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The Proton Sponge Effect: Substitution of Quino[7,8-*h*]quinoline and the First Structurally Characterised Derivatives

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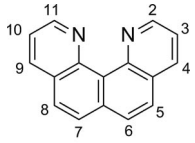
A new route to unsymmetrical derivatives of quino[7,8-*h*]-quinoline was developed. Substitutions at the 2,11-, 4,9- and 6,7-positions of quino[7,8-*h*]quinoline were also successfully performed. X-ray crystal structure determinations of the resulting products revealed the propensity for derivatives of this molecule to exist in either stabilised keto or imino forms as a result of the formation of a strong intramolecular N–H···N hydrogen bond.

Introduction

Quino[7,8-*h*]quinoline (Figure 1) is known for its association with the class of molecules known as proton sponges. These are a class of molecules classified according to the destabilising overlap of the lone pair of electrons on adjacent nitrogen atoms within the molecule. This strained orientation is released upon binding of a proton that forms a strong hydrogen bond between these nitrogen atoms. 1,8-Bis(dimethylaminonaphthalene) (DMAN),[1] trademarked by Aldrich as Proton Sponge was the original, and investigations into derivatives of DMAN is now well established and covered by numerous reviews.[2]



I

Figure 1. Quino[7,8-*h*]quinoline (**I**) showing the atom-numbering scheme.

The synthesis of quino[7,8-*h*]quinoline was first reported 25 years ago by Zirnstein and Staab.[3] During the intervening quarter century, very few research groups have explored the coordination ability of this intriguing ligand, with just a handful of reports on the subject to date.[4,5,6] The ability to functionalise heterocyclic compounds greatly enhances their utility, especially in the field of supramolecular chemistry where heterocyclic compounds similar to quino[7,8-*h*]-quinoline such as 1,10-phenantholrolene and 2,2′-bipyridine are important building blocks. In this study, we were interested in the extent to which quino[7,8-*h*]quinoline could be functionalised, with the eventual aim of enhancing the photophysical properties of this potentially useful ligand. The unusual structural features of quino[7,8-*h*]quinoline molecules make X-ray crystallography a valuable technique in elucidating the behavior and solid-state forms of these molecules. We have therefore recorded single-crystal X-ray structures of as many of the substituted ligands as possible in both their neutral and protonated forms. We have previously reported on boron difluoride[5] and Cu^{II}[4b] complexes of quino[7,8-*h*]quinoline.

Results and Discussion

2,11-Substitution of Quino[7,8-*h*]quinoline

Given the rarity of quino[7,8-*h*]quinoline derivatives in general, we were interested in developing synthetic protocols for peripheral modification of the ring; ideally we wanted to be able to alter the substitution at any position. Our initial studies started with an attempt to form compounds with substitution at the 2,11-positions, which are situated at either side of the potentially chelating nitrogen atoms, to see whether this would influence the binding site of these nitrogen atoms. An attractive route appeared to be the use of the double Skaup cyclisation with 3-bis(methylthio)acrolein and 1,8-diaminonaphthalene (**1**), which was reported to give **2** in 40% yield (Scheme 1).[7]

Despite numerous attempts, we were unable to reproduce this reaction. The failure was identified to be specific to **1**, as repeating the reported reaction conditions with other simple anilines gave the expected quinolines. In our hands, the reported experimental conditions resulted in intractable

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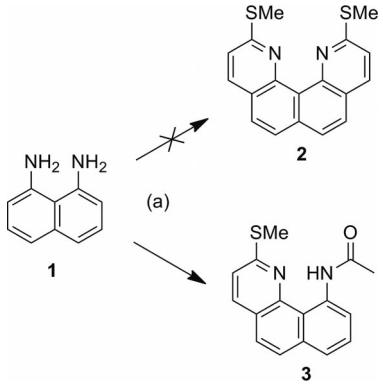


Scheme 1. Attempted double Skraup condensation of **1**. Reagents and conditions: (a) 3,3-bis(methylthio)acrylaldehyde, HOAc, reflux, 8 h.

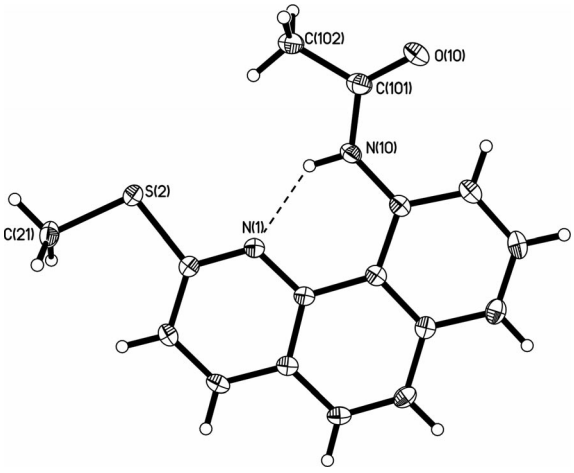
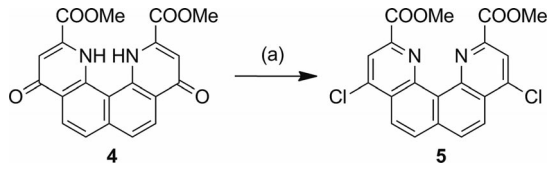


Figure 2. Crystal structure of **3** showing the internal H-bond; ellipsoids are drawn at the 50% probability level.

black tar; however, we were able to isolate and purify a small quantity of a white compound, which, once characterised, was identified as compound **3**; the result of both a single condensation and acetylation reaction. Subsequent single-crystal X-ray structure analysis confirmed this assignment (Figure 2). The asymmetric unit of the crystal structure of **3** consisted of one molecule of **3** and no solvent molecules (Figure 2). Analysis of the structure revealed that the acetamide group is oriented such that there exists a moderate electrostatic hydrogen bond[8] (located from the Fourier difference map) between the central nitrogen atoms; N(10)–H 1.940(1) Å, N(1)–N(10) 2.639(1) Å, N(1)–H–N(10) 138.0(1)°. The ^{1}H NMR chemical shift for this hydrogen was found at δ = 14.3 ppm, which indicates that this hydrogen bond is also present in solution. As no spectroscopic or analytical data was supplied in the original paper to support the formation of **2**, we could not compare it to the product we isolated. The purification method described for **2** used silica gel chromatography eluting with a very nonpolar solvent gradient (hexanes/ethyl acetate, 9:1), and we have not yet synthesised a quino[7,8-*h*]quinoline compound that elutes under these conditions. This led us to believe that **3** may have been mistakenly characterised as **2** in the original report.

The failure of this route led us to look at the original synthesis of **I** (Figure 1) that proceeded via **4**.[9] By directly treating **4** with phosphorus oxychloride, new methyl ester substituted proton sponge **5** (Scheme 2) was conveniently formed and fully characterised.



Scheme 2. Synthesis of 2,11-substituted **5**. Reagents and conditions: (a) $POCl_3$, 130 °C, 9 min.

The molecular structure of the protonated form of **5** (obtained from the reaction with $BF_3{\cdot}OEt_2$ in the presence of trace amounts of water) confirmed the ester groups were retained during the reaction (Figure 3).

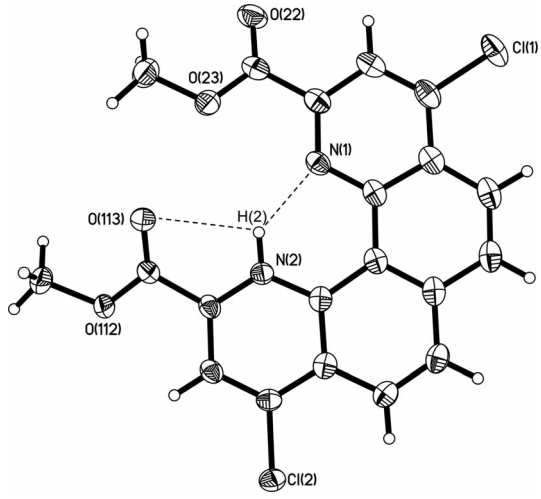


Figure 3. Crystal structure of the cation [H(**5**)]$^+$ showing the close contacts of H(2); ellipsoids are drawn at the 50% probability level.

