A New Route to Ring-Fused Pyrazines: Imidazo[4,5-b]Quinoxalines by a Simple Oxidation–Annulation Sequence

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Abstract: Novel tricyclic 4H-imidazo[4,5-b]quinoxalines were synthesized by a new ortho-annulation process starting from 4H-imidazoles and cerammonium nitrate (CAN) as oxidation reagent in the presence of potassium carbonate as base. This reaction is interpreted as a multi-step reaction involving oxidative radical formation, a radical aromatic substitution and a subsequent redox process. The analysis is supported by high level DFT calculations. This novel transformation opens the way for the construction of ring-fused derivatives of pyrazine. The new tricyclic products display strong fluorescence in solution and, in addition, show reversible redox activity.

Key words: amines, heterocycles, oxidations, radical reactions, ring-closure

Ring-annulation reactions of nitrogen-containing systems play an important role in the construction of pharmacologically active compounds as well as for new innovative materials. Besides ‘classical’ condensation reactions, increasingly elegant pericyclic processes have been applied. As a result, laborious multi-step procedures with low yields could therefore be replaced.

A special case among aza-heterocycles, however, are the pyrazines where ring formation is based, almost without exception, on condensation reactions. Cycloaddition reactions of 1,4-diazadienes are quite rare and the results have to be viewed critically. Particularly, intermediate electron-rich alkene substructures (ene-diamines) are capable of undergoing subsequent redox processes. Other synthetic approaches such as electrocyclization with subsequent elimination applied to diazahexatriene systems mainly resulted in the formation of pyrimidines and quinazolines with only a few publications on the formation of pyrazines.

The concept of electrocyclization of 1,n-dipoles and positively or negatively charged unsaturated systems was successfully applied for azepines and larger ring systems.

Since vicinal diamines/diimines and the corresponding hybrids are easily accessible, oxidative cyclization reactions have gained increasing interest. In the past, some such cyclizations have been employed for the construction of phenazines, fluoflavines, fluorindines and other ring-fused derivatives. Observations made by a cooperating group as well as our own experimental findings inspired us to study such reactions in more detail.

Our starting point was the observation that derivatization reactions of the deep-red 4H-imidazoles of type 2 often led to yellow, strongly fluorescent by-products. Since, initially, ring-annulation processes were suspected to cause the formation of these by-products, first, the ortho-fluorosubstituted derivative 2a was synthesized. The ortho-fluorine atom should facilitate an intramolecular nucleophilic substitution thus leading to tricycles of type 3.

All compounds of type 2 were prepared by the standard method developed in our group (Scheme 1) – the cyclization reaction of benzamidine hydrochloride and bis-arylimidoyl chlorides. The bis-electrophiles of type 1 are easily accessible by a two-step, one-pot reaction. The new bis-arylimidoyl chloride 1j, which possesses propargyl ether groups (Ar = C6H4OCH2C≡CH), was isolated as yellow crystals in good yields. These newly introduced functional groups offered the opportunity for further modifications (e.g. cycloadditions and cross-coupling reactions). The new derivatives 2h and 2o, which possess n-octyl groups, were synthesized in order to obtain compounds with better solubility in nonpolar solvents (Scheme 1).

The starting compound 2a was isolated in good yields and was characterized by elemental analysis, MS, 1H NMR and 19F NMR data. Even during its synthesis, traces of a strongly blue fluorescent substance were detected by TLC, which could be isolated by column chromatogra-
phy, in ~1% yield; this substance was identical to 3a. Subsequent treatment of 2a with various bases primarily formed the deep-purple anion of 2a which, however, proved to be stable towards cyclization processes. In contrast, heating 2a in acetic acid under reflux formed a green solution which, upon work-up and purification, gave the new derivative 3a in ~20% yield (Scheme 2). Compound 3a was isolated as slightly yellow crystals which showed strong blue fluorescence in solution. Most likely, in this reaction, the protonated cyanine-like form 2aH⁺ was generated which easily undergoes an SN₂ type reaction at the aromatic core. However, all further attempts to improve the yield of this ring-annulation reaction failed. In all cases, mixtures of decomposition products derived from the starting heterocycle 2a were obtained and the desired imidazoquinoxaline 3a was isolated only in low yield (1–20%). Due to these experimental findings and in order to introduce other functional groups into heterocycles 3, we focused our further studies on a different synthetic strategy.

