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A simple and efficient method for the synthesis of highly substituted imidazoles using 3-aroylquinoxalin-2(1*H*)-ones

Vakhid A. Mamedov *, Nataliya A. Zhukova, Tat'yana N. Beschastnova, Aidar T. Gubaidullin, Dimitry V. Rakov, Il'dar Kh. Rizvanov

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences, Arbuzov Str. 8, 420088 Kazan, Russian Federation

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NMR data
X-ray diffraction analysis

ABSTRACT

3-Aroylquinoxalin-2(1*H*)-ones were found to be hetero analogues of α-diketones for the efficient, one-pot, three component synthesis of 2,4,5-trisubstituted imidazoles and imidazo[1,5-*a*]quinoxalin-4(5*H*)-ones in boiling methanol. The key advantages of this process are high yields, ready availability and low cost of 3-aroylquinoxalin-2(1*H*)-ones and easy work-up and separation of the products by non-chromatographic methods. Furthermore, the presence of an *ortho*-iminoanilide fragment at position 4 of the imidazoles obtained has made it possible to produce 2-(imidazol-4-yl)benzimidazoles in almost quantitative yields.

Naturally occurring and synthetic derivatives of imidazole exhibit a wide range of biological activity, making them attractive compounds for organic chemists.[1] They act as inhibitors of p38 MAP kinase[2a] and B-Raf kinase,[2b] by transforming the growth factor of the β1 (TGF-β1) type 1 activin receptor-like kinase (ALK5),[2c] cyclooxygenase-2 (COX-2)[2d] and biosynthesis of interleukin-1 (IL-1).[2e] Appropriately substituted imidazoles are used extensively as glucagon receptors[3a] and CB1 cannabinoid receptor antagonists,[3b] modulators of P-glycoprotein (P-gp)-mediated multidrug resistance (MDR),[3c] antibacterial[3d] and antitumor[3e] agents and pesticides.[3f] Recent advances in green chemistry and organometallic catalysis has extended the application of imidazoles as ionic liquids[4] and *N*-heterocyclic carbenes.[5] This appears to be the reason why the largest amount of modifications on the synthesis of imidazole derivatives refer to the classical Debus,[6] Radziszewski[7] and Japp[8] papers, on the syntheses of highly substituted imidazoles from a 1,2-dicarbonyl compound, various aldehydes, and ammonia. Multicomponent reactions (MCRs) have attracted considerable attention since they are performed without the need to isolate any intermediate. They save both energy and raw materials and also reduce the reaction time.[9] 2,4,5-Trisubstituted imidazoles are generally synthesized by a three component cyclocondensation of a 1,2-diketone, an α-hydroxyketone or α-ketomonoxime with an aldehyde and ammonium acetate, using microwaves,[10a–d] ionic liquids,[10e] refluxing in acetic acid,[10f–h] silica sulfuric acid,[10i] or $NiCl_2$–$6H_2O$/Al_2O_3.[10j] They have also been prepared by the reaction of aryl nitriles and α,α-dilithioarylnitromethanes,[11a] or by multistep syntheses.[11b,c] Most of these synthetic methods have one or more serious drawbacks, such as laborious and complex work-up and purification, generation of significant amounts of waste materials, strongly acidic conditions, low yields and the use of expensive reagents. Besides, most of them require elevated temperatures using microwave irradiation[10a–d,12a,c,13a] at 180–200 °C, or by refluxing[10g–j,11a–c,12b,13b] or heating[10e,12c,d,13c] the reaction mixture at high temperatures. However, the principal drawback of these methods is the inability to introduce various functional groups on the imidazoles using traditional reagents that supply the C(4)–C(5) fragment for construction of the imidazole ring system. The development of a new system to overcome these shortcomings and comply with the criteria of a mild, efficient and environmentally benign protocol for the synthesis of highly substituted imidazoles is an important task for organic chemists.

In continuation of our efforts to develop quinoxalin-2(1*H*)-one[14a–e] based synthetic methodologies, herein we report for the first time, a simple, mild and expeditious synthesis of

* Corresponding author. Fax: +7 843 2 73 2253.
E-mail addresses: mamedov@iopc.knc.ru, mamedov@iopc.ru (V.A. Mamedov).

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2,4,5-trisubstituted imidazoles in high yields using 3-aroylquinoxalin-2(1*H*)-ones as hetero analogues of α-diketones.

