



# Reinvestigating the synthesis of *N*-arylbenzamidines from benzonitriles and anilines in the presence of AlCl<sub>3</sub>

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## ABSTRACT

The preparation of *N*-phenylbenzamide **3a** from the reaction between benzonitrile **1a** and aniline in the presence of AlCl<sub>3</sub> is reinvestigated with respect to mode of reagent addition, reaction temperature and Lewis acid catalysis. Pre-forming the nitrile-Lewis acid complex prior to the addition of aniline allows for milder reaction conditions, allowing for the higher yielding synthesis of *N*-phenylbenzamide **3a** (83%). Using these modified conditions several *N*-(4-substituted phenyl)benzamidines can be prepared including the *N*-(4-methoxyphenyl)benzamide **3b** (93%) and the previously unobtainable 2-amino-*N*-(4-methoxyphenyl)benzamide **3i** (56%). All new compounds are fully characterised.

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## 1. Introduction

*N*-Arylbenzamidines are useful building blocks for a number of heteroarenes including imidazoles,<sup>1</sup> benzimidazoles,<sup>2</sup> pyrimidines,<sup>3</sup> quinazolines,<sup>4</sup> 4*H*-1,2,4-thiadiazines,<sup>5</sup> 1,2,4-benzothiadiazines<sup>6</sup> and benzothiazoles,<sup>6a,f</sup> 4,5-dihydro-1,2,4-oxadiazoles,<sup>7</sup> 4*H*-[1,4,2]diazaphospholes,<sup>8</sup> 4*H*-1,3-oxazin-4-ones<sup>9</sup> and 2,5-dihydro-1,2,4,6-thiatriazines.<sup>10</sup> Furthermore, several *N*-arylbenzamidines have interesting biological properties, including inhibitor activity towards tyrosine kinases<sup>11</sup> and nitric oxide synthetase<sup>12</sup> and as selective D<sub>1</sub> dopamine receptor antagonists.<sup>13</sup> Antimicrobial<sup>14</sup> and antiparasitic<sup>15</sup> activities have also been reported.

We recently needed access to a series of *N*-arylbenzamidines and found a number of preparations described in the literature.<sup>16</sup> These included the addition of anilines to benzonitriles using bases such as BuLi,<sup>17</sup> sodamide,<sup>1c,d,18</sup> sodium hydride,<sup>6e,f</sup> or sodium alkoxide (Pinner method)<sup>19</sup> and also the addition of anilines to benzonitriles catalysed by acids such as methanesulfonic<sup>6e,f</sup> or toluenesulfonic acid<sup>6c</sup> or Lewis acids.<sup>2b,4c,6b,20</sup> Recently a high yielding synthesis was reported using catalytic quantities of ytterbium amides but these are not commercially available reagents.<sup>21</sup> Surprisingly no single procedure stood out as superior. On the basis of the available literature we focused our investigation on the simple reaction of benzonitrile with aniline in the presence of aluminium trichloride. This reaction has been described in detail in the series *Organic Synthesis*.<sup>20c</sup>

A search of the surrounding literature revealed some interesting information: (1) the reactions were typically carried out at high temperatures (180–200 °C); (2) the mode of addition was

predominantly addition of the Lewis acid to a mixture of aniline and benzonitrile; (3) the work-ups involved the use of sometimes very caustic solutions of NaOH (50%); and (4) the presence of alkoxy or nitro groups was reported to be incompatible with the use of Lewis acids such as AlCl<sub>3</sub>.<sup>4c</sup>

A partial re-optimisation of the reaction conditions as reported herein provided useful results that included the AlCl<sub>3</sub> mediated synthesis of previously unobtainable 2-amino-4-methoxyphenylbenzamide **3i**.

## 2. Results and discussion

Nucleophilic addition to unactivated nitriles was not considered to be facile and as such the reactions of anilines with benzonitriles was often conducted at elevated temperatures (180–200 °C). Surprisingly, the addition of Lewis acid catalysts to these reaction mixtures was typically carried out after the benzonitriles were mixed with anilines and heated to relatively high temperatures.<sup>6b,20a</sup> The alternative addition of Lewis acid catalyst to the benzonitrile prior to the addition of aniline has received considerably less attention.<sup>20d</sup> It seemed rational to us that pre-forming the nitrile-Lewis acid complex<sup>22</sup> at near ambient temperatures prior to addition of the amine could allow these reactions to take place at lower temperatures, via the now activated nitrile, which could lead to better recoveries of benzamidines.

As such we investigated the mode of addition for the classical preparation of *N*-phenylbenzamide **3a**, described by Cooper and Partridge.<sup>20c</sup> At first the original conditions (mixing of benzonitrile **1a** with aniline, heating to 200 °C, followed by addition of AlCl<sub>3</sub>) were reproduced to confirm the literature yields and to examine the effect of reaction time and temperature. Furthermore, we

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varied the concentrations of NaOH used in the work-up for decomposing the AlCl<sub>3</sub> reaction complexes. At best, with this mode of addition, the *N*-phenylbenzamidinium **3a** could be obtained in yields of ca. 70% (lit.<sup>20c</sup> 74%) when the reaction was heated to 200 °C prior to the addition of AlCl<sub>3</sub>. The use of lower reaction temperatures (100 °C) and longer reaction times (6 h) gave reduced yields of the desired benzamidinium **3a**. The use of varying concentrations of NaOH during the reaction work-up did little to affect the product yields (Table 1). Switching the mode of addition gave interesting results. When powdered AlCl<sub>3</sub> was added to benzonitrile **1a** at ca. 20 °C a solid complex rapidly formed that could not be stirred. Heating the reaction mixture to ca. 100 °C gave a uniform melt. Adding aniline to this melt at ca. 200 °C, led to poor recoveries of the desired *N*-phenylbenzamidinium **3a** and surprisingly higher recoveries of the benzonitrile trimer 1,3,5-triphenyl[1,3,5]triazine **4**. As such the aniline was added to the melt at the lowest possible melt temperature ca. 100 °C and the reaction was left to heat for 4 h. Under these conditions the recovery of *N*-phenylbenzamidinium **3a** increased to 83–84%. Adding the aniline at ca. 100 °C and then raising the reaction temperature to ca. 200 °C gave a reduced yield. Conversely adding the aniline prior to the melt temperature at ca. 50–70 °C and allowing the reaction to stand for 12 h also led to reduced recoveries of *N*-phenylbenzamidinium **3a**. Alternative combinations that were investigated including mixing all three reagents or mixing the AlCl<sub>3</sub> with the aniline at ca. 20 °C and then heating to ca. 100 °C failed to give superior yields of *N*-phenylbenzamidinium **3a** (Table 1).