Since radical cations were discussed as being alternative intermediates in other cyclization reactions, oxidation reactions were tested. Moreover, we recently demonstrated that oxygen is necessary in certain types of ortho-annulation processes.

Several oxidants, combined with potassium carbonate (the addition of a base results in shorter reaction times and higher yields), were employed successfully in the ring-forming reactions of compounds 2, e.g. cerammonium nitrate (CAN), lead(IV) acetate and potassium hexacyanoferrate(III). In these experiments, the combination of CAN and potassium carbonate proved to be the best for this transformation. This protocol is distinguished by short reaction times, high yields and non-toxic by-products.

The oxidation with lead(IV) acetate resulted in comparably high yields but, due to the formation of toxic waste products, this pathway was not pursued further. Using potassium hexacyanoferrate(III), longer reaction times, excess of oxidant and higher temperatures were necessary in order to obtain comparable yields. In a recent publication we demonstrated that other oxidants able to transfer oxygen (dimethyldioxirane, peroxyacids) selectively reacted with 2 at the imino nitrogen atom with formation of β-aminonitrones. Consequently, under these conditions (CAN, K₂CO₃, MeCN, r.t.), 2a exclusively gave 3b as the main product. Analogously, oxidation reactions of all the other 4H-imidazoles 2 resulted in the selective formation of yellow cyclization products 3 (Scheme 3). Depending on the substituents on the aryl residues, the yields varied from traces (3n and 3o) up to 90% (3d; Table 1). The low yield for 3n and 3o may be explained by the steric demand exerted by the two neighboring trifluoromethyl/ester groups. The new derivatives were isolated in analytically pure form after recrystallization/column chromatography. Elemental analysis and MS data confirmed the loss of two hydrogen atoms. The ¹H- and ¹³C NMR spectra of derivatives 3 exhibited two sets of signals for the former aryl residues at the =N/NH-atoms, indicating an unsymmetrical structure. In the ¹H NMR spectrum of derivative 3d, the signal at δ = 7.16 ppm was the key signal for this ortho-annulation process. In the ¹³C NMR spectra, the C-2 of the imidazole ring absorbs in the downfield region, similar to the starting compounds (δ: 189 ppm; 3: δ = 181 ppm).

A single-crystal X-ray analysis of 3d allowed an unambiguous structural assignment of these compounds, as shown in Figure 1. Hence, the cyclization products 3 have the structure of 2-phenyl-4-aryl-4H-imidazo[4,5-b]quinoxalines. Compound 3d is a monomer in the solid state with the bond lengths and angles being within the expected range. Typically, an alternation of bond lengths in the 4H-imidazol core was detected. The C2–C3 bond length (1.46 Å) lies in the range of single carbon–carbon bonds in a butadiene system. The π-system of the 4-tolyl ring is nearly perpendicular with respect to the central 4H-imidazoquinoxaline functionality.

It is noteworthy that only a few literature reports on imidazo[4,5-b]quinoxalines exist; 2-substituted derivatives with additional substituents at the pyrazine ring are unknown.
The new tricyclic compounds were well soluble in common solvents and proved to be stable towards air. In contrast to the deep red-colored 4H-imidazoles (2d; \( \lambda_{\text{max}} = 490 \text{ nm} \)), their long-wavelength UV/Vis absorptions are shifted hypsochromically (\( \Delta \lambda \approx 100 \text{ nm} \)). Additions display a strong blue fluorescence in solution (3d; \( \lambda_{\text{em}} = 488 \text{ nm} \)) with Stokes shifts (v) of approximately 5500 cm\(^{-1}\) and quantum yields between 5 and 40\%. The bromo-substituted derivative 3k offers the preconditions needed for subsequent modifications as exemplified here for the Sonogashira cross-coupling method. Upon treatment of 3k with trispropylsilyl acetylene or phenyl acetylene under standard Sonogashira conditions, the new, highly fluorescent bis-acetylenes 3p and 3q were isolated in high yields. It is noteworthy that all efforts to cross-couple the parent compounds 2 itself failed so far. This can be explained by the excellent chelating properties of the 4H-imidazoles 2, which prevent the formation of catalytically active palladium species.