Initially, we condensed 3-benzoylquinoxalin-2(1*H*)-one (**1a**) (1 mmol), benzaldehyde (**2a**) (1 mmol) and ammonium acetate (2 mmol) in boiling methanol for 9 h, which led to a very poor yield (5%) of a mixture of 2,4,5-trisubstituted imidazole **3a** and imidazo[1,5-*a*]quinoxalin-4(5*H*)-one **4a** in the ratio 2:1 (Table 1, entry 1). To enhance the yield of the desired product the reaction time was increased to 15 h, but no appreciable increase in the product yield was observed (Table 1, entry 1). There remained a large amount of the unreacted 3-benzoylquinoxalin-2(1*H*)-one (**1a**) and benzaldehyde (**2a**) in the reaction mixture. It was considered worthwhile to carry out the reaction using various ratios of 3-benzoylquinoxalin-2(1*H*)-one (**1a**), benzaldehyde (**2a**) and ammonium acetate starting with 1:1:10 (Table 1, entry 2). A maximum yield (79%) of a mixture of imidazole **3a** and imidazo[1,5-*a*]quinoxalin-4(5*H*)-one **4a** was obtained with a 1:2:10 ratio of the reagents (Table 1, entry 3). A further increase in the amount of benzaldehyde **2a** (ratio of 1:3:10) led to products **3** and **4** in the same ratio, but in lower yield (52%). Unreacted benzaldehyde (**2a**) remained in the reaction mixture (Table 1, entry 4). When the reaction was carried out in the presence of the organocatalyst L-proline no improvement in the yield of the desired product was observed. When 3-{α-[2-(or 4)-methylphenylimino)benzylidene}quinoxalin-2(1*H*)-ones) **1b**,**c** were used instead of **1a** the total yields of the mixture remained approximately the same, but in the case of quinoxalin-2(1*H*)-one **1c** the ratio of products **3a** and **4a** increased in favor of the former and reached 4:1 (Table 1, entry 8). When the reaction was carried out with 1-(*n*-butyl)-3-benzoylquinoxalin-2-one (**1d**) the formation of 1,3-diphenyl-5-butylimidazo[1,5-*a*]quinoxalin-4-one (**4d**) was observed as almost the sole product (Table 1, entry 10).

To determine the scope and generality of this reaction, we utilized various substituted aldehydes and 3-pyridinecarboxaldehyde. The desired products were obtained and the results are summarized in Table 2.

The presence of the *ortho*-iminoanilide substituent at position 4 of imidazoles **3** makes it possible to use them in further syntheses. Herein, using the four imidazole derivatives **3a**,**c**,**e**,**h**, we have shown that the reaction of these compounds with ammonium acetate in acetic acid proceeds with the formation of 2-(imidazol-4-yl)benzimidazoles **5a–d** in almost quantitative yields (Table 3).

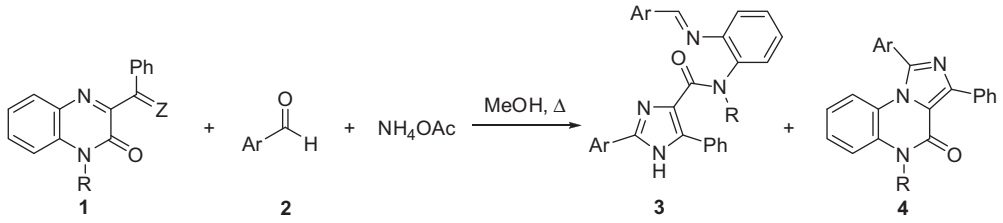
The structures of compounds **3a–c**,**e–h**, **4a–h,** and **5a–d** were deduced from their elemental analyses and ^{1}H NMR data.[15,16] The mass spectra of these compounds displayed molecular ion peaks at appropriate *m*/*z* values. The initial fragmentation of compounds **3a–c**,**e–h,** and **4a–h** involved scission of the imidazole and imidazo[1,5-*a*]quinoxaline ring systems, and for compounds **5a–d** of both the imidazole and benzimidazole ring systems.[15,16]

