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

Svenja Herzog,[a] Gunther Buehrdel,[a] Rainer Beckert,*[a] Susann Klimas,[a] Ernst-Ulrich Würthwein,*[b] Stefan Grimme,[b] Helmar Görls[c]

[a] Institute of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Humboldtstr. 10, 07743 Jena, Germany
Fax +49(3641)948212; E-mail: C6bera@uni-jena.de

[b] Organic-Chemistry Institute, University Münster, Corrensstr. 40, 48149 Münster, Germany
Fax +49(251)8339772; E-mail: wurthwe@uni-muenster.de

[c] Institute of Inorganic and Analytical Chemistry, Friedrich-Schiller-University Jena, Lessingstr. 8, 07743 Jena, Germany

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Abstract: Novel tricyclic 4*H*-imidazo[4,5-*b*]quinoxalines were synthesized by a new *ortho*-annulation process starting from 4*H*-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.

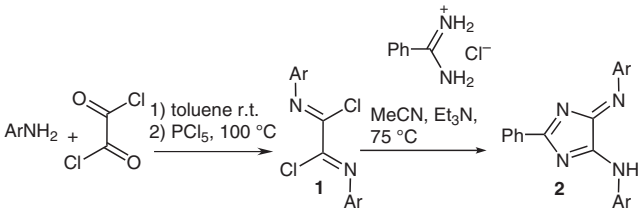
A special case among aza-heterocycles, however, are the pyrazines where ring formation is based, almost without exception, on condensation reactions. Cycloaddition reactions of 1,4-diazadienes are quite rare and the results have to be viewed critically.[1] Particularly, intermediate electron-rich alkene substructures (ene-diamines) are capable of undergoing subsequent redox processes. Other synthetic approaches such as electrocyclization with subsequent elimination[2] applied to diazahexatriene systems mainly resulted in the formation of pyrimidines[3] and quinazolines[4] with only a few publications on the formation of pyrazines.[5]

The concept of electrocyclization of 1,n-dipoles and positively or negatively charged unsaturated systems was successfully applied for azepines and larger ring systems.[6]

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.[7] Observations made by a cooperating group[8a,b] as well as our own experimental findings[8c,d] inspired us to study such reactions in more detail.

Our starting point was the observation that derivatization reactions of the deep-red 4*H*-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*-fluoro-substituted 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 **1**.[9] The bis-electrophiles of type **1** are easily accessible by a two-step, one-pot reaction.[10] The new bis-arylimidoyl chloride **1j**, which possesses propargyl ether groups (Ar = $C_6H_4OCH_2C{\equiv}CH$), 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).



Scheme 1 Synthesis of the 4*H*-imidazoles **2**

The starting compound **2a** was isolated in good yields and was characterized by elemental analysis, MS, ^{1}H NMR and ^{19}F NMR data. Even during its synthesis, traces of a strongly blue fluorescent substance were detected by TLC, which could be isolated by column chromatogra-

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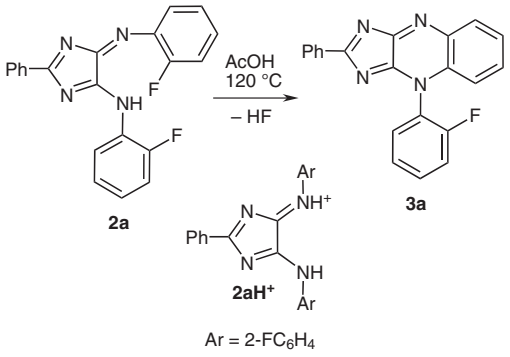
phy, in ~1% yield; this substance was identical to **3a**. Subsequent treatment of **2a** with various bases primarily formed the deep-purple anion of **2a** which, however, proved to be stable towards cyclization processes. In contrast, heating **2a** in acetic acid under reflux formed a green solution 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 S_{Ni}-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.



Scheme 2 Cyclization of *ortho*-fluoro-substituted 4*H*-imidazoles

Since radical cations were discussed as being alternative intermediates in other cyclization reactions,[11] oxidation reactions were tested. Moreover, we recently demonstrated that oxygen is necessary in certain types of *ortho*-annulation processes.[8d]

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.[12] Consequently, under these conditions (CAN, K_2CO_3, MeCN, r.t.), **2a** exclusively gave **3b** as the main product. Analogously, oxidation reactions of all the other 4*H*-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 ^{1}H- and ^{13}C 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 ^{1}H NMR spectrum of derivative **3d**, the signal at δ = 7.16 ppm was the key signal for this *ortho*-annulation process. In the ^{13}C NMR spectra, the C-2 of the imidazole ring absorbs in the downfield region, similar to the starting compounds (**2**: 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-4*H*-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 4*H*-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 4*H*-imidazoquinoxaline functionality.

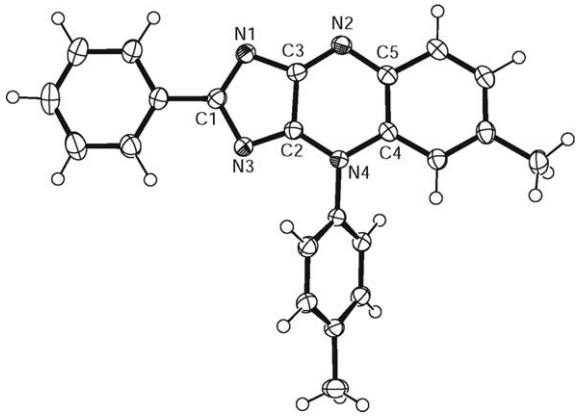


Figure 1 ORTEP plot (50% probability ellipsoids) of the solid-state molecular structure (X-ray crystal structure analysis) of derivative **3d**, selected bond lengths in Å: N1–C1, 1.343(2); N1–C3, 1.372(2); N2–C3, 1.3095(19); N2–C5, 1.379(2); N3–C1, 1.391(2); N3–C2, 1.3172(19); N4–C2, 1.3520(19); N4–C4, 1.4049(19); C2–C3, 1.461(2); C4–C5, 1.417(2).