Due to their inherent merocyanine-type structures, compounds 3 are likely to behave as multi-step redox systems according to Scheme 4. We could recently demonstrate that 4H-imidazoles 2 and other cross-conjugated systems behave as electrophores that can easily be switched between oxidized and reduced forms. The cyclic voltammograms, as well as difference pulse polarographic measurements of 3d, revealed two reversible reduction waves that correspond to two single-electron transfer steps (3d; \(-0.782 \text{ V} \) and \(-0.986 \text{ V} \) ). In the first step, it is likely that the radical anion was generated. The second electron-transfer step then leads to the formation of the di-anion (3-red), which can be protonated to yield the leuco (3-leuco) form (Scheme 4). The quasi-reversibility of the reduction was confirmed by cyclovoltammetric measurements (\( \Delta E_{\text{RED,OX}} = 0.128 \text{ V} \) and \( \Delta E_{\text{RED,OX}} = 0.082 \text{ V} \) ). 3d-leuco could also be obtained by the reduction of 3d in tetrahydrofuran, in the presence of small amounts of aqueous sodium dithionite, however, this is rapidly reoxidized by air. Furthermore, the cyclovoltammogram of 3d showed two irreversible oxidation waves at 0.903 V and 1.372 V.

We postulate the following mechanism (Scheme 5) for the formation of the imidazo[4,5-b]quinazolines of type 3. First, oxidation takes place through intermediate formation of the radical cation A derived from a secondary amine. A relatively strong acidity has been predicted for these radical cations and, consequently, deprotonation may result in the aminyl radical B. Finally, radical B is...
able to attack the attached aromatic ring intramolecularly to give 3 via C.

In order to investigate the mechanism of the ring-closure reaction, high-level quantum chemical gas-phase calculations were performed using the program packages GAUSSIAN 03,17 employing the DFT B3LYP/6-311+G(d,p) method for geometry optimization and energy determination including zero-point correction and TURBOMOLE,18 using the recently developed B2PLYP-D hybrid functional,19 with the def2-TZVP-basis set, 20 and the B3LYP/6-311+G(d,p) geometries for the energy determinations. Many DFT calculations of (charged) open-shell species using standard hybrid functionals suffer from the well-known problem of self-interaction error,21 that typically leads to reaction barriers that are too low and to over-delocalization effects in unsaturated systems.22 These problems can be significantly alleviated by increasing the amount of Fock-exchange admixture as, for example, in the double-hybrid functionals which have about 50% Fock-exchange compared to 20% in B3LYP.

Among other conceivable mechanisms compatible with the reaction conditions (presence of base and oxidant at room temperature), we took three possible pathways for the cyclization reaction into account computationally (Scheme 6). If the oxidation takes place first, a radical cation will be formed, which may either undergo the ring-closure reaction or might be deprotonated to give the corresponding radical. Alternatively, initial oxidative removal of a hydrogen atom may take place, producing the radical, which will then cyclize. A third possibility involves initial deprotonation by the base, whereby anionic ring-closure reaction might occur. All three modes are expected to lead to the product observed after additional oxidation and deprotonation steps.

With respect to the cyclization reaction, the calculations (B2PLYP-D data, B3LYP values in parentheses) clearly favor the radical mechanism, which shows the lowest activation barrier of 8.6 (18.1) kcal/mol, followed by the anionic mechanism [25.1 (32.4) kcal/mol] and the radical cation mode [42.3 (45.8) kcal/mol]. Thus, the radical cyclization with its pronounced exothermicity [−12.1 (−11.3) kcal/mol] seems to be the favored mode of ring-formation. In contrast, the energy-rich transition-state and the product of the radical cation cyclization suffer significantly from a lack of resonance due to the four-coordinate nitrogen atom present in these structures. The anionic mechanism, despite its moderate energy barrier, seems to be less likely since this mode is expected to require a stronger base than is present in the reaction mixture.

Scheme 5 Proposed mechanism for the ortho-ring-annulation process

Scheme 6 Overview of the three possible cyclization mechanisms studied using DFT-calculations. Relative energies (kcal/mol) at the B2-PLYP-D/def2-TZVP/B3LYP/6-311+G(d,p)-level. Numbers in parentheses refer to B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p)-calculations.
Thus, in good agreement with the experimental conditions and the considerations discussed above, we suggest the radical pathway for the cyclization reaction. The idea of a radical mechanism proceeding through a step-wise initial oxidation to the radical cation, then deprotonation to the radical seems especially attractive due to the enhanced acidity of nitrogen-containing radical cations in comparison to the neutral aromatic amines.