The asymmetric unit consists of two molecules of **5** and two tetrafluoroborate anions. The protons on N(2) and N(2B) (from the second molecule in the asymmetric unit) were found by way of the Fourier difference map. An important distinction between **5** and the crystal structures of other protonated proton sponges was that there was no auxiliary three-centred hydrogen bonding from anions or solvent to the central proton.[10] The three-centred hydrogen bond now consisted of an interaction between N(1) and N(2) and between N(2) and O(113) (Table 1). The methyl esters appear to shield the proton binding site. In a review chapter on proton sponges,[2a] the authors proposed that four criteria needed to be met for a molecule to be classified as a proton sponge and that unsubstituted quino[7,8-*h*] quinoline was in violation of the fourth requirement. That is, there needed to be the presence of a hydrophobic environment at the nitrogen atoms to account for the low rate of proton addition–elimination and to prevent coordination of all Lewis acids except the proton. In reality, there is no

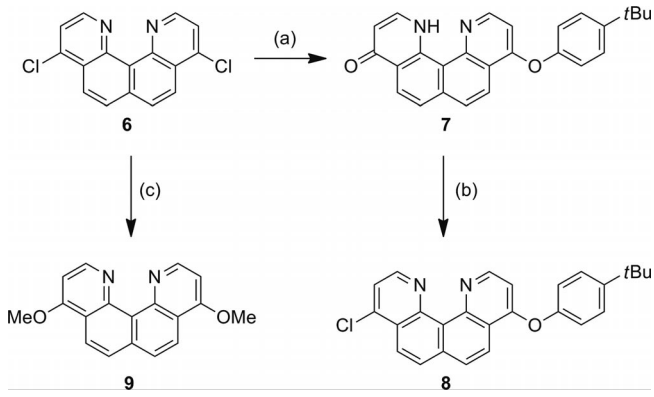
Table 1. Important bond lengths and angles associated with the hydrogen bonding of H(2) and H(2B) in [H(**5**)][BF_4].

N–H [Å]		N–X [Å]		N–H–X [°]	
N2–H2	1.9500(3)	N2–N1	2.643(3)	N2–H2–N1	135.00(3)
O113–H2	2.4800(3)	O113–N1	2.790(3)	N2–H2–O113	101.00(3)
N1–H2B	1.9600(3)	N1–N2	2.646(3)	N1–H2B–N1	135.00(3)
O31B-H2B	2.3900(3)	O31B–N1	2.730(3)	N2–H2B–O31B	103.00(3)

molecule that matches all the criteria perfectly. The original proton sponge, 1,8-bis(dimethylamino)naphthalene,[1] has been shown to complex to boron.[11] It would appear that **5** meets the criteria of a proton sponge more effectively in this case, as the cavity can only support a proton because of the greater steric influence of the methyl esters. The previously reported crystal structure of the analogous tetrafluoroborate salt of 1,8-bis(dimethylamino)naphthalene also reveals that there were no significant auxiliary hydrogen-bonding interactions.[12] A symmetry-generated tetrafluoroborate anion lies above the proton cavity in the crystal structure of [H(**5**)][BF_4], but the short contacts exceed what would be considered weak hydrogen bonding. For a molecule based on quino[7,8-*h*]quinoline, **5** replicates this shielding of the proton well. To the best of our knowledge, **5** is currently the only confirmed quino[7,8-*h*]quinoline derivative with 2,11-substitution, and the ester groups offer great potential for elaboration and also fine-tuning of the binding site.

4,9-Substitution of Quino[7,8-*h*]quinoline

The known compound 4,9-dichloroquino[7,8-*h*]quinoline (**6**) was synthesised by a modification[5] of the original preparation by Staab and co-workers.[3] We discovered that it was possible to simultaneously improve the yield and decrease the reaction time of the critical de-esterification step by employing hydrothermal conditions.[5] Our modification gave us a reliable and large-scale route to **6**. The 4,9-substituted chlorides present an opportunity to further functionalise the ring system. Initially, we were interested in elaborating the rings by nucleophilic aromatic substitution, as this would give us a route to selectively functionalise the rings.[13] The very properties that make **6** intriguing also hamper its usability; purification by standard techniques is highly problematic, and so reactions were optimised to produce high-yielding reactions with simple workup procedures. We first investigated the substitution of the 4,9-chlorides on **6** with oxygen-donor nucleophiles (Scheme 3). Direct substitution of the chlorides with phenol unexpectedly led to nearly quantitative conversion to **7** (Scheme 3a). The preference for **7** over the quinoline-4-ol tautomer is easy to understand: the high basicity of the proton sponge analogues favours protonation of the nitrogen atoms with concomitant formation of the keto form of the heterocycle. What is less explicable is the formation of either tautomer from **6** in the first place. The most logical explanation is the direct substitution of the chloride by a hydroxide anion under the harsh conditions followed by tautomerism. Interestingly, mass spectrometric analysis of the crude material indicates the presence of the double phenol addition product and suggests that this may decompose on workup. To convert **7** back into a dipyridine-type donating ligand, treatment with phosphorus oxychloride gave unsymmetrical **8** (Scheme 3b).



Scheme 3. Nucleophilic substitution of **6** with oxygen donors. Reagents and conditions: (a) *t*BuC_6H_4OH, KOH, 150 °C, 4 h; (b) $POCl_3$, 120 °C, 9 min; (c) NaOMe, MeOH reflux, 2 h.

We subsequently found that both of the chlorides could be substituted by sodium methoxide leading to the isolation of disubstituted quino[7,8-*h*]quinoline **9** (Scheme 3c). The success of this reaction supports the theory that the hydroxide anion is directly responsible for the formation of **7**. The 4,9-substitution patterns of **7** and **9** were confirmed by elucidation of their X-ray crystal structures.

Attempts to crystallise **7** in the presence of copper perchlorate by vapour diffusion of diethyl ether in acetonitrile resulted in the isolation of protonated **7** as the perchlorate salt and no metal complex (Figure 4). CHN analysis of the bulk crystallised material suggested the formulation [H(**7**)][ClO_4]; however, upon analysis of a single crystal suitable for X-ray determination, the asymmetric unit was found to consist of two molecules of **7** and only one perchlorate. The charge was balanced by a central proton (located by the difference Fourier map) that formed a bridge between the two molecules of **7** (Figure 4). Both carbonyl groups associated with this bridging hydrogen were elongated to a partial double bond length of 1.300(3) Å. The difference map placed the proton as a formal bond to O(9A) with a strong hydrogen bond[8] to O(9) [O(9A)–H(9AA) 1.610(2) Å, O(9A)–O(9) 2.444(2) Å] and an O(9A9–H(9AA)–O(9) angle of 175.00(2)°. Although this single crystal was a minor product compared to the bulk material, it allowed identification of the structural features of **7** to reinforce the NMR and MS structural assignments.

The bulk material of formula [H(**7**)][ClO_4] most likely had all O(9) positions protonated with the charge balanced by a perchlorate anion.

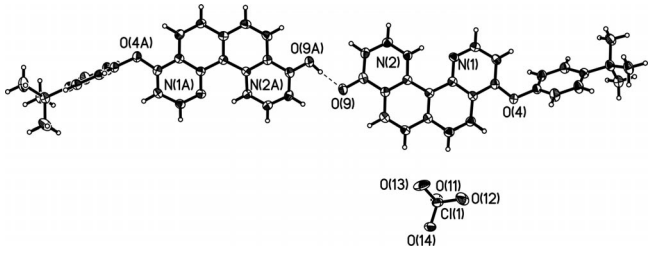


Figure 4. Crystal structure depicting the hydrogen-bond dimer [H(**7**)$_2$]ClO_4 showing the bridging proton, H(9AA), between O(9) and O(9A); ellipsoids are drawn at the 50% probability level.