It is noteworthy that only a few literature reports on imidazo[4,5-*b*]quinoxalines exist;[13] 2-substituted derivatives with additional substituents at the pyrazine ring are unknown.

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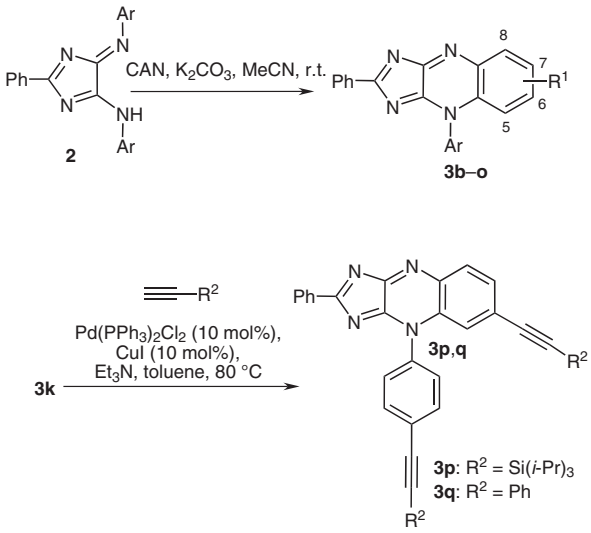


Scheme 3 Synthesis of 4*H*-imidazo[4,5-*b*]quinoxalines and modification by Sonogashira cross-coupling reaction

Table 1 Substitution Pattern of **2** and **3**

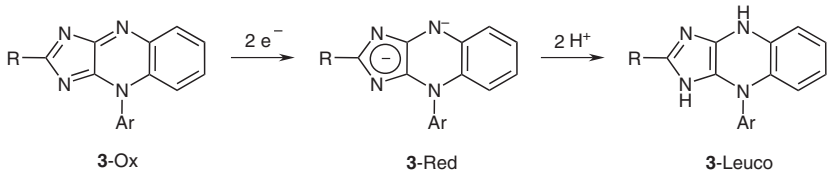
2	Ar	R	Product	Yield (%)
2a	2-FC_6H_4	H	**3a**[a]	20
2a	2-FC_6H_4	8-F	**3b**	52
2c	Ph	H	**3c**	84
2d	4-Tolyl	6-Me	**3d**	92
2e	4-(EtO_2C)C_6H_4	6-EtO_2C	**3e**	65
2f	4-$F_3CC_6H_4$	6-F_3C	**3f**	78
2g	4-*t*-BuC_6H_4	6-*t*-Bu	**3g**	90
2h	4-*n*-$OctOC_6H_4$	6-*n*-OctO	**3h**	75
2i	4-$MeOC_6H_4$	6-MeO	**3i**	91
2j	4-HC≡$CCH_2OC_6H_4$	6-HC≡CCH_2O	**3j**	87
2k	4-BrC_6H_4	6-Br	**3k**	93
2l	2-BrC_6H_4	8-Br	**3l**	97
2m	3-$F_3CC_6H_4$	7-F_3C	**3m**	71
2n	3,5-$(F_3C)_2C_6H_3$	5,7-$(F_3C)_2$	**3n**	trace
2o	3,5-(*n*-$OctO_2C)_2C_6H_3$	5,7-(*n*-$OctO_2C)_2$	**3o**	trace

[a] Formed by S_N-reaction on the *ortho*-F-position (Scheme 2).

The new tricyclic compounds were well soluble in common solvents and proved to be stable towards air. In contrast to the deep red-colored 4*H*-imidazoles (**2d**; λ_{max} = 490 nm, shoulder 520 nm), their long-wavelength UV/Vis absorptions are shifted hypsochromically ($\Delta\lambda$ = ~100 nm; **3d**: λ_{max} = 385 nm, shoulder 400 nm). In addition, they display a strong blue fluorescence in solution (**3d**: λ_{Em} = 488 nm) with Stokes shifts (ν) 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 triisopropylsilyl 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 4*H*-imidazoles **2**,[14] 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 4*H*-imidazoles **2** and other cross-conjugated systems behave as electrophores that can easily be switched between oxidized and reduced forms.[12,15,16] 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**; –0.728 V and –0.986 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 dianion (**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 ($\Delta E^1_{RED,OX}$ = 0.128 V and $\Delta E^2_{RED,OX}$ = 0.082 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*]quinoxalines 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



Scheme 4 4*H*-Imidazo[4,5-*b*]quinoxalines **3** as two-electron redox systems

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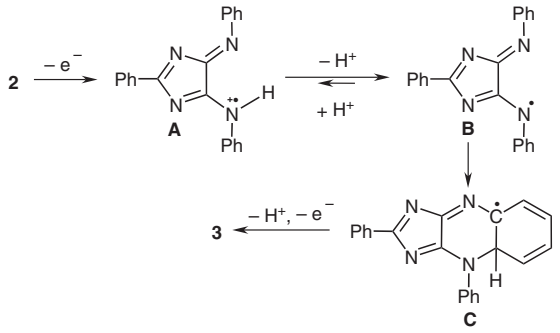


