mmol) according to the procedure described for **3a** (5 hours reaction time); the yield was 3.00 g (88 %), colorless microprisms, mp. 283 °C dec. (dimethylformamide); calorimetric data for thermolysis: decomposition onset 278.1 °C, peak maximum 283.6 °C, ΔH = –686 mJ/mg; ir: 3100 br, 1660 s, 1600 m 1540 s cm^{-1}; ^1H nmr (DMSO-d_6): δ = 1.01 (s, Me), 1.13 (s, Me), 2.27 (d, J = 7.0 Hz, CH_2), 2.57 (d, J = 7.0 Hz, CH_2), 3.73 (s, NMe), 7.34 (t, J = 6.1 Hz, 7-H), 7.53 (d, J = 6.0 Hz, 8-H), 7.67 (t, J = 6.5 Hz, 6-H), 7.75 (d, J = 6.5 Hz, 8-H), 11.60 (s, OH, exchangeable with D_2O); ^{13}C nmr (DMSO-d_6): δ 26.8 and 29.7 (dimedone-Me), 30.5 (NMe), 32.1 (dimedone-C5), 54.0 (dimedone-CH_2), 105.9 (dimedone-C2), 116.0-143.5 (ArC), 154.4 (amide-CO); ^1H nmr of dimedone (**2g**) (DMSO-d_6): δ 0.98 (s, 2 Me), 2.11 (s, 2 CH_2), 5.18 (s, 2-H as enol), 10.97 (s, OH); ms: *m/z* (%) 343 (23, M+1), 342 (100, M), 296 (10, M – NO_2).

Anal. Calcd. for $C_{18}H_{18}N_2O_5$: C, 63.15; H, 5.30; N, 8.18. Found: C, 62.78; H, 5.34; N, 8.24.

4-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-3-nitro-1-phenylquinolin-2(1*H*)-one (**8b**).

This compound was prepared from 4-chloro-3-nitroquinolone **1f** (3.01 g, 10 mmol) and dimedone (**2g**) (2.10 g, 15 mmol) according to the procedure described for **3a** (5 hours reaction time); the yield was 3.95 g (98 %), colorless microprisms, mp 273 °C dec (1-propanol); calorimetric data for thermolysis: decomposition onset 268.1 °C, peak maximum 273.4 °C, ΔH = –573 mJ/mg; ir: 3300 br, 3000 m, 1660 s, 1630 m, 1530 s cm^{-1}; ^1H nmr (DMSO-d_6): δ = 1.07 (s, Me), 1.16 (s, Me), 2.30 and 2.40 (2 s, 2 CH_2), 6.70 (d, J = 7.0 Hz, 1 Ar), 7.20-7.60 (m, 8 ArH), 11.60 (s, b, OH); ms: *m/z* (%) 405 (34, M+1), 404 (100, M), 358 (5, M – NO_2).

Anal. Calcd. for $C_{23}H_{20}N_2O_5$: C, 68.31; H, 4.98; N, 6.93. Found: C, 67.60; H, 4.98; N, 5.99.

1-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-2-nitro-6,7-dihydro-5*H*-benzo[*ij*]quinolizin-3-one (**8c**).

This compound was prepared from 1-chloro-2-nitrobenzo-quinolizinone **1g** (2.64 g, 10 mmol) and dimedone (**2g**) (2.10 g,

15 mmol) according to the procedure described for **3a** (5 hours reaction time); the yield was 3.31 g (90 %), colorless microprisms, mp 278 °C dec (ethanol); calorimetric data for thermolysis: decomposition onset 272.4 °C, peak maximum 277.6 °C, ΔH = –848 mJ/mg; ir: 3000 w, 1660 s, 1590 m cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 1.00 (s, Me), 1.10 (s, Me), 2.20 (s, 2 CH_2), 2.40-2.60 (m, 2 CH_2), 3.00 (m, Ar-CH_2), 4.10 (m, NCH_2), 7.05-7.15 (m, 1 ArH), 7.30 (d, J = 6.0 Hz, 1 ArH), 7.50 (d, J = 6.1 Hz, 1 H, ArH), 11.50 (s, b, OH); ms: *m/z* (%) 369 (23, M+1), 368 (100, M), 322 (5, M – NO_2).