A heated DMSO solution of **9** followed by slow cooling gave single crystals of **9**. The asymmetric unit consists of three molecules of the neutral form of **9**; one molecule is shown in Figure 5. The three molecules of **9** in the asymmetric unit have N(1)–C(17)–C(13)–N(2) torsion angles of 13.73(49), 8.83(49) and 8.13(50)°, which are smaller than the angles found in the neutral form of **6** with a 20.02(9)° torsional twist.[5] This significant difference in the torsional angle of these neutral forms of this ligand can be attributed to the weak hydrogen bonding that is present in both crystal structures. In **9**, weak hydrogen bonds between the nitrogen atoms of one molecule and the hydrogen atoms in the 2,11-positions or on the methoxy groups of an adjacent molecule exist, which aid in reducing the lone pair–lone pair interaction between the two nitrogen atoms. This arrangement of molecules is not possible in **6** where instead the lone electron pairs on the heteroatoms are orientated towards the chloroform solvent molecules.[5]

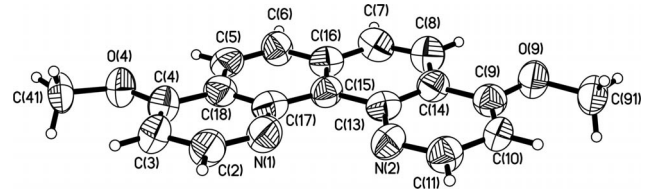
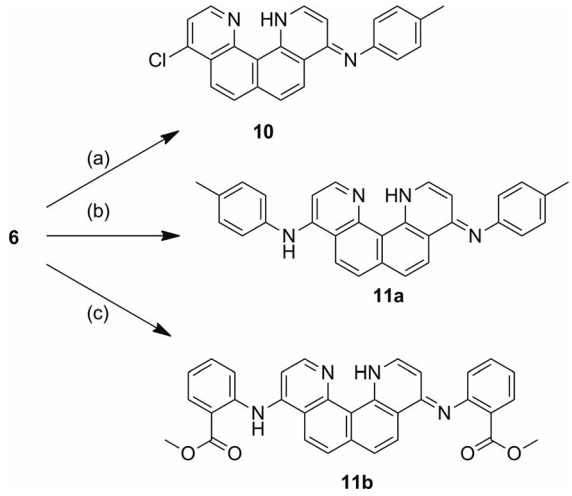


Figure 5. Crystal structure of **9** showing the atom labels, ellipsoids are drawn at the 50% probability level.

Next, we investigated the substitution of the chlorides on **6** with nitrogen-donor nucleophiles (Scheme 4). The substitution of the 4,9-chlorides on **6** with anilines was attempted; *p*-toluidine was used to test the reaction methodology, as it was hoped that the methyl group would provide improved solubility. Addition of a single toluidine unit was achieved by heating a fourfold excess to reflux in toluene (Scheme 4a). The insolubility of product **10** allowed for simple purification: the reagents were simply heated together and the product was filtered off to remove the excess amounts of the starting materials. We established the location of the proton by ^{1}H NMR spectroscopy, as **10** was sparingly soluble in hot [D_6]DMSO and a peak at δ = 14.62 ppm confirmed the highly deshielded position typical for protons bound to proton sponges.[1,3b,14] Disubstitution with *p*-toluidine to form **11a** could be achieved as a melt in neat *p*-toluidine. Purification proved to be more complicated than that of **10** (Scheme 4b), but purification was eventually achieved by silica gel column chromatography whereby compound **11a** was slowly eluted (CH_2Cl_2/MeOH/NEt_3, 8:8:1 gradient).



Scheme 4. Nucleophilic substitution of **6** with nitrogen donors. Reagents and conditions: (a) *p*-toluidine, toluene, reflux, 4 h; (b) *p*-toluidine, 150 °C, 4 h or (c) methyl anthranilate, 120 °C, 2 h.

HRMS and NMR spectroscopy confirmed the presence of **11a** as did the measurement of several different X-ray crystal structures (Figures 6 and 7). Finally, we were interested in constructing a substituted derivative of **6** with extended conjugation capable of enhanced fluorescence, and so we prepared compound **11b** (Scheme 4c). The methyl ester group on the aromatic ring on this molecule allows H-bonding back to the secondary amines or imines depending on the tautomeric form and both help to enhance the rigidity and maintain the planarity of the whole system. The combination of which may provide a pathway to electron delocalisation across the molecule. Molecules **11a** and **11b** were sparingly soluble in hot [D_6]DMSO and their ^{1}H NMR spectra showed highly deshielded protons at δ = 16.41 and 15.69 ppm, respectively; the large downfield shifts are typical for highly deshielded protons located between the ring nitrogen atoms. This NMR evidence offers further confirmation that these molecules adopt a partial imino tautomeric form in their neutral state and that one of the protons is located between the two ring nitrogen atoms rather than localised on the aniline substituent. A crystal structure of **11a** was obtained by cooling a solution at 4 °C in CH_2Cl_2/MeOH overnight. The asymmetric unit (Figure 6) revealed that, upon crystallisation, **11a** exists in the partial tautomer form with a hydrogen atom located on the ring N(2) nitrogen atom rather than on the imino N(91) nitrogen atom (the hydrogen was located by the Fourier difference map). The C(9)–N(91) bond length at 1.311(2) Å has significant double-bond character relative to C(4)–N(41) 1.367(2) Å. This arrangement appears to be further stabilised by one methanol solvent molecule. The methanol solvent interacts with a moderate electrostatic hydrogen

bond[8] with O(21)–H(21) 0.820(2) Å, N(91)–H(21) 1.950(2) Å, O(21)–N(91) 2.753(2) Å and an O(21)–H(21)–N(91) angle of 167.00(2)°. There are several instances where simple quinolines showed similar tautomerism after nucleophilic aromatic substitution of an aniline.[15] In these papers, the tautomerism was reversible; however, as a result of the basicity of **10**, **11a** and **11b**, the thermodynamic equilibrium sits firmly in favour of one of the two aniline groups present adopting the imino form, as evidenced in both the solution and solid-state studies.

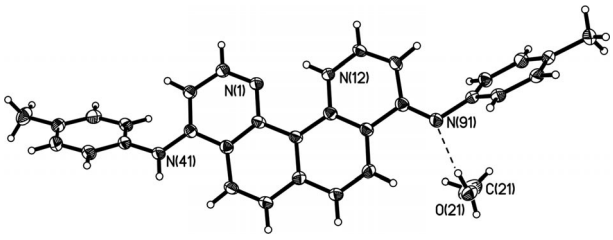


Figure 6. Crystal structure of **11a**; ellipsoids are drawn at the 50% probability level.

Further protonation of these molecules is possible. This results in the equilibrium being driven back towards the secondary amine form. The evidence for this comes from both NMR spectroscopy and X-ray studies on the protonated form of **11a**, which was synthesised by treating **11a** with $BF_3{\cdot}OEt_2$ in the presence of trace amounts of water. Upon crystallisation, a compound with the formula [H(**11a**)]BF_4 was obtained. Analysis of the ^{1}H NMR spectrum of this tetrafluoroborate salt revealed chemical shifts corresponding to the central NH proton at δ = 18.79 ppm and two secondary amine proton signals at δ = 10.11 ppm. Notably, the ^{1}H NMR shift corresponding to the central NH proton is now further downfield than that of the similarly positioned proton in the neutral form of **11a** (δ =16.41 ppm). Crystals of [H(**11a**)]BF_4 were formed by vapour diffusion of diethyl ether into a methanolic solution containing the salt. The asymmetric unit consists of one molecule of protonated **11a** and one tetrafluoroborate anion (Figure 7). The hydrogen atoms on N(4) and N(9) and the proton on N(1) were located by the Fourier difference map. As expected, the C(4)–N(4) [1.354(4) Å] and C(9)–N(9) [1.374(4) Å] bond lengths are no longer significantly different and both are significantly longer than those found for C(9)–N(91) in the neutral form of **11a** (Figure 6), that is, the molecule is no longer in the tautomeric imino form. The tetrafluoroborate anion interacts with a moderately strong hydrogen bond to the secondary amine N4[8] [F(4)–H(4A) 2.080(3) Å, N(4)–F(4) 2.869(3) Å] and an N(4)–H(4A)–F(4) angle of 152.00(3)°.