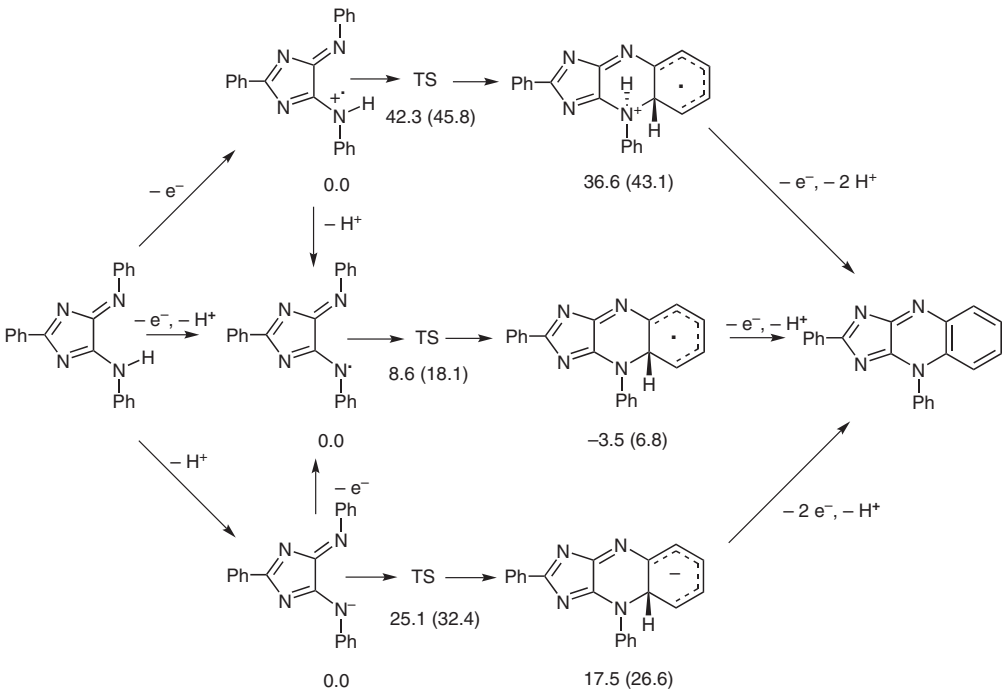
Scheme 5 Proposed mechanism for the *ortho*-ring-annulation process

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 then is present in the reaction mixture.



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.

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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.[23]

In conclusion, starting from easily accessible 4*H*-imidazoles, a new synthesis of tricyclic 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 F_{254}). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE 250 and 400 spectrometers, shifts (δ) are given relative to signals arising from the solvent. Melting points were measured with a Galen III apparatus (Boëtius system) or with a Kofler apparatus and are uncorrected. Electrochemical measurements were carried out in CH_2Cl_2 with a Metrohm 663 VA Stand using platinum electrodes (reference electrode SCE) and tetrabutylammonium hexafluorophosphate as conductive salt.

Bis-aryloxaldiimidoyl Chlorides 1; General Procedure

To a solution of the corresponding aniline (0.1 mol) in toluene (50 mL), oxalyl chloride (4.6 mL, 6.6 g, 0.052 mol), dissolved in toluene (50 mL) was added within 10 min (a slurry of the corresponding oxanilide was formed). The mixture was stirred for 20 min at r.t. then PCl_5 (22.0 g, 0.105 mol) was added. The mixture was heated under reflux until no further hydrogen chloride was formed. The dark-yellow reaction mixture was concentrated in vacuo to dryness and the crude product was recrystallized from *n*-heptane/toluene.

Bis(2-fluorophenyl)oxaldiimidoyl Chloride (1a)

Yield: 62%; yellow crystals; mp 105–107 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.59–8.55 (m, 2 H, CH-Ar), 7.68–7.51 (m, 2 H, CH-Ar), 7.32–7.12 (m, 4 H, CH-Ar).

^{19}F NMR (188 MHz, $CDCl_3$): δ = –122.9 (s, 2 F).

MS (EI): *m*/*z* (%) = 312 (10) [M^+], 156 (100) [$M/2^+$].

Anal. Calcd for $C_{14}H_8Cl_2F_2N_2$: C, 53.70; H, 2.58; N, 8.95. Found: C, 53.37; H, 2.72; N, 8.61.

Bis(2-bromophenyl)oxaldiimidoyl Chloride (1b)

Yield: 74%; yellow crystals; mp 182–183 °C.

^{1}H NMR (250 MHz, $CDCl_3$): 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).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 145.0, 141.1, 133.1, 127.9, 127.5, 120.1, 114.3.

MS (EI): *m*/*z* (%) = 434 (1) [M^+], 355/353 (70/50) [M – Br]$^+$, 317 (50), 218/216 (100/90) [$M/2^+$], 157/155 (60/70).

Anal. Calcd for $C_{14}H_8Br_2Cl_2N_2$: C, 38.66; H, 1.85; N, 6.44. Found: C, 39.07; H, 2.01; N, 6.44.

Bis[4-(propargyloxy)phenyl]oxaldiimidoyl Chloride (1j)

Yield: 83%; yellow crystals; mp 174–175 °C.

^{1}H NMR (250 MHz, $CDCl_3$): 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, CH_2), 2.56 (t, *J* = 2.4 Hz, 2 H, C≡CH).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 156.7, 138.9, 136.7 (Cl-C=N), 123.5, 115.2, 78.2, 75.8, 56.1.

MS (EI): *m*/*z* (%) = 388/386/384 (10/40/70) [M^+], 192 (100) [$M/2^+$], 188 (60), 153 (20).

Anal. Calcd for $C_{20}H_{14}Cl_2N_2O_2$: C, 62.35; H, 3.66; N, 7.27. Found: C, 62.44; H, 3.86; N, 7.15.

2-Phenyl-4-arylamino-5-arylimino-4*H*-imidazoles (2); General Procedure

A solution of the corresponding bis-aryloxaldiimidoyl chloride **1** (10 mmol), benzamidine hydrochloride (1.7 g, 11 mmol) and Et_3N (7.0 mL, 5.1 g, 50 mmol) in MeCN (50 mL) was heated under reflux until no starting material **1** was detected (TLC; 2–5 h). The formed Et_3N·HCl was filtered off, the solvent was removed in vacuo and the crude product was recrystallized or purified by column chromatography on silica gel ($CHCl_3$–*n*-heptane).