**Table 1**

Investigation of the reaction between benzonitrile **1a** (553 mg, 5.36 mmol), AlCl<sub>3</sub> (1 equiv) and aniline **2** (1 equiv) protected from moisture with a CaCl<sub>2</sub> drying tube

PhCN + PhNH <sub>2</sub> $\xrightarrow{\text{AlCl}_3}$ Ph-N=C(Ph)-NH <sub>2</sub> + Ph-N=C(Ph)-N=C(Ph)-N=C(Ph)					
1	2	3a	4		
Reagents	Time (h)	Temp. (°C)	NaOH <sup>a</sup> (mol%)	Yields (%)	
				3a	4
(PhCN+PhNH <sub>2</sub> )+AlCl <sub>3</sub>	1	200	50	70	Trace
(PhCN+PhNH <sub>2</sub> )+AlCl <sub>3</sub> <sup>b</sup>	1	200	19	69	nd <sup>d</sup>
(PhCN+PhNH <sub>2</sub> )+AlCl <sub>3</sub>	1	200	12.5	66	Trace
(PhCN+PhNH <sub>2</sub> )+AlCl <sub>3</sub>	6	100	12.5	60	3
(PhCN+AlCl <sub>3</sub> )+PhNH <sub>2</sub>	1	200	12.5	58	6
(PhCN+AlCl <sub>3</sub> )+PhNH <sub>2</sub> <sup>c</sup>	1	200	12.5	49	6
(PhCN+AlCl <sub>3</sub> )+PhNH <sub>2</sub>	4	100	12.5	83	3
(PhCN+AlCl <sub>3</sub> )+PhNH <sub>2</sub>	4	100	50	84	3
(PhCN+AlCl <sub>3</sub> )+PhNH <sub>2</sub>	12	70	12.5	72	Trace
(PhCN+AlCl <sub>3</sub> )+PhNH <sub>2</sub>	12	50	12.5	66	Trace
(AlCl <sub>3</sub> +PhNH <sub>2</sub> )+PhCN	6	100	12.5	55	1.5
(PhCN+AlCl <sub>3</sub> +PhNH <sub>2</sub> )	6	100	12.5	53	1.5

<sup>a</sup> NaOH used during work up.

<sup>b</sup> Cooper and Partridge *Org. Syn.* procedure (lit.<sup>20c</sup> 69–74% yield).

<sup>c</sup> Aniline added at 100 °C then heated to 200 °C.

<sup>d</sup> nd=no data.

### 3. Optimisation using different Lewis acids

While AlCl<sub>3</sub> appears to be the Lewis acid most commonly used for catalysing the nucleophilic addition of anilines to benzonitriles, other Lewis acids, including ZnCl<sub>2</sub>,<sup>20a</sup> AlMe<sub>3</sub><sup>11c,23</sup> and ytterbium amides<sup>21</sup> have also been used. We premixed benzonitrile with a range of commonly available Lewis acids that differ from each other by the hardness of the metal and that are typically found in a synthesis laboratory, to examine their effect on the amidine synthesis (Table 2).

**Table 2**

Reaction of benzonitrile **1a** (553 mg, 5.36 mmol) with Lewis acids (LA) (1 equiv) and aniline **2** (1 equiv) protected from moisture with a CaCl<sub>2</sub> drying tube

PhCN + LA $\xrightarrow{\text{PhNH}_2}$ Ph-N=C(Ph)-NH <sub>2</sub> + Ph-N=C(Ph)-N=C(Ph)-N=C(Ph)					
1a	LA	2	3a	4	
LA	Time (h)	Temp. (°C)	Yields (%)		
			3a	4	
AlCl <sub>3</sub>	4	100	83	3	
FeCl <sub>3</sub>	2	100	<sup>b</sup>	—	
TiCl <sub>4</sub>	5	135	68	36	
Ti( <sup>i</sup> PrO) <sub>4</sub>	7	100	nr <sup>c</sup>	—	
SnCl <sub>4</sub>	5	100	6	—	
ZnCl <sub>2</sub>	5	100	6	—	
Sml <sub>2</sub> <sup>a</sup>	48	100	nr <sup>c</sup>	—	

<sup>a</sup> In a solution of THF (1.0 M).

<sup>b</sup> Complex reaction mixture.

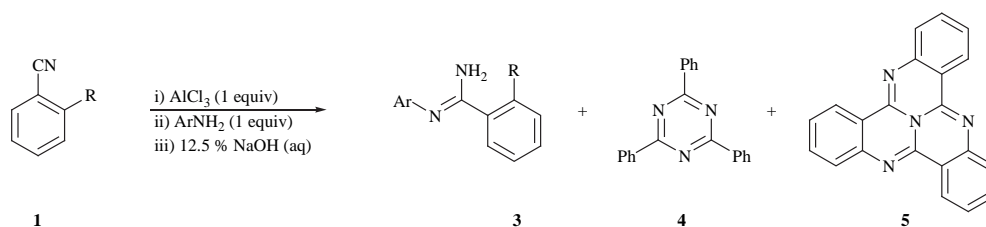
<sup>c</sup> nr=no reaction.

In our hands, the softer Lewis acids [ZnCl<sub>2</sub>, SnCl<sub>4</sub>, Ti(<sup>i</sup>PrO)<sub>4</sub>] were ineffective leading to little or no reaction. TiCl<sub>4</sub> did afford a respectable yield of *N*-phenylbenzamidinium **3a** (68%) but the complex formed between the benzonitrile **1a** and the TiCl<sub>4</sub> required higher temperatures to generate a homogenous melt and led to comparatively high recoveries of the 2,4,6-triphenyl-1,3,5-triazine **4** (36%). FeCl<sub>3</sub> led to complex reaction mixtures that could not be resolved. In light of this study, we retained the use of AlCl<sub>3</sub> as Lewis acid for further studies.

### 4. Benzamidinium formation in the presence of methoxy, nitro and halogen substituents

It was reported recently that the presence of alkoxy or nitro groups were incompatible with the use of Lewis acids such as AlCl<sub>3</sub>, for the synthesis of benzamidines.<sup>4c</sup> In light of this we examined our modified reaction conditions to the preparation of several more challenging targets (Table 3).

