Imidazoquinolinethiones from 8-aminoquinolines by a novel *peri*-participation

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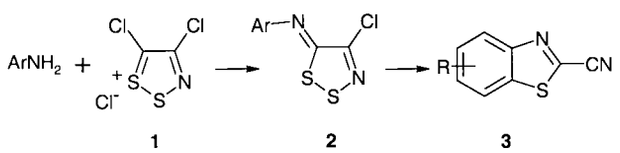
8-Aminoquinolines and 4,5-dichloro-1,2,3-dithiazolium chloride **1** give *N*-(quinolin-8-yl)iminodithiazoles **6** and **15a–c** which undergo a novel thermal rearrangement to give imidazo[4,5,1-*ij*]quinoline-4-thiones **13** and **16a–c** respectively. Normal cyclisation of the dithiazolo group onto the carbocyclic ring to form a benzothiazole (*e.g.* **6**→**5**) is averted by *peri*-participation of the quinoline ring nitrogen. This participation results in formation of the imidazole ring and delivery of a sulfur atom to the quinoline 2-position; delivery of this sulfur appears to be intramolecular and possibly involves a [1,3] sigmatropic shift of a carbon–sulfur bond (Scheme 4). The same overall reaction is observed, at much lower temperature, on treatment of the quinolinyliminodithiazoles (**15a** and **c**) with sodium hydride in THF (Scheme 5), thus providing a ready route to imidazo[4,5,1-*ij*]quinoline-4-thiones. These thiones are rapidly oxidised to the corresponding 4-ones, such as **25**; **25** was also formed, rapidly and quantitatively, from the analogous iminodithiazole derivative **23** of 8-aminoquinolin-2-one in boiling ethanol (Scheme 6). Mechanisms are proposed for all the new rearrangements reported.

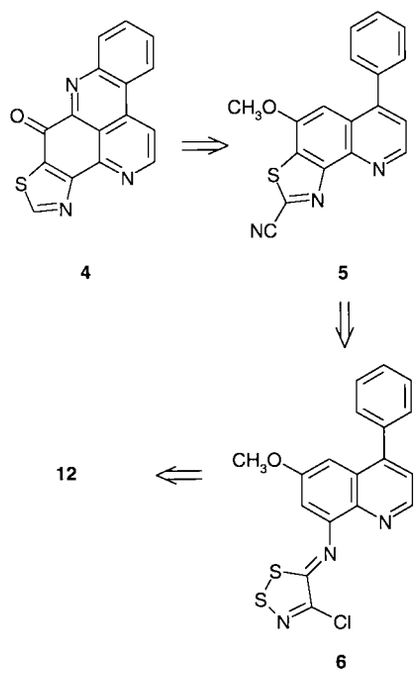
We have shown that thermolysis of 5-arylimino-1,2,3-dithiazoles **2**, easily prepared from primary aromatic amines and 4,5-dichloro-1,2,3-dithiazolium chloride† (Appel salt) **1**,



1 **2** **3**

gives 2-cyanobenzothiazoles **3**.[1] This provides a simple and general synthesis of 2-cyanobenzothiazoles from anilines in two steps and, if desired, the cyano group can be cleanly removed in one step with concentrated hydrochloric acid. This reaction sequence suggested a potentially simple and versatile construction of the pentacyclic ring system of a group of pyridoacridine alkaloids which have an unsubstituted thiazole ring fused to the acridine. These highly cytotoxic marine natural products include the kuanoniamines and dercitins.[2] We envisaged that kuanoniamine A **4** could be derived from the thiazoloquinoline **5** by nitration at the quinoline 5-position and conversion of the nitro group into an azide *via* the primary amine, followed by azide decomposition and nitrene insertion into the phenyl ring, as demonstrated for a closely related compound.[3] By analogy with many earlier reactions,[1] **5** would be the expected thermolysis product of the iminodithiazole **6** formed from 8-amino-6-methoxy-4-phenylquinoline **12** and Appel salt **1**. This amine was prepared as shown in Scheme 1.

Condensation of 4-methoxy-2-nitroaniline, triethyl orthoformate and Meldrum's acid in the orthoformate at reflux gave the adduct **7** in 90% yield, easily allowing the preparation of multigram amounts of material. Thermolysis of **7** to give carbon dioxide, acetone and the quinolin-4-one proceeded well, under milder and more dilute conditions than those recommended,[4] though the product was still difficult to isolate entirely free from diphenyl ether. The crude quinolinone was converted into the 4-chloro compound **8** with phosphorus pentachloride in phosphorus oxychloride; on a large scale most of the latter was removed by distillation before work up. Cyclisation and chlorination (about 60% overall) could be scaled up readily. The nitro compound **8** was reduced almost quantitatively with stannous chloride in ethanol to the amine **9** which was acetylated in high yield. Treatment of the 4-chloroacetamide **10** with phenylboronic acid under standard conditions,[3] but with 5 rather than 3 mol% of catalyst, gave 96% of the 4-phenyl-



4 **5** **6** **12**

† IUPAC name: 4,5-dichloro-1λ^4-1,2,3-dithiazol-1-ylium chloride.

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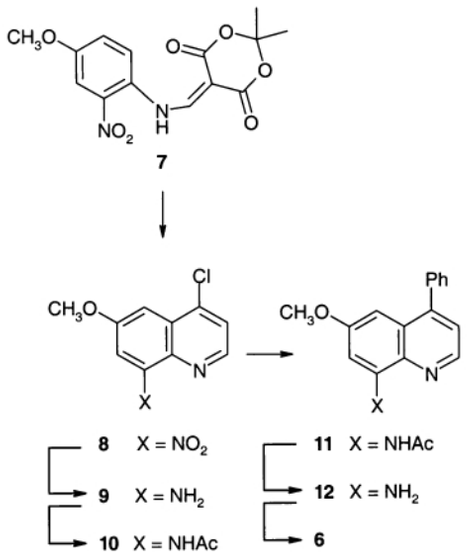
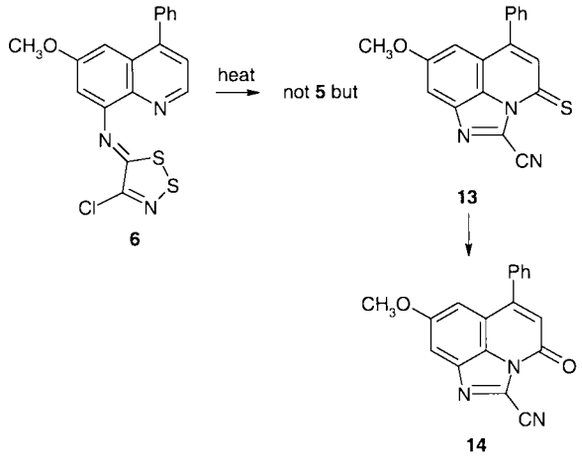


Scheme 1

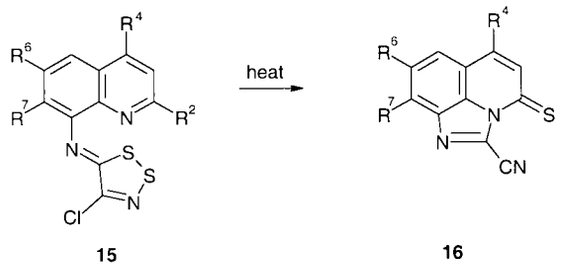
quinoline **11** which was hydrolysed with hot concentrated hydrochloric acid to give the amine **12** as a not very stable oil. Treatment of this (and other 8-aminoquinolines) with Appel salt **1** and pyridine in DCM at room temperature in the usual way[1] gave very low yields of the imino-1,2,3-dithiazoles like **6**. However at lower temperatures (−20 °C or below) under argon and with rapid work up and purification, the imine yields were raised, to 42% for **6**. Atypically, the imine **6** was also somewhat unstable to storage.