In conclusion, starting from easily accessible 4H-imidazo[4,5-b]quinoxalines 3 has been developed. Their structure was determined by elemental analysis, MS, NMR and, additionally, by X-ray crystal structural analysis. The compounds are air-stable and well soluble in common solvents and display a strong blue fluorescence in solution. These features make them of interest as multifunctional dyes. High-level quantum chemical DFT-calculations are in good agreement with a radical cyclization mechanism, which may operate after oxidation to the radical cation and subsequent deprotonation to produce the intermediate radical.

The reagents were purchased from commercial sources and were used directly unless otherwise stated in the text. All solvents were of reagent grade and were dried according to common practice and distilled prior to use. Reactions were monitored by TLC, carried out on 0.2 mm Merck silica gel plates (60 F254). 1H and 13C NMR spectra were recorded on Bruker AVANCE 250 and 400 spectrometers, shifts (δ) are given relative to signals arising from the solvent. Melt points were measured with a Galen III apparatus (Boëtius system) or with a Kofler apparatus and are uncorrected. Electrochemical measurements were carried out in CH2Cl2 with a Metrohm 663 VA Stand using platinum electrodes (reference electrode SCE) and tetrabutylammonium hexafluorophosphate as conductive salt.

Bis(arylaldimidoyl) Chlorides 1; General Procedure
To a solution of the corresponding bis-aryloxaldiimidoyl chloride (10 mmol), benzamidine hydrochloride (1.7 g, 11 mmol) and Et3N (7.0 mL, 51 g, 50 mmol) in MeCN (50 mL) was heated under reflux until no starting material was detected (TLC; 2–5 h). The formed Et3N·HCl was filtered off, the solvent was removed in vacuo and the crude product was recrystallized or purified by column chromatography on silica gel (CHCl3–n-heptane).

Bis(2-fluorophenyl)aldimidoyl Chloride (1a)
Yield: 62%; red crystals; mp 105–107 °C.
1H NMR (250 MHz, CDCl3): δ = 8.55–8.51 (m, 2 H, C-Ph), 7.68–7.51 (m, 2 H, CH-Ar), 7.32–7.12 (m, 4 H, CH-Ar).
19F NMR (188 MHz, CDCl3): δ = -122.9 (s, 2 F).
MS (EI): m/z (%) = 312 (10) [M+], 156 (100) [M/2+].

Bis(2-bromophenyl)aldimidoyl Chloride (1b)
Yield: 74%; yellow crystals; mp 182–183 °C.
1H NMR (250 MHz, CDCl3): δ = 7.71–7.37 (m, 4 H, CH-Ar), 7.18–7.11 (m, 2 H, CH-Ar), 7.07–7.04 (m, 2 H, CH-Ar).
13C NMR (63 MHz, CDCl3): δ = 145.0, 141.1, 133.1, 127.9, 127.5, 120.1, 114.3.

Bis(4-propargylxylophenyl)aldimidoyl Chloride (1j)
Yield: 83%; yellow crystals; mp 174–175 °C.
1H NMR (250 MHz, CDCl3): δ = 7.29 (d, J = 8 Hz, 4 H, CH-Ar), 7.06 (d, J = 8 Hz, 4 H, CH-Ar), 4.74 (d, J = 2.4 Hz, 4 H, CH3), 2.56 (t, J = 2.4 Hz, 2 H, C=C-H).
13C NMR (63 MHz, CDCl3): δ = 156.7, 138.9, 136.7 (Cl-C=N), 123.5, 115.0, 72.8, 75.2, 56.1.
MS (EI): m/z (%) = 388/386/384 (10/40/70) [M+], 192 (100) [M2+] 188 (60), 153 (20).
Anal. Calcld for C25H14BrCl2N2O2: C, 38.69; H, 3.87; N, 15.27. Found: C, 38.82; H, 3.86; N, 15.27.