Anal. Calcd. for $C_{20}H_{20}N_2O_5$: C, 65.21; H, 5.47; N, 7.60. Found: C, 64.83; H, 5.36; N, 8.40.

Diethyl 2-Hydroxy-2-(1-methyl-2-oxo-3-phenylsulfinyl-1,2-dihydroquinolin-4-yl)malonate (**9a**).

To a solution of 4-chloro-3-phenylsulfonylquinolone **1i** (1.67 g, 5 mmol) and diethyl malonate (**2a**) (1.60 g, 10 mmol) in dimethylformamide (40 mL), anhydrous potassium carbonate (2.8 g, 20 mmol) was added at 20 °C. The mixture was stirred at 60-70 °C for 4 hours, then poured into ice/water (100 mL) and acidified with 6 *M* hydrochloric acid to pH = 1. After standing for 12 hours at room temperature, the formed precipitate was filtered by suction, washed with water until acid-free and dried. The yield was 1.83 g (80 %) orange microprisms, mp 283 °C (ethanol); ir: 3300 m, 1660 s, 1540 s cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 0.91 (t, J = 7.0 Hz, 2 ethyl-CH_3), 3.43 (s, NMe), 3.75 (q, J = 7.1 Hz, 2 ethyl-CH_2), 7.18 (t, J = 7.2 Hz, 8-H), 7.35-7.50 (m, 4 ArH), 7.58 (t, 2 ArH), 7.79 (d, J = 7.1 Hz, 2 ArH), 8.03 (d, J = 7.2 Hz, 5-H); ^{13}C nmr (DMSO-d_6): δ 15.5 (ethyl-CH_3), 29.3 (NMe), 56.2 (ethyl-CH_2; inversion by DEPT-135 experiment), 69.9 (quartery malonyl-C; missing in DEPT-135 experiment), 114.6 (Ar-CH), 121.7 (Ar-CH), 123.8 (Ar-C), 126.7 (Ar-C), 127.4 (Ar-CH), 128.3 (Ar-CH), 130.4 (Ar-CH), 132.1 (Ar-CH), 132.3 (Ar-CH), 140.3 (Ar-C), 144.9 (Ar-C), 157.9 (SO-C), 158.6 (ester-C=O), 166.3 (amide-C=O); ms: *m/z* (%) 458 (15, M+1), 457 (100, M), 385 (40, M – COOEt), 313 (89, M – 2 COOEt).

Anal. Calcd. for $C_{23}H_{23}NO_7S$: C, 60.38, H, 5.07; N, 3.06. Found: C, 60.02, H, 5.34; N, 3.38.

Diethyl 2-Hydroxy-2-(2-oxo-1-phenyl-3-phenylsulfinyl-1,2-dihydroquinolin-4-yl)malonate (**9b**).

This compound was prepared from 4-chloro-3-phenylsulfonylquinolone **1j** (1.98 g, 5 mmol) and diethyl malonate (**2a**) (1.60 g, 10 mmol) according to the procedure described for **9a**; the yield was 1.97 g (76 %) pale yellow microprisms, mp 122 °C (ethanol); calorimetric data for thermolysis: mp onset 116.6 °C, peak maximum 122.0 °C, ΔH = 11 mcal/mg; decomposition onset 247.0 °C, peak maximum 276.7 °C, ΔH = –14 mcal/mg; ir: 2950 m, 1730 s, 1660 s, cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 1.35 (t, J = 7.0 Hz, 2 ethyl-CH_3), 4.20-4.45 (m, 2 ethyl-CH_2), 6.65 (d, J = 7.1 Hz, 8-H), 7.10-7.30 (m, 3 ArH), 7.30-7.70 (m, 8 ArH), 7.95 (d, J = 7.1 Hz, 1 ArH), 8.10 (d, J = 7.0 Hz, 5-H); ms: *m/z* (%) 520 (32, M+1), 519 (100, M), 447 (39, M – COOEt), 375 (76, M – 2 COOEt).