2-Phenyl-4-(2-fluorophenylamino)-5-(2-fluorophenylimino)-4*H*-imidazole (2a)

Yield: 62%; red crystals; mp 170–176 °C ($CHCl_3$–*n*-heptane).

IR (ATR): 3391, 3369, 3069, 1592, 1496, 1434, 1341, 1245, 1230, 1086, 754, 716 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.31–7.09 (m, 13 H, CH-Ar).

^{19}F NMR (188 MHz, $CDCl_3$): 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 ($CHCl_3$): λ_{max} (log ε) = 481 nm (4.1).

Anal. Calcd for $C_{21}H_{14}N_4F_2$: C, 69.99; H, 3.92; N, 15.55. Found: C, 69.61; H, 3.87; N, 15.27.

2-Phenyl-4-(4-tolylamino)-5-(4-tolylimino)-4*H*-imidazole (2d)

Yield: 92%; red crystals; mp 209 °C (MeCN).[9]

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.55 (m, 2 H, CH-Ph), 7.89 (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).

^{13}C NMR (63 MHz, $CDCl_3$): 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.

2-Phenyl-4-(4-octanoxyphenylamino)-5-(4-octanoxyphenylimino)-4*H*-imidazole (2h)

Yield: 67%; red crystals; mp 101–103 °C ($CHCl_3$–*n*-heptane).

IR (ATR): 3369, 3304, 2956, 2920, 2853, 1614, 1574, 1533, 1504, 1237, 1168, 1031, 1000, 830 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): 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, OCH_2), 1.85–1.78 (m, 4 H, CH_2), 1.48–0.74 (m, 26 H, CH).

^{13}C NMR (63 MHz, $CDCl_3$): 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 (OCH_2), 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 ($CHCl_3$): λ_{max} (log ε) = 423 (4.0), 508 (4.2), 538 nm (4.1).

Anal. Calcd for $C_{37}H_{48}N_4O_2$: 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]-4*H*-imidazole (2j)

Yield: 74%; red crystals; mp 171 °C ($CHCl_3$–*n*-heptane).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.58 (m, 2 H, CH-Ph), 8.05 (d, *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, OCH_2), 2.56 (t, *J* = 2.4 Hz, 2 H, C≡CH).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 188.0 (C-2), 156.2, 133.4, 132.1, 130.4, 128.5, 125.5, 125.4, 125.3, 115.5, 78.3, 75.8, 56.1.

MS (EI): *m*/*z* (%) = 432 (40) [M^+], 393 (60) [$M - C_3H_3^+$], 158 (20), 133 (100).

Anal. Calcd for $C_{27}H_{20}N_4O_2$: C, 74.99; H, 4.66; N, 12.95. Found: C, 74.58; H, 4.42; N, 12.46.

2-Phenyl-4-(2-bromophenylamino)-5-(2-bromophenylimino)-4*H*-imidazole (2l)

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

IR (ATR): 3301, 3062, 1615, 1592, 1566, 1538, 1423, 1327, 1267 1060, 1022, 747 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.51 (s, 1 H, NH), 8.60–8.58 (m, 2 H, CH-Ph), 7.70–7.47 (m, 7 H, CH-Ar), 7.27–7.13 (m, 4 H, CH-Ar).

MS (DEI): *m*/*z* (%) = 484/482/480 (5/10/5) [M^+], 403/401 (80/100) [$M - Br]^+$, 300 (35).

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 405 (4.0), 491 nm (4.2).

Anal. Calcd for $C_{21}H_{14}N_4Br_2$: C, 52.31; H, 2.93; N, 11.62. Found: C, 52.07; H, 2.65; N, 11.31.

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

Yield: 76%; red solid; mp 60–65 °C.

^{1}H NMR (250 MHz, acetone-d_6): δ = 8.69 (s, 4 H, CH-Ar), 8.30–8.23 (m, 4 H, CH-Ar), 7.57–7.35 (m, 3 H, CH-Ph), 4.32–4.22 (m, 8 H, OCH_2), 1.77–1.74 (m, 8 H, CH_2), 1.40–1.30 (m, 40 H, CH_2), 0.89–0.87 (m, 12 H, CH_3).

^{13}C NMR (63 MHz, acetone-d_6): δ = 189.1, 165.0, 134.3, 132.0, 131.8, 131.0, 128.8, 65.6 (OCH_2), 32.2, 29.6, 28.6, 28.4, 26.3, 22.9, 14.1 (CH_3).

MS (ESI, MeOH/$CHCl_3$): *m*/*z* (%) = 971 (100) [M + Na^+], 949 (60) [M + H^+].

Anal. Calcd for $C_{57}H_{80}N_4O_8$: C, 72.12; H, 8.49; N, 5.90. Found: C, 71.81; H, 8.34; N, 5.99.

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

A solution of **2a** (1.0 g, 2.7 mmol) in glacial AcOH (10 mL) was heated to 120 °C until no starting material **2a** could be detected (TLC; ~4 h). A green solution formed. Most of the solvent was removed in vacuo and the residue was added to H_2O (50 mL). After neutralization with Na_2CO_3, the crude product was extracted with $CHCl_3$ (3 × 50 mL) and the organic layer was dried (Na_2SO_4). After removing the solvent in vacuo, the product was purified by column chromatography on silica gel ($CHCl_3$–MeOH).

Yield: 20%; yellow crystals; mp 257 °C (dec).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.59–8.57 (m, 2 H, CH-Ph), 8.38–8.35 (m, 1 H, CH-Ar), 7.77–7.44 (m, 9 H, CH-Ar), 7.30 (m, 1 H, CH-Ar).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 182.5 (C-2), 162.0, 159.3, 151.5 (^1J = 440 Hz), 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, 128.4, 125.9, 125.7 (d, *J* = 4 Hz), 123.2 (d, *J* = 14 Hz), 117.5 (d, *J* = 18 Hz), 115.9.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –119.6 (s, 1 F).