Using our optimised reaction conditions, *N*-(4-methoxyphenyl)benzamidinium **3b** was obtained in 93% yield. This was notable since the reported base (NaNH<sub>2</sub>) catalysed preparation of this benzamidinium was low yielding (14%).<sup>1d</sup> Disappointingly, the analogous preparation of *N*-(4-nitrophenyl)benzamidinium **3c** gave the product only in low yield (16–21%), although it was worth noting that after 4 h, based on recovered unreacted aniline the yield was a more respectable 59%. *N*-(4-Tolyl)- and *N*-(4-halophenyl)benzamidines **3d–i** were readily prepared in high yields (78–93%) although the 4-iodophenyl analogue did require additional benzonitrile. The previously reported attempt to synthesize both the 2-amino-*N*-(4-methoxyphenyl)benzamidinium **3l** and the 2-amino-*N*-(4-nitrophenyl)benzamidinium **3m** concluded that these two compounds could not be prepared using AlCl<sub>3</sub>,<sup>4c</sup> but in our hands 2-amino-*N*-(4-methoxyphenyl)benzamidinium **3l** was obtained in 56% yield when 2 equiv of the benzonitrile were used; longer reaction times did not improve the yield. Unfortunately, 2-amino-*N*-(4-nitrophenyl)benzamidinium **3m** could not be isolated from the analogous reaction mixture. Generally, the reaction conditions were quite tolerant of halogen substituents providing the 4-fluoro-, chloro- and bromophenyl analogues **3n–p** (43–58%), however, in one case (Ar=4-IC<sub>6</sub>H<sub>4</sub>, **1b** R=NH<sub>2</sub>) the reaction gave a complex mixture. Both the 4-phenyl and 4-tolyl analogues could be isolated in comparatively good 64 and 66% yields, respectively. Interestingly, increasing the temperature of the anthranilonitrile **1b** reactions to ca. 150 °C led to complex mixtures that could not be resolved. Furthermore, while the unsubstituted benzonitrile gave the expected triazine

**Table 3**Reaction of benzonitriles **1a** or **1b** (1 equiv) with anilines (500 mg) at ca. 100 °C protected from moisture with a CaCl<sub>2</sub> drying tube

Ar	<b>1</b> (R)	Time (h)	Yields (%)		
			<b>3</b>	<b>4</b>	<b>5</b>
4-MeOC <sub>6</sub> H <sub>4</sub>	<b>1a</b> (H)	4	<b>3b</b> (93)	3	—
4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>1a</b> (H)	4	<b>3c</b> (16) (59) <sup>a</sup>	Trace	—
4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>1a</b> (H)	8	<b>3c</b> (21)	Trace	—
4-MeC <sub>6</sub> H <sub>4</sub>	<b>1a</b> (H)	6	<b>3d</b> (93)	—	—
4-FC <sub>6</sub> H <sub>4</sub>	<b>1a</b> (H)	6	<b>3e</b> (82)	—	—
4-ClC <sub>6</sub> H <sub>4</sub>	<b>1a</b> (H)	6	<b>3f</b> (89)	—	—
4-BrC <sub>6</sub> H <sub>4</sub>	<b>1a</b> (H)	6	<b>3g</b> (78)	—	—
4-IC <sub>6</sub> H <sub>4</sub>	<b>1a</b> (H)	6	<b>3h</b> (85) <sup>b</sup>	—	—
3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<b>1a</b> (H)	6	<b>3i</b> (91)	—	—
Ph	<b>1b</b> (NH <sub>2</sub> )	6	<b>3j</b> (64)	—	—
4-MeC <sub>6</sub> H <sub>4</sub>	<b>1b</b> (NH <sub>2</sub> )	6	<b>3k</b> (66)	—	12
4-MeOC <sub>6</sub> H <sub>4</sub>	<b>1b</b> (NH <sub>2</sub> )	8	<b>3l</b> (49)	—	18
4-MeOC <sub>6</sub> H <sub>4</sub>	<b>1b</b> (NH <sub>2</sub> )	8	<b>3l</b> (56) <sup>c</sup>	—	30
4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>1b</b> (NH <sub>2</sub> )	12	<b>3m</b> (0) <sup>d</sup>	—	—
4-FC <sub>6</sub> H <sub>4</sub>	<b>1b</b> (NH <sub>2</sub> )	6	<b>3n</b> (58)	—	—
4-ClC <sub>6</sub> H <sub>4</sub>	<b>1b</b> (NH <sub>2</sub> )	6	<b>3o</b> (48)	—	—
4-BrC <sub>6</sub> H <sub>4</sub>	<b>1b</b> (NH <sub>2</sub> )	6	<b>3p</b> (43)	—	—
4-IC <sub>6</sub> H <sub>4</sub>	<b>1b</b> (NH <sub>2</sub> )	6	<b>3q</b> (0) <sup>d</sup>	—	—
3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<b>1b</b> (NH <sub>2</sub> )	6	<b>3r</b> (35)	—	—

<sup>a</sup> 59% Based on recovered 4-nitroaniline<sup>b</sup> Benzonitrile (2 equiv).<sup>c</sup> 2-Aminobenzonitrile (2 equiv).<sup>d</sup> Complex reaction mixture.

by-product **4** in trace amounts, anthranilonitrile gave instead traces of tricycloquinazoline **5** (mp 322–323 °C)<sup>24</sup> on three individual occasions. The high temperature (290 °C) treatment of anthranilonitrile with AlCl<sub>3</sub> is known to give tricycloquinazoline **5** in 75% yield.<sup>25</sup>

## 5. Conclusion

By modifying the mode of addition (benzonitrile+Lewis acid, followed by aniline) and by moderating the reaction temperatures, the Lewis acid (AlCl<sub>3</sub>) catalysed reaction of benzonitriles and anilines has been shown to produce significantly improved yields of benzamidines. The reaction conditions are not compatible with nitro-substituted anilines, but do tolerate *p*-anisidine, allowing for the preparation of the previously unobtainable 2-amino-*N*-(4-methoxyphenyl)benzamidine.

## 6. Experimental

### 6.1. General methods and materials

Reactions were protected from atmospheric moisture by CaCl<sub>2</sub> drying tubes. Anhydrous Na<sub>2</sub>SO<sub>4</sub> was used for drying organic extracts, and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F<sub>254</sub>). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm). Melting points were determined using a PolyTherm-A, Wagner & Munz, Koeffler-Hotstage Microscope apparatus. Solvents used for

recrystallization are indicated after the melting point. UV spectra were obtained using a Perkin–Elmer Lambda-25 UV/vis spectrophotometer and inflections are identified by the abbreviation ‘inf’. IR spectra were recorded on a Shimadzu FTIR–NIR Prestige-21 spectrometer with a Pike Miracle Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w, respectively. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 300 machine (at 300 and 75 MHz, respectively). <sup>13</sup>C NMR CH assignments were supported by DEPT-135 NMR studies. Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Low resolution (EI) mass spectra were recorded on a Shimadzu Q2010 GC/MS with direct inlet probe. 2,4,6-Triphenyl-1,3,5-triazine **4**<sup>26</sup> and tricycloquinazoline **5**,<sup>24</sup> were identical to authentic samples.

