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Reactions of tetracyanoethylene with *N*′-arylbenzamidines: A route to 2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitriles

Styliana I. Mirallai, Maria Manoli and Panayiotis A. Koutentis*

Department of Chemistry, University of Cyprus, P. O. Box 20537, 1678 Nicosia, Cyprus, koutenti@ucy.ac.cy

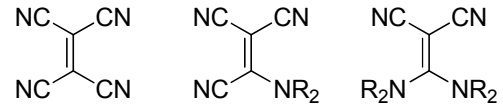
Eight 2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitriles **15** are prepared in four steps from *N*′-arylbenzamidines **11** and tetracyanoethylene (TCNE) in ~70-90% yields. The transformation involves the initial formation of *N*-aryl-*N*′-(1,2,2-tricyanovinyl)-benzamidines **12** in 87-99% yields, which in MeCN undergo a 5-exo-dig cyclization to give the 2-[1-aryl-5-imino-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitriles **13** in 84-92% yields, while in MeOH the (*Z*)-2-[2-phenyl-4-(arylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitriles **14** are formed in 85-94% yields. The imidazoles **14** can also be prepared directly from imidazoles **13** *via* a Dimroth rearrangement in either neat MeOH or in DCM with DBU. Subsequent thermolysis of imidazoles **14** in diphenyl ether affords 2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitriles **15** in near quantitative yields. Mechanistic rationale is provided for all transformations.

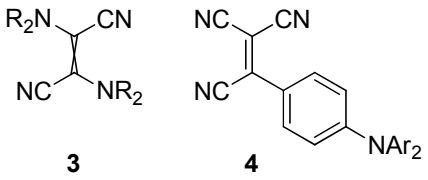
1. Introduction

Tetracyanoethylene (TCNE)[1,2] a cyanocarbon,[3] is the simplest of the percyano alkenes. It is highly electron-deficient and strongly electrophilic. Not surprisingly, TCNE can act as a powerful electron acceptor forming charge transfer complexes with various donors,[4,5] or it can participate in pericyclic chemistry as an electron deficient dienophile in Diels-Alder reactions[4] or enophile in 2+2 cycloadditions.[6,7]

Furthermore, it can act as an umpolung source of dicyanomethylene.[8-10] Its most common reaction is that of addition to its double bond and subsequent loss of the cyanide (tricyanovinylation). Direct addition to the nitrile can also occur but is less common.[11,12] The chemistry of TCNE has been extensively reviewed.[7,13-19]

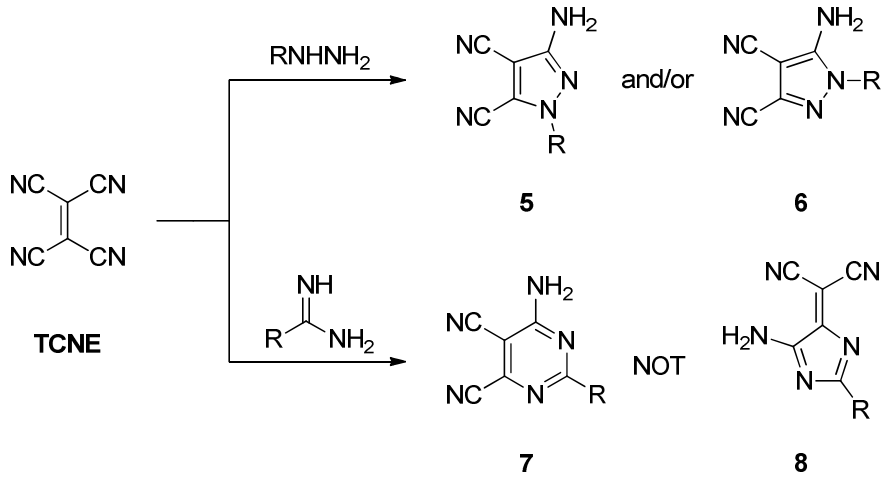
With primary or secondary aliphatic amines and with most primary and secondary aromatic amines, the reaction with TCNE gives *N*-tricyanovinylamines **1**, although with an excess of amine 1,1-diamino-2,2-dicyanoethylenes **2**[13,20,21] or 1,2-diamino-1,2-dicyanoethylenes **3**[22] are formed. TCNE does not react with tertiary aliphatic amines, but it readily reacts with both tertiary and secondary aromatic amines, attacking the arene to give 4-tricyanovinyl-arylamines **4** *via* the initial formation of a 1:1 π complex.[21]