The enhanced fluorescence of the protonated form of **11b** over that of **11a** is best illustrated by Figure 8. The neutral imino form of **11a** is not fluorescent (Figure 8a). Upon protonation, the imino form is converted into the secondary amine tautomer, and in the process the rigidity of the core quino[7,8-*h*]quinoline ring system is enhanced, which leads to a mild fluorescent response (Figure 8b). As in the case

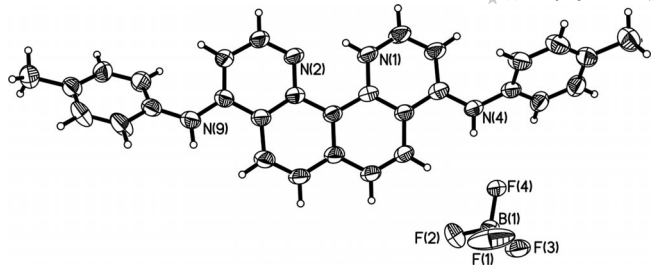


Figure 7. Crystal structure of [H(**11a**)][BF_4]; ellipsoids are drawn at the 50% probability level.

of **11a**, the neutral form of **11b** (Figure 8c) is also not fluorescent. Although no crystals were grown, it is reasonable to assume that protonation occurs at the same position for molecule **11b**. The crystal structures of [H(**11a**)][BF_4] and neutral **11a** both show that the substituted anilines are rotated away from the plane of the heterocyclic ring. Although no crystal structure was obtained, the hydrogen bonding present between the secondary amines and the methyl esters of [H(**11b**)][BF_4] may align the aniline substituents with the central heterocycle. The optimised geometries of both [H(**11a**)][BF_4] and [H(**11b**)][BF_4] were calculated at the B3LYP/6-311++g(2d,p) level (Supporting Information). The angles between the aniline substituents and the heterocyclic ring for [H(**11a**)][BF_4] were 67.57 and 71.37°, which were reduced to 43.90 and 41.20° for [H(**11b**)][BF_4] suggesting that this is in fact the case.

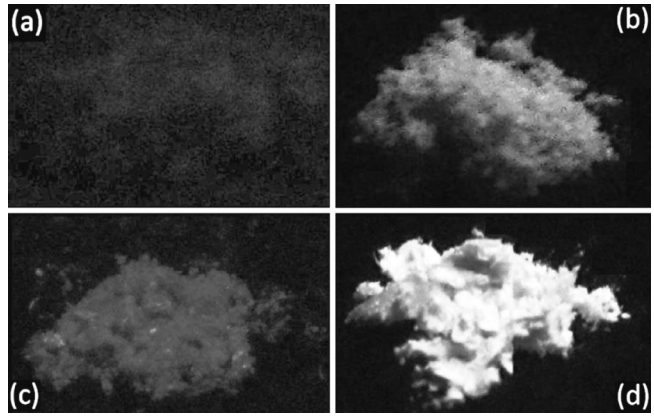


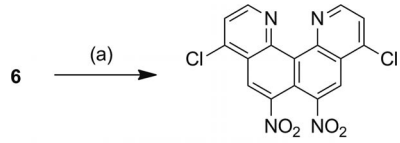
Figure 8. Compounds (a) **11a**, (b) [H(**11a**)][BF_4], (c) **11b** and (d) [H(**11b**)][BF_4] viewed in the dark under a longwave 385-nm UV lamp.

Analysis of the molecular orbitals involved in the π–π* transitions for [H(**11a**)][BF_4] and [H(**11b**)][BF_4] provide more evidence for these empirical observations (Supporting Information, Figure S1). The weak fluorescence observed for [H(**11a**)][BF_4] appears to be due to partial intramolecular charge transfer from one aniline substituent back into the heterocyclic ring. In contrast, the strong fluorescence observed for [H(**11b**)][BF_4] appears to be due to an increase in the delocalisation of the intramolecular charge over two thirds of the molecule (Supporting Information, Figure S2). The strong fluorescence of [H(**11b**)][BF_4] must, therefore, arise from both an increase in the structural rigidity and

the electron delocalisation across the molecule and shows that with careful choice of substituent, quino[7,8-*h*]quinoline may show utility as a fluorescence-active compound.

6,7-Substitution of Quino[7,8-*h*]quinoline

To access the 6,7-positions of quino[7,8-*h*]quinoline, we found that nitration of **6** in fuming HNO_3/H_2SO_4 gave selective electrophilic substitution of two NO_2 groups (Scheme 5). The mass spectra revealed the chlorides had remained intact and that the NO_2 groups had replaced two hydrogen atoms somewhere on the ring.



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Scheme 5. Electrophilic substitution of **6** with nitrogen donors. Reagents and conditions (a) HNO_3, H_2SO_4, 120 °C, 2 min.

Not unsurprisingly, the compound showed poor solubility in all solvents; however, a ^{1}H NMR spectrum recorded in hot [D_6]DMSO of a protonated form of **12** revealed that the product possesses C_2 symmetry, and this allowed assignment of the protons in the 2,3- and 10,11-positions on the ring, leaving the 5,6- and 7,8-positions as likely points of NO_2 substitution. In the absence of a crystal structure, it is only possible to speculate exactly which positions were substituted; however, nitration reactions under similar conditions of a related proton sponge led to substitution at the *para*-positions to the nitrogen, as confirmed by X-ray crystal structure determination.[16] In addition, quinolines undergo nitration at the 6-position;[17] therefore, on the basis of this additional evidence, we propose that the substitution of **12** is more likely to have occurred at the 6- and 7-positions. Reduction of the nitro groups to amines may provide additional sites for further functionalisation; for example, DMAN was grafted onto silica for use as a base catalyst for the Knoevenagel condensation between benzaldehyde and different active methylene compounds as well as for the Claisen–Schmidt condensation of benzaldehyde and 2-hydroxyacetophenone to chalcones and flavanones.[18]

Conclusions

This report outlines the first successful syntheses of 2,11- and 6,7-substituted quino[7,8-*h*]quinoline derivatives that have shown, despite poor solubility and poor elution behaviour of the quino[7,8-*h*]quinoline moiety, that it is possible to substitute and purify this molecule in positions other than the 4,9-positions. We have also shown that direct substitution at the 4,9-positions is possible with a number of derivatives that were successfully formed and characterised. The propensity for the molecule to tautomerise, as evidenced by X-ray crystallography, was explored and ultimately provides a pathway to unsymmetrical mixed derivative examples. Some progress in the preparation of functionalised quino[7,8-*h*]quinolines derivatives has been observed. Preliminary results with Pd^0 coupling reactions show promise and will be reported at a later date.