**6.1.1. (Z)-N-Phenylbenzamidine 3a (typical procedure).** To stirred benzonitrile **1a** (550 μL, 5.36 mmol) at ca. 20 °C was added portionwise powdered anhydrous AlCl<sub>3</sub> (706 mg, 5.36 mmol). The reaction mixture was then heated (ca. 100 °C) until a homogenous melt formed. To this was added aniline **2** (489 μL, 5.36 mmol) and the mixture was heated for 4 h and then allowed to cool to ca. 20 °C. The resultant solid mass was then crushed and slurried in 12.5% NaOH (40 mL). The resulting mixture was extracted (DCM), washed (H<sub>2</sub>O) and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the volatiles followed by chromatography of the residue gave 2,4,6-triphenyl-1,3,5-triazine **4** (16.4 mg, 3%) as light yellow needles, mp 231–232 °C (lit.,<sup>26</sup> 231–232 °C) (PhH); *R*<sub>f</sub> (hexane/DCM, 9:1) 0.36; (found: C, 81.42; H, 4.77; N, 13.61. C<sub>21</sub>H<sub>15</sub>N<sub>3</sub> requires C, 81.53; H, 4.89; N, 13.58%); λ<sub>max</sub> (DCM)/nm 271 (log ε 1.84); ν<sub>max</sub>/cm<sup>-1</sup> 1589m, 1517s, 1447m, 1368s, 1300w, 1175w, 1146w, 1069w, 1028m, 841m, 743s; δ<sub>H</sub>(300 MHz; CDCl<sub>3</sub>) 8.79 (6H, d, J 7.5, Ph H), 7.63–7.56 (9H, m, Ph CH), 5.30 (2H, s); δ<sub>C</sub>(75 MHz; CDCl<sub>3</sub>) 171.6, 136.2, 132.5 (CH), 129.0

(CH), 128.6 (CH);  $m/z$  (EI) 309 ( $M^+$ , 37%), 103 (100), 76 (19), 44 (59). Further elution (*t*-BuOMe) gave the title compound **3a** (871 mg, 83%) as colourless plates, mp 115.5–116 °C (lit.,<sup>20a</sup> 116 °C) (PhH);  $R_f$  (*t*-BuOMe) 0.71;  $\lambda_{\max}$ (DCM)/nm 232 (log  $\epsilon$  3.32), 269 (3.12);  $\nu_{\max}/\text{cm}^{-1}$  3468w and 3350w (NH<sub>2</sub>), 3039w (Ar CH), 1616s, 1589m, 1570s, 1496m, 1489m, 1448m, 1379m, 1296w, 1238m, 1170m, 1076m, 1024m, 975w, 948w, 929w, 914w, 837m, 777m, 750m;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.87 (2H, d, *J* 6.6, Ar H), 7.51–7.41 (3H, m, Ar H), 7.38–7.33 (2H, m, Ar H), 7.06 (1H, dd, *J* 7.4, 7.4, Ar H), 6.99 (2H, d, *J* 7.2, Ar H), 4.87 (2H, br s, NH<sub>2</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 155.0, 149.7, 135.8, 130.5 (CH), 129.5 (CH), 128.5 (CH), 126.8 (CH), 122.9 (CH), 121.6 (CH);  $m/z$  (EI) 196 ( $M^+$ , 100%), 193 (56), 180 (35), 178 (13), 152 (4), 119 (9), 104 (38), 93 (76), 77 (98), 66 (10), 51 (39).

**6.1.2. (Z)-N-(4-Methoxyphenyl)benzamidinium 3b.** Similar treatment of benzonitrile **1a** (417  $\mu\text{L}$ , 4.06 mmol) with AlCl<sub>3</sub> (536 mg, 4.06 mmol) and *p*-anisidine (500 mg, 4.06 mmol) heated at ca. 100 °C for 4 h gave the title compound **3b** (853 mg, 93%) as colourless plates, mp 114 °C (lit.,<sup>27</sup> 115.5 °C) (cyclohexane/EtOH, 95:05);  $R_f$  (*t*-BuOMe) 0.36;  $\lambda_{\max}$ (DCM)/nm 233 (log  $\epsilon$  4.27), 276 (3.92);  $\nu_{\max}/\text{cm}^{-1}$  3439m, and 3294w (NH<sub>2</sub>), 3125w, 3003w (Ar CH), 2833w, 1638m, 1601m, 1566m, 1502s, 1466m, 1439m, 1381m, 1288m, 1242m, 1223m, 1182m, 1169w, 1128w, 1103m, 1088w, 1036m, 1001w, 978w, 930w, 862m, 847w, 829w, 814w, 789m, 754m, 718m;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.87 (2H, d, *J* 5.4, Ar H), 7.49–7.41 (3H, m, Ar H), 6.92 (4H, br s, Ar H), 4.86 (2H, br s, NH<sub>2</sub>), 3.80 (3H, s, OCH<sub>3</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 155.5, 155.0, 142.6, 135.9, 130.4 (CH), 128.4 (CH), 126.7 (CH), 122.4 (CH), 114.8 (CH), 55.4 (OCH<sub>3</sub>);  $m/z$  (EI) 226 ( $M^+$ , 91%), 211 (26), 182 (2), 167 (4), 123 (40), 108 (98), 104 (100), 92 (8), 80 (15), 77 (38), 64 (11), 51 (13).

**6.1.3. (Z)-N-(4-Nitrophenyl)benzamidinium 3c.** Similar treatment of benzonitrile **1a** (371  $\mu\text{L}$ , 3.62 mmol) with AlCl<sub>3</sub> (477 mg, 3.62 mmol) and 4-nitroaniline (500 mg, 3.62 mmol) heated at ca. 100 °C for 8 h gave the title compound **3c** (180 mg, 21%) as yellow needles, mp 164.5–165 °C (lit.,<sup>28</sup> 167–168 °C) (PhH); (found: C, 64.82; H, 4.51; N, 17.38. C<sub>13</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub> requires C, 64.72; H, 4.60; N, 17.42%);  $R_f$  (*t*-BuOMe) 0.74;  $\lambda_{\max}$ (DCM)/nm 232 (log  $\epsilon$  5.40), 334 (5.36);  $\nu_{\max}/\text{cm}^{-1}$  3477m and 3363m (NH<sub>2</sub>), 1643m, 1607m, 1574m, 1491m, 1447w, 1373m, 1335s, 1317m, 1301m, 1258m, 1173m, 1109m, 1078w, 1059w, 1030w, 1001w, 926w, 870m, 858m, 808w, 791m, 783m, 748m;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 8.20 (2H, d, *J* 8.4, Ar H), 7.84 (2H, br s, Ar H), 7.54–7.43 (3H, m, Ar H), 7.06 (2H, d, *J* 7.8, Ar H), 4.98 (2H, br s, NH<sub>2</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 156.8, 154.8, 143.2, 134.7, 131.2 (CH), 128.7 (CH), 126.8 (CH), 125.5 (CH), 122.1 (CH);  $m/z$  (EI) 241 ( $M^+$ +1, 100%), 240 (53), 225 (10), 194 (20), 179 (18), 167 (4), 151 (5), 138 (14), 118 (6), 108 (27), 104 (100), 92 (13), 76 (45), 65 (22), 50 (19).