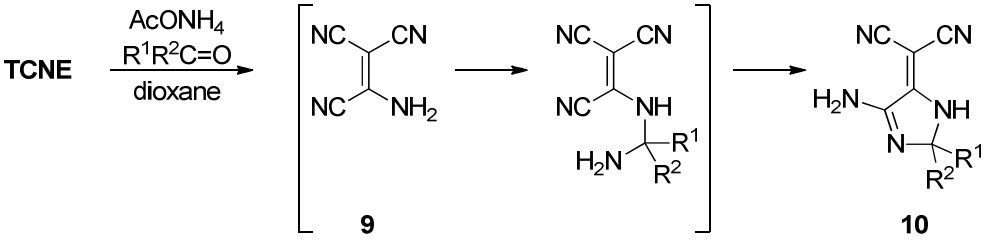
TCNE also reacts with a variety of bis-amino nucleophiles to give, after the initial addition to the double bond, intramolecular cyclizations typically on the vicinal nitrile that lead to various heterocyclic systems. For example, TCNE reacts with substituted hydrazines to give pyrazoles **5** and/or **6**,[11,12,23] or with 2-amidines to give 2-substituted 6-aminopyrimidine-4,5-dicarbonitriles **7**. The latter 6-exo-dig cyclization is somewhat

surprising since a 5-exo-dig cyclization could in theory occur on the geminal nitrile to yield five membered imidazoles of type **8** (Scheme 1).



Scheme 1. Typical reaction products of TCNE with hydrazines and amidines.

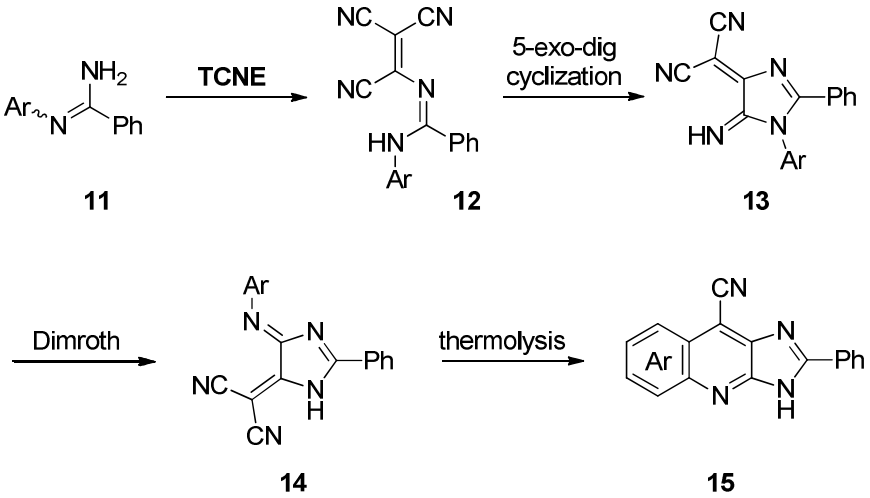
To the best of our knowledge, only one report on the preparation of imidazolines from TCNE has appeared whereby N-methylamino functionalization of the intermediate tricyanovinylamine **9** led to a geminal (5-exo-dig) heterocyclization to give 2-[5-amino-2,3-dihydro-4*H*-imidazol-4-ylidene]malononitriles **10** (Scheme 2).[24]



Scheme 2. Formation of imidazoles **10** from TCNE.

In light of this and our interest in preparing cyano substituted heteroarenes,[10,25-29] we report below our complementary study on the reaction of TCNE with readily available *N′*-arylbenzamidines **11**,[30] which affords *(Z)-N*-aryl-*N′*-(1,2,2-tricyanovinyl)benzamidines **12** that readily undergo a 5-exo-dig cyclization to the (imidazolylidene)-

malononitriles **13**, that in two steps, *via* the Dimroth rearrangement product **14**, can be converted into 2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitriles **15** (Scheme 3).



11 **12** **13**

14 **15**

Scheme 3. Four step conversion of TCNE and benzamidines **11** into imidazo[4,5-*b*]-quinolines **15**.

Previous syntheses of imidazo[4,5-*b*]quinolines include the one-pot Beckmann rearrangement of 3-acyl-2-(alkylamino)quinolin-4-(1*H*)-ones,[31] the reductive cyclization of 5-(2-nitrobenzylidene)-3,5-dihydro-imidazol-4-ones,[32,33] from lithiated 3-aminoquinolines with nitriles,[34] and from 2,3-diaminoquinolines.[35] Several imidazo[4,5-*b*]quinolines behave as NO synthase inhibitors[35] or as analogues of antiviral polyhalogenated benzimidazole ribonucleosides,[36] furthermore, fused 3*H*-imidazo[4,5-*b*]quinoline-9-carbonitriles have been investigated as fluorescent dyes.[37]