2-Phenyl-4-arylamino-5-arylimino-4H-imidazoles (2); General Procedure
A solution of the corresponding bis-aryloxaldiimidoyl chloride 1 (10 mmol), benzamidine hydrochloride (1.7 g, 11 mmol) and Et3N (7.0 mL, 51 g, 50 mmol) in MeCN (50 mL) was heated under reflux until no starting material 1 was detected (TLC; 2–5 h). The formed Et3N·HCl was filtered off, the solvent was removed in vacuo and the crude product was recrystallized or purified by column chromatography on silica gel (CHCl3–n-heptane).

Bis(2-fluorophenyl)aldimidoyl Chloride (2a)
Yield: 62%; red crystals; mp 170–176 °C (CHCl3–n-heptane).
IR (ATR): 3391, 3369, 3069, 1592, 1496, 1434, 1341, 1245, 1230, 1086, 754, 716 cm–1.
1H NMR (250 MHz, CDCl3): δ = 7.31–7.09 (m, 13 H, CH-Ar).
19F NMR (188 MHz, CDCl3): δ = -125.4 (s, 2 F).
MS (EI): m/z (%) = 360 (35) [M+], 341 (25) [M – F]+, 136 (40), 121 (100), 103 (35).
UV/Vis (CHCl3): λmax (log ε) = 481 nm (4.1).

Bis(4-(4-tolyloxy)phenyl)aldimidoyl Chloride (2d)
Yield: 92%; red crystals; mp 209 °C (MeCN).9
1H NMR (250 MHz, CDCl3): δ = 8.55 (d, J = 8 Hz, 4 H, CH-Ph), 7.79 (d, J = 8 Hz, 4 H, CH-Tol), 7.61–7.49 (m, 3 H, CH-Ph), 7.25 (d, J = 8 Hz, 4 H, CH-Tol), 2.39 (s, 6 H, CH-Tol).
13C NMR (63 MHz, CDCl3): δ = 188.6 (C-2), 163.6, 139.5, 136.7, 133.6, 132.1, 130.5, 129.8, 128.5, 123.6, 21.2.

Bis(4-(4-octanoyloxy)phenyl)aldimidoyl Chloride (2f)
Yield: 67%; red crystals; mp 101–103 °C (CHCl3–n-heptane).
IR (ATR): 3369, 3304, 2956, 2920, 2853, 1614, 1574, 1533, 1504, 1237, 1168, 1031, 1000, 830 cm–1.
1H NMR (250 MHz, CDCl3): δ = 9.25 (s, 1 H, NH), 8.57 (m, 2 H, CH-Ph), 8.02 (d, J = 8 Hz, 4 H, CH-Ar), 7.59–7.53 (m, 5 H, CH-Ph), 6.98 (d, J = 8 Hz, 4 H, CH-Ar), 4.01 (t, J = 7 Hz, 4 H, OCH2), 1.95–1.78 (m, 4 H, CH2), 1.48–0.74 (m, 26 H, CH3).
13C NMR (63 MHz, CDCl3): δ = 187.5 (C-2), 162.6 (C-4), 135.2, 133.2, 132.3, 130.2, 128.4, 125.4, 121.2, 115.0, 68.3 (OCH2), 31.8, 30.1, 29.7, 29.1, 26.0, 22.6, 14.0.
MS (EI): m/z (%) = 580 (100) [M+], 467 (57), 451 (49).

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UV/Vis (CHCl₃): λ_max (log ε) = 423 (4.0), 508 (4.2), 538 nm (4.1).
Anal. Calcd for C₉H₇N₃O₃C: C, 76.51; H, 8.33; N, 9.65. Found: C, 76.90; H, 8.74; N, 9.23.

2-Phenyl-4-[4-(propargyloxy)phenylamino]-5-[4-(propargyloxy)phenylimino]-4H-imidazole (2)

Yield: 74%; red crystals; mp 171 °C (CHCl₃–heptane).

1H NMR (250 MHz, CDCl₃): δ = 8.58 (m, 2 H, CH-Ph), 8.05 (m, J = 8 Hz, 4 H, CH-Ar), 7.62–7.51 (m, 3 H, CH-Ph), 7.08 (d, J = 8 Hz, 4 H, CH-Ar), 4.76 (d, J = 2.4 Hz, 4 H, OCH₂), 2.56 (t, J = 2.4 Hz, 2 H, CH₂).