Thermolysis of the neat imine **6**, $C_{18}H_{12}ClN_3OS_2$, at 200 °C was complete within 1 min to give a red product, $C_{18}H_{11}N_3OS$, in about 50% yield. Although it had the expected analysis and accurate mass for the thiazole **5**, and showed a characteristic IR signal for a cyanide, its colour and insolubility were unexpected. Furthermore, the ^{1}H NMR spectrum was different from the normal quinoline pattern, and the characteristic signal for the quinoline 2-H and its coupling with the 3-H had disappeared. It became apparent that the thermolysis product could not be the fused thiazole **5** when we attempted its nitration with cupric nitrate–acetic anhydride or nitric acid–acetic acid, and its bromination with bromine in acetic acid. All of these reactions were rapid and almost quantitative at room temperature and all gave the *same* product in which one sulfur atom had been replaced by one oxygen atom. The spectral data for the sulfur and the oxygen compounds were remarkably similar indicating that sulfur had been replaced by oxygen with no other structural change. This suggested the possible *oxidation* of a thiocarbonyl to a carbonyl compound; the product had a $\nu_{C=O}$ at 1692 cm^{-1} and this taken with the ^{1}H NMR evidence for the absence of a quinoline 2-H, suggested a quinolin-2-one structure. All the spectroscopic data fitted well for the quinoline-2-thione structure **13** for the thermolysis product and the quinolin-2-one structure **14** for its oxidation product (Scheme 2). Thus, in the thermolysis of iminodithiazole **6** into **13**, the dithiazole ring has opened, with the elimination of hydrogen chloride and sulfur, but neighbouring group participation by the quinoline ring nitrogen has diverted the 'normal' reaction pathway; none of the normal thermolysis product, thiazole **5**, was detected. This conversion is a new decomposition for arylimino-1,2,3-dithiazoles which, if it is general, would be a useful route to the unknown imidazo[4,5,1-*ij*]quinolin-4-ones and -4-thiones from 8-aminoquinolines.[5]

In order to explore the scope and the mechanism of this rearrangement we synthesised a few less substituted 8-aminoquinolines and converted them with Appel salt **1** at −20 °C into the corresponding iminodithiazoles **15** which were then thermolysed (Scheme 3). The thermolyses were of the neat material at 200–250 °C for 1 min (Method A) or for concentrated solutions



Scheme 2



Scheme 3

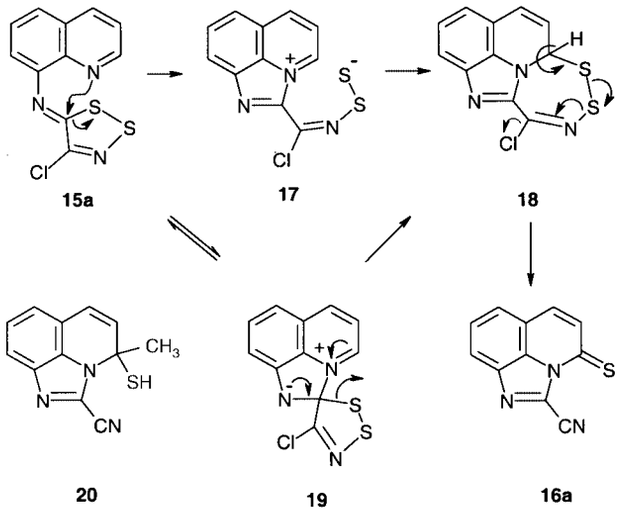
Table 1

	R^2	R^4	R^6	R^7	Yield of thione (%)	
6	H	Ph	MeO	H	**13**	49
15a	H	H	H	H	**16a**	52
15b	H	Ph	H	H	**16b**	38
15c	H	H	H	Me	**16c**	40
15d	Me	H	H	H	No thione detected	
15e	Cl	H	H	H	No thione detected	

in a minimum of toluene in sealed tubes at 250 °C for 3 h (Method B). Thermolyses in boiling toluene or chlorobenzene were cleaner, allowing the recovery of unchanged starting material, but slower. Although the reaction mixtures were often dark and complex, in all cases (**15a**–**c**) where the quinoline 2-position was unsubstituted the same rearrangement occurred to give the red or brown imidazoquinoline-4-thiones **16a**–**c** in modest yields (40–50%) (Scheme 3 and Table 1) whose structures followed from their analytical and spectroscopic properties. A few preliminary experiments on the decomposition of the simplest quinoline derivative **15a** under microwave irradiation neat, in toluene, and in 2,6-lutidine, and by photolysis in toluene, showed that in all cases the same thermolysis product **16a** was formed in approximately the same yield.

When the quinoline 2-position was blocked by chlorine **15e** or a methyl group **15d** the reactions did not revert to the 'normal' thiazole ring fusion pathway to any noticeable extent. These two reactions were particularly complex and it is possible that the quinoline nitrogen atom still participates in the dithiazole ring opening which is accompanied by various decomposition reactions. Furthermore, with these substrates, no thione products were detected. With the other substrates, **15a**–**c**, the source of the thione sulfur must be the dithiazole ring, and this sulfur could be delivered inter- or intra-molecularly. If it were intermolecular, one might expect that with the quinoline 2-position blocked the sulfur would be delivered to the 4-position to give the corresponding γ-thione, but this was not observed.

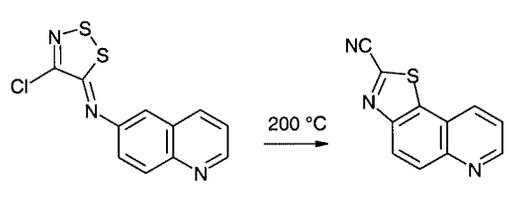
A possible rearrangement mechanism is proposed for the parent compound **15a** in Scheme 4. Rather than the 'normal'