The presence of singlets due to the proton of the CH imine fragment at 8.84–9.04 ppm, the NH carbamoyl group at 10.79–10.92 ppm and the imidazole ring at 13.00–13.10 ppm, along with the signals of the protons of the benzene rings were characteristic of compounds **3a–c**,**e–h**. An almost constant value of the proton chemical shifts of the phenyl group at position 3 and the protons of the benzene ring of the quinoxalinone system were characteristic of the ^{1}H NMR spectra of compounds **4a–h**. The ^{1}H NMR spectra of the compounds **4a–h** were distinguished by the signals of the protons of the substituents at position 1. The assignment of the signals for the protons of the imidazo[1,5-*a*]quinoxalin-4(5*H*)-one were made by comparing the spectra of all the compounds obtained in this work with those published in our previous papers.[17a–d] The ^{1}H NMR spectral characteristics of imidazolylbenzimidazoles **5a–d** include multiplets for protons H(5), H(6) and H(4), H(7) at 7.12–7.19 and 7.51–7.60 ppm, respectively.[16]

The molecular structures of imidazole **3a**, imidazo[1,5-*a*]quinoxalin-4(5*H*)-one **4a** and 2-(imidazol-4-yl)benzimidazole **5a** were confirmed unambiguously by single-crystal X-ray analyses (Figs. 1a–c).[18–21]

A plausible mechanism for the synthesis of imidazoles, imidazo[1,5-*a*]quinoxalin-4(5*H*)-ones and benzimidazoles is proposed (Scheme 1). The formation of the diamine intermediate **A** takes

Table 1
Condensation of quinoxalin-2(1*H*)-ones **1**, arylaldehydes and ammonium acetate under various conditions



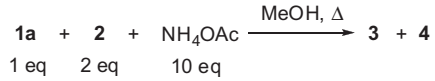
1 2 3 4

1a R = H, Z = O **2a** Ar = Ph
1b R = H, Z = NC_6H_4Me-2 **2b** Ar = 4-BrC_6H_4
1c R = H, Z = NC_6H_4Me-4 **2c** Ar = 4-$O_2NC_6H_4$
1d R = *n*-Bu, Z = O

Entry	Substrates		Ratio **1**:**2**:NH_4OAc	Time (h)	Products	Ratio **3**:**4**[a]	Yield[b] (%)
1	**1a**	**2a**	1:1:2	9	**3a** + **4a**	2:1	5 (7)[c]
2	**1a**	**2a**	1:1:10	9	**3a** + **4a**	1.8:1	30
3	**1a**	**2a**	1:2:10	7	**3a** + **4a**	2:1	79 (79)[d]
4	**1a**	**2a**	1:3:10	7	**3a** + **4a**	2:1	52
5	**1a**	**2b**	1:2:10	7	**3b** + **4b**	1.4:1	83
6	**1a**	**2c**	1:2:10	7	**3c** + **4c**	2.7:1	70
7	**1b**	**2a**	1:2:10	7	**3a** + **4a**	1:1.2	61
8	**1c**	**2a**	1:2:10	7	**3a** + **4a**	4:1	64
9	**1c**	**2b**	1:2:10	7	**3b** + **4b**	2:1	59
10	**1d**	**2a**	1:2:10	7	**3d** + **4d**[e]	Trace:1	52

[a] The ratio of compounds **3** and **4** was determined by ^{1}H NMR spectroscopy.
[b] Isolated yield of the mixture of **3** and **4**.
[c] Isolated yield after reflux for 15 h.
[d] Isolated yield when the reaction was carried out in the presence of L-proline.
[e] Isolated yield of **4d** = 42%, mp 210–212 °C.

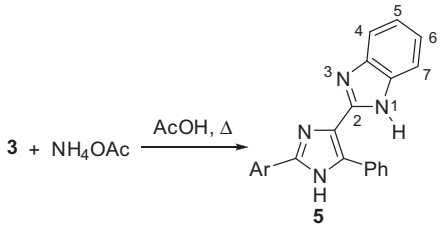
Table 2
3-Aroylquinoxalin-2(1*H*)-one derivatives as hetero analogues of α-diketones in the synthesis of functionalized imidazoles



Entry	Aldehyde (Ar)	Products[a] (yield, %)	Mp (°C)
1	**2a** (Ph)	**3a** + **4a** (49) (26)	234–237 (**3a**) 318–319(**4a**)
2	**2b** (4-BrC_6H_4)	**3b** + **4b** (47) (33)	267–270 (**3b**) 357–358 (**4b**)
3	**2c** (4-$O_2NC_6H_4$)	**3c** + **4c** (47) (17)	299–302 (**3c**) >360 (**4c**)
4	**2d** (4-FC_6H_4)	**3e** + **4e** (45) (26)	261–262 (**3e**) 315–316 (**4e**)
5	**2e** (4-ClC_6H_4)	**3f** + **4f** (40) (28)	258–260 (**3f**) 338–340 (**4f**)
6	**2f** (4-IC_6H_4)	**3g** + **4g** (44) (29)	287–290 (**3g**) >360 (**4g**)
7	**2g** (Pyridin-3-yl)	**3h** + **4h** (38) (42)	238–239 (**3h**) 320–321 (**4h**)

[a] Isolated yield.