MS (EI): *m*/*z* (%) = 340 (50) [M^+], 321 (20) [$M - F]^+$, 121 (80), 111 (100).

Emission ($CHCl_3$): λ = 450 nm; λ = 470 nm.

Anal. Calcd for $C_{21}H_{13}N_4F$: C, 74.11; H, 3.85; N, 16.46. Found: C, 73.81; H, 3.61; N, 16.16.

2-Phenyl-4-aryl-4*H*-imidazo[4,5-*b*]quinoxalines (3); General Procedure

A mixture of the corresponding 2-phenyl-4*H*-imidazole **2** (2 mmol), K_2CO_3 (1.4 g, 10 mmol) and CAN (3.3 g, 6 mmol) in MeCN (50 mL) was stirred at r.t. (less reactive/less soluble derivatives of type **2** at 50 °C) until no starting material **2** could be detected (TLC, 0.5–4 h; in the case of **2l** and **2m** even after 24 h only a conversion of 25% could be observed). Most of the solvent was removed in vacuo and the residue was added to H_2O (100 mL). The crude product was extracted with $CHCl_3$ (3 × 100 mL), the insoluble solid was filtered off and washed with MeOH. The organic layers were combined and dried (Na_2SO_4). After removing the solvent in vacuo, the product was purified by column chromatography on silica gel ($CHCl_3$–MeOH).

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

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

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61–8.58 (m, 2 H, CH-Ph), 7.75–7.38 (m, 9 H, CH-Ar), 7.11 (m, 1 H, CH-Ar).

^{19}F NMR (188 MHz, $CDCl_3$): δ = –119.6 (s, 1 F), –119.8 (s, 1 F).

MS (EI): *m*/*z* (%) = 358 (100) [M^+], 339 (22) [$M - F]^+$, 255 (32).

Emission ($CHCl_3$): λ_{max} = 496 nm.

Anal. Calcd for $C_{21}H_{12}N_4F_2$: C, 70.39; H, 3.38; N, 15.63. Found: C, 70.06; H, 3.11; N, 15.33.

2-Phenyl-4-phenyl-4*H*-imidazo[4,5-*b*]quinoxaline (3c)

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

IR (ATR): 3073, 1596, 1566, 1454, 1431, 1345, 1245, 1136, 1096, 1064, 917, 753, 716, 689 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (m, 2 H, CH-Ph), 8.38 (d, *J* = 8 Hz, 1 H, CH-Ar), 7.78–7.38 (m, 11 H, CH-Ar).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.5 (C-2), 162.0, 148.3, 138.0, 135.7, 133.0, 132.4, 130.9, 130.4, 130.3, 130.0, 128.9, 128.8, 128.5, 127.6, 125.8, 116.6.

MS (EI): *m*/*z* (%) = 322 (73) [M^+], 321 (100) [$M - H^+$].

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 379 nm (4.5).

Anal. Calcd for $C_{21}H_{14}N_4$: C, 78.24; H, 4.38; N, 17.38. Found: C, 77.83; H, 4.21; N, 17.11.

2-Phenyl-4-tolyl-6-methyl-4*H*-imidazo[4,5-*b*]quinoxaline (3d)

Yield: 92%; yellow crystals; mp 296 °C (dec).

IR (ATR): 3047, 2983, 2953, 2927, 1592, 1563, 1514, 1480, 1431, 1342, 814, 713 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.57 (m, 2 H, CH-Ph), 8.25 (d, *J* = 8 Hz, 1 H, CH-8), 7.56–7.42 (m, 8 H, CH-Ar), 7.16 (s, 1 H, CH-5), 2.59 (s, 3 H, CH_3), 2.49 (s, 3 H, CH_3).

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^{13}C NMR (63 MHz, $CDCl_3$): δ = 181.4, 161.1, 148.2, 140.6, 139.9, 136.5, 133.2, 133.1, 132.2, 130.9, 130.5, 129.9, 129.0, 128.4, 127.7, 127.3, 116.2, 22.1, 21.5.

MS (EI): *m*/*z* (%) = 350 (100) [M^+], 335 (70).

MS (micro-ESI): *m*/*z* (%) = 373 (100) [M + Na^+], 351 (20) [M + H^+].

HRMS: *m*/*z* calcd for $C_{24}H_{19}N_4$: 351.161; found: 351.163.

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 385 (4.5) nm.

Emission ($CHCl_3$): λ_{max} = 488 nm.

Anal. Calcd for $C_{23}H_{18}N_4$: C, 78.83; H, 5.18; N, 15.99. Found: C, 78.52; H, 5.06; N, 15.76.

2-Phenyl-4-(4-ethoxycarbonylphenyl)-6-ethoxycarbonyl-4*H*-imidazo[4,5-*b*]quinoxaline (3e)
Yield: 65%; yellow crystals; mp 265 °C.

IR (ATR): 3395, 2987, 2930, 2852, 1717 (C=O), 1664, 1592, 1531, 1437, 1345, 1273, 1229, 1101, 1021, 919, 851, 765 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56–8.36 (m, 5 H, CH-Ar), 8.25–8.06 (m, 3 H, CH-Ar), 7.74–7.45 (m, 4 H, CH-Ar), 4.52 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.39 (q, *J* = 7.1 Hz, 2 H, OCH_2), 1.50 (q, *J* = 7.1 Hz, 3 H, CH_3), 1.40 (q, *J* = 7.1 Hz, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.1 (C-2), 165.2 (C=O), 163.3 (C=O), 161.5, 148.7, 140.2, 140.1, 138.7, 133.1, 132.8, 132.5, 131.7, 131.1, 130.4, 128.6, 127.8, 126.0, 119.0, 118.4, 61.8, 60.9, 14.4.