Scheme 4

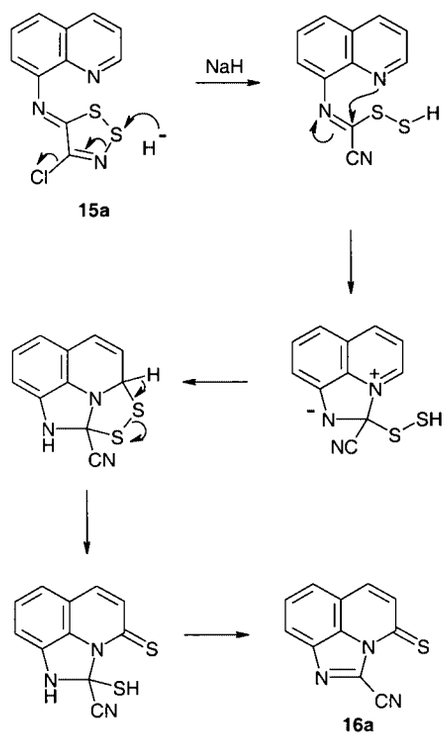
cyclisation of the iminodithiazole ring onto the adjacent benzo position,[1] the quinoline nitrogen atom participates as a neighbouring nucleophile, diverting the reaction to the imidazoquinolinium species **17**. This would then collapse to the tetracyclic compound **18**, delivering sulfur to the pyridinium ring intramolecularly. Elimination of hydrogen chloride and sulfur (possibly *via* a nitrile sulfide) from the 7-membered ring in **18** would yield the very stable cyano compound **16a** isolated. It is also possible that C–S bond breaking, in **15a**, and C–S bond making, in **18**, could be concerted *via* the spiro intermediate **19**; this could be in thermal equilibrium with the starting material and could rapidly neutralise its dipolar charges by a 1,3-sigmatropic shift, as shown. In accord with this general mechanism was the isolation from the decomposition mixture of the 2-methyl compound **15d** of a minor product with a molecular weight 227. This was assigned the structure **20** on the basis of its MS and HRMS, IR spectrum, and ^{1}H and ^{13}C NMR spectra, including δ_C DEPT 135 which showed the presence of 5 sp^2 carbon atoms (=**C**–H) and one sp^3 carbon atom (–**C**H$_3$). Another very minor product of this reaction had a molecular weight of 225; on the basis of its MS and ^{1}H NMR spectra this could be the fused thiazoloquinoline analogous to **5**, indicating that the 'normal' cyclisation pathway was not totally supressed in this case.

In the mechanism of Scheme 4 we have assumed that the new rearrangement pathway arises simply because of faster attack of the dithiazole ring in **15a** by the *peri* nitrogen atom than by the *ortho* carbon atom, C-7, of the quinoline ring. The latter would have resulted in formation of a fused 2-cyanothiazole ring. To check that there was no inherent barrier to this reaction, we studied the thermolysis of the isomeric 6-iminodithiazoloquinoline **21**. This isomer was chosen because the electronic interactions between the quinoline hetero atom and the dithiazole groups in **15a** and **21** are similar, but *intra*molecular participation by the hetero atom is not possible in **21**. Iminodithiazoloquinoline **21** (75%) was prepared from 6-aminoquinoline and Appel salt **1** by the general procedure, and was heated at 200 °C for 2 min (Method A). The only product isolated was the normal, expected fused thiazole **22** (51%), in accord with the above proposals.



Since the quinoline nitrogen atom is seen to participate effectively in the thermolysis of the imines **6** and **15a–c**, it is possible that it could participate in other reactions of these imines. We have reported, for example, that sodium hydride in hot THF readily opens the dithiazole ring of *N*-arylimines **2**; one equivalent gives the corresponding cyanothioanilide, ArNHCSCN, and a second equivalent gives the aryl isothiocyanate, ArNCS.[6] We therefore treated the quinolinylimines **15a** and **15c** with an equivalent of sodium hydride in refluxing THF; again the quinoline nitrogen participated to give the imidazoquinolinethiones **16a** and **16c**, identical with the thermolysis products and in comparable yield, 40 and 51% respectively. This sodium hydride reaction provides an attractive alternative to pyrolysis for the preparation of the imidazoquinolines **16**.

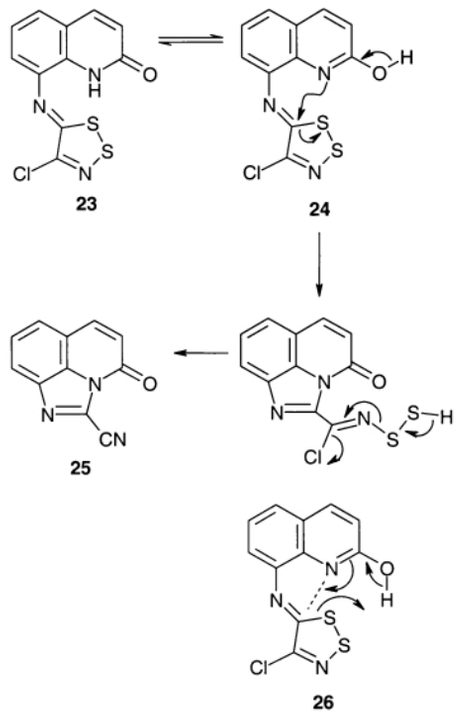
A mechanism is proposed for this hydride initiated reaction in Scheme 5. The reaction proceeds at a much lower temper-



Scheme 5

ature (boiling THF) than the thermolyses since the dithiazole ring is first opened by sodium hydride. The proposed mechanism follows the same general pattern as that for the thermal reaction (Scheme 4), with formation of the imidazole ring followed by intramolecular transfer of sulfur to the quinoline 2-position.

Conversion of the quinolinethione **13** into the quinolinone **14** (96%) with cupric nitrate in acetic anhydride has been mentioned above. The thione **16b** similarly gave the corresponding quinolinone (92%). The two series were further interrelated by conversion of quinolinone **25** (Scheme 6) into thione **16a** (78%) by treatment with one equivalent of Lawesson's reagent in toluene at reflux. The quinolinone **25**, and hence the quinolinethione **16a**, was independently synthesised as shown in Scheme 6. 8-Aminoquinolin-2-one, prepared by the stannous chloride reduction of the nitro compound, gave the iminodithiazole **23** (50%) with Appel salt under the low temperature conditions. This imine proved to be quite labile thermally, decomposing during crystallisation. On heating in boiling ethanol at 65 °C for 35 min, it was cleanly converted into the imidazoquinolinone **25** which with Lawesson's reagent gave the thione **16a**, both being identical with the compounds above. This thermolysis reaction is also considered to be initiated by



Scheme 6

the quinoline nitrogen (Scheme 6) which in the hydroxy tautomer **24** will be strongly nucleophilic, hence the mildness of the decomposition conditions. Opening of the dithiazole ring could possibly be assisted by the hydroxy group in a concerted manner (arrows in **26**).

Thus the reactions of the imines derived from 8-aminoquinolines and Appel salt **1**, described in this paper, not only construct the fused cyanoimidazole ring but also introduce functionality into the quinoline ring. This new, mechanistically interesting reaction provides a novel route to imidazo[4,5,1-*ij*]quinolines; various dihydro and tetrahydro derivatives of this ring system are known[7] but not the thio compounds reported here, and even the oxo compounds are rare.