Anal. Calcd. for $C_{28}H_{25}NO_7S$: C, 64.73; H, 4.85; N, 2.70. Found: C, 64.72; H, 4.61; N, 2.65.

Dimethyl 2-Hydroxy-2-(3-oxo-2-phenylsulfinyl-6,7-dihydro-5*H*-benzo[*ij*]quinolizin-1-yl)malonate (**9c**).

This compound was prepared from 1-chloro-2-phenylsulfonylbenzoquinolizinone **1k** (1.30 g, 3.6 mmol) and dimethyl malonate (**2b**) (1.10 g, 8 mmol) according to the procedure described for **9a**; the yield was 1.01 g (61 %) beige microprisms, mp 197 °C (ethanol); calorimetric data for thermolysis: mp onset 191.7 °C, peak maximum 196.6 °C, ΔH = 16 mcal/mg; decomposition onset 258.6 °C, peak maximum 279.8 °C, ΔH = –10 mcal/mg; ir: 2900 m, 1760 s, 1730 s, 1640 s cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 1.90 (m, CH_2), 2.91-2.94 (m, Ar-CH_2), 3.62 (s, 2 MeO), 3.86-89 (m, N-CH_2), 7.27 (t, J = 7.5 Hz, 1 Aryl-H), 7.50-7.70 (m, 6 ArH), 7.92 (d, J = 7.5 Hz, 5-H).

Anal. Calcd. for $C_{23}H_{21}NO_7S$: C, 60.65; H, 4.65; N, 3.08. Found: C, 60.48; H, 4.66; N, 3.01.

Diethyl 2-Hydroxy-2-(3-oxo-2-phenylsulfinyl-6,7-dihydro-5*H*-benzo[*ij*]quinolizin-1-yl)malonate (**9d**).

This compound was prepared from 1-chloro-2-phenylsulfonylbenzoquinolizinone **1k** (1.79 g, 5 mmol) and diethyl malonate (**2a**) (1.60 g, 10 mmol) according to the procedure described for **9a** (4 hours reaction time); the yield was 1.89 g (78 %), fine yellow needles, mp. 177 °C (ethanol); ir: 3000 m, 1780 s, 1730 m, 1640 s, cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 1.25 (t, J = 6.4 Hz, 2 ethyl-CH_3), 2.10 (m, CH_2), 3.00 (t, J = 6.1 Hz, Ar-CH_2), 4.05 (t, J = 6.2 Hz, N-CH_2), 4.20-4.45 (m, 2 ethyl-CH_2), 7.10 (t, J = 6.5 Hz, 1 ArH), 7.40 (d, J = 6.1 Hz, 1 ArH), 7.45-7.65 (m, 3 PhH), 7.75 (d, J = 6 Hz, 1 ArH), 8.10 (d, J = 6.0 Hz, 2 ArH); ms: *m/z* (%) 484 (27, M+1), 483 (100, M), 411 (39, M – COOEt), 339 (83, M – 2 COOEt).

Anal. Calcd. for $C_{25}H_{25}NO_7S$: C, 62.10; H, 5.21; N, 2.90. Gef.: C, 62.18; H, 5.01; N, 2.84.

2,3,4-Trichloroquinoline and (**10a**) 2,4-Dichloro-3-nitroquinoline (**10b**).

These compounds were synthesized according to ref. [8].

Diethyl 2-(2,3-Dichloroquinolin-4-yl)malonate (**11a**).