Table 3
An efficient method for synthesizing 2-(imidazol-4-yl)benzimidazoles **5a–d**



Entry	Imidazole (Ar)	Product	Yield (%)	Mp (°C)
1	**3a** (Ph)	**5a**	94	220–222
2	**3c** (4-$O_2NC_6H_4$)	**5b**	99	355–358
3	**3e** (4-FC_6H_4)	**5c**	98	264–265
4	**3h** (pyridin-3-yl)	**5d**	95	280–281

place during the initial stage of the reaction. Intermediate **A** condenses with the 3-aroylquinoxalin-2(1*H*)-one **1** followed by dehydration to afford the imino intermediate **B**, which is transformed into compounds **3** and **4** via two different ways (**pathway I** and **pathway II**). **Pathway I** proceeds by cascade reactions involving: (a) acid-catalyzed ring-closure of intermediate **C** with the formation of spiro-compound **D**, (b) acid-catalyzed ring-opening of spiro-compound **E** with formation of the imidazole derivative **F**, which rearranges into the imidazole derivative **G** via a [1,5] hydrogen shift, and (c) reaction of the latter with the aldehyde to form compound **3**. **Pathway II** involves tautomerism of intermediate **B** with formation of compound **H**, which under acid catalysis undergoes intramolecular cyclization to give **J**. The final product **4** is formed following the elimination of ammonia from intermediate **K**.

It is apparent that the formation of 2-(imidazol-4-yl)benzimidazoles **5a–d** involves ammoniolysis of imidazoles **3a,c,e,h** to form the corresponding *ortho*-aminoanilide derivative **G** as the first step. The next step involves intramolecular nucleophilic attack by the amino group on the carbonyl with the formation of intermediate hydroxy-derivative **L**, and then elimination of water (Scheme 2).

To summarize, we have described a simple and efficient one-pot multicomponent methodology for the synthesis of 2,4,5-trisubstituted imidazoles and imidazo[1,5-*a*]quinoxalin-4(5*H*)-ones with the use of 3-aroylquinoxalin-2(1*H*)-one derivatives as hetero analogues of α-diketones. This was accomplished by the novel