Experimental

IR spectra were recorded on a Perkin-Elmer Paragon 1000PC instrument. ^{1}H and ^{13}C NMR were recorded on the following machines: JEOL JNM LA400 (400 MHz) spectrometer (Centre Commun d'Analyses, Université de la Rochelle, France); Bruker WM 500 (500 MHz/125 MHz) spectrometer (Imperial College, UK); chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane, which was used as internal standard. Mass spectra were recorded on an AE1 MS12 or a VG Micromass 7070B mass spectrometers (Imperial College); or on a Varian MAT311 in the Centre Régional de Mesures Physiques de l'Ouest (C.R.M.P.O., Université de Rennes, France). Chromatography was carried out on silica gel 60 at medium pressure and the sample mixtures were applied to the column preadsorbed onto silica. Light petroleum refers to the fraction bp 40–60 °C. Toluene was dried over sodium. Thin-layer chromatography was performed on Merck Kieselgel 60 F_{254} aluminium backed plates eluting with a gradient of dichloromethane–ethyl acetate. The following compounds were made by literature methods: 8-amino-4-phenylquinoline;[8] 2-methyl-8-nitroquinoline,[9] 7-methyl-8-nitroquinoline[10] and 2-chloro-8-nitroquinoline[11] were reduced to the amino compounds by stannous chloride in AcOH–HCl;[12] 2-chloro-8-nitroquinoline was hydrolysed with hot dilute aqueous hydrochloric acid to the quinolin-2(1*H*)-one which was reduced[12] to 8-aminoquinolin-2(1*H*)-one.[13] New spectroscopic data are given below.

8-Nitroquinolin-2(1*H*)-one

2-Chloro-8-nitroquinoline (0.4 g, 1.9 mmol) was stirred at reflux in aqueous HCl (10%, 10 ml) during 24 h. After cooling, the reaction mixture was neutralised with saturated sodium bicarbonate solution to pH 8 and extracted with ethyl acetate (2 × 20 ml). The extracts were combined and dried over magnesium sulfate and the solvent removed *in vacuo*. Chromatography of the residue with light petroleum–ethyl acetate (8:2) gave the title compound as yellow needles (94%), mp 160–162 °C (from ethanol) (lit.,[14] 163 °C) (Found: M^+, 190.0375. $C_9H_6N_2O_3$ requires *M*, 190.0378); ν_{max} (KBr)/cm^{-1} 3341 (NH), 1685 (C=O), 1524 (NO_2); δ_H (400 MHz, $CDCl_3$) 6.75 (1H, dd, *J* 1.8 and 9.7 Hz, H-3), 7.30 (1H, t, *J* 8.1 Hz, H-6), 7.79 (1H, d, *J* 9.7 Hz, H-4), 7.87 (1H, dd, *J* 1.3 and 7.6 Hz, H_{arom}), 8.50 (1H, dd, *J* 1.2 and 8.4 Hz, H_{arom}), 11.25 (1H, s, NH); *m*/*z* 190 (M^+, 100%), 116 (61).

8-Aminoquinolin-2(1*H*)-one

Elution with light petroleum–ethyl acetate (8:2) gave the title compound as colourless needles (87%), mp 244–246 °C (from ethanol) (Found: M^+, 160.0633. $C_9H_8N_2O$ requires *M*, 160.0636); ν_{max} (KBr)/cm^{-1} 3452 (NH_2), 3358 (NH), 1679 (C=O); δ_H (400 MHz, $CDCl_3$) 4.70 (2H, s, NH_2), 6.68 (1H, d, *J* 9.3 Hz, H-3), 6.89 (1H, dd, *J* 1.3 and 7.4 Hz, H_{arom}), 7.01 (1H, dd, *J* 1.3 and 7.4 Hz, H_{arom}), 7.06 (1H, t, *J* 7.7 Hz, H-6), 7.80 (1H, d, *J* 9.3 Hz, H-4), 12.50 (1H, s, NH); *m*/*z* 160 (M^+, 100%).

2,2-Dimethyl-5-(4-methoxy-2-nitrophenylaminomethylene)-1,3-dioxane-4,6-dione 7

A mixture of isopropylidene malonate (Meldrum's acid) (8.57 g, 59.5 mmol) and triethyl orthoformate (60 ml) was heated at reflux for 1 h and then allowed to cool slightly. Solid 4-methoxy-2-nitroaniline (10 g, 59.5 mmol) was added in one portion and the reaction mixture was then heated at reflux for 3.5 h and again allowed to cool to room temperature. The orange crystals were filtered off, washed with a little methanol and dried under vacuum to give the *title compound* as orange plates (17.2 g, 90%), mp 203–205 °C (Found: C, 51.9; H, 4.2; N, 8.6. $C_{14}H_{14}N_2O_7$ requires C, 52.1; H, 4.3; N, 8.7%); ν_{max} (KBr)/cm^{-1} 1728 (C=C), 1690 (C=O); δ_H (270 MHz, $CDCl_3$) 1.76 (6H, s, ^{i}Pr), 3.92 (3H, s, OMe), 7.31 (1H, dd, *J* 3.0 and *J* 9.0 Hz, H-5), 7.55 (1H, d, *J* 8.0 Hz, H-6), 7.76 (1H, d, *J* 3.0 Hz, H-3), 8.64 (1H, d, *J* 13.9 Hz, =CHN); δ_C (100 MHz, $CDCl_3$) 27.2, 56.2, 90.2, 105.3, 109.9, 119.5, 123.3, 127.5, 138.7, 151.4, 157.2, 163.4, 164.3; *m*/*z* 322 (M^+, 2.5%), 264 ($M^+ - CH_3COCH_3$, 22), 220 ($M^+ - CH_3COCH_3 - CO_2$, 9).

4-Chloro-6-methoxy-8-nitroquinoline 8

A solution of 2,2-dimethyl-5-(4-methoxy-2-nitrophenylaminomethylene)-1,3-dioxane-4,6-dione **7** (20 g, 62 mmol) in diphenyl ether (200 ml) was heated at 180 °C for 10 min then allowed to cool to room temperature. To this solution was slowly added dropwise light petroleum (bp 60–80 °C) (250 ml) over 20 min with stirring. The resulting precipitate was filtered off and washed thoroughly with more light petroleum and then dried *in vacuo* to give a solid (12.2 g, 89%). This was dissolved in phosphorus oxychloride (165 ml) and to this mixture was added phosphorus pentachloride (11.55 g, 55.5 mmol, 1 eq.). The reaction mixture was heated to reflux for 1 h and then most of the phosphorus oxychloride was removed by distillation to leave a thick oily residue. This residue was poured into iced water and neutralised to pH 8 using 10% sodium hydroxide. The resulting precipitate was filtered off, washed with water and dried *in vacuo*. Recrystallisation from ethyl acetate gave the title compound as pale yellow needles (8.31 g, 56% overall), mp 176–177 °C (Found: C, 50.2; H, 2.8; N, 11.7. $C_{10}H_7ClN_2O_3$ requires C, 50.3; H, 2.9; N, 11.7%); ν_{max} (KBr)/cm^{-1} 1628 (NO_2); δ_H (270 MHz, $CDCl_3$) 4.03 (3H, s, OMe), 7.59 (1H, d, *J* 4.6 Hz, H-3),

7.64 (1H, d, *J* 2.7 Hz, H-5), 7.71 (1H, d, *J* 2.7 Hz, H-7), 8.75 (1H, d, *J* 4.6 Hz, H-2); δ_C (100 MHz, $CDCl_3$) 56.4, 105.6, 117.2, 123.0, 128.3, 136.3, 141.3, 149.1, 149.3, 157.1; *m*/*z* 238 (M^+, 100%), 208 ($M^+ - OCH_3$, 20), 180 ($M^+ - CH_3 - NO_2$, 39).