Experimental Section

General Procedures: Unless otherwise stated, all reagents and solvents were purchased from commercial sources and used without further purification. NMR spectra were collected with Bruker Avance 400 and 500 MHz spectrometers. All chemical shifts are reported relative to residual solvent (^{1}H, ^{13}C). Microanalyses were performed at the Campbell Microanalytical Laboratory at the University of Otago. Electrospray mass spectra were recorded with a Mircomass ZMD spectrometer run in the positive ion mode. High-resolution mass spectra were recorded with a microTOF-Q mass spectrometer operating at a nominal voltage of 3500 V. This service was provided by The University of Auckland. IR spectra were recorded with a Bruker Alpha-P diamond anvil system. Single-crystal X-ray data were collected at reduced temperature with a Rigaku Spider diffractometer equipped with a copper rotating anode X-ray source and a curved image plate detector. The crystals were mounted in an inert oil, transferred into the cold gas stream of the detector and irradiated with graphite monochromated Cu-K_α (k = 1.54178 Å) X-rays. The data was collected by the Crystal Clear program (v.1.4.0) and processed with FS-PROCESS to apply the Lorentz and polarisation corrections to the diffraction spots (integrated 3 dimensionally). The structures were solved by direct methods by using SHELXS-97 and refined by using the SHELXL-97 program.[19] Absorption correction was carried out empirically. Hydrogen atoms were calculated at their ideal positions unless otherwise stated.

Computational: Density functional theory (DFT) calculations were carried out by using the Gaussian09 package of programs.[20] Becke's three-parameter hybrid exchange correlation function containing the non-local gradient correction of Lee, Yang and Parr (B3LYP),[21] in conjunction with the 6-311G++(2d,p) basis set were used to obtain the optimised geometries.

***N*-[2-(Methylthio)benzo[*h*]quinolin-10-yl]acetamide (3):** A mixture of 3,3-bis(methylthio)acrylaldehyde (0.300 g, 2.00 mmol) and **1** (0.174 g, 1.10 mmol) in glacial acetic acid (30 mL) was heated under reflux for 8 h. The excess amount of acetic acid was removed in vacuo, and the residue was quenched with a saturated $NaHCO_3$ solution. The residue was extracted with CH_2Cl_2 (200 mL), and the organic layer was washed with water (2× 200 mL), filtered and dried with $MgSO_4$. Purification by silica gel column chromatography (hexanes/EtOAc, 9:1) gave **3** as a pale brown solid, which darkened upon storing. R_f = 0.21 (hexanes/EtOAc, 2:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, $COCH_3$), 2.69 (s, 3 H, SCH_3), 7.33 (d, $^3J_{5,6}$ = 8.5 Hz, 1 H, 6-*H*), 7.51–7.68 (m, 4 H, 3,7,8,9-*H*), 8.05 (d, $^3J_{5,6}$ = 8.5 Hz, 1 H, 5-*H*), 9.02 (d, $^3J_{3,4}$ = 7.9 Hz, 1 H, 4-*H*), 14.3 (s, 1 H, N*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.7 (t), 25.9 (t), 116.6 (q), 117.0 (s), 118.0 (s), 122.8 (s), 124.3 (q), 124.8 (s), 128.1 (s), 129.0 (s), 135.4 (q), 136.9 (s), 139.2 (q), 147.3 (q), 158.0 (q), 169.4 (q) ppm.

Crystal Data for 3: $C_{16}H_{14}N_2OS$, colourless block, dimensions 0.55 × 0.34 × 0.33 mm, triclinic, space group $P\bar{1}$, a = 7.2715(2) Å, b = 9.8011(2) Å, c = 10.4908(2) Å, α = 106.4320(10)°, β = 99.5190(10)°, γ = 106.4390(10)°, U = 662.88(3) Å^3, μ = 0.240 mm^{-1}, Z = 2, D_c = 1.415 g cm^{-3}, F(000) = 296, T = 173(2) K. A total of 7336 reflections were collected by using a Bruker SMART four

circle diffractometer in the range $2.31 < 2\theta < 66.50°$. A semiempirical absorption correction (SADABS-2004/1) was applied. The 2603 independent reflections were used to solve the structure by direct methods (SHELXS-97), which resulted in the location of all non-hydrogen atoms. All non-hydrogen atoms were made anisotropic and the refinement (SHELXL-97) of 181 parameters converged to $R_1 = 0.0310$ [for 2603 reflections having $I > 4\sigma(I)$], w$R_2 = 0.0854$ and goodness of fit 1.090 (for all 2603 F^2 data). Peak/hole 0.335/–0.244 e Å^{-3}.

Dimethyl 4,9-Dichloroquinolino[7,8-*h*]quinoline-2,11-dicarboxylate (5): Phosphorus oxychloride (1.25 mL, 13.5 mmol) was added to **4** (0.394 g, 1.06 mmol), and the reaction mixture was stirred at 130 °C for 9 min. The reaction mixture was poured into ice–water (200 mL), basified with 6 M KOH (20 mL) and extracted with CH_2Cl_2 (200 mL). The organic layer was filtered and dried with $MgSO_4$ to give **5** (0.315 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.19 (s, 6 H, COCH_3), 8.20 (d, $^3J_{5,6}$ = 8.9 Hz, 2 H, 6,7-*H*), 8.55 (s, 2 H, 3,10-*H*), 8.60 (d, $^3J_{5,6}$ = 8.8 Hz, 2 H, 5,8-*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 53.3 (t), 122.5 (s), 125.0 (s), 127.1 (q), 127.9 (q), 130.9 (s), 136.9 (q), 144.0 (q), 147.8 (q), 148.1 (q), 165.2 (q) ppm. LRMS: *m*/*z* = 415.02 [M]$^+$. $C_{20}H_{12}Cl_2N_2O_4{\cdot}0.5H_2O$ (423.02): calcd. C 56.62, H 3.09, N 6.60; found C 56.73, H 3.08, N 6.60.

[H(5)][BF$_4$]: $BF_3{\cdot}OEt_2$ (0.121 mL, 0.964 mmol) was added to **5** (0.100 g, 0.241 mmol) in dry CH_2Cl_2 (5 mL) under an atmosphere of Ar, and the mixture was stirred at room temperature for 8 h. The reaction mixture was diluted with CH_2Cl_2, and the solvent was separated from deposited [H(**5**)][BF_4] and dried under vacuum. The product was then set up for crystallisation by vapour diffusion of diethyl ether into a MeCN solution containing [H(**5**)][BF_4]. Brown crystals suitable for X-ray crystallography were obtained after 1 d. ^{1}H NMR (500 MHz, CD_3CN): δ = 4.23 (s, 6 H, COCH_3), 8.43 (d, $^3J_{5,6}$ = 9.1 Hz, 2 H, 6,7-*H*), 8.64 (d, *J* = 9.1 Hz, 2 H, 5,8-*H*), 8.68 (s, 2 H, 3,10-*H*), 19.14 (s, 1 H, N*H*) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ = 55.5 (t), 117.3 (q), 125.2 (s), 128.1 (s), 129.7 (q), 133.7 (s), 140.2 (q), 143.4 (q), 145.4 (q), 152.3 (q), 162.1 (q) ppm. LRMS: *m*/*z* = 415.53 [M]$^+$. $C_{20}H_{13}N_2O_4Cl_2H^+{\cdot}BF_4^-$ (503.04): calcd. C 47.75, H 2.60, N 5.57; found C 47.78, H 2.33, N 5.64.

Crystal Data for [H(5)][BF$_4$]: $C_{20}H_{13}N_2O_2Cl_2BF_4$, yellow prism, dimensions $0.2 \times 0.15 \times 0.1$ mm, triclinic, space group $P2_1/c$, a = 11.0327(2) Å, b = 13.5997(2) Å, c = 15.1206(3) Å, α = 113.4460(10)°, β = 99.4340(10)°, γ = 97.8210(10)°, U = 2001.82(7) Å^3, μ = 3.573 mm^{-1}, Z = 4, D_c = 1.669 g cm^{-3}, F(000) = 1016, T = 100(2) K. A total of 10378 reflections were collected by using a Rigaku MM007 rotating anode in the range $6.58 < 2\theta < 144.00°$. A semiempirical absorption correction (ABSCOR; Higashi, 1995) was applied. The 5797 independent reflections were used to solve the structure by direct methods (SHELXS-97), which resulted in the location of all non-hydrogen atoms. All non-hydrogen atoms were made anisotropic and the refinement (SHELXL-97) of 596 parameters converged to $R_1 = 0.0406$ [for 5280 reflections having $I > 4\sigma(I)$], w$R_2 = 0.1095$ and goodness of fit 1.080 (for all 5280 F^2 data). Peak/hole 0.336/–0.391 e Å^{-3}.