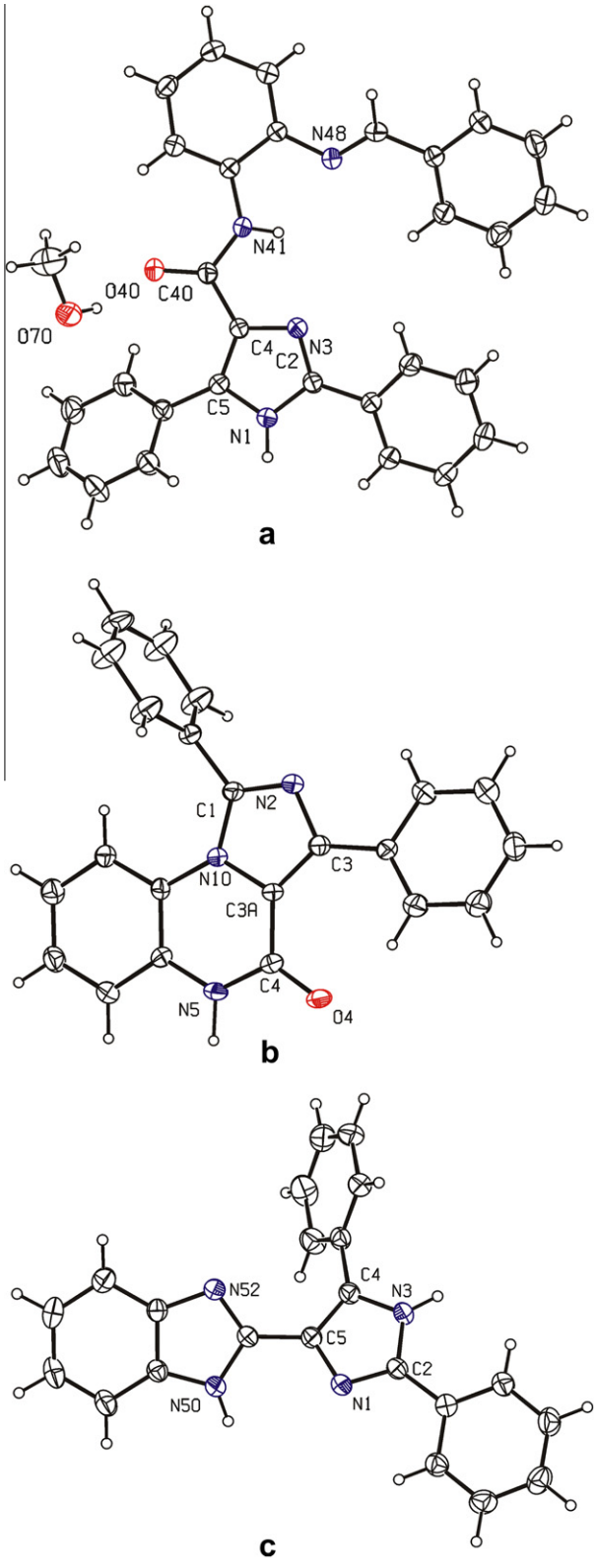
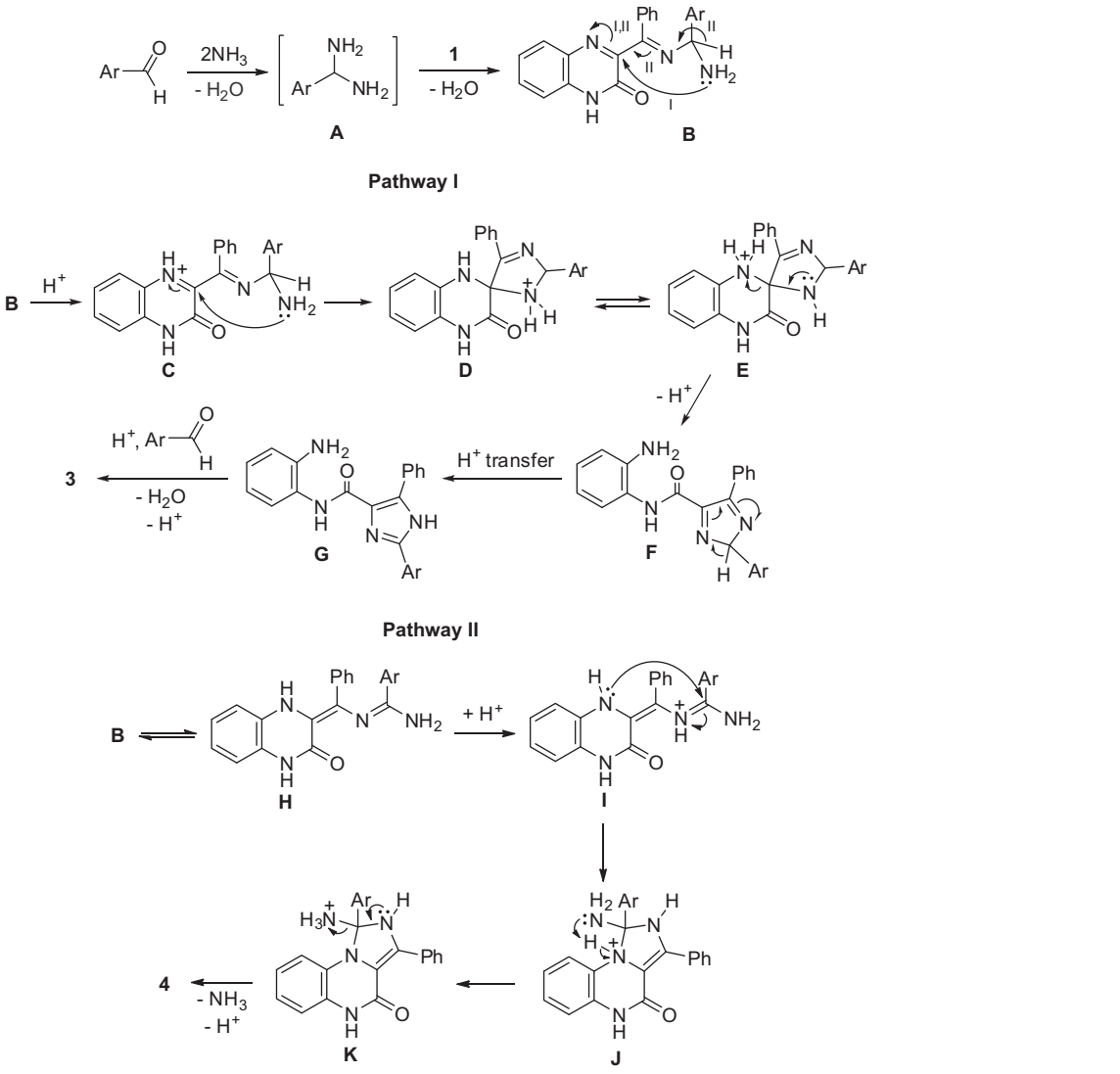
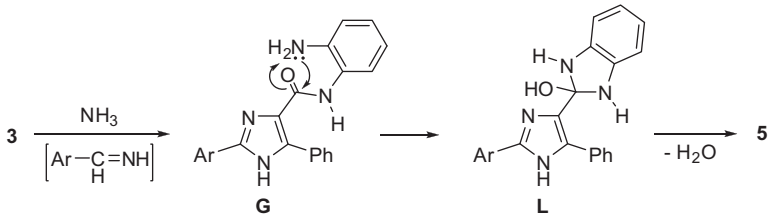