8-Amino-4-chloro-6-methoxyquinoline 9

To a solution of 4-chloro-6-methoxy-8-nitroquinoline **8** (1.0 g, 4.2 mmol) in ethanol (10 ml) at room temperature was added $SnCl_2 \cdot 2H_2O$ (5.29 g, 21 mmol). The mixture was heated at reflux for 30 min and then allowed to cool to room temperature, poured into iced water and then neutralised with 10% sodium bicarbonate solution to pH 9. The resulting suspension was extracted with ethyl acetate and the combined extracts were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. Recrystallisation of the residue from light petroleum (bp 60–80 °C) gave the *title compound* as pale yellow needles (0.84 g, 96%), mp 94–95 °C (Found: C, 57.5; H, 4.1; N, 13.3. $C_{10}H_9ClN_2O$ requires C, 57.6; H, 4.3; N, 13.4%); ν_{max} (KBr)/cm^{-1} 3427 (NH_2); δ_H (270 MHz, $CDCl_3$) 3.89 (3H, s, OMe), 5.05 (2H, br s, NH_2), 6.56 (1H, d, *J* 2.4 Hz, H-5), 6.77 (1H, d, *J* 2.4 Hz, H-7), 7.38 (1H, d, *J* 4.7 Hz, H-3), 8.41 (1H, d, *J* 4.7 Hz, H-2); δ_C (100 MHz, $CDCl_3$) 55.3, 91.1, 102.0, 121.8, 128.1, 136.1, 140.7, 143.8, 145.5, 159.7; *m*/*z* 208 (M^+, 100%), 179 ($M^+ - OCH_3$, 47), 165 ($M^+ - NO_2$, 25).

8-Acetamido-4-chloro-6-methoxyquinoline 10

To a suspension of 8-amino-4-chloro-6-methoxyquinoline **9** (1.0 g, 4.8 mmol) in glacial acetic acid (3 ml) was added acetic anhydride (1 ml). The mixture was heated at reflux for 30 min then allowed to cool and poured into iced water. The resulting white solid was filtered off, washed with water and dried under vacuum. The solid was recrystallised from ethyl acetate to give colourless needles (1.0 g, 92%), mp 202 °C (subl.) (Found: C, 57.6; H, 4.3; N, 11.1. $C_{12}H_{11}ClN_2O_2$ requires C, 57.6; H, 4.4; N, 11.2%); ν_{max} (KBr)/cm^{-1} 3311 (NH), 1674 (C=O); δ_H (270 MHz, $CDCl_3$) 2.34 (3H, s, CH_3CO), 3.96 (3H, s, OMe), 7.10 (1H, d, *J* 2.7 Hz, H-5), 7.48 (1H, d, *J* 4.9 Hz, H-3), 8.47 (1H, d, *J* 4.9 Hz, H-2), 8.53 (1H, d, *J* 2.7 Hz, H-7), 9.65 (1H, br s, NH); δ_C (100 MHz, $CDCl_3$) 25.1, 55.6, 96.1, 109.6, 122.2, 127.3, 135.7, 135.8, 141.3, 144.5, 159.5, 168.7; *m*/*z* 250 (M^+, 45%), 235 ($M^+ - CH_3$, 24), 208 ($M^+ - CH_3C{=}O$, 100).

8-Acetamido-6-methoxy-4-phenylquinoline 11

A mixture of 8-acetamido-4-chloro-6-methoxyquinoline **10** (0.355 g, 1.42 mmol), phenylboronic acid (0.173 g, 1.56 mmol), tetrakis(triphenylphosphine)palladium(0) (0.082 g, 5 mol%), benzene (3.5 ml), ethanol (0.48 ml), 2 M sodium carbonate solution (3.12 ml) was heated at reflux for 48 h and then allowed to cool to room temperature. The mixture was extracted with DCM three times and the combined organic solution was washed with water three times and brine before being dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The solid was filtered through a short pad of silica gel using ethyl acetate as eluent and the solvents again removed under reduced pressure to give the title compound as colourless needles (0.398 g, 96%), mp 167–168 °C (ethyl acetate–light petroleum, bp 60–80 °C) (Found: C, 73.7; H, 5.4; N, 9.6. $C_{18}H_{16}N_2O_2$ requires C, 73.9; H, 5.5; N, 9.6%); ν_{max} (KBr)/cm^{-1} 3292 (NH), 1668 (C=O); δ_H (270 MHz, $CDCl_3$) 2.35 (3H, s, CH_3CO), 3.77 (3H, s, OMe), 6.86 (1H, d, *J* 2.7 Hz, H-5), 7.28 (1H, d, *J* 4.4 Hz, H-3), 7.46–7.52 (5H, m, Ph), 8.53 (1H, d, *J* 2.7 Hz, H-7), 8.62 (1H, d, *J* 4.4 Hz, H-2), 9.88 (1H, br s, NHAc); δ_C (100 MHz, $CDCl_3$) 25.1, 55.43, 98.4, 108.3, 122.4, 127.3, 128.4, 128.6, 129.2, 135.2, 135.7, 138.2, 144.9, 147.4, 158.4, 168.8; *m*/*z* 292 (M^+, 76%), 277 ($M^+ - CH_3$, 82), 250 ($M^+ - CH_3C{=}O$, 100), 221 ($M^+ - CH_3C{=}O - OCH_3$, 56).

8-Amino-6-methoxy-4-phenylquinoline 12

A suspension of 8-acetamido-6-methoxy-4-phenylquinoline **11** (1.5 g, 5.1 mmol) in hydrochloric acid (37%, 20 ml) was heated at 80 °C for 15 min and then allowed to cool to room temperature, poured into iced water and then neutralised with 10% sodium bicarbonate solution to pH 8. The resulting suspension was extracted with ethyl acetate and the combined extracts were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude material was separated by flash column chromatography using light petroleum–ethyl acetate (5:5) to give the title compound as colourless needles (86%), mp 28–30 °C; ν_{max} (KBr)/cm^{-1} 3354 (NH_2), 1620, 1560, 1515, 1370; δ_H (270 MHz, $CDCl_3$) 3.71 (3H, s, CH_3O), 5.07 (2H, br s, NH_2), 6.54 (1H, d, *J* 2.5 Hz, H-5 or H-7), 6.58 (1H, d, *J* 2.5 Hz, H-7 or H-5), 7.22–7.24 (1H, m, H_{arom}), 7.42–7.50 (5H, m, H_{phen}), 8.61 (1H, d, *J* 4.2 Hz, H-2); *m*/*z* 250 (M^+, 100%).

Imino-1,2,3-dithiazoles: general procedure

Under an inert atmosphere (argon), dithiazolium salt **1** (0.208 g, 1 mmol) was added to a solution of the 8-aminoquinoline (1 mmol) in dichloromethane (5 ml). The mixture was cooled (−20 °C) and pyridine (2 mmol) added. The mixture was stirred until all of the amine had been used up. The mixture was warmed to room temperature and then was either filtered through acidic alumina eluting with DCM, or poured into ice–water–DCM to separate the organic layer. In the latter case, the aqueous layer was extracted with DCM and the combined organic solution was washed with HCl, water, brine and dried over magnesium sulfate. The filtered solvents were removed under reduced pressure and the residue was separated by chromatography using DCM–ethyl acetate as eluent.