9-(4-*tert*-Butylphenoxy)quinolino[7,8-*h*]quinolin-4(1*H*)-one (7): A mixture of 4-*tert*-butylphenol (7.72 g, 51.2 mmol), potassium hydroxide (0.460 g, 9.35 mmol) and **6** (0.200 g, 0.668 mmol) was stirred at 150 °C for 4 h. The reaction mixture was diluted with CH_2Cl_2 (200 mL) and washed with 7 M HCl (10 mL) in water (200 mL) then basified with 6 M KOH (10 mL). The organic layer was dried with $MgSO_4$ and filtered. The product was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 95:5) to give **2** (0.258 g, 98%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.42 [s, 9 H, C(CH_3)$_3$], 6.84 (d, $^3J_{10,11}$ = 6.2 Hz, 1 H, 11-H), 6.87 (d, $^3J_{2,3}$ = 5.4 Hz, 1 H, 3-*H*), 7.21 (d, $^3J_{2,3}$ = 8.6 Hz, 2 H, 2-Ph*H*), 7.56 (d, $^3J_{2,3}$ = 8.6 Hz, 2 H, 3-Ph*H*), 7.78 (d, $^3J_{5,6}$ = 8.7 Hz, 1 H, 6-*H*), 7.93 (d, $^3J_{10,11}$ = 6.2 Hz, 1 H, 10-*H*), 8.09 (d, $^3J_{7,8}$ = 6.2 Hz, 1 H, 7-*H*), 8.50 (d, $^3J_{7,8}$ = 6.2 Hz, 1 H, 8-*H*), 8.62 (d, $^3J_{5,6}$ = 8.7 Hz, 1 H, 5-*H*), 8.80 (d, $^3J_{2,3}$ = 5.4 Hz, 1 H, 2-*H*); 16.30 (s, 1 H, N*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.5 (t), 34.6 (q), 105.4 (s), 111.1 (s), 115.0 (q), 116.7 (q), 119.5 (q), 120.6 (s), 122 (s), 124.1 (s), 125.6 (s), 126.1 (q), 127.4 (s), 127.7 (s), 137.0 (q), 138.4 (s), 140.4 (q), 148.5 (q), 148.7 (s), 149.3 (q), 151.4 (s), 162.8 (s) ppm. IR: $\tilde{\nu}$ = 2957, 1615, 1583, 1527, 1505, 1492, 1432, 1422, 1386, 1275, 1216, 1198, 1184, 855, 827 cm^{-1}. LRMS: *m*/*z* = 395.55 [M]$^+$. $C_{26}H_{22}N_2O_2$ (394.47): calcd. C 79.16, H 5.62, N 7.10; found C 79.68, H 5.99, N 6.36. The product was recrystallised by vapour diffusion of diethyl ether into a MeCN solution containing **7** with an equimolar quantity of copper perchlorate. $C_{26}H_{22}N_2O_2{\cdot}HClO_4$ (494.93): calcd. C 63.10, H 4.68, N 5.66; found C 63.00, H 4.60, N 5.70.

Crystal Data for 7: $C_{52}H_{45}N_4ClO_4$, colourless needle, dimensions $0.5 \times 0.1 \times 0.05$ mm, monoclinic, space group $P2_1/c$, a = 16.964(3) Å, b = 10.938(2) Å, c = 24.162(5) Å, α = 90.00°, β = 101.65(3)°, γ = 90.00°, U = 4391.2(15) Å^3, μ = 1.282 mm^{-1}, Z = 4, D_c = 1.345 g cm^{-3}, F(000) = 1864, T = 100(2) K. A total of 17488 reflections were collected by using a Rigaku MM007 rotating anode in the range $6.65 < 2\theta < 144.18°$. A semiempirical absorption correction (ABSCOR; Higashi, 1995) was applied. The 10421 independent reflections were used to solve the structure by direct methods (SHELXS-97), which resulted in the location of all non-hydrogen atoms. All non-hydrogen atoms were made anisotropic and the refinement (SHELXL-97) of 587 parameters converged to $R_1 = 0.0643$ [for 8316 reflections having $I > 4\sigma(I)$], w$R_2 = 0.1569$ and goodness of fit 1.050 (for all 8316 F^2 data). Peak/hole 0.403/–0.426 e Å^{-3}.

4-(4-*tert*-butylphenoxy)-9-chloroquinolino[7,8-*h*]quinoline (8): Phosphorus oxychloride (1.00 mL, 10.7 mmol) was added to **7** (0.258 g, 0.655 mmol), and the reaction mixture was stirred at 120 °C for 9 min under an atmosphere of Ar. The reaction mixture was poured into water (200 mL) and basified with 6 M KOH (20 mL) and extracted with CH_2Cl_2 (200 mL). A small portion of decolourising carbon was added, and the organic layer was dried with $MgSO_4$ and filtered to give **8** (0.264 g, 98%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.42 [s, 9 H, C(CH_3)$_3$], 7.25 (d, $^3J_{2,3}$ = 8.7 Hz, 2 H, 2-Ph*H*), 7.30 (d, $^3J_{2,3}$ = 6.5 Hz, 1 H, 3-*H*), 7.64 (d, $^3J_{2,3}$ = 8.7 Hz, 3-Ph*H*), 8.00 (d, $^3J_{10,11}$ = 4.9 Hz, 1 H, 10-*H*), 8.32 (d, $^3J_{7,8}$ = 9.0 Hz, 1 H, 7-*H*), 8.40 (d, $^3J_{5,6}$ = 8.9 Hz, 1 H, 6-*H*), 8.70 (d, $^3J_{5,6}$ = 8.9 Hz, 1 H, 5-*H*), 8.83 (d, $^3J_{7,8}$ = 9.0 Hz, 1 H, 8-*H*), 9.44 (d, $^3J_{10,11}$ = 4.9 Hz, 1 H, 11-*H*), 9.61 (d, $^3J_{2,3}$ = 6.5 Hz, 1 H, 2-*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.1 (t), 34.6 (q), 105.7 (s), 116.6 (q), 120.0 (s), 120.1 (q), 122.6 (s), 123.6 (s), 126.0 (q), 126.7 (q), 127.1 (s), 127.9 (s), 128.8 (s), 129.8 (s), 137.6 (q), 140.0 (q), 145.0 (q), 146.5 (s), 146.6 (q), 149.8 (q), 150.0 (s), 151.1 (q) ppm. IR: $\tilde{\nu}$ = 2957, 1595, 1496, 1475, 1417, 1262, 1218, 1205, 842 cm^{-1}. HRMS (ESI+): calcd. for $C_{26}H_{21}N_2OCl$ [M + H]$^+$ 413.1415; found 413.1415.

4,9-Dimethoxyquino[7,8-*h*]quinoline (9): Sodium methoxide (0.072 g, 1.338 mmol) was added to **6** (0.050 g, 0.167 mmol) in MeOH (10 mL), and the mixture was heated at reflux for 2 h under an atmosphere of Ar. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and MeOH (10 mL), and the solution was then washed with 2 M KOH (10 mL) in water (100 mL). The organic layer was dried with $MgSO_4$, filtered and concentrated to give **9** (0.048 g, 100%). The product was recrystallised by heating to dissolution in hot DMSO then slowly cooling. ^{1}H NMR (500 MHz, MeOD): δ = 3.35 (s, 6 H, OCH_3), 7.20 (d, $^3J_{2,3}$ = 5.0 Hz, 2 H, 3,10-

H), 7.90 (d, $^3J_{5,6}$ = 8.7 Hz, 2 H, 6,7-*H*), 8.35 (d, $^3J_{5,6}$ = 8.7 Hz, 2 H, 5,8-*H*), 8.99 (d, $^3J_{2,3}$ = 5.0 Hz, 2 H, 2,11-*H*) ppm. ^{13}C NMR (125 MHz, MeOD): δ = 50.0 (t), 102.9 (s), 121.7 (q), 123.1 (s), 125.7 (q), 128.2 (s), 137.9 (q), 148.4 (q), 151.6 (s), 164.4 (q) ppm. IR: $\tilde{\nu}$ = 3322, 1600, 1519, 1443, 1416, 1281, 1129, 1007, 837, 811 cm^{-1}. HRMS (ESI+): calcd. for $C_{18}H_{14}N_2O_2$ [M + H]$^+$ 291.1128; found 291.1128.