**6.1.4. (Z)-N-(4-Methylphenyl)benzamidinium 3d.** Similar treatment of benzonitrile **1a** (479  $\mu\text{L}$ , 4.66 mmol) with AlCl<sub>3</sub> (615 mg, 4.66 mmol) and *p*-toluidine (500 mg, 4.66 mmol) heated at ca. 100 °C for 6 h gave the title compound **3d** (906 mg, 93%) as colourless needles, mp 102–103 °C (lit.,<sup>29</sup> 103–105 °C) (cyclohexane);  $R_f$  (*t*-BuOMe) 0.86;  $\lambda_{\max}$ (DCM)/nm 233 (log  $\epsilon$  4.27), 278 (3.92);  $\nu_{\max}/\text{cm}^{-1}$  3449w (NH<sub>2</sub>), 3292w, 3123w, 3055w, 2918w, 2860w, 1633s, 1601m, 1568m, 1504m, 1447w, 1383m, 1234m, 1105w, 1024w, 926w, 866m, 793m, 777m, 758w, 714m;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.83 (2H, d, *J* 6.6 Ar H), 7.51–7.40 (3H, m, Ar H), 7.15 (2H, d, *J* 8.1 Ar H), 6.89 (2H, d, *J* 8.1 Ar H), 4.81 (2H, br s, NH<sub>2</sub>), 2.33 (3H, s, CH<sub>3</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 155.1, 146.7, 135.8, 132.2, 130.4 (CH), 130.0 (CH), 128.4 (CH), 126.7 (CH), 121.4 (CH), 20.8 (CH<sub>3</sub>);  $m/z$  (EI) 211 ( $M^+$ +1, 13%), 210 ( $M^+$ , 85), 194 (24), 165 (3), 133 (5), 107 (100), 103 (66), 91 (43), 77 (38), 65 (25), 51 (28).

**6.1.5. (Z)-N-(4-Fluorophenyl)benzamidinium 3e.** Similar treatment of benzonitrile **1a** (462  $\mu\text{L}$ , 4.50 mmol) with AlCl<sub>3</sub> (593 mg, 4.50 mmol) and 4-fluoroaniline (432  $\mu\text{L}$ , 4.50 mmol) heated at ca. 100 °C for 6 h gave the title compound **3e** (794 mg, 82%) as colourless needles, mp

124.5–125 °C (lit.,<sup>21</sup> 126–128 °C) (cyclohexane/EtOH, 95:05);  $R_f$  (*t*-BuOMe) 0.57;  $\lambda_{\max}$ (DCM)/nm 231 (log  $\epsilon$  4.23), 278 (3.83);  $\nu_{\max}/\text{cm}^{-1}$  3470w and 3344w (NH<sub>2</sub>), 3202w (Ar CH), 1614s, 1570m, 1499s, 1473w, 1445w, 1410w, 1379m, 1238w, 1213s, 1092w, 1076w, 1028w, 1011w, 979w, 928w, 862w, 851w, 802w, 779m, 762s, 706s;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.84 (2H, d, *J* 6.6, Ar H), 7.48–7.40 (3H, m, Ar H), 7.07–7.01 (2H, m, Ar H), 6.94–6.89 (2H, m, Ar H), 4.88 (2H, br s, NH<sub>2</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 159.0 (d, <sup>1</sup>*J*<sub>CF</sub> 240.8, CF), 155.2, 145.6, 135.6 (CH), 130.6 (CH), 128.5 (CH), 126.7 (CH), 122.7 (d, <sup>2</sup>*J*<sub>CF</sub> 7.6, CH), 116.1 (d, <sup>2</sup>*J*<sub>CF</sub> 22.7, CH);  $m/z$  (EI) 214 ( $M^+$ , 55%), 198 (21), 169 (93), 156 (78), 147 (51), 129 (26), 119 (31), 111 (77), 104 (40), 95 (41), 77 (40), 69 (100), 57 (70), 51 (28).

**6.1.6. (Z)-N-(4-Chlorophenyl)benzamidinium 3f.** Similar treatment of benzonitrile **1a** (406  $\mu\text{L}$ , 3.92 mmol) with AlCl<sub>3</sub> (517 mg, 3.92 mmol) and 4-chloroaniline (500 mg, 3.92 mmol) heated at ca. 100 °C for 6 h gave the title compound **3f** (807 mg, 89%) as colourless needles, mp 116.5 °C (lit.,<sup>27</sup> 115.5 °C) (cyclohexane/EtOH, 95:05);  $R_f$  (*t*-BuOMe) 0.86;  $\lambda_{\max}$ (DCM)/nm 241 (log  $\epsilon$  4.34), 284 (3.94);  $\nu_{\max}/\text{cm}^{-1}$  3470w and 3346w (NH<sub>2</sub>), 1612s, 1568s, 1485m, 1447w, 1404w, 1379m, 1238w, 1171w, 1097m, 1011m, 858m, 779m, 723w, 708s;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.81 (2H, d, *J* 6.9, Ar H), 7.51–7.40 (3H, m, Ar H), 7.30 (2H, d, *J* 8.7, Ar H), 6.90 (2H, d, *J* 8.7, Ar CH), 4.79 (2H, br s, NH<sub>2</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 155.4, 148.0, 135.3, 130.7 (CH), 129.5 (CH), 128.6 (CH), 128.1, 126.8 (CH), 123.0 (CH);  $m/z$  (EI) 232 ( $M^+$ +2, 28%), 230 ( $M^+$ , 85), 216 (7), 214 (31), 169 (14), 149 (7), 147 (9), 129 (27), 127 (61), 113 (11), 111 (29), 104 (68), 97 (15), 77 (33), 69 (11), 51 (13).

**6.1.7. (Z)-N-(4-Bromophenyl)benzamidinium 3g.** Similar treatment of benzonitrile **1a** (298  $\mu\text{L}$ , 2.91 mmol) with AlCl<sub>3</sub> (386 mg, 2.91 mmol) and 4-bromoaniline (500 mg, 2.91 mmol) heated at ca. 100 °C for 6 h gave the title compound **3g** (624.5 mg, 78%) as colourless needles, mp 122–123 °C (lit.,<sup>30</sup> 124 °C) (cyclohexane/EtOH, 95:05);  $R_f$  (*t*-BuOMe) 0.71;  $\lambda_{\max}$ (DCM)/nm 246 (log  $\epsilon$  4.38);  $\nu_{\max}/\text{cm}^{-1}$  3470w and 3345w (NH<sub>2</sub>), 1614s, 1568m, 1497w, 1481m, 1447w, 1400w, 1379m, 1298w, 1238m, 1172w, 1099w, 1072m, 1007m, 858m, 779m, 719w, 706s;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.81 (2H, d, *J* 6.9, Ar H), 7.51–7.40 (5H, m, Ar H), 6.86 (2H, d, *J* 8.7, Ar H), 4.72 (2H, br s, NH<sub>2</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 155.3, 148.5, 135.3, 132.5 (CH), 130.8 (CH), 128.6 (CH), 126.8 (CH), 123.5 (CH), 115.8;  $m/z$  (EI) 276 ( $M^+$ +2, 65%), 274 ( $M^+$ , 73), 260 (15), 258 (19), 194 (7), 173 (50), 171 (53), 157 (15), 155 (17), 104 (100), 97 (28), 92 (15), 84 (11), 77 (58), 65 (11), 51 (28).