To a solution of 2,3,4-trichloroquinoline (**10a**) (1.66 g, 5 mmol) and diethyl malonate (**2a**) (1.60 g, 10 mmol) in dimethylformamide (40 mL), anhydrous potassium carbonate (2.8 g, 20 mmol) was added at 20 °C. The mixture was stirred at 60 °C for 4 hours, then poured into ice/water (100 mL) and acidified with conc. hydrochloric acid to pH = 1. After standing for 12 hours at room temperature, the formed precipitate was filtered by suction, washed with water until acid-free and dried. The yield was

0.85 g (48 %), colorless prisms, mp. 103 °C (ethanol); calorimetric data for thermolysis: mp onset 100.3 °C, peak maximum 103.0 °C, ΔH = 46 mJ/mg; decomposition onset 305.4 °C, peak maximum 312.2 °C, ΔH = –326 mJ/mg; ir: 2980 s, 1760 s, 1750 s cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 1.20 (t, J = 7.0 Hz, 2 Me), 4.25 (q, J = 7.1 Hz, 2 CH_2), 5.80 (s, CH), 7.60 (t, J = 7.0 Hz, 1 ArH), 7.75 (t, J = 7.1 Hz, 1 ArH), 7.95 (d, J = 7.2 Hz, 1 ArH), 8.05 (d, J = 5.0 Hz, 1 ArH); ^{13}C nmr ($CDCl_3$): δ 15.1 (Me), 46.8 (CH), 58.3 (CH_2), 122.9 (Ar-CH), 126.1 (Ar-CH), 127.8 (Ar-CH), 128.0 (Ar-CH), 130.5 (Ar-CH), 140.6 (C-4), 145.5 (C-8a), 147.6 (C-2), 158.6 (ester-C=O).

Anal. Calcd. for $C_{16}H_{15}Cl_2NO_4$: C, 53.95; H, 4.24; N, 3.93. Found: C, 53.96; H, 4.14; N, 3.86.

Dimethyl 2-(2-Chloro-3-nitroquinolin-4-yl)malonate (**11b**).

This compound was prepared from 2,4-dichloro-3-nitroquinoline (**10b**) (1.21 g, 5 mmol) and dimethyl malonate (**2b**) (1.60 g, 10 mmol) according to the procedure described for **3a** (5 hours reaction time); the yield was 1.04 g (61 %), colorless needles, mp 152 °C (ethanol); calorimetric data for thermolysis: mp onset

146.1 °C, peak maximum 151.8 °C, ΔH = 75 mJ/mg; decomposition onset 170.6 °C, peak maximum 178.6 °C, ΔH = –378 mJ/mg; decomposition onset 249.1 °C, peak maximum 268.6 °C, ΔH = –159 mJ/mg; ir: 2960 m, 1760 s, 1740 m, 1540 s cm^{-1}; ^1H nmr (DMSO-d_6): δ 3.70 (s, 2 Me), 5.95 (s, CH), 7.90 (t, J = 7.0 Hz, 1 ArH), 8.10 (t, J = 7.1 Hz, 1 ArH), 8.20 (d, J = 7.0 Hz, 2 ArH); ^{13}C nmr ($CDCl_3$): δ = 14.9 (Me), 47.3 (CH), 59.1 (CH_2), 124.3 (Ar-CH), 126.2 (Ar-CH), 128.3 (Ar-CH), 128.9 (Ar-CH), 134.5 (Ar-CH), 140.2 (C-4), 146.6 (C-2), 149.5 (C-8a), 159.1 (ester-C=O).

Anal. Calcd. for $C_{14}H_{11}ClN_2O_6$: C, 49.65; H, 3.27; N, 8.27; Cl, 10.47. Found: C, 49.77; H, 3.44; N, 8.13, Cl, 10.40.

Ethyl 3-(6-Chloropyridin-3-ylmethylamino)-2-(1-methyl-3-nitro-2-oxo-1,2-dihydroquinolin-4-yl)-3-oxopropanoate (**13a**).