13C NMR (63 MHz, CDCl₃): δ = 137.8, 132.8 (d, J = 11 Hz), 132.7, 132.6 (d, J = 2.5 Hz), 131.0, 130.1, 129.5, 129.2, 128.5, 124.8, 125.9, 125.7 (d, J = 4 Hz), 123.2 (d, J = 14 Hz), 117.5 (d, J = 18 Hz), 115.9.

19F NMR (188 MHz, CDCl₃): δ = −116.9 (s, 1 F).

Anal. Calcd for C₂₆H₁₉N₅F₂: C, 74.71; H, 4.42; N, 12.46. Found: C, 74.58; H, 4.42; N, 12.46.

2-Phenyl-4-(2-bromophenylamino)-5-(2-bromophenylimino)-4H-imidazole (2b)

Yield: 84%; red crystals; mp 214 °C (MeCN).

IR (ATR): 3073, 1596, 1566, 1454, 1431, 1345, 1245, 1136, 1096, 814, 713 cm⁻¹.

UV/Vis (CHCl₃): λ_max (log ε) = 322 (73) [M⁺], 339 (22) [M – F⁺], 255 (32).


Anal. Calcd for C₂₇H₂₀N₄O₂: C, 74.99; H, 4.42; N, 12.46. Found: C, 74.58; H, 4.42; N, 12.46.

2-Phenyl-4-[3,5-di(carboxyloxy)phenylamino]-5-[3,5-di(carboxyloxy)phenylimino]-4H-imidazole (2o)

Yield: 76%; red solid; mp 60–65 °C.

1H NMR (250 MHz, acetone-d₆): δ = 8.69 (s, 4 H, CH-Ar), 8.30–8.23 (m, 4 H, CH-Ph), 7.57–7.35 (m, 3 H, CH-Ph), 4.32–4.22 (m, 2 H, OCH₂), 1.77–1.74 (m, 8 H, CH₂), 1.40–1.30 (m, 30 H, CH₃), 0.89–0.87 (m, 12 H, CH₃).

13C NMR (63 MHz, acetone-d₆): δ = 189.1, 165.0, 134.3, 132.0, 131.8, 131.0, 128.8, 65.6 (OCH₂), 32.2, 29.6, 28.6, 28.4, 26.3, 22.9, 14.1 (CH₂).

UV/Vis (CHCl₃): λ_max (%): 358 (100) [M⁺], 339 (22) [M – F⁺], 255 (32).

Emission (CHCl₃): λ_max = 496 nm.

Anal. Calcd for C₂₃H₁₈N₄O₂F: C, 70.39; H, 3.38; N, 15.63. Found: C, 70.06; H, 3.11; N, 15.33.

2-Phenyl-4-(2-fluorophenyl)-8-fluoro-4H-imidazo[4,5-b]quinoxaline (3b)

Yield: 52%; yellow crystals; mp 256 °C.

1H NMR (400 MHz, CDCl₃): δ = 8.61–8.58 (m, 2 H, CH-Ph), 7.75–7.38 (m, 9 H, CH-Ph), 7.11 (m, 1 H, CH-Ph).

19F NMR (188 MHz, CDCl₃): δ = −119.6 (s, 1 F), −119.8 (s, 1 F).


2-Phenyl-4-(2-fluorophenyl)-4H-imidazo[4,5-b]quinoline (3c)

Yield: 84%; yellow crystals; mp 304 °C (dec).

IR (ATR): 3073, 1596, 1544, 1341, 1354, 1254, 1204, 1096, 914, 767, 716, 689 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 8.60 (m, 2 H, CH-Ph), 8.38 (d, J = 8 Hz, 1 H, CH-Ar), 7.78–7.39 (m, 11 H, CH-Ph).

UV/Vis (CHCl₃): λ_max (%): 322 (73) [M⁺], 339 (22) [M – H⁺].

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2-Phenyl-4-(4-ethoxycarbonylphenyl)-6-ethoxycarbonyl-4H-imidazo[4,5-b]quinoline (3e)

Yield: 76%; yellow crystals; mp 208–209 °C.