**6.1.8. (Z)-N-(4-Iodophenyl)benzamidinium 3h.** Similar treatment of benzonitrile **1a** (468  $\mu\text{L}$ , 4.56 mmol) with AlCl<sub>3</sub> (301 mg, 2.28 mmol) and 4-iodoaniline (500 mg, 2.28 mmol) heated at ca. 100 °C for 6 h gave the title compound **3h** (622.5 mg, 85%) as colourless needles, mp 137 °C (lit.,<sup>30</sup> 139 °C) (cyclohexane/EtOH, 95:05);  $R_f$  (*t*-BuOMe) 0.86;  $\lambda_{\max}$ (DCM)/nm 231 (log  $\epsilon$  4.91), 246 (5.03), 280 inf (4.70);  $\nu_{\max}/\text{cm}^{-1}$  3470w and 3345w (NH<sub>2</sub>), 3071 (Ar CH), 1612s, 1568s, 1481w, 1470w, 1447w, 1396w, 1375m, 1298w, 1238m, 1177w, 1101w, 1076w, 1063w, 1001m, 858m, 777m, 717m, 704s;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.83–7.78 (3H, m, Ar H), 7.63 (2H, d, *J* 8.1, Ar H), 7.48–7.39 (2H, m, Ar H), 6.73 (2H, d, *J* 8.1, Ar H), 4.89 (2H, br s, NH<sub>2</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 155.0, 149.5, 138.4 (CH), 135.4, 130.7 (CH), 128.5 (CH), 126.7 (CH), 124.0 (CH), 86.3;  $m/z$  (EI) 323 ( $M^+$ +1, 13%), 322 ( $M^+$ , 100), 306 (15), 245 (4), 219 (76), 194 (6), 179 (6), 104 (80), 98 (27), 92 (33), 76 (48), 65 (12), 51 (10).

**6.1.9. (Z)-N-(3,4-Dichlorophenyl)benzamidinium 3i.** Similar treatment of benzonitrile **1a** (317  $\mu\text{L}$ , 3.09 mmol) with AlCl<sub>3</sub> (407 mg, 3.09 mmol) and 3,4-dichloroaniline (500 mg, 3.09 mmol) heated at ca. 100 °C for 6 h gave the title compound **3i** (746 mg, 91%) as colourless plates, mp 108–109 °C (lit.,<sup>6b</sup> 110–111 °C) (cyclohexane/EtOH, 95:05);  $R_f$  (*t*-BuOMe) 0.79;  $\lambda_{\max}$ (DCM)/nm 231 (log  $\epsilon$  4.46), 246 (4.43), 285 (4.13);  $\nu_{\max}/\text{cm}^{-1}$  3449w and 3326w (NH<sub>2</sub>), 1614s, 1568s, 1470m, 1458m, 1387m, 1371m, 1227w, 1128m, 1024m, 930w, 897m,

879m, 847w, 831w, 797m, 777s, 725m, 712m;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.79 (2H, d, *J* 6.9, Ar H), 7.52–7.37 (4H, m, Ar H), 7.08 (1H, d, *J* 2.1, Ar H), 6.81 (1H, dd, *J* 8.4, 2.1, Ar H), 4.77 (2H, br s, NH<sub>2</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 155.6, 149.2, 135.0, 133.0, 131.0 (CH), 130.9 (CH), 128.6 (CH), 126.8 (CH), 126.3, 123.6 (CH), 121.5 (CH); *m/z* (EI) 268 (M<sup>+</sup>+4, 8%), 266 (M<sup>+</sup>+2, 51), 264 (M<sup>+</sup>, 78), 250 (13), 248 (23), 163 (38), 161 (57), 147 (12), 145 (18), 109 (20), 104 (100), 97 (10), 77 (54), 52 (23).

**6.1.10. (Z)-2-Amino-N-(*N*-phenyl)benzamidinium 3j.** Similar treatment of anthranilonitrile **1b** (634 mg, 5.37 mmol) with AlCl<sub>3</sub> (708 mg, 5.37 mmol) and aniline (489  $\mu$ L, 5.37 mmol) heated at ca. 100 °C for 6 h gave the title compound **3j** (722 mg, 64%) as colourless plates, mp 146–147 °C (lit.<sup>4c</sup> 146–147 °C) (PhH); *R<sub>f</sub>* (*t*-BuOMe) 0.62;  $\lambda_{\text{max}}$ (DCM)/nm 232 (log  $\epsilon$  3.56), 327 (2.92);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3493w and 3433m (NH<sub>2</sub>), 3385w, 3205w, 1600s (Ar CH), 1579m, 1568m, 1539m, 1483m, 1446m, 1375m, 1325m, 1271m, 1238m, 1149m, 1072m, 1022m, 908m, 839m, 781m, 740s, 700m;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.43–7.35 (3H, m, Ar CH), 7.22–7.17 (1H, m, Ar CH), 7.12–7.06 (1H, m, Ar CH), 7.02–6.99 (2H, m, Ar CH), 6.74–6.67 (2H, m, Ar CH), 5.99 (2H, s, NH<sub>2</sub>), 4.81 (2H, s, NH<sub>2</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) one peak missing 155.8, 148.8, 147.8, 131.1 (CH), 129.5 (CH), 127.3 (CH), 123.1 (CH), 121.8 (CH), 117.1 (CH), 116.6 (CH); *m/z* (EI) 211 (M<sup>+</sup>+1, 63%), 210 (25), 196 (27), 167 (4), 119 (40), 105 (4), 93 (100), 92 (24), 77 (19), 65 (22), 51 (16).