2. Results and Discussion

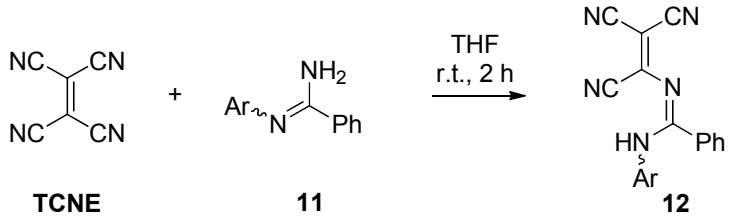
2.1. Preparation of N-*aryl*-N'-*(1,2,2-tricyanovinyl)benzamidines* ***12***

The reaction of *N′*-phenylbenzamidine **11a** with TCNE was investigated in a variety of solvents and temperatures and in almost all cases three products were observed in varying ratios by TLC: a colorless, a yellow and an orange product **12a**, **13a** and **14a**, respectively. The order of formation was determined (by TLC) to be first the colorless, then the yellow and finally the orange colored compound. It was noted that the colorless product **12a** converted rapidly into the yellow product **13a** during a 2D TLC study, furthermore, polar protic solvents such as MeOH or EtOH strongly promoted the formation of the orange product **14a**. Both mass spectrometry and elemental analysis of these three products showed they were isomers with a molecular formula of $C_{18}H_{11}N_5$ indicating that an addition between TCNE and *N′*-phenylbenzamidine **11a** followed by loss of HCN had occurred.

Since silica promoted the conversion of the colorless compound into the isomeric yellow we pursued a non chromatographic work up to isolate a clean sample of the colorless compound **12a**: Treating *N′*-phenylbenzamidine **11a** with TCNE (1 equiv) in dry THF at *ca.* 20 ^{o}C led to the exclusive formation of the colorless compound **12a** (by TLC). By carefully evaporating the THF, redissolving the residue in a small quantity of Et_2O and diluting with *n*-pentane we were able to precipitate a microanalytically pure sample of the colorless product **12a** in 97% yield. The spectroscopic and analytical data (see Structure Elucidation Discussion for **12a** in Supporting Information) tentatively suggested the product to be *N*-phenyl-*N′*-(1,2,2-tricyanovinyl)benzamidine (**12a**), which could originate from simple substitution of one nitrile by the least sterically hindered *N′*-arylbenzamidine amino group. The

reaction was general and in total nine analogues were prepared (Table 1). Interestingly, where the benzamidines contained *N′*-aryl substituents with either chloro, bromo, iodo or nitro substituents (entries 5-9) the reactions required a slight excess (1.2 equiv) of TCNE to come to completion.

Table 1 Reaction of TCNE with *N′*-arylbenzamidines **11**.



TCNE **11** **12**

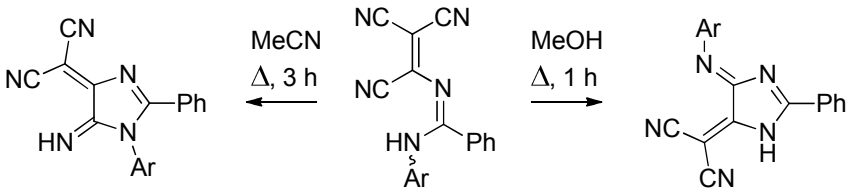
entries	TCNE (mmol)	Ar	yields **12** (%)
1	1.0	Ph	**12a** (97)
2	1.0	4-$MeOC_6H_4$	**12b** (98)
3	1.0	4-MeC_6H_4	**12c** (99)
4	1.0	4-FC_6H_4	**12d** (95)
5	1.2	4-ClC_6H_4	**12e** (93)
6	1.2	3,4-$Cl_2C_6H_3$	**12f** (91)
7	1.2	4-BrC_6H_4	**12g** (92)
8	1.2	4-IC_6H_4	**12h** (87)
9	1.2	4-$O_2NC_6H_4$	**12i** (88)

*2.2. Conversion of tricyanovinylbenzamidines **12** into imidazoles **13** and **14***

Solutions of the tricyanovinylbenzamidine **12a** in DMF or DMSO at *ca.* 20 ^oC or heated to reflux in a range of solvents such as DCM, PhMe or THF led to mixtures of both yellow and orange products **13a** and **14a**, respectively. Furthermore, treatment with either base (Hünig's base or DBU) or acid catalysis ($TsOH.H_2O$, H_2SO_4 or Lewis acids like $AlCl_3$, $FeCl_3$, $ZnCl_2$) gave more complex mixtures. Fortunately, simply heating a solution of the tricyanovinylbenzamidine **12a** in dry acetonitrile led to the formation of the yellow isomer **13a** in 88% yield while in MeOH the orange

isomer **14a** was formed in 92% yield. These conversions were generally high yielding for all nine analogues (Table 2).