A solution of quinolinylmalonate **3f** (1.81 g, 5 mmol) and 6-chloro-3-pyridylmethanamine (**12a**) (1.42 g, 10 mmol) in toluene (30 mL) was heated under reflux for 30 min. After cooling, hexane (40 mL) was added and the resulting precipitate filtered by suction. The yield was 2.17 g (78 %), light yellow microprisms, mp 116 °C (toluene/hexane); ir: 3300 m, 1740 m, 1640 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.03 (t, J = 7.1 Hz, ethyl-CH_3), 3.72 (s, NMe), 4.12-4.14 (m, ethyl-CH_2), 4.39-4.40 (m, N-CH_2), 5.10 (s, CH), 7.36 (d, J = 7.7 Hz, 1 ArH), 7.48 (t, J = 8.0 Hz, 1 ArH), 7.55 (d, J = 8.5 Hz, 1 ArH), 7.71-7.79 (m, 2 ArH), 8.27-8.32 (m, 2 ArH); ms: *m/z* (%) 460 (25, M+2), 458 (60, M), 370 (43), 368 (100), 342 (15), 340 (31), 168 (33), 142 (55), 144 (21).

Anal. Calcd. for $C_{21}H_{19}ClN_4O_6$: C, 54.97; H, 4.17; N, 12.21. Found: C, 54.81; H, 3.87; N, 12.13.

Ethyl 3-[*N*-(6-Chloropyridin-3-ylmethyl)-*N*-methylamino]-2-(1-methyl-3-nitro-2-oxo-1,2-dihydroquinolin-4-yl)-3-oxopropanoate (**13b**).

This compound was obtained from quinolinylmalonate **3f** (1.81 g, 5 mmol) and *N*-methyl-6-chloro-3-pyridylmethanamine (**12b**) (1.56 g, 10 mmol) according to the method described for **13a**; the yield was 2.43 g (83 %), light yellow prisms, mp 148 °C (ligroin); ir: 2950 w, 1740 s, 1650 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.15 (t, J = 7.1 Hz, ethyl-CH_2), 3.69 (s, NMe), 3.79 (s, NMe), 4.18-4.29 (m, ethyl-CH_2), 4.63 (s, N-CH_2), 5.00 (s, CH), 7.28-7.33 (m, 2 ArH), 7.45 (d, J = 8.6 Hz, 1 ArH), 7.60 (dd, J = 8.1 and 2.1 Hz, 1 ArH), 7.68-7.71 (m, 1 ArH), 7.98 (d, J = 8.2 Hz, 1 ArH), 8.29 (s, 1 ArH).

Anal. Calcd. for $C_{22}H_{21}ClN_4O_6$: C, 55.88; H, 4.48; N, 11.85. Found: C, 56.01; H, 4.31; N 11.50

Ethyl 2-(1-Methyl-3-nitro-2-oxo-1,2-dihydroquinolin-4-yl)-3-morpholino-3-oxopropanoat (**14**).

This compound was obtained from quinolinylmalonate **3f** (1.81 g, 5 mmol) and morpholine (0.87 g, 10 mmol) according to the method described for **13a**; the yield was 1.57 g (78 %) light yellow prisms, mp 91 °C (toluene); ir: 2900 m, 1740 s, 1650 s, 1540 s cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.20 (t, J = 7.5 Hz, ethyl-CH_3), 3.40-3.70 (m, 4 CH_2), 3.85 (s, NMe), 4.25 (q, J = 7. 5 Hz, ethyl-CH_2), 4.90 (s, CH), 7.35 (t, J = 7.0 Hz, 1 ArH), 7.45 (d, 7.5 Hz, 1 ArH), 7.70 (t, J = 7.5 Hz, 1 ArH), 8.05 (d, J = 7.5 Hz, 1 ArH); ms: *m/z* (%) 404 (18, M+1), 403 (100, M), 314 (7).

Anal. Calcd. for $C_{19}H_{21}N_3O_7$: C, 56.57; H, 5.25; N, 10.42. Found: C, 56.97; H, 5.27; N, 10.03.

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