Crystal Data for 9: $C_{18}H_{14}N_2O_2$, colourless chip, dimensions 0.6 × 0.05 × 0.05 mm, monoclinic, space group $P2_1/c$, a = 6.9964(14) Å, b = 12.597(3) Å, c = 46.260(9) Å, α = 90.00°, β = 94.19(3)°, γ = 90.00°, U = 4066.3(14) Å^3, μ = 0.762 mm^{-1}, Z = 12, D_c = 1.423 g cm^{-3}, F(000) = 1824, T = 123(2) K. A total of 7370 reflections were collected by using a Rigaku MM007 rotating anode in the range 6.70 < 2θ < 143.20°. A semiempirical absorption correction (ABSCOR; Higashi, 1995) was applied. The 6224 independent reflections were used to solve the structure by direct methods (SHELXS-97), which resulted in the location of all non-hydrogen atoms. All non-hydrogen atoms were made anisotropic and the refinement (SHELXL-97) of 601 parameters converged to R_1 = 0.0940 [for 1963 reflections having $I > 4\sigma$ (I)], wR_2 = 0.1984 and goodness of fit 0.828 (for all 1963 F^2 data). Peak/hole 0.299/–0.487 e Å^{-3}.

(*E*)-*N*-[9-Chloroquinolino[7,8-*h*]quinolin-4(1*H*)-ylidene]-4-methylaniline (10): A solution of *p*-toluidine (0.143 g, 1.338 mmol) and **6** (0.100 g, 0.334 mmol) was heated at reflux for 4 h in toluene (20 mL). The precipitate of crude **10** was filtered and dissolved in CH_2Cl_2 (200 mL) and MeOH (20 mL) and then washed with water (200 mL) and 6 M KOH (20 mL). The organic layer was dried with $MgSO_4$ and filtered. Compound **10** was precipitated from hot DMSO by addition of EtOAc and filtered (0.099 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$, MeOD): δ = 2.37 (s, 3 H, C*H*$_3$), 6.97 (d, $^3J_{5,6}$ = 7.0 Hz, 2 H, 6-*H*), 7.28 (m, 4 H, 2,3-Ph*H*), 7.84 (d, $^3J_{10,11}$ = 5.0 Hz, 2 H, 10-*H*), 8.09 (d, $^3J_{7,8}$ = 9.0 Hz, 2 H. 7-*H*), 8.12 (d, $^3J_{2,3}$ = 9.0 Hz, 2 H, 3-*H*), 8.40 (d, $^3J_{2,3}$ = 9.0 Hz, 2 H, 2-*H*), 8.57 (d, $^3J_{5,6}$ = 7.0 Hz, 2 H, 5-*H*), 8.68 (d, $^3J_{7,8}$ = 9.0 Hz, 2 H, 8-*H*), 9.03 (d, $^3J_{10,11}$ = 5.0 Hz, 2 H, 11-*H*); (in [D$_6$]DMSO) 14.62 (s, 1 H, N*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, MeOD): δ = 20.0 (t), 101.3 (s), 115.7 (q), 115.9 (q), 122.3 (s), 122.6 (s), 124.7 (s), 125.3 (s), 125.4 (s), 127.3 (q), 128.6 (s), 130.1 (s), 133.6 (q), 136.7 (q), 137.7 (q), 138.3 (q), 140.6 (s), 144.1 (q), 146.5 (q), 148.1 (s), 155.2 (q) ppm. IR: $\tilde{\nu}$ = 2999, 1627, 1596, 1552, 1515, 1496, 1475, 1426, 1398, 1365, 1346, 1220, 1180, 1148, 845, 825 cm^{-1}. LRMS: *m*/*z* = 370.72 [M + H]$^+$. Elemental analysis was measured for the tetrafluoroborate salt. $C_{23}H_{17}ClN_3{\cdot}BF_4{\cdot}0.75H_2O$ (471.17): calcd. C 58.63, H 3.96, N 8.92; found C 58.59, H 3.68, N 8.82.

(*E*)-*N*-*p*-Tolyl-9-(*p*-tolylimino)-9,12-dihydroquinolino[7,8-*h*]quinolin-4-amine (11a): A solution of *p*-toluidine (2.75 g, 25.6 mmol) and **6** (0.100 g, 0.334 mmol) was stirred at 150 °C for 4 h. The reaction mixture was diluted with CH_2Cl_2 (200 mL) and washed with water (200 mL) and 6 M KOH (20 mL). The organic layer was dried with $MgSO_4$ and filtered. The product was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 90:10; CH_2Cl_2/MeOH, 50:50; CH_2Cl_2/MeOH/NEt_3, 47:47:6) to give **11a** (0.136 g, 92%). The product was recrystallised by cooling to 4 °C in CH_2Cl_2/MeOH overnight. ^{1}H NMR (500 MHz, $CDCl_3$, [D$_6$]DMSO): δ = 2.33 (s, 6 H, C*H*$_3$), 6.66 (d, $^3J_{5,6}$ = 6.4 Hz, 2 H, 6,7-*H*), 7.12 (d, $^3J_{2,3}$ = 7.9 Hz, 4 H, 2-Ph*H*), 7.23 (d, $^3J_{2,3}$ = 7.9 Hz, 4 H, 3-Ph*H*), 7.95 (d, $^3J_{2,3}$ = 8.8 Hz, 2 H, 3,10-*H*), 8.25 (d, $^3J_{2,6}$ = 6.4 Hz, 2 H, 5,8-*H*), 8.61 (d, $^3J_{2,3}$ = 8.8 Hz, 2 H, 2,11-*H*), 16.41 (s, 1 H, N*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, [D$_6$]DMSO): δ = 20.6 (t), 101.8 (s), 116.2 (q), 118.3 (q), 123.1 (s), 123.2 (q), 124.7 (s), 130.0 (s), 133.0 (s), 135.8 (q), 141.4 (q), 142.6 (q), 143.4 (q), 152.2 (s) ppm. IR: $\tilde{\nu}$ = 2920, 1594, 1560, 1512, 1457, 1421, 1388, 1326, 822, 800 cm^{-1}. HRMS (ESI+): calcd. for $C_{30}H_{24}N_4$ [M + H]$^+$ 441.2074; found 441.2068 .

Crystal Data for 11a: $C_{31}H_{28}N_4O$, yellow chip, dimensions 0.4 × 0.15 × 0.15 mm, orthorhombic, space group $P2_12_12_1$, a = 7.8131(16) Å, b = 14.208(3) Å, c = 22.211(4) Å, α = 90.00°, β = 90.00°, γ = 90.00°, U = 2465.6(9) Å^3, μ = 0.617 mm^{-1}, Z = 4, D_c = 1.273 g cm^{-3}, F(000) = 1000, T = 100(2) K. A total of 9733 reflections were collected by using a Rigaku MM007 rotating anode in the range 6.54 < 2θ < 143.80°. A semiempirical absorption correction (ABSCOR; Higashi, 1995) was applied. The 4104 independent reflections were used to solve the structure by direct methods (SHELXS-97), which resulted in the location of all non-hydrogen atoms. All non-hydrogen atoms were made anisotropic and the refinement (SHELXL-97) of 329 parameters converged to R_1 = 0.0392 [for 3788 reflections having $I > 4\sigma$ (I)], wR_2 = 0.1030 and goodness of fit 1.066 (for all 3788 F^2 data). Peak/hole 0.178/–0.271 e Å^{-3}.