Table 2 Conversion of tricyanovinylbenzamidines **12** into imidazoles **13** and **14**.

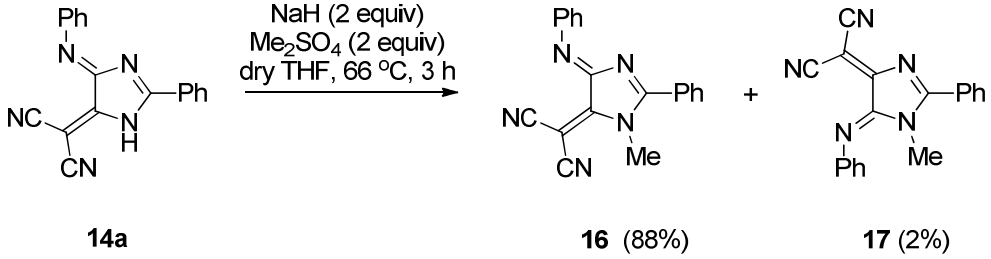


13 **12** **14**

entries	Ar	yields **13** (%)	yields **14** (%)
1	Ph	**13a** (88)	**14a** (92)
2	4-$MeOC_6H_4$	**13b** (89)	**14b** (91)
3	4-MeC_6H_4	**13c** (89)	**14c** (94)
4	4-FC_6H_4	**13d** (89)	**14d** (88)
5	4-ClC_6H_4	**13e** (87)	**14e** (86)
6	3,4-$Cl_2C_6H_3$	**13f** (87)	**14f** (90)
7	4-BrC_6H_4	**13g** (85)	**14g** (87)
8	4-IC_6H_4	**13h** (84)	**14h** (85)
9	4-$O_2NC_6H_4$	**13i** (92)	**14i** (93)

The ^{13}C NMR spectroscopic data for both the yellow and orange isomers **13a** and **14a**, respectively suggested one less nitrile group which indicated a cyclization had occurred. As mentioned above, cyclizations to give either six membered pyrimidines (*via* a 6-exo-dig cyclization) or five membered imidazoles (*via* a 5-exo-dig) were possible (Scheme 1), however, a study of the available spectroscopic data was inconclusive (see Structure Elucidation Discussion for **13a** and **14a** in Supporting Information). To identify these isomers we collected single crystal X-ray data, which supported the yellow isomer to be 2-[5-imino-1,2-diphenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**13a**) (see Supporting Information, Figure S1) and the orange isomer to be (*Z*)-2-[2-phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (**14a**) (see Supporting Information, Figure S2).

To study the chemistry of the imidazole **14a** further, it was N-methylated using methyl sulfate in dry THF. The products obtained were (*Z*)-2-[1-methyl-2-phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (**16**) and (*Z*)-2-[1-methyl-2-phenyl-5-(phenylimino)-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**17**) in 88 and 2% yields, respectively (Scheme 4).

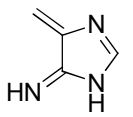


Scheme 4. ***N*-**Methylation of imidazole **14a**.

Unlike the non-methylated imidazole **14a** the ^{1}H and ^{13}C NMR spectra of both methylated isomers were well resolved, showing the expected eight quaternary, six CH and one CH_3 carbon signals. The assigned regioselectivity for the methylation of the major isomer **16** was determined by single crystal X-ray spectroscopy (see Supporting Information, Figure S4), while 2D-NOESY ^{1}H NMR spectroscopy was used to support the assignment for the imidazole **17** (see Supporting Information). The UV/vis spectra for the N-methylated imidazoles **16** and **17**, which cannot suffer from prototautomerism, showed only minor solvatochromic effects (see Supporting Information, Figures S5 and S6).

Both the above imidazoles are examples of *ortho* quinone methide imines (QMI's) which typically are reactive species and not readily isolated.[38] Not surprisingly, very few examples of this ring system have been reported: 4-Methylene-1*H*-imidazol-5(4*H*)-imines **18** have been proposed as possible intermediates in the conversion of

(*Z*)-N^1-{1,2-dicyano-2-[(*N*,*N*-dimethylamino)methylamino]vinyl}formamidines **19** into purines or imino-pyrroles,[39] and as intermediates in the preparation of purine-N^9-acetic acids from HCN and glycine.[40] More recently, a series of prototautomerically closely related 4-imino-5-methyleneimidazolidin-2-ones **20** have been isolated and characterized.[41,42] Interestingly, the ^{1}H NMR in DMSO-d_6 indicated the imine NH was present as two broad singlets (δ_H 9.1-8.8 ppm) in a 1:1 ratio, which was attributed to *E/Z* isomers of the exocyclic methylene (*cf.* the ^{1}H NMR of imidazole **13a**). To the best of our knowledge, only one related X-ray structure has been reported, that of (*E*)-4-[5-imino-1-phenyl-1*H*-imidazol-4(5*H*)-ylidene]-2,2-dimethyl-oxazolidin-5-imine (**21**).[43]