6-Methoxy-4-phenyl-8-[*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)amino]quinoline 6. Elution with DCM–ethyl acetate (8:2) gave the compound as a brown oil (42%) (Found: M^+, 385.0103 $C_{18}H_{12}ClN_3OS_2$ requires *M*, 385.0110); ν_{max} (KBr)/cm^{-1} 1606, 1565, 1465, 1155; δ_H (270 MHz, $CDCl_3$) 3.81 (3H, s, CH_3O), 7.12 (1H, d, *J* 2.7 Hz, H-7), 7.21 (1H, d, *J* 2.7 Hz, H-5), 7.42 (1H, d, *J* 4.7 Hz, H-3), 7.48–7.50 (5H, m, H_{phen}), 8.87 (1H, d, *J* 4.7 Hz, H-2); δ_C (100 MHz, $CDCl_3$) 55.6, 93.3, 102.4, 110.1, 122.5, 128.5, 128.7, 129.3, 135.9, 138.1, 143.4, 146.6, 147.8, 149.7, 157.8, 161.2; *m*/*z* 385 (M^+, 10%), 292 ($M^+ - ClCNS$, 48), 286 ($M^+ - Cl - S_2$, 100).

8-[*N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)amino]quinoline 15a. Elution with DCM–ethyl acetate (8:2) gave the compound as brown needles (65%), mp 144–146 °C (decomp.) (Found: M^+, 278.9698. $C_{11}H_6ClN_3S_2$ requires *M*, 278.9692); ν_{max} (KBr)/cm^{-1} 1724, 1592, 862, 793; δ_H (270 MHz, $CDCl_3$) 7.46–7.54 (2H, m, H_{arom}), 7.62 (1H, t, *J* 7.6 Hz, H-6), 7.75 (1H, dd, *J* 1.1 and 8.4 Hz, H_{arom}), 8.25 (1H, dd, *J* 1.6 and 8.4 Hz, H_{arom}), 8.96 (1H, dd, *J* 1.6 and 4.2 Hz, H-2); δ_C (100 MHz, $CDCl_3$) 118.3, 121.9, 125.8, 127.0, 128.7, 129.5, 130.9, 136.9, 147.9, 149.7, 167.6; *m*/*z* 279 (M^+, 14%), 244 ($M^+ - Cl$, 27), 180 ($M^+ - S_2$, Cl, 100).

4-Phenyl-8-[*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)amino]-quinoline 15b. Elution with DCM–ethyl acetate (8:2) gave the compound as a brown–yellow oil (40%) (Found: M^+, 355.6847. $C_{17}H_{10}ClN_3S_2$ requires *M*, 355.6849); ν_{max} (KBr)/cm^{-1} 1607, 1565, 1465, 1155; δ_H (270 MHz, $CDCl_3$) 7.06 (1H, d, *J* 4.5 Hz, 3-H), 7.10–7.23 (7H, m, H_{arom}, H_{phen}), 7.46 (1H, dd, *J* 9 and 1.2 Hz, H-6), 8.60 (1H, d, *J* 4.5 Hz, H-2); *m*/*z* 355 (M^+, 5%), 320 ($M^+ - Cl$, 2), 287 ($M^+ - HCl - S$, 100), 262 ($M^+ - ClCNS$, 38).

7-Methyl-8-[*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)amino]-quinoline 15c. Elution with DCM–ethyl acetate (8:2) gave the compound as a brown oil (35%) (Found: M^+, 292.9846. $C_{12}H_8ClN_3S_2$ requires *M*, 292.9849); ν_{max} (KBr)/cm^{-1} 1603,

1568, 1463, 1150; δ_H (270 MHz, $CDCl_3$) 2.86 (3H, s, CH_3), 7.45 (1H, d, *J* 7.6 Hz, H_{arom}), 7.50 (1H, dd, *J* 4.2 and 8.4 Hz, H-3), 7.65 (1H, dd, *J* 0.8 and 7.6 Hz, H_{arom}), 8.71 (1H, dd, *J* 1.8 and 8.4 Hz, H-4), 9.04 (1H, dd, *J* 1.8 and 4.2 Hz, H-2); δ_C (100 MHz, $CDCl_3$) 18.4, 112.1, 119.6, 121.7, 123.9, 129.3, 133.1, 136.2, 144.4, 148.8, 149.9, 157.1; *m*/*z* 293 (M^+, 10%), 258 ($M^+ - Cl$, 10), 225 ($M^+ - HCl - S$, 20), 200 ($M^+ - ClCNS$, 100).

2-Methyl-8-[*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)amino]-quinoline 15d. Elution with DCM–ethyl acetate (8:2) gave the compound as brown needles (53%), mp 168–170 °C (decomp.) (Found: M^+, 292.9847. $C_{12}H_8ClN_3S_2$ requires *M*, 292.9849); ν_{max} (KBr)/cm^{-1} 1605, 1565, 1465, 1155; δ_H (270 MHz, $CDCl_3$) 2.73 (3H, t, CH_3), 7.32 (1H, d, *J* 8.8 Hz, H-3), 7.45–7.53 (2H, m, H_{arom}), 7.65 (1H, dd, *J* 7.8 and 1.2 Hz, H-7), 8.07 (1H, d, *J* 8.8 Hz, H-4); δ_C (100 MHz, $CDCl_3$) 25.2, 118.2, 119.5, 123.1, 123.6, 125.5, 125.6, 125.9, 126.3, 127.7, 136.8, 158.7; *m*/*z* 293 (M^+, 10%), 258 ($M^+ - Cl$, 7), 225 ($M^+ - HCl - S$, 30), 200 ($M^+ - ClCNS$, 100).

2-Chloro-8-[*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)amino]-quinoline 15e. Elution with DCM–ethyl acetate (8:2) gave the compound as a brown oil (46%); ν_{max} (film)/cm^{-1} 1600, 1565, 1465, 1155; δ_H (400 MHz, $CDCl_3$) 6.92 (1H, d, *J* 8.8 Hz, H-3), 7.40–7.60 (2H, m, H_{arom}), 7.72 (1H, dd, *J* 8.6 and 1.4 Hz, H-7), 8.16 (1H, d, *J* 8.6 Hz, H-4); *m*/*z* 313 (M^+, 17%), 278 ($M^+ - Cl$, 65), 220 ($M^+ - ClCNS$, 25), 214 (100).

6-[*N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)amino]quinoline 21. Elution with DCM–ethyl acetate (8:2) gave the *title compound* as yellow needles (75%), mp 158–160 °C (Found: M^+, 278.9698. $C_{11}H_6ClN_3S_2$ requires *M*, 278.9691); ν_{max} (KBr)/cm^{-1} 1626, 1557, 1412, 1155; δ_H (400 MHz, $CDCl_3$) 7.44 (1H, dd, *J* 8.2 and 4.2 Hz, H-3), 7.58–7.64 (2H, m, H_{arom}), 8.12–8.27 (2H, m, H_{arom}), 8.92 (1H, d, *J* 2.8 Hz, H-2); δ_C (100 MHz, $CDCl_3$) 115.4, 121.8, 123.8, 128.9, 131.5, 136.0, 146.6, 147.9, 149.3, 150.1, 159.7; *m*/*z* 279 (M^+, 10%), 244 ($M^+ - Cl$, 10), 211 ($M^+ - HCl - S$, 20), 186 ($M^+ - ClCNS$, 100).