Figure 1. ORTEP plots of compounds **3a** (a), **4a** (b) and **5a** (c) and partial numbering schemes. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented by spheres of arbitrary radii. The DMSO molecule in (c) is not shown.

ring-opening of 3-aroylquinoxalin-2(1*H*)-ones on exposure to diaminoarylmethanes generated from arylaldehydes and ammonium acetate. The introduction of the *ortho*-iminoanilide fragment at position 4 of the imidazole derivatives with the help of this



Scheme 1. A plausible mechanism for the formation of imidazoles **3** and **4**. **Pathway I**—acid catalysis through ring-closure and ring-opening processes. **Pathway II**—via a novel acid catalysis imidazoannulation of quinoxalin-2(1*H*)-ones.



Scheme 2. A possible mechanism for the formation of 2-(imidazol-4-yl)benzimidazoles **5a**–**d**.

method made it possible to synthesize 2-(imidazol-4-yl)benzimidazoles. The simplicity of this method, high yields, easy work-up and purification of the products by crystallization are key advantages. The application of this methodology for the synthesis of other heterocyclic ring systems is currently under investigation and the results will be published in due course.

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15. *Illustrative experimental procedure for the preparation of compounds* ***3*** *and* ***4***: 4-Fluorobenzaldehyde **2d** (0.2 g, 1.6 mmol) was added to a suspension of benzoylquinoxalinone **1a** (0.2 g, 0.8 mmol) and NH_4OAc (0.62 g, 8 mmol) in MeOH (10 mL). The mixture was stirred at reflux until complete dissolution of the reagents was observed (ca. 2 h). After ca. 10–15 min the precipitation of light-yellow crystals occurred gradually and precipitation continued for 5 h. The mixture was cooled to room temperature and the precipitate filtered and dried in air, to give 0.29 g (77%) of a mixture of compounds **3e** and **4e** in the ratio of 1.7:1. These were separated by fractional crystallization (AcOH) to give analytically pure 2-(4-fluorophenyl)-5-phenyl-1*H*-imidazole-4-carboxylic acid 2-(4-fluorobenzylidene)aminoanilide (**3e**) and 1-(4-fluorophenyl)-3-phenylimidazo[1,5-*a*]quinoxalin-4(5*H*)-one (**4e**). Compound **3e**: yield 0.17 g (45%), yellow powder, mp 261–262 °C. [Found: C, 72.88; H, 4.24; N, 11.67. $C_{29}H_{20}F_2N_4O$ requires C, 72.79; H, 4.21; N, 11.71]; ν_{max} (KBr) 3316, 1643, 1587, 1517, 1495, 1437, 1228, 841, 751 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ 7.11 (1H, dd, *J* 7.5, 7.1 Hz), 7.27 (1H, dd, *J* 7.8, 7.5 Hz), 7.37 (2H, dd, $^3J_{HH}$ 8.9, $^3J_{HF}$ 8.9 Hz), 7.39 (2H, dd, $^3J_{HH}$ 8.9, $^3J_{HF}$ 8.9 Hz), 7.44–7.52 (4H, m), 7.89 (2H, d, *J* 7.1 Hz), 8.13 (2H, dd, $^3J_{HH}$ 8.6, $^4J_{HF}$ 5.4 Hz), 8.22 (2H, dd, $^3J_{HH}$ 8.4, $^4J_{HF}$ 5.8 Hz), 8.53 (1H, d, *J* 7.8 Hz), 8.86 (1H, s), 10.79 (1H, s), 13.01 (1H, br s); $^{13}C\{^1H\}$ NMR (150.9 MHz, DMSO-d_6) δ 116.3 (d, $^2J_{FC}$ 28.8 Hz), 116.49, 116.52 (d, $^2J_{FC}$ 22.4 Hz), 116.6, 117.5, 118.5, 122.4, 123.5, 126.5 (d, $^4J_{FC}$ 2.9 Hz), 127.4, 127.9, 128.1 (d, $^3J_{FC}$ 9.2 Hz), 128.2, 128.3, 128.6, 129.0, 129.6, 130.0, 131.4, 131.5 (d, $^3J_{FC}$ 8.8 Hz), 132.5, 132.6, 133.3 (d, $^4J_{FC}$ 2.7 Hz), 134.4, 136.3, 138.4, 144.6, 158.9, 160.5, 163.1 (d, $^1J_{FC}$ 246.8 Hz), 164.7 (d, $^1J_{FC}$ 250.5 Hz). MS (EI), *m*/*z* [I(%)]: 479 (1), 478 (4) $[M]^{+\cdot}$, 461 (4), 460 (11), 265 (24), 239 (13), 238 (44), 214 (42), 213 (100), 212 (82), 211 (18), 119 (41), 116 (12), 90 (18), 89 (23). Compound **4e**: yield 73 mg (26%), white solid, mp 315–316 °C. [Found: C, 74.59; H, 3.93; N, 11.87. $C_{22}H_{14}FN_3O$ requires C, 74.36; H, 3.97; N, 11.82]; ν_{max} (KBr) 3031, 2983, 2903, 2868, 1659, 1605, 1488, 1392, 1228, 842, 747, 689 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ 6.92 (1H, dd, *J* 8.5, 7.3 Hz), 7.02 (1H, d, *J* 8.1 Hz), 7.27–7.48 (7H, m), 7.78 (2H, dd, $^3J_{HH}$ 8.3, $^4J_{HF}$ 5.4 Hz), 8.19 (2H, d, *J* 7.3 Hz), 11.43 (1H, s). $^{13}C\{^1H\}$ NMR (150.9 MHz, DMSO-d_6) δ 116.5 (d, $^2J_{FC}$ 22.0 Hz), 117.6, 117.7, 119.4, 122.3, 122.8, 127.9, 128.6, 128.9, 129.2 (d, $^4J_{FC}$ 3.4 Hz), 130.4, 130.7, 132.4 (d, $^3J_{FC}$ 8.4 Hz), 133.8, 144.1, 144.4, 156.1, 163.9 (d, $^1J_{FC}$ 247.9 Hz). MS (EI), *m*/*z* [I(%)]: 356 (28), 355 (100) $[M]^{+\cdot}$, 354 (11), 327 (4), 252 (27), 206 (25), 205 (32), 103 (4), 89 (9), 77 (7).