[H(11a)][BF$_4$]: $BF_3{\cdot}OEt_2$ (0.484 mL, 3.856 mmol) was added to **11a** (0.100 g, 0.227 mmol) in dry CH_2Cl_2 (5 mL) under an atmosphere of Ar, and the mixture was stirred at room temperature for 10 min. The reaction mixture was diluted with diethyl ether, and the solvent was separated from deposited [H(**11a**)][BF$_4$], which was dried under vacuum. The product was then set up for crystallisation by vapour diffusion of diethyl ether into a MeOH solution containing [H(**11a**)][BF$_4$]. Yellow crystals suitable for X-ray crystallography were obtained after 1 d. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.40 (s, 6 H, C*H*$_3$), 7.06 (d, $^3J_{5,8}$ = 6.3 Hz, 2 H, 6,7-*H*), 7.38 (m, 8 H, 2,3-Ph*H*), 8.26 (d, $^3J_{2,3}$ = 9.1 Hz, 2 H, 3,10-*H*), 8.72 (d, $^3J_{5,6}$ = 6.3 Hz, 2 H, 5,8-*H*), 8.78 (d, $^3J_{2,3}$ = 9.1 Hz, 2 H, 2,11-*H*), 10.11 (s, 2 H, N*H*), 18.79 (s, 1 H, N*H*) ppm. ^{13}C NMR (125 MHz, [D$_6$]-DMSO): δ = 21.1 (t), 102.8 (s), 116.5 (q), 116.7 (q), 123.6 (s), 125.3 (s), 126.6 (s), 130.8 (s), 136.1 (q), 136.3 (q), 136.8 (q), 143.6 (q), 145.7 (s), 153.0 (q) ppm. HRMS (ESI+): calcd. for $C_{30}H_{24}N_4$ [M + H]$^+$ 441.2074; found 441.2068.

Crystal Data for [H(11a)][BF$_4$]: $C_{30}H_{25}N_4BF_4$, yellow rod, dimensions 0.8 × 0.3 × 0.05 mm, monoclinic, space group $P2_1/c$, a = 16.076(3) Å, b = 17.296(4) Å, c = 9.1906(18) Å, α = 90.00°, β = 97.00(3)°, γ = 90.00°, U = 2536.3(9) Å^3, μ = 0.858 mm^{-1}, Z = 4, D_c = 1.384 g cm^{-3}, F(000) = 1096, T = 123(2) K. A total of 8257 reflections were collected by using a Rigaku MM007 rotating anode in the range 6.52 < 2θ < 143.40°. A semi-empirical absorption correction (ABSCOR; Higashi, 1995) was applied. The 4242 independent reflections were used to solve the structure by direct methods (SHELXS-97), which resulted in the location of all non-hydrogen atoms. All non-hydrogen atoms were made anisotropic and the refinement (SHELXL-97) of 355 parameters converged to R_1 = 0.0660 [for 2736 reflections having $I > 4\sigma$ (I)], wR_2 = 0.1710 and goodness of fit 1.085 (for all 2736 F^2 data). Peak/hole 0.425/–0.371 e Å^{-3}.

(*E*)-Methyl 2-[9-(*o*-Tolylamino)quinolino[7,8-*h*]quinolin-4(1*H*)-ylideneamino]benzoate (11b): A mixture of methyl anthranilate (6.65 mL, 51.4 mmol) and **6** (0.200 g, 0.668 mmol) was stirred at 120 °C for 2 h. The reaction mixture was diluted with CH_2Cl_2 (200 mL) and washed with water (200 mL) and 6 M KOH (20 mL). The organic layer was dried with $MgSO_4$ and filtered. The product was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 90:10; CH_2Cl_2/MeOH, 50:50; CH_2Cl_2/MeOH/NEt_3, 47:47:6) to give **11b** (0.093 g, 26%). ^{1}H NMR (500 MHz, $CDCl_3$, MeOD): δ = 3.97 (s, 6 H, COC*H*$_3$), 7.17 (t, $^3J_{5,6}$ = 7.6 Hz, 2 H, 6-Ph*H*), 7.57 (m, 4 H, 4,5-Ph*H*), 7.68 (d, $^3J_{3,4}$ = 8.0 Hz, 2 H, 3-Ph*H*), 7.99 (d, $^3J_{5,6}$ = 8.8 Hz, 2 H, 6,7-*H*), 8.04 (d, $^3J_{2,3}$ = 7.9 Hz, 2 H, 3,10-*H*),

8.28 (d, $^3J_{5,6}$ = 8.8 Hz, 2 H, 5,8-*H*) 8.89 (m, 2 H, 2,11-*H*); (in [D$_6$]DMSO) 15.69 (s, 1 H, N*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, MeOD): δ = 52.5 (t), 104.4 (s), 116.2 (q), 118.1 (q), 118.2 (q), 119.5 (s), 121.8 (s), 123.5 (s), 127.3 (s), 131.9 (s), 134.3 (s), 136.1 (q), 141.4 (q), 143.1 (q), 145.5 (s), 149.3 (q), 168.5 (q) ppm. IR: $\tilde{\nu}$ = 3243, 1585, 1552, 1527, 1491, 1452, 1416, 1390, 1321, 1252, 1082, 738 cm^{-1}. HRMS (ESI+): calcd. for $C_{32}H_{24}N_4O_8$ [M + H]$^+$ 529.1870; found 529.1866.

4,9-Dichloro-6,7-dinitroquinolino[7,8-*h*]quinoline (12): To a mixture of fuming nitric acid (1 mL) and concentrated sulfuric acid (1 mL) heated briefly to initiate NO_2 generation was added **6** (0.050 g), and the reaction mixture was stirred for 2 min at 120 °C. The mixture was poured onto ice. The mixture was diluted with CH_2Cl_2 (100 mL) and MeOH (10 mL) and washed with 6 M KOH (20 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated to give **12** (0.023 g, 35%). ^{1}H NMR (500 MHz, 70 °C, [D$_6$]DMSO): δ = 6.52 (d, $^3J_{2,3}$ = 7.4 Hz, 1 H, 3-*H*), 8.34 (d, $^3J_{5,6}$ = 5.0 Hz, 1 H, 10-*H*), 8.37 (dd, $^3J_{1,2}$ = 5.2 Hz, $^3J_{2,3}$ = 7.4 Hz, 1 H, 2-*H*), 9.09 (s, 1 H, 8-*H*), 9.15 (s, 1 H, 5-*H*), 9.31 (d, $^3J_{10,11}$ = 5.0 Hz, 1 H, 11-*H*), 15.59 (d, $^3J_{1,2}$ = 5.2 Hz, 1 H, N*H*) ppm. ^{13}C NMR (125 MHz, 70 °C, [D$_6$]DMSO): δ = 111.1 (q), 113.4 (s), 120.1 (q), 121.3 (q), 123.7 (q), 123.8 (q), 124.9 (s), 125.1 (s), 126.3 (s), 140.5 (q), 141.8 (s), 142.8 (q), 145.3 (q), 145.6 (q), 148.3 (q), 152.8 (s) ppm. HRMS (ESI+): calcd. for $C_{16}H_6Cl_2N_4O_4$ [M + H]$^+$ 388.9839; found 388.9832.

CCDC-893097 (for **3**), -893098 (for [H(**5**)][BF_4]), -893099 (for **11a**), -893100 (for **7**), -893101 (for [H(**11a**)][BF_4]) and -893102 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR and ^{13}C NMR spectra for compounds **3**, **5**, H(**5**)BF_4, **7**, **8**, **9**, **10**, **11a**, H(**11a**)BF_4, **11b** and **12**; molecular orbital plots for compounds H(**11a**)BF_4 and H(**11b**)BF_4.

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