8-[*N*-(4-Chloro-5*H*-1,2,3-dithiazol-5-ylidene)amino]quinolin-2(1*H*)-one 23. Elution with DCM–ethyl acetate (8:2) gave the compound as a brown oil (50%) (Found: M^+, 294.9684. $C_{11}H_6ClN_3OS_2$ requires *M*, 294.9682); ν_{max} (KBr)/cm^{-1} 3345, 1673; δ_H (400 MHz, $CDCl_3$) 6.75 (1H, dd, *J* 1.9 and 9.5 Hz, H-3), 7.32 (1H, t, *J* 7.8 Hz, H-6), 7.52 (1H, d, *J* 8.6 Hz, H_{arom}), 7.66 (1H, dd, *J* 1.0 and 7.4 Hz, H_{arom}), 7.80 (1H, d, *J* 9.5 Hz, H-4), 9.60 (1H, s, NH); *m*/*z* 295 (M^+, 10%), 260 ($M^+ - Cl$, 30), 195 ($M^+ - S_2$, Cl, 100).

Thermolysis of imino-1,2,3-dithiazoles: general procedures

Method A. The 8-[*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-amino]quinoline (0.1 g) was heated neat under nitrogen at 200–250 °C for 1 min. The product was isolated by flash chromatography using light petroleum–ethyl acetate (6:4) as eluting solvent.

Method B. The 8-[*N*-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-amino]quinoline (0.5 mmol) was heated at 250 °C under nitrogen in a minimum amount of toluene (5 drops) in a sealed tube for 3 h. The product was isolated by flash chromatography using light petroleum–ethyl acetate (6:4) as eluting solvent.

2-Cyano-8-methoxy-6-phenyl-4*H*-imidazo[4,5,1-*ij*]quinoline-4-thione 13

Method A. Compound **6** gave compound **13** as red needles (42%), mp 258–262 °C (from ethanol) (Found: M^+, 317.0623. $C_{18}H_{11}N_3OS$ requires *M*, 317.0618); ν_{max} (KBr)/cm^{-1} 2230 (CN), 1261; δ_H (270 MHz, $CDCl_3$) 3.92 (3H, s, CH_3O), 7.36 (1H, s, H-3), 7.45 (1H, d, *J* 1.9 Hz, H-5 or H-7), 7.51–7.60 (6H, m, H_{phen}, H-5 or H-7); *m*/*z* 317 (M^+, 100%), 302 ($M^+ - Me$, 9), 284 ($M^+ - Me - H_2O$, 8). Thermolysis in boiling toluene (12 h) gave 49% yield.

2-Cyano-4*H*-imidazo[4,5,1-*ij*]quinoline-4-thione 16a

Method B. Compound **15a** gave compound **16a** as red needles (52%), mp 230–232 °C (from ethanol) (Found: M^+, 211.0204. $C_{11}H_5N_3S$ requires *M*, 211.0203); ν_{max} (KBr)/cm^{-1} 2233 (CN), 1600, 1533, 1162; δ_H (400 MHz, $CDCl_3$) 7.34 (1H, d, *J* 9.3 Hz, H_{arom}), 7.59 (1H, d, *J* 9.3 Hz, H_{arom}), 7.62 (1H, d, *J* 8.1 Hz, H_{arom}), 7.84 (1H, d, *J* 7.5 Hz, H_{arom}), 8.09 (1H, d, *J* 8.1 Hz, H_{arom}); δ_C (100 MHz, $CDCl_3$) 111.2, 120.6, 124.8, 125.9, 127.6, 127.9, 129.5, 130.5, 136.5, 139.6, 182.3; *m*/*z* 211 (M^+, 100%), 153 ($M^+ - CN - S$, 95).

Hydride procedure. A solution of the iminodithiazole **15a** (0.2 g, 0.7 mmol) in dry THF (5 ml) was stirred at 67 °C for 18 h in the presence of sodium hydride (60% dispersion in mineral oil, 27 mg, 0.7 mmol). The reaction mixture was filtered and the solvent evaporated from the filtrate. The residue was dissolved in ethyl acetate, washed with water, dried over sodium sulfate and purified by column chromatography with light petroleum–ethyl acetate (60:40) as eluent to give **16a** (50%) identical with that described above.

Microwave irradiation. The iminodithiazole **15a** (0.1 g, 0.36 mmol) in 2,6-lutidine (1 ml) or in toluene (1 ml) was placed in the microwave oven in a glass vial (10 ml) with a screw-cap lid. The irradiation was programmed for 3 min with a delay of 5 s to obtain 100% power output (300 W). The initial temperature (infrared measurement) was constant over a period of 15 to 30 s followed by a sharp increase over a period of 45 s. The irradiation was stopped 2 min later. After cooling, the brown reaction mixture was purified by column chromatography as above. Compound **15a** gave **16a** identical with that described above in 42 or 20% yield respectively.

Photolysis procedure. A stirred solution of iminodithiazole **15a** (0.1 g, 0.36 mmol) in toluene (3 ml) was heated with a lamp bulb (100 W) at reflux for 6 h. The mixture was allowed to cool. The crude material was purified by column chromatography as above to give **16a** (38%) identical with that described above.

Thionation procedure. A stirred solution of 2-cyano-4*H*-imidazo[4,5,1-*ij*]quinolin-4-one **25** (0.1 g, 0.5 mmol) in anhydrous toluene (5 ml) was treated with commercially available Lawesson's reagent (0.29 g, 0.5 mmol). The mixture was refluxed for 6 h, evaporated to dryness and the resulting material purified by column chromatography with light petroleum–ethyl acetate (60:40) as eluent to give **16a** (78%) identical with that described above.

2-Cyano-6-phenyl-4*H*-imidazo[4,5,1-*ij*]quinoline-4-thione 16b

Method B. Compound **15b** gave compound **16b** as brown needles (38%), mp 236–238 °C (from ethanol) (Found: M^+, 287.0517. $C_{17}H_9N_3S$ requires *M*, 287.0517); ν_{max} (KBr)/cm^{-1} 2237 (CN), 1229; δ_H (270 MHz, $CDCl_3$) 7.38 (1H, s, H-5), 7.54–7.68 (6H, m, H_{phen}, H_{arom}), 7.89 (1H, d, *J* 8.0 Hz, H_{arom}), 8.11 (1H, d, *J* 8.0 Hz, H_{arom}); *m*/*z* 287 (M^+, 100%), 229 ($M^+ - CN - S$, 35).

2-Cyano-9-methyl-4*H*-imidazo[4,5,1-*ij*]quinoline-4-thione 16c

Method B. Compound **15c** gave compound **16c** as red needles (40%), mp >250 °C (from ethanol) (Found: M^+, 225.0362. $C_{12}H_7N_3S$ requires *M*, 225.0361); ν_{max} (KBr)/cm^{-1} 2923, 2229 (CN), 1600, 1532, 1304, 1163; δ_H (270 MHz, $CDCl_3$) 2.76 (3H, s, CH_3), 7.29 (1H, d, *J* 9.0 Hz, H_{arom}), 7.39 (1H, d, *J* 7.9 Hz,

H_{arom}), 7.53 (1H, d, *J* 9.1 Hz, H_{arom}), 7.70 (1H, d, *J* 7.9 Hz, H_{arom}); δ_C (100 MHz, $CDCl_3$) 16.8, 111.3, 118.5, 127.7, 128.7, 129.8, 130.5, 130.8, 135.4, 138.7, 139.2, 183.4; *m*/*z* 225 (M^+, 100%), 167 ($M^+ - CN - S$, 35).