16. *Illustrative experimental procedure for the preparation of compounds* ***5***: A solution of **3e** (0.2 g, 0.42 mmol) and NH_4OAc (0.19 g, 2.51 mmol) in AcOH (4 mL) was refluxed for 6 h. The solvent was concentrated to dryness under reduced pressure and the solid residue was treated with H_2O (5 mL). The resulting white precipitate was collected, washed with H_2O and dried in air to give 0.15 g (98%) of 2-[2-(4-fluorophenyl)-5-phenylimidazol-4-yl]benzimidazole (**5c**), mp 264–265 °C. [Found: C, 69.83; H, 4.54; N, 13.47. $C_{22}H_{15}FN_4{\cdot}AcOH$ requires C, 69.57; H, 4.59; N, 13.53]; ν_{max} (KBr) 1689, 1498, 1289, 1275, 1232, 1163 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ 7.12–7.19 (2H, m), 7.37–7.43 (3H, m), 7.49–7.56 (4H, m), 8.16 (2H, d, *J* 6.8 Hz), 8.23 (2H, dd, $^3J_{HH}$ 8.1, $^4J_{HF}$ 5.6 Hz), 12.46 (1H, br s), 12.90 (1H, br s); $^{13}C\{^1H\}$ NMR (150.9 MHz, DMSO-d_6) δ 112.1, 116.6 (d, $^2J_{FC}$ 22.0 Hz), 119.4, 122.4, 127.3 (d, $^4J_{FC}$ 2.6 Hz), 128.6 (d, $^3J_{FC}$ 8.4 Hz), 128.9, 129.7, 130.5, 132.8, 135.1, 144.6, 149.2, 162.1, 164.3 (d, $^1J_{FC}$ 246.1 Hz). MS (EI), *m*/*z* [I(%)]: 355 (19), 354 (71) $[M]^{+\cdot}$, 353 (100), 205 (21), 177 (12), 103 (10), 60 (8).
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18. The X-ray diffraction data for crystals of **3a** were collected on a Bruker AXS Smart Apex II CCD diffractometer at 296 K. *Crystallographic data for* ***3a***. $C_{29}H_{22}N_4O{\cdot}CH_3OH$, yellow crystalline plates, formula weight 474.55, orthorhombic, Pbca, a = 7.5316(6) Å, b = 23.637(2) Å, c = 27.950(2) Å, V = 4975.8(7) $Å^3$, Z = 8, ρ_{calc} = 1.267 g cm^{-3}, $\mu(\lambda MoK_\alpha)$ = 0.81 cm^{-1}, F(0 0 0) = 2000, reflections collected = 49021, unique = 5924, $R_{(int)}$ = 0.1279, full-matrix least-squares on F^2, parameters = 338, restraints = 0. Final indices R_1 = 0.0594, wR_2 = 0.1074 for 2696 reflections with $I > 2\sigma(I)$; R_1 = 0.1587, wR_2 = 0.1393 for all data, goodness-of-fit on F^2 = 0.978, largest difference in peak and hole (0.178 and −0.199 $eÅ^{-3}$).
19. The X-ray diffraction data for crystals of **4a** were collected on a Bruker AXS Smart Apex II CCD diffractometer at 296 K. *Crystallographic data for* ***4a***. $C_{22}H_{15}N_3O$, colorless needles, formula weight 337.37, monoclinic, P 2_1/c, a = 15.074(5) Å, b = 5.078(2) Å, c = 23.490(8) Å, β = 107.785(5)°, V = 1712.2(9) $Å^3$, Z = 4, ρ_{calc} = 1.309 g cm^{-3}, $\mu(\lambda$Mo $K_\alpha)$ = 0.83 cm^{-1}, F(000) = 704, reflections collected = 12388, unique = 3677, $R_{(int)}$ = 0.2111, full-matrix least-squares on F^2, parameters = 227, restraints = 1. Final indices R_1 = 0.0731, wR_2 = 0.1250 for 1132 reflections with $I > 2\sigma(I)$; R_1 = 0.2718, wR_2 = 0.1823 for all data, goodness-of-fit on F^2 = 0.891, largest difference in peak and hole (0.172 and −0.235 $eÅ^{-3}$).
20. The X-ray diffraction data for crystals of **5a** were collected on a Bruker AXS Smart Apex II CCD diffractometer at 296(2) K. *Crystallographic data for* ***5a***. $C_{22}H_{16}N_4$, C_2H_6OS, colorless prisms, 0.40 × 0.13 × 0.08 mm, formula weight 414.52, orthorhombic, $P2_12_12_1$, a = 7.8844(5), b = 13.3793(8), c = 20.1173(13) Å, V = 2122.1(2) $Å^3$, Z = 4, ρ_{calc} = 1.297 g·cm^{-3}, $\mu(\lambda MoK_\alpha)$ = 1.76 cm^{-1}, F(000) = 872, reflections collected = 16538, unique = 4983, R(int) = 0.0470, full-matrix least-squares on F^2, parameters = 279, restraints = 0. Final indices R_1 = 0.0419, wR_2 = 0.0921 for 3630 reflections with $I > 2\sigma(I)$; R_1 = 0.0674, wR_2 = 0.1027 for all data, goodness-of-fit on F^2 = 1.028, largest difference in peak and hole (0.158 and −0.270 $eÅ^{-3}$).
21. Crystallographic data (excluding structure factors) for the structures **3a**, **4a** and **5a** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 815371, 815372 and 815373, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).