MS (EI): *m*/*z* (%) = 466 (59) [M^+], 437 (23), 409 (20), 393 (43), 365 (36), 320 (12).

UV/Vis ($CDCl_3$): λ_{max} (log ε) = 387 nm (4.3).

Anal. Calcd for $C_{27}H_{22}N_4O_4$: C, 69.52; H, 4.75; N, 14.01. Found: C, 69.15; H, 4.54; N, 13.64.

2-Phenyl-4-(4-trifluoromethylphenyl)-6-trifluoromethyl-4*H*-imidazo[4,5-*b*]quinoxaline (3f)
Yield: 78%; yellow crystals; mp 190–192 °C.

IR (ATR): 3395, 3298, 2927, 2855, 1670, 1599, 1530, 1508, 1442, 1411, 1321, 1250, 1109, 1067, 1019, 833, 719 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (m, 2 H, CH-Ph), 8.51 (d, ^3J = 8 Hz, 1 H, CH-8), 8.10 (d, *J* = 8 Hz, 2 H, CH-Ar), 7.91 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1 H, CH-7), 7.80 (m, 2 H, CH-Ar), 7.61–7.49 (m, 4 H, CH-Ar).

^{19}F NMR (188 MHz, $CDCl_3$): δ = –62.48 (s, 3 F), –63.21 (s, 3 F).

MS (EI): *m*/*z* (%) = 458 (20) [M^+], 389 [M – CF_3]$^+$, 376 (100), 188 (73), 161 (85), 145 (46).

UV/Vis ($CDCl_3$): λ_{max} (log ε) = 380 nm (4.3).

Emission ($CHCl_3$): λ_{max} = 503 nm.

Anal. Calcd for $C_{23}H_{12}F_6N_4$: C, 60.27; H, 2.64; N, 12.22. Found: C, 59.84; H, 2.25; N, 12.01.

2-Phenyl-4-(4-*tert*-butylphenyl)-6-*tert*-butyl-4*H*-imidazo[4,5-*b*]quinoxaline (3g)
Yield: 90%; yellow crystals; mp 243–245 °C.

IR (ATR): 3065, 2959, 2908, 2867, 1595, 1565, 1482, 1423, 1341, 1248, 1154, 1091, 919, 823, 718 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (m, 2 H, CH-Ph), 8.31 (d, *J* = 8 Hz, 1 H, CH-8), 7.74 (m, 3 H, CH-Ar), 7.53–7.46 (m, 5 H, CH-Ar), 7.37 (d, *J* = 2 Hz, 1 H, CH-5), 1.50 (s, 9 H, CH_3), 1.32 (s, 9 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.5 (C-2), 161.5, 153.6, 152.8, 148.3, 136.4, 133.3, 133.0, 132.1, 130.3, 129.9, 128.7, 128.4, 127.1, 127.0, 124.2, 112.6, 35.4, 35.1, 31.3, 31.0.

MS (EI): *m*/*z* (%) = 434 (100) [M^+], 419 (85), 403 (10), 377 (20), 202 (20), 188 (20), 174 (10).

UV/Vis ($CDCl_3$): λ_{max} (log ε) = 385 nm (4.4).

Emission ($CHCl_3$): λ_{max} = 487 nm.

Anal. Calcd for $C_{29}H_{30}N_4$: C, 80.15; H, 6.96; N, 12.89. Found: C, 79.73; H, 6.56; N, 12.66.

2-Phenyl-4-(4-octyloxyphenyl)-6-octyloxy-4*H*-imidazo[4,5-*b*]quinoxaline (3h)
Yield: 79%; yellow crystals; mp 243–244 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (m, 2 H, CH-Ph), 8.22 (d, *J* = 8 Hz, 1 H, CH-8), 7.48–7.45 (m, 5 H, CH-Ar), 7.22 (m, 3 H, CH-Ar), 6.75 (d, *J* = 2 Hz, 1 H, CH-5), 4.14 (t, *J* = 7.1 Hz, 2 H, OCH_2), 3.90 (t, *J* = 7.1 Hz, 2 H, OCH_2), 1.92–1.73 (m, 4 H, CH_2), 1.54–0.73 (m, 26 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.8, 162.7, 161.3, 146.0, 143.2, 135.6, 134.8, 132.3, 132.2, 131.8, 131.2, 129.2, 128.5, 127.4, 126.9, 126.2, 120.8, 116.2, 115.1, 99.0, 69.4, 68.8, 31.8, 31.7, 29.6, 29.3, 29.2, 28.8, 26.0, 25.9, 22.6, 14.0.

MS (EI): *m*/*z* (%) = 578 (30) [M^+], 353 (10), 248 (20), 221 (11), 135 (48), 109 (86), 28 (100).

Anal. Calcd for $C_{37}H_{46}N_4O_2$: C, 76.78; H, 8.01; N, 9.68. Found: C, 76.19; H, 7.75; N, 9.46.

2-Phenyl-4-(4-methoxyphenyl)-6-methoxy-4*H*-imidazo[4,5-*b*]quinoxaline (3i)
Yield: 91%; yellow crystals; mp 270–274 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.56 (m, 2 H, CH), 8.26 (d, *J* = 8 Hz, 1 H, CH-8), 7.51–7.22 (m, 8 H, CH-Ar), 6.77 (d, *J* = 2 Hz, 1 H, CH-5), 3.99 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 180.0 (C-2), 160.8, 160.2, 148.3, 133.4, 133.3, 132.1, 130.8, 129.7, 128.6, 128.4, 128.3, 115.7, 115.5, 98.6, 55.8, 55.7.

MS (EI): *m*/*z* (%) = 382 (100) [M^+], 344 (10), 248 (20).