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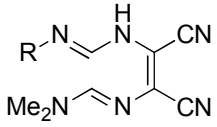

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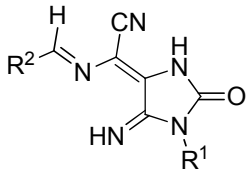

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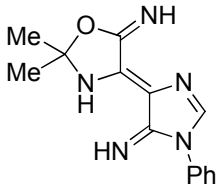

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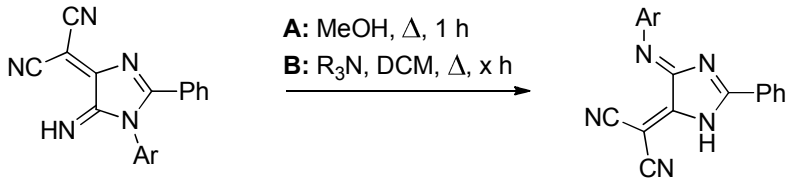
*2.3. Dimroth rearrangement of imidazole **13** into imidazole **14***

A close analysis of the two imidazoles **13a** and **14a** indicated that the latter was probably the product of a Dimroth rearrangement of the former. Dimroth rearrangements are typically thermally induced or initiated by acids or bases.[44] Nevertheless, a pure sample of the imidazole **13a** dissolved in MeOH and left to stir at *ca.* 20 °C for 38 h was converted into the imidazole **14a** in high yield. The reaction

time could be considerably shortened to 1 h by heating the reaction mixture to *ca.* 67 ^{o}C. Furthermore, in a non-protic non-nucleophilic solvent such as DCM heated to *ca.* 40 ^{o}C the conversion of imidazole **13a** into imidazole **14a** required the addition of base with DBU (1 equiv) giving the best results (Table 3). When DBU was replaced by pyridine, DMAP or lutidine or DABCO (1 equiv) the Dimroth rearrangement could not be driven to completion, while the use of trialkylamines, such as Et_3N (2-4 equiv) or Hünig's base (*i*-Pr_2NEt) led to no reaction. The reaction with DBU could also be carried out at *ca*. 20 ^{o}C but the reaction time increased to 22 h while the yield decreased to 84-86%. Finally, reducing the equivalents of DBU led to incomplete reactions (entry 1) while no significant advantage was observed in using more than one equivalent (entry 3). Interestingly, the use of sterically hindered Barton's base also gave the imidazole **14a** in 91% (entry 4).

Table 3 Dimroth rearrangement of 2-(1-aryl-5-imino-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene)malononitriles **13** into (*Z*)-2-[4-(arylimino)-2-phenyl-4-1*H*-imidazol-5(4*H*)-ylidene]malononitriles **14**.

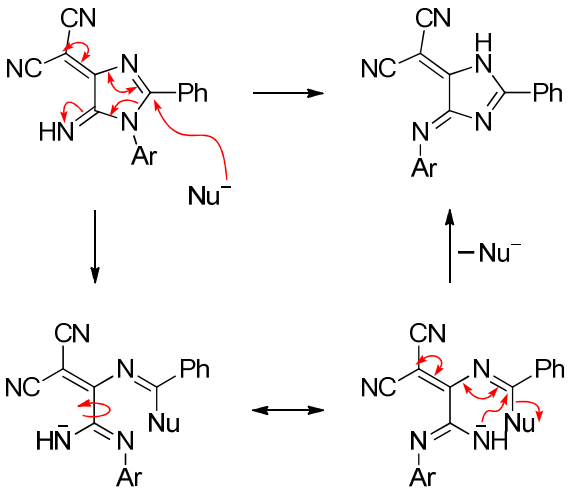


13 **14**

entries	Ar	cond. B base (equiv), time (h)	yields **14** (%) cond. A	cond. B
1	Ph	DBU (0.5), 48	-	ir[a]
2	Ph	DBU (1), 4	-	**14a** (97)
3	Ph	DBU (2), 3	-	**14a** (96)
4	Ph	Barton's base (1),[b] 10	**14a** (99.6)	**14a** (91)
5	4-$MeOC_6H_4$	DBU (1), 4	**14b** (99)	**14b** (90)
6	4-MeC_6H_4	DBU (1), 4	**14c** (94)	**14c** (91)
7	4-FC_6H_4	DBU (1), 6	**14d** (98)	**14d** (92)
8	4-ClC_6H_4	DBU (1), 6	**14e** (98)	**14e** (92)
9	3,4-$Cl_2C_6H_3$	DBU (1), 6	**14f** (96)	**14f** (93)
10	4-BrC_6H_4	DBU (1), 6	**14g** (94)	**14g** (88)
11	4-IC_6H_4	DBU (1), 6	**14h** (95)	**14h** (91)
12	4-$O_2NC_6H_4$	DBU (1), 6	**14i** (95)	**14i** (95)

[a] ir = incomplete reaction; [b] 2-*tert*-butyl-1,1,3,3-tetramethylguanidine.