IR (ATR): 3428, 2927, 2847, 1717 (C=O), 1664, 1592, 1531, 1437, 1345, 1273, 1229, 1101, 1021, 919, 851, 765 cm

MS (EI): m/z (%): 342 (100) [M+], 324 (50), 246 (20), 222 (11), 135 (41), 117 (30), 99 (23), 71 (12).

MS (micro-ESI): m/z (%): 340 (100) [M+], 322 (70), 244 (40), 220 (30), 136 (20), 118 (15), 99 (13).

UV/Vis (CDCl3): λ_{max} (log ε) = 342 nm (4.0).

Emission (CHCl3): λ_{max} = 385 nm (4.4).

Analytical Calcd for C27H18N4O4: C, 73.02; H, 4.75; N, 13.02. Found: C, 72.96; H, 4.65; N, 13.01.

2-Phenyl-4-(4-trifluoromethylphenyl)-6-trifluoromethyl-4H-imidazo[4,5-b]quinoline (3f)

Yield: 75%; yellow crystals; mp 230–231 °C.

IR (ATR): 3432, 2927, 2847, 1717 (C=O), 1664, 1592, 1531, 1437, 1345, 1273, 1229, 1101, 1021, 919, 851, 765 cm

MS (EI): m/z (%): 342 (100) [M+], 324 (50), 246 (20), 222 (11), 135 (41), 117 (30), 99 (23), 71 (12).

MS (micro-ESI): m/z (%): 339 (100) [M+], 322 (70), 244 (40), 220 (30), 136 (20), 118 (15), 99 (13).

UV/Vis (CDCl3): λ_{max} (log ε) = 339 nm (4.0).

Emission (CHCl3): λ_{max} = 344 nm (4.0).

Analytical Calcd for C27H18N4O4: C, 73.03; H, 4.75; N, 13.01. Found: C, 72.06; H, 4.58; N, 12.95.
2-Phenyl-4-(4-bromophenyl)-6-bromo-4H-imidazo[4,5-b]quinoline (3k)
Yield: 93%; yellow crystals; mp 377 °C (dec).

IR (ATR): 3050, 1675, 1589, 1560, 1468, 1425, 1338, 1238, 820 cm⁻¹.

Yield: 93%; yellow crystals; mp 218 °C.

UV/Vis (CHCl₃): \( \lambda_{\text{max}} = 492 \text{ nm} \) (4.6).

Emission (CHCl₃): \( \lambda_{\text{max}} (\text{log } e) = 410 (4.6), 428 (4.6) \text{ nm} \).

3H NMR (400 MHz, CDCl₃): \( \delta = 8.59 \) (m, 2 H, CH-Ph), 8.32 (d, \( J = 8 \) Hz, 1 H, CH-8), 7.94 (d, \( J = 8 \) Hz, 2 H, CH-Ar), 7.77–7.37 (m, 17 H, CH-Ar).

\[ \text{EMI} \] 1: \( \text{EMI} \text{I} \] 2: \( \text{EMI} \text{I} \] 3: \( \text{EMI} \text{I} \] 4: \( \text{EMI} \text{I} \] 5: \( \text{EMI} \text{I} \] 6: \( \text{EMI} \text{I} \] 7: \( \text{EMI} \text{I} \] 8: \( \text{EMI} \text{I} \] 9: \( \text{EMI} \text{I} \] 10: \( \text{EMI} \text{I} \] 11: \( \text{EMI} \text{I} \] 12: \( \text{EMI} \text{I} \] 13: \( \text{EMI} \text{I} \] 14: \( \text{EMI} \text{I} \] 15: \( \text{EMI} \text{I} \] 16: \( \text{EMI} \text{I} \] 17: \( \text{EMI} \text{I} \] 18: \( \text{EMI} \text{I} \] 19: \( \text{EMI} \text{I} \] 20: \( \text{EMI} \text{I} \] 21: \( \text{EMI} \text{I} \] 22: \( \text{EMI} \text{I} \]
the range 2.11° ≤ Θ ≤ 27.47°, completeness Θobs = 99.7%, 3947 independent reflections, R = 0.0447, 2774 reflections with Fo > 4σ(Fo); 305 parameters, 0 restraints, Rs = 0.0495, wR2 = 0.1184, R1 = 0.0796, wR2 = 0.1334, GOOF = 1.034, largest difference peak and hole: 0.306–0.269 e Å⁻³.

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References