Anal. Calcd for $C_{23}H_{18}N_4O_2$: C, 72.24; H, 4.74; N, 14.65. Found: C, 71.89; H, 4.52; N, 14.35.

2-Phenyl-4-(4-propargyloxyphenyl)-6-propargyloxy-4*H*-imidazo[4,5-*b*]quinoxaline (3j)
Yield: 87%; yellow crystals; mp 289 °C (dec).

^{1}H NMR (200 MHz, DMSO-d_6): δ = 8.35 (m, 2 H, CH), 8.22 (d, *J* = 8 Hz, 1 H, CH-8), 7.70 (d, *J* = 8 Hz, 2 H, CH-Ar), 7.54–7.51 (m, 3 H, CH-Ph), 7.45 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1 H, CH-7), 7.35 (d, *J* = 8 Hz, 2 H, CH-Ar), 6.80 (d, *J* = 2 Hz, 1 H, CH-5), 4.98 (d, *J* = 2.4 Hz, 2 H, OCH_2), 4.84 (d, *J* = 2.4 Hz, 2 H, OCH_2), 3.67 (t, *J* = 2.4 Hz, 1 H, C≡CH), 3.59 (t, *J* = 2.4 Hz, 1 H, C≡CH).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.58–8.26 (m, 3 H, CH-Ar), 7.75–6.69 (m, 9 H, CH-Ar), 4.87 (d, *J* = 2.4 Hz, 2 H, OCH_2), 4.71 (d, *J* = 2.4 Hz, 2 H, OCH_2), 2.65 (t, *J* = 2.4 Hz, 1 H, C≡CH), 2.53 (d, *J* = 2.4 Hz, 1 H, C≡CH).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 178.7 (C-2), 159.8, 158.2, 157.5, 148.2, 133.2, 133.0, 132.0, 131.4, 130.7, 128.9, 128.8, 128.7, 116.1, 115.9, 100.5, 79.2, 78.9, 78.7, 78.2, 56.2, 55.9.

MS (EI): *m*/*z* (%) = 430 (100) [M^+], 391 (80) [M – $C_3H_3^+$], 352 (50), 207 (40), 83 (80).

Anal. Calcd for $C_{27}H_{18}N_4O_2$: C, 75.39; H, 4.21; N, 13.02. Found: C, 75.05; H, 3.96; N, 12.76.

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2-Phenyl-4-(4-bromophenyl)-6-bromo-4*H*-imidazo[4,5-*b*]quinoxaline (3k)
Yield: 93%; yellow crystals; mp 350 °C (dec).

IR (ATR): 3050, 1675, 1589, 1560, 1468, 1425, 1338, 1238, 820 cm^{-1}.

^1H NMR (250 MHz, DMSO-d_6): δ = 8.39 (m, 2 H, CH-Ph), 8.23 (d, *J* = 8 Hz, 1 H, CH-Ar), 8.03–7.93 (m, 4 H, CH-Ar), 7.74 (d, *J* = 8 Hz, 1 H, CH-Ar), 7.56–7.53 (m, 3 H, CH-Ar), 7.40 (d, *J* = 2 Hz, 1 H, CH-5).

MS (EI): *m*/*z* (%) = 482/480/478 (30/70/30) [M^+], 401/399 (40/45) [M – Br]$^+$, 217 (40), 193 (40), 165 (30).

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 387 (4.5), 403 nm (4.5).

Anal. Calcd for $C_{21}H_{12}N_4Br_2$: C, 52.53; H, 2.50; N, 11.67. Found: C, 52.24; H, 2.68; N, 11.72.

2-Phenyl-4-(2-bromophenyl)-8-bromo-4*H*-imidazo[4,5-*b*]quinoxaline (3l)
Yield: 97%; yellow crystals; mp 377 °C (dec).

^1H NMR (400 MHz, DMSO-d_6): δ = 8.44 (m, 2 H, CH-Ph), 8.16–8.09 (m, 2 H, CH-Ar), 7.93–7.76 (m, 3 H, CH-Ar), 7.67–7.56 (m, 4 H, CH-Ar), 7.20 (m, 1 H, CH-Ar).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 182.7 (C-2), 162.5, 148.2, 135.1, 135.0, 134.5, 133.6, 133.3, 132.8, 130.5, 130.4, 129.9, 129.8, 129.5, 129.0, 128.5, 125.1, 121.0, 117.0.

MS (EI): *m*/*z* = 482/480/478 (6/13/7) [M^+], 402/401/399 (3/13/14), 217 (43), 103 (22).

Anal. Calcd for $C_{21}H_{12}N_4Br_2$: C, 52.53; H, 2.50; N, 11.67. Found: C, 52.19; H, 2.27; N, 11.42.

2-Phenyl-4-(3-trifluoromethylphenyl)-7-trifluoromethyl-4*H*-imidazo[4,5-*b*]quinoxaline (3m)
Note: the isomeric 5-trifluoromethyl derivative was only detected in trace amounts (TLC).

Yield: 71%; yellow crystals; mp 252 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 2 Hz, 1 H, CH-8), 8.48 (m, 2 H, CH-Ph), 8.07–7.92 (m, 4 H, CH-Ar), 7.75 (dd, *J* = 8 Hz, *J* = 2 Hz, 1 H, CH), 7.55–7.53 (m, 1 H, CH-Ph), 7.47–7.39 (m, 3 H, CH-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.8 (C-2), 162.7, 148.7, 137.0, 135.7, 133.5, 133.3 (q, ^2J = 32 Hz, CCF_3), 133.0 (q, ^2J = 32 Hz, CCF_3), 132.4, 131.4, 130.3, 129.1, 128.7, 128.1, 127.8 (q, ^3J = 4 Hz), 127.5, 125.0 (q, ^3J = 4 Hz), 124.9 (q, ^3J = 4 Hz), 123.5 (q, ^1J = 270 Hz), 123.2 (q, ^1J = 270 Hz), 117.1.