**6.1.11. (Z)-2-Amino-N-(4-methylphenyl)benzamidinium 3k.** Similar treatment of anthranilonitrile **1b** (551 mg, 4.66 mmol) with AlCl<sub>3</sub> (615 mg, 4.66 mmol) and *p*-toluidine (500 mg, 4.66 mmol) heated at ca. 100 °C for 6 h gave first tricycloquinazoline **5** (60 mg, 12%) as yellow cotton like fibres, mp 322–323 °C (lit.<sup>24</sup> 322–323 °C); *R<sub>f</sub>* (DCM) 0.51;  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3480w, 3360m (NH), 1630m, 1597m, 1587m, 1506w, 1470m, 1445w, 1294s, 1182m, 1111s, 841m, 754m;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 8.50 (3H, d, *J* 8.1, Ar CH), 7.63 (1H, dd, *J* 7.5, 7.5, Ar CH), 7.55 (1H, d, *J* 8.1, Ar CH), 7.37 (1H, dd, *J* 7.5, 7.5, Ar CH); *m/z* (EI) 320 (M<sup>+</sup>, 18%), 311 (27), 293 (78), 167 (41), 149 (13), 127 (89), 118 (11), 97 (56), 91 (27), 77 (19), 71 (25). Further elution (*t*-BuOMe) gave the title compound **3k** (688.5 mg, 66%) as colourless plates, mp 150–151 °C (lit.<sup>4c</sup> 152–153 °C) (cyclohexane/EtOH, 95:05); *R<sub>f</sub>* (*t*-BuOMe) 0.33;  $\lambda_{\text{max}}$ (DCM)/nm 232 (log  $\epsilon$  4.51), 285 (3.84), 326 (3.91);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3493w, 3433w and 3387w (NH<sub>2</sub>), 3179w, 1609s, 1572m, 1537m, 1504m, 1448w, 1375m, 1325m, 1271w, 1238m, 1157m, 1105w, 1053w, 1034w, 1015w, 868w, 849w, 825m, 779w, 741s, 712w;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.41 (1H, dd, *J* 7.8, 1.2, Ar H), 7.22–7.15 (3H, m, Ar H), 6.90 (2H, *J* 8.1, Ar H), 6.74–6.66 (2H, m, Ar H), 5.81 (2H, br s, NH<sub>2</sub>), 4.86 (2H, br s, NH<sub>2</sub>), 2.35 (3H, s, CH<sub>3</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 156.1, 147.7, 146.0, 132.5, 131.0 (CH), 130.1 (CH), 127.3 (CH), 121.7 (CH), 117.1 (CH), 116.6, 116.6 (CH), 20.8 (CH<sub>3</sub>); *m/z* (EI) 226 (M<sup>+</sup>+1, 10%), 225 (M<sup>+</sup>, 99), 208 (16), 119 (22), 107 (100), 106 (94), 92 (27), 77 (11), 65 (28).

**6.1.12. (Z)-2-Amino-N-(4-methoxyphenyl)benzamidinium 3l.** Similar treatment of anthranilonitrile **1b** (959 mg, 8.12 mmol) with AlCl<sub>3</sub> (535 mg, 4.06 mmol) and *p*-anisidine (500 mg, 4.06 mmol) heated at ca. 100 °C for 8 h gave first tricycloquinazoline **5** (260 mg, 30%) as yellow cotton like fibres, mp 322–323 °C (lit.<sup>24</sup> 322–323 °C); identical to that described above. Further elution (*t*-BuOMe) gave the title compound **3l** (545 mg, 56%) as cream coloured plates, mp 148–149 °C (PhH); *R<sub>f</sub>* (*t*-BuOMe) 0.41; (found: C, 69.66; H, 6.30; N, 17.37. C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>O requires C, 69.69; H, 6.27; N, 17.41%);  $\lambda_{\text{max}}$ (DCM)/nm 231 (log  $\epsilon$  5.26), 296 (4.70), 327 (4.67);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3482w, 3441w and 3383w (NH<sub>2</sub>), 3192w (Ar CH), 2962w, 2926w and 2835w (CH<sub>3</sub>), 1606s, 1574m, 1537m, 1500s, 1470m, 1456w, 1414w, 1373m, 1327m, 1285m, 1234s, 1182m, 1169m, 1155m, 1099m, 1032m, 932m, 901m, 870m, 849m, 827m, 783m, 737s, 714m;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.41 (1H, dd, *J* 8.0, 1.1, Ar H), 7.18 (1H, ddd, *J* 7.7, 7.7, 1.5, Ar H), 6.92 (4H, br s, Ar H), 6.73–6.66 (2H, m, Ar H), 5.99 (2H, br s, NH<sub>2</sub>), 4.86 (2H, br s, NH<sub>2</sub>), 3.81 (3H, s, CH<sub>3</sub>O);  $\delta_{\text{C}}$ (75 MHz;

CDCl<sub>3</sub>) 156.4, 155.7, 147.8, 141.7, 131.0 (CH), 127.3 (CH), 122.7 (CH), 117.1 (CH), 116.6, 116.5 (CH), 114.8 (CH), 55.5 (OCH<sub>3</sub>); *m/z* (EI) 241 (M<sup>+</sup>, 71%), 224 (10), 209 (7), 181 (3), 154 (2), 123 (66), 119 (40), 108 (100), 92 (27), 80 (12), 65 (19), 52 (6).

**6.1.13. (Z)-2-Amino-N-(4-fluorophenyl)benzamidinium 3n.** Similar treatment of anthranilonitrile **1b** (531 mg, 4.50 mmol) with AlCl<sub>3</sub> (593 mg, 4.50 mmol) and 4-fluoroaniline (432  $\mu$ L, 4.50 mmol) heated at ca. 100 °C for 6 h gave the title compound **3n** (593.5 mg, 58%) as colourless plates, mp 143.4–145 °C (cyclohexane/EtOH, 95:05); *R<sub>f</sub>* (*t*-BuOMe) 0.67; (found: C, 68.18; H, 5.35; N, 18.21. C<sub>13</sub>H<sub>12</sub>FN<sub>3</sub> requires C, 68.11; H, 5.28; N, 18.33%);  $\lambda_{\text{max}}$ (DCM)/nm 232 (log  $\epsilon$  4.35), 283 (3.82), 330 (3.71);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3495w, 3435w and 3377w (NH<sub>2</sub>), 3204w, 1610s, 1572m, 1537m, 1495s, 1450w, 1406w, 1375m, 1327m, 1267w, 1234w, 1211s, 1159m, 1088w, 1009w, 872w, 839m, 789m, 744s, 710w;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.39 (1H, d, *J* 7.5, Ar H), 7.22–7.17 (1H, m, Ar H), 7.08–7.02 (2H, m, Ar H), 6.95–6.90 (2H, m, Ar H), 6.73–6.66 (2H, m, Ar H), 5.78 (2H, br s, NH<sub>2</sub>), 4.91 (2H, br s, NH<sub>2</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 159.1 (d, <sup>1</sup>J<sub>CF</sub> 241.6, CF), 156.5, 147.7, 144.5, 131.2 (CH), 127.3 (CH), 123.0 (d, <sup>3</sup>J<sub>CF</sub> 7.6, CH), 117.1 (CH), 116.6 (CH), 116.3, 116.2 (d, <sup>2</sup>J<sub>CF</sub> 21.9, CH); *m/z* (EI) 229 (M<sup>+</sup>, 52%), 212 (19), 185 (3), 119 (61), 111 (100), 92 (31), 84 (9), 75 (15), 65 (27), 57 (5).