The rearrangement was irreversible since treating (*Z*)-2-[2-phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (**14a**) with either NaOH (0.5 mol%) in MeOH at *ca.* 67 ^{o}C or with DBU (1 equiv) in dry DCM at *ca*. 40 ^{o}C for 24 h led to no reaction. The reaction presumably is initiated by nucleophilic attack by either methanol/methoxide or even DBU, which can act as a nucleophile,[45] at the imidazole C-2 position which is strongly electrophilic, activated by both the exocyclic ylidenemalononitrile and the imidazole imine which have constructively aligned dipoles. Subsequent ring opening *via* cleavage of the imidazole N(1)–C(2) bond affords a ring opened species that can rotate and undergo ring closure to afford the new imidazole **14** (Scheme 5).



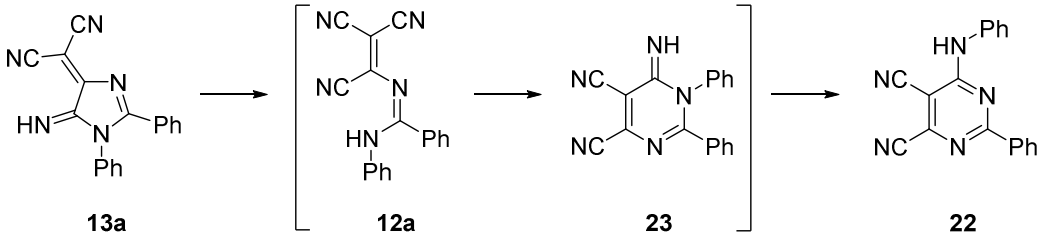
Scheme 5. Mechanistic rational for the Dimroth rearrangement of imidazoles **13**.

*2.4. Thermal behavior studies of imidazoles **13** and **14***

The thermal behavior of both imdiazoles **13a** and **14a** was also investigated: Differential scanning calorimetry (DSC) studies under an argon atmosphere showed that the imidazole **13a** immediately decomposed after melting. On heating a bulk sample under argon atmosphere at *ca.* 220 °C for 20 min a reaction mixture was obtained from which the imidazole **14a** was isolated in low yield (33%) together with two new products 2-phenyl-6-(phenylamino)pyrimidine-4,5-dicarbonitrile (**22**) (11%) and traces of 2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15a**) (see Structural Elucidation Discussion of **15a** and **22** in Supporting Information).

Tentatively, pyrimidine **22** can form from imidazole **13a** in three steps: Firstly imidazole **13a** ring opens to give the tricyanovinylamidine intermediate **12a** which subsequently undergoes a 6-exo-dig heterocyclization on the vicinal nitrile to give 6-imino-1,2-diphenyl-1,6-dihydropyrimidine-4,5-dicarbonitrile (**23**), that under the reaction conditions Dimroth rearranges to the observed pyrimidine **22** (Scheme 6).

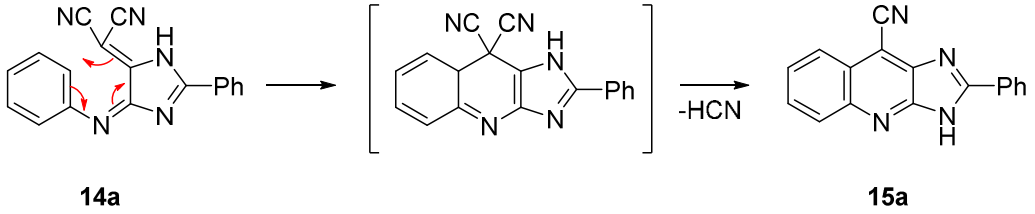
Unfortunately, no trace of the pyrimidine **23** could be identified and isolated from the reaction mixture.



Scheme 6. Proposed route for the formation of pyrimidine **22**.

Surprisingly, complex reaction mixtures were also obtained when the reaction was carried out using inert solvents such as toluene, xylene, chlorobenzene or diphenyl ether at reflux, while in benzene heated to reflux the yellow imidazole **13a** was stable.

As for 2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15a**), based on the carbon-nitrogen connectivity, we tentatively suggest that the product could have formed from imidazole **14a** *via* an electrocyclic ring closure and subsequent loss of HCN (Scheme 7).