^{19}F NMR (188 MHz, $CDCl_3$): δ = –62.4 (s, 3 F), –63.1 (s, 3 F).

MS (EI): *m*/*z* (%) = 458 (100) [M^+], 439 (10) [M – F]$^+$, 389 (80) [M – CF_3]$^+$, 229 (60), 145 (80).

UV/Vis ($CDCl_3$): λ_{max} (log ε) = 378 nm (4.6).

Emission ($CHCl_3$): λ_{max} = 492 nm.

Anal. Calcd for $C_{23}H_{12}F_6N_4$: C, 60.27; H, 2.64; N, 12.22. Found: C, 60.01; H, 2.43; N, 12.42.

2-Phenyl-4-[3,5-bis(trifluoromethyl)phenylamino]-5,7-bis(trifluoromethyl)-4*H*-imidazo[4,5-*b*]quinoxaline (3n)
MS (EI): *m*/*z* (%) = 595/594 (50/100) [M^+], 575 (10) [M – F]$^+$, 526/525 (20/90) [M – CF_3]$^+$, 300 (90), 229 (60), 213 (50).

Sonogashira Cross-Coupling Reaction with 3k; General Procedure
To a suspension of 4*H*-imidazo[4,5-*b*]quinoxaline **3k** (2 mmol), $Pd(PPh_3)_2Cl_2$ (73 mg, 0.1 mmol), Ph_3P (55 mg, 0.2 mmol) and CuI (20 mg, 0.1 mmol) in degassed toluene, was added the corresponding acetylene (3 mmol) and Et_3N (5 mL, 36 mmol). The mixture was stirred at 80 °C for 4 h under argon, then the mixture was filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel ($CHCl_3$–MeOH).

2-Phenyl-4-(4-triisopropylsilylethynylphenyl)-6-triisopropylsilylethynyl-4*H*-imidazo[4,5-*b*]quinoxaline (3p)
Yield: 95%; yellow crystals; 238 °C (dec).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.70 (m, 2 H, CH-Ph), 7.97–7.44 (m, 10 H, CH-Ar), 1.22–1.15 (m, 42 H, *i*-Pr).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.8, 149.4, 144.6, 139.5, 135.4, 133.9, 133.4, 132.4, 132.0, 131.9, 129.7, 129.3, 128.4, 127.5, 127.2, 126.8, 120.1, 105.3, 105.2, 99.2, 95.0, 18.7, 18.6, 11.4, 11.3.

MS (DEI): *m*/*z* (%) = 683 (10) [M + H^+], 277 (75), 183 (100).

UV/Vis ($CDCl_3$): λ_{max} (log ε) = 422 (4.5), 448 nm (4.6).

Emission ($CHCl_3$): λ_{max} = 473 nm.

Anal. Calcd for $C_{43}H_{54}N_4Si_2$: C, 75.61; H, 7.97; N, 8.26. Found: C, 75.14; H, 7.55; N, 7.95.

2-Phenyl-4-(4-phenylethynylphenyl)-6-phenylethynyl-4*H*-imidazo[4,5-*b*]quinoxaline (3q)
Yield: 93%; yellow crystals; mp 218 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1, 137.7, 134.7, 133.5, 133.1, 132.8, 132.7, 132.1, 132.0, 131.8, 131.0, 130.1, 128.9, 128.5, 128.4, 127.8, 126.1, 124.1, 122.6, 122.3, 119.2, 93.0, 92.1, 88.6, 87.9.

MS (DEI): *m*/*z* (%) = 522 (78) [M^+], 521 (90) [M – H^+], 277 (100), 261 (30).

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 410 (4.6), 428 nm (4.6).

Emission ($CHCl_3$): λ_{max} = 483 nm; λ_{max} = 502 nm.

Anal. Calcd for $C_{37}H_{22}N_4$: C, 85.04; H, 4.24; N, 10.72. Found: C, 84.59; H, 4.01; N, 10.42.

X-ray Crystal Structure Determination for 3d
The intensity data for the compound was collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[24] The structure was solved by direct methods (SHELXS),[25] and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97).[26] The hydrogen atoms for the molecule were located by difference Fourier synthesis and refined isotropically. Only the hydrogen atoms of the 6-methyl group were included at calculated positions with fixed thermal parameters. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[26] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

CCDC-735167 (for **3d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033; or deposit@ccdc.cam.ac.uk].

X-ray Crystal Data for 3d
Empirical formula: $C_{23}H_{18}N_4$; Mr = 350.41 $gmol^{-1}$; yellow prism; crystal size 0.05 × 0.05× 0.05 mm^3; monoclinic; space group $P2_1/n$; unit cell dimensions: *a* = 9.0370(4) Å, *b* = 12.2704(6) Å, *c* = 15.6333(5) Å, β = 94.637(3)°; *V* = 1727.86(13) Å^3; *T* = –90 °C; *Z* = 4; $\rho_{calcd.}$ = 1.347 g/cm^3; μ(Mo-K_α) = 0.82 cm^{-1}; *F*(000) = 736; 12078 reflections in *h*(–11/11), *k*(–15/15), *l*(–20/20), measured in

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the range $2.11° \le \Theta \le 27.47°$, completeness $\Theta_{max} = 99.7\%$, 3947 independent reflections, $R_{int} = 0.0447$, 2774 reflections with $F_o > 4\sigma(F_o)$; 305 parameters, 0 restraints, $R1_{obs} = 0.0495$, $wR2_{obs} = 0.1184$, $R1_{all} = 0.0796$, $wR2_{all} = 0.1334$, GOOF = 1.034, largest difference peak and hole: 0.306/–0.269 e Å^{-3}.

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