**6.1.14. (Z)-2-Amino-N-(4-chlorophenyl)benzamidinium 3o.** Similar treatment of anthranilonitrile **1b** (463 mg, 3.92 mmol) with AlCl<sub>3</sub> (517 mg, 3.92 mmol) and 4-chloroaniline (500 mg, 3.92 mmol) heated at ca. 100 °C for 6 h gave the title compound **3o** (461 mg, 48%) as colourless plates, mp 162–163 °C (lit.<sup>4c</sup> 161–162 °C) (cyclohexane/EtOH, 95:05); *R<sub>f</sub>* (*t*-BuOMe) 0.78;  $\lambda_{\text{max}}$ (DCM)/nm 230 (log  $\epsilon$  4.30), 242 (4.21), 272 (3.69);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3495w, 3435w and 3381w (NH<sub>2</sub>), 3206w (Ar CH), 1611s, 1580m, 1566m, 1537m, 1481m, 1400w, 1375m, 1327w, 1265w, 1240m, 1159m, 1088m, 1009m, 868w, 847w, 824w, 766w, 746m;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.39 (1H, dd, *J* 7.8, 0.9, Ar CH), 7.31 (2H, d, *J* 8.7, Ar CH), 7.20 (1H, dd, *J* 7.7, 1.5, Ar CH), 6.93 (2H, d, *J* 8.7, Ar CH), 6.74–6.66 (2H, m, Ar CH), 5.82 (2H, br s, NH<sub>2</sub>), 4.79 (2H, br s, NH<sub>2</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 156.3, 147.7, 147.2, 131.4 (CH), 129.6 (CH), 128.4, 127.3 (CH), 123.3 (CH), 117.2 (CH), 116.7 (CH), 116.2; *m/z* (EI) 247 (M<sup>+</sup>+2, 15%), 245 (M<sup>+</sup>, 51), 230 (9), 228 (27), 209 (3), 192 (3), 166 (3), 136 (24), 129 (29), 127 (100), 119 (97), 105 (14), 92 (53), 75 (15), 65 (33).

**6.1.15. (Z)-2-Amino-N-(4-bromophenyl)benzamidinium 3p.** Similar treatment of anthranilonitrile **1b** (344 mg, 2.91 mmol) with AlCl<sub>3</sub> (3.84 mg, 2.91 mmol) and 4-bromoaniline (500 mg, 2.91 mmol) heated at ca. 100 °C for 6 h gave the title compound **3p** (358 mg, 43%) as colourless plates, mp 167–168 °C (lit.<sup>4c</sup> 167–168 °C) (cyclohexane/EtOH, 95:05); *R<sub>f</sub>* (*t*-BuOMe) 0.76;  $\lambda_{\text{max}}$ (DCM)/nm 232 (log  $\epsilon$  4.48), 241 (4.46), 280 (4.13), 331 (3.88);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3495w, 3433w and 3383w (NH<sub>2</sub>), 3211w (Ar CH), 1609s, 1574m, 1566m, 1537m, 1479m, 1396w, 1375m, 1327w, 1242m, 1159m, 1095w, 1070m, 1005m, 868w, 847w, 822w, 766w, 746s, 710w;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.46 (2H, d; *J* 8.4, Ar H), 7.39 (1H, d, *J* 7.8, Ar H), 7.23–7.16 (1H, m, Ar H), 6.87 (2H, d, *J* 8.4, Ar H), 6.74–6.66 (2H, m, Ar H), 5.80 (2H, br s, NH<sub>2</sub>), 4.80 (2H, br s, NH<sub>2</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) one peak missing 156.3, 147.8, 132.6 (CH), 131.4 (CH), 127.4 (CH), 123.8 (CH), 117.2 (CH), 116.8 (CH), 116.2, 116.1; *m/z* (EI) 291 (M<sup>+</sup>+2, 34%), 289 (M<sup>+</sup>, 35), 274 (14), 272 (14), 236 (17), 209 (4), 193 (5), 173 (54), 171 (56), 119 (100), 105 (18), 92 (57), 76 (16), 65 (52), 52 (10).

**6.1.16. (Z)-2-Amino-N-(3,4-dichlorophenyl)benzamidinium 3r.** Similar treatment of anthranilonitrile **1b** (364 mg, 3.09 mmol) with AlCl<sub>3</sub> (407 mg, 3.09 mmol) and 3,4-dichloroaniline (500 mg, 3.09 mmol) heated at ca. 100 °C for 6 h gave the title compound **3r** (305.5 mg, 35%) as colourless plates, mp 129–130 °C (lit.<sup>4c</sup> 130–131 °C) (cyclohexane/EtOH, 95:05); *R<sub>f</sub>* (*t*-BuOMe) 0.90; (found: C, 55.64; H, 3.98; N, 14.98. C<sub>13</sub>H<sub>11</sub>Cl<sub>2</sub>N<sub>3</sub> requires C, 55.73; H, 3.96; N, 15.00%);  $\lambda_{\text{max}}$ (DCM)/nm 230 (log  $\epsilon$  4.35), 242 (4.27), 287 (3.75);  $\nu_{\text{max}}$ /cm<sup>-1</sup>

3495m, 3453w and 3395m (NH<sub>2</sub>), 3277w, 1632s, 1576m, 1574m, 1547m, 1495w, 1468m, 1450m, 1387s, 1375m, 1321m, 1261w, 1252m, 1223w, 1157w, 1119m, 1020w, 889s, 852m, 835m, 771m, 750s, 717w;  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>) 7.42–7.35 (2H, m, Ar H), 7.21 (1H, dd, *J* 7.8, 1.2, Ar H), 7.10 (1H, d, *J* 1.8, Ar H), 6.83 (1H, dd, *J* 8.4, 1.8, Ar H), 6.73–6.67 (2H, m, Ar H), 5.65 (2H, br s, NH<sub>2</sub>), 4.88 (2H, br s, NH<sub>2</sub>);  $\delta_{\text{C}}$ (75 MHz; CDCl<sub>3</sub>) 156.6, 148.3, 147.7, 133.0, 131.6 (CH), 131.1 (CH), 127.3 (CH), 126.4, 123.8 (CH), 121.7 (CH), 117.2 (CH), 116.8 (CH), 115.8; *m/z* (EI) 283 (M<sup>+</sup>+2, 4%), 281 (M<sup>+</sup>+1, 13), 279 (M<sup>+</sup>, 35), 264 (9), 262 (11), 236 (17), 208 (2), 192 (3), 163 (28), 161 (49), 119 (100), 92 (29), 75 (5), 65 (22).

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## Supplementary data

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