2-Cyano-4-methyl-4*H*-imidazo[4,5,1-*ij*]quinoline-4-thiol 20

Method B. Compound **15d** gave compound **20** as a dark oil (<5%) (Found: M^+, 227.0517. $C_{12}H_9N_3S$ requires *M*, 227.0512); ν_{max} (KBr)/cm^{-1} 3203, 2981, 2935, 2227, 1596, 1321, 1269, 1103, 841, 807; δ_H (400 MHz, $CDCl_3$) 2.80 (3H, s, CH_3), 7.44 (1H, d, *J* 8.4 Hz, H_{arom}), 7.52 (1H, t, *J* 8.0 Hz, H_{arom}), 7.72 (1H, d, *J* 8.3 Hz, H_{arom}), 8.13 (1H, d, *J* 8.4 Hz, H_{arom}), 9.57 (1H, d, *J* 7.8 Hz, H_{arom}); δ_C (100 MHz, $CDCl_3$) 25.2, 114.0, 118.1, 123.6, 125.5, 125.7, 125.9, 133.4, 136.7, 137.7, 158.6, 159.8; δ_C (100 MHz, $CDCl_3$) DEPT (Distortionless Enhancement by Polarisation Transfer, angle 135°) 25.2, 118.1, 123.6, 125.5, 125.7, 136.7; *m*/*z* 227 (M^+, 8%), 226 ($M^+ - H$, 11), 200 ($M^+ - H - CN$, 35), 193 ($M^+ - H_2S$, 100), 140 (25). Further elution gave traces of a compound (<0.5%) tentatively assigned as 2-cyano-5-methylthiazolo[5,4-*h*]quinoline; δ_H (400 MHz, $CDCl_3$) 2.75 (3H, s, CH_3), 7.40 (1H, d, *J* 7.9 Hz, H_{arom}), 7.45 (1H, d, *J* 8.6 Hz, H_{arom}), 7.60 (1H, d, *J* 8.2 Hz, H_{arom}), 8.49 (1H, d, *J* 8.6 Hz, H_{arom}); *m*/*z* 225 (M^+).

Thiazolo[5,4-*f*]quinoline-2-carbonitrile 22

Method B. Compound **21** gave compound **22** as yellow needles (51%); mp 218–220 °C (Found: M^+, 211.0204. $C_{11}H_5N_3S$ requires *M*, 211.0196); ν_{max} (KBr)/cm^{-1} 3035, 2232, 1600, 1555, 1497, 1380, 1314, 1267, 1140, 830, 805; δ_H (400 MHz, $CDCl_3$) 7.62 (1H, dd, *J* 8.3 and 4.4 Hz, H-3), 8.27 (1H, d, *J* 9.2 Hz, H-8), 8.35–8.45 (2H, m, H-4, H-7), 9.11 (1H, dd, *J* 1.6 and 4.4 Hz, H-2); δ_C (100 MHz, $CDCl_3$) 112.7, 122.4, 122.7, 125.6, 130.9, 133.4, 133.6, 136.0, 147.6, 151.0, 151.6; *m*/*z* 211 (M^+, 100%), 185 ($M^+ - CN$, 10).

2-Cyano-4*H*-imidazo[4,5,1-*ij*]quinolin-4-one 25

Method B. Compound **23** gave compound **25** as colourless needles (40%), mp >240 °C (from ethanol) (Found: M^+, 195.0435. $C_{11}H_5N_3O$ requires *M*, 195.0433; ν_{max} (KBr)/cm^{-1} 2242 (CN), 1702 (C=O), 1640, 1605, 1305, 1134; δ_H (400 MHz, $CDCl_3$) 6.77 (1H, d, *J* 9.7 Hz, H-5), 7.67 (1H, t, *J* 7.5 Hz, H-8), 7.85 (1H, d, *J* 7.5 Hz, H_{arom}), 7.95 (1H, d, *J* 9.7 Hz, H-6), 8.12 (1H, d, *J* 8.1 Hz, H_{arom}); δ_C (100 MHz, $CDCl_3$) 117.7, 121.4, 123.7, 124.3, 125.7, 127.3, 127.6, 127.9, 139.7, 140.1, 156.6; *m*/*z* 195 (M^+, 100%). The crude material **23** in refluxing ethanol gave cleanly compound **25** identical with that described above.

Oxidation of thiones

To a suspension of the 4*H*-imidazo[4,5,1-*ij*]quinoline-4-thione (1 mmol) in acetic anhydride (5 ml) was added $Cu(NO_3)_2 \cdot 3H_2O$ (2 mmol) in one portion. The mixture was stirred at room temperature for 2 h and then poured into a DCM and saturated aqueous sodium hydrogen carbonate solution bilayer and stirred for 10 min. The organic layer was separated and the aqueous layer extracted with DCM twice. The combined organic extracts were washed with saturated sodium hydrogen carbonate and brine, dried over magnesium sulfate and the solvents removed under reduced pressure. Column chromatography of the residue, eluting with light petroleum–ethyl acetate (6:4) gave the following compounds.

2-Cyano-8-methoxy-6-phenyl-4*H*-imidazo[4,5,1-*ij*]quinolin-4-one 14. Compound **13** gave compound **14** as yellow needles (96%), mp 242–244 °C (from ethanol) (Found: M^+, 301.0834. $C_{18}H_{11}N_3O_2$ requires *M*, 301.0851); ν_{max} (KBr)/cm^{-1} 2226 (CN), 1692 (C=O); δ_H (400 MHz, $CDCl_3$) 3.93 (3H, s, CH_3O), 6.73 (1H, s, H-5), 7.46 (1H, d, *J* 2.0 Hz, H_{arom}), 7.58–7.60 (6H, m, H_{phen}, H_{arom}); *m*/*z* 301 (M^+, 100%), 286 ($M^+ - Me$, 29), 270 ($M^+ - OMe$, 9).

2-Cyano-6-phenyl-4*H*-imidazo[4,5,1-*ij*]quinolin-4-one. Compound **16b** gave the *title compound* as colourless needles (92%), mp >240 °C (from ethanol) (Found: M^+, 271.0735. $C_{17}H_9N_3O$ requires *M*, 271.0745); ν_{max} (KBr)/cm^{-1} 2258 (CN), 1698 (C=O); δ_H (400 MHz, $CDCl_3$) 6.81 (1H, s, H-5), 7.66 (5H, m, H_{phen}), 7.73 (1H, dd, *J* 8.2 and 7.8 Hz, H-8), 7.94 (1H, d, *J* 7.8 Hz, H-7), 8.21 (1H, d, *J* 8.2 Hz, H-9); *m*/*z* 271 (M^+, 93), 270 ($M^+ - 1$, 100%).

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