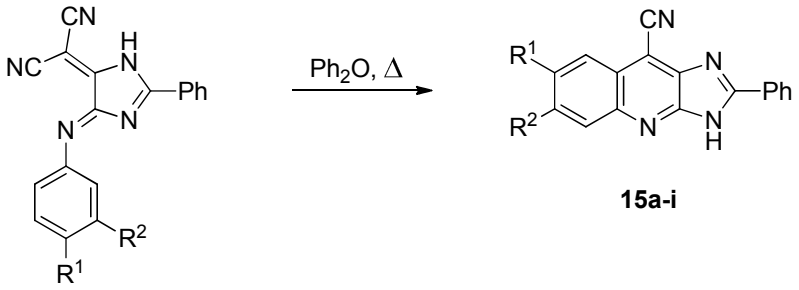


Scheme 7. Proposed mechanism for the formation of imidazo[4,5-*b*]quinoline **15a**.

In light of this, we carried out a DSC study of a pure sample of the imidazole **14a** that showed only an exothermic transition (onset 255.8 °C peak 256.7 °C). On cooling to *ca.* 20 °C, a TLC analysis of the contents of this DSC pan revealed only one product, compound **15a**. Subsequent thermolysis of the imidazole **14a** in diphenyl ether at *ca.*

280 °C, for 4 h protected from moisture with $CaCl_2$ drying tube, gave compound **15a** quantitatively. The reaction temperature could be lowered to 215 °C without affecting the product yield, although this led to longer reaction times (26 h). In boiling benzene or toluene no 2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15a**) was obtained, while chlorobenzene led to an incomplete reaction even after 2 d. The reaction was general and nearly all of the imidazoles **14** could be converted into the their corresponding 2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitriles **15** (Table 4).

Table 4 Thermolysis of (*Z*)-2-[4-(arylimino)-2-phenyl-4-1*H*-imidazol-5(4*H*)-ylidene]malononitriles **14** to give 2-phenyl-3*H*-imidazo[4,5-*b*]-quinoline-9-carbonitriles **15**.



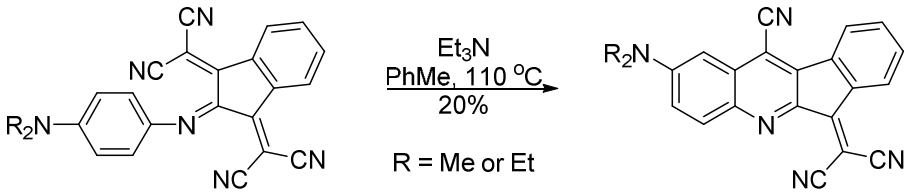
14a-i **15a-i**

entries	R^1	R^2	temp. (°C)	time (h)	yields (%)
1	H	H	280	4	**15a** (98)
2	H	H	260	6	**15a** (99)
3	H	H	240	18	**15a** (99.5)
4	H	H	215	26	**15a** (99)
5	MeO	H	280	2	**15b** (99)
6	Me	H	280	2	**15c** (99)
7	F	H	280	6	**15d** (99)
8	Cl	H	280	6	**15e** (98)
9	Cl	Cl	280	6	**15f** (84)[a]
10	Br	H	280	4	**15h** (98)
11	I	H	280	4	**15i** (98)
12	O_2N	H	280	6	[b]

[a] 7,8-Dichloro-2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15g**) was also isolated as a side product (12%).
[b] A complex and unresolvable reaction mixture was observed.

Worthy of note was that the imidazoles **14** supporting electron donating substituents on the arylimino group (entries 5 & 6) reacted faster than analogs supporting electron withdrawing groups (entries 7 & 8). Furthermore, the thermolysis of the unsymmetrically substituted dichlorophenylimidazole **14f** (entry 9) gave as expected the two possible isomeric products: 6,7-dichloro-2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15f**) and 7,8-dichloro-2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15g**) in 84 and 12% yields, respectively where the product ratio presumably reflects the steric demands for the respective cyclizations. Disappointingly, thermolysis of the nitrophenyl analogue (entry 12) led to a very complex reaction mixture (by TLC) which could not be resolved.

While there are many examples of the preparation of quinolines *via* electrocyclic ring closures followed by elimination of a leaving group to regain aromaticity,[46-52] there are very few examples which afford quinolines fused to five[53,54] and six membered rings,[55,56] and only one example involving an ylidenemalononitrile; cyclization of 2,2'-(2-{[4-(dialkylamino)phenyl]-imino}-1*H*-indene-1,3(2*H*)-diylidene)dimalononitriles **24** affords 2-[2-(dialkylamino)-11-cyano-6*H*-indeno[2,1-*b*]quinolin-6-ylidene)malononitriles **25** in low yields (Scheme 8).[57]

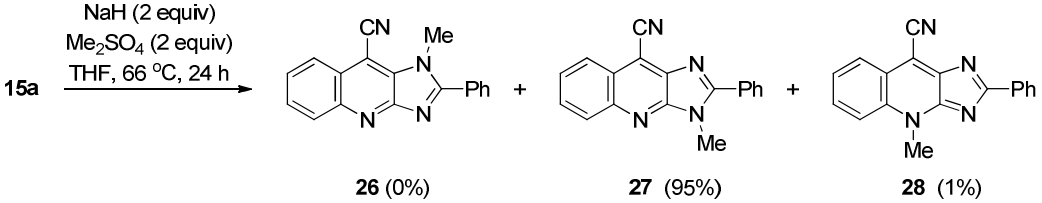


24 **25**

Scheme 8. Example of a quinoline synthesis *via* electrocylic ring closure.

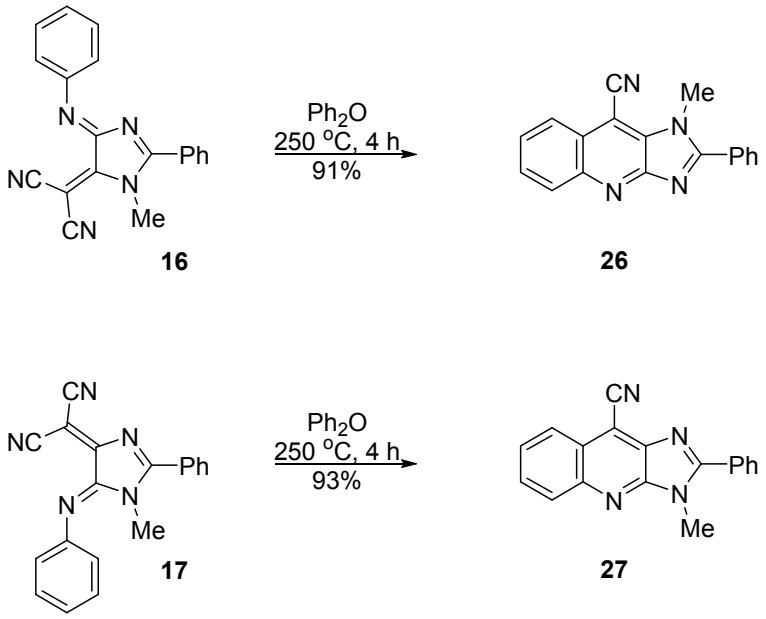
2.5. Preparation of N-*methylated 2-phenyl-3*H-*imidazo[4,5-*b*]quinoline-9-carbonitriles*

The regioselectivity of 2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15a**) towards N-methylation was investigated. As such, methylation of 2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15a**) using NaH (2 equiv) and dimethyl sulfate (2 equiv) in dry THF at *ca.* 66 ^{o}C gave two products: 3-methyl-2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**27**) and 4-methyl-2-phenyl-4*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**28**) in 95 and 1% yields, respectively (Scheme 9). No trace of 1-methyl-2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**26**) was observed. The regioselectivity of the methylations was supported by 2D-NOESY ^{1}H NMR experiments (see Supporting Information).



Scheme 9. *N*-Methylation of imidazo[4,5-*b*]quinoline-9-carbonitrile **15a**.

Since both the methylated imidazoles (*Z*)-2-[1-methyl-2-phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (**16**) and (Z)-2-[1-methyl-2-phenyl-5-(phenyl-imino)-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**17**) were in our possession these were also independently thermolyzed to give 1-methyl-2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**26**) and 3-methyl-2-phenyl-3*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**27**) in high yields, respectively (Scheme 10).



16 **26**

17 **27**

Scheme 10. Thermolysis of *N*-methylated imidazoles **16** and **17**.

3 Conclusions

The reaction of TCNE and *N*′-arylbenzamidines affords a densely functionalized adduct which on standing or gentle heating undergoes a 5-exo-dig cyclization to give the novel imidazoles **13**. These in turn in neat refluxing MeOH or in DCM with DBU suffer Dimroth rearrangements to give imidazoles **14**. The latter compounds readily undergo thermal mediated electrocyclic ring closures to give 3*H*-imidazo[4,5-*b*]-quinolines **15** in almost quantitatively yields. As such, the synthetic route outlined above affords a new 4-step but high yielding route to this useful ring system *via* readily available TCNE and *N*′-arylbenzamidines.

4 Experimental

4.1 General methods and materials

Reactions were protected from atmospheric moisture by $CaCl_2$ drying tubes. All reaction mixtures and column eluents were monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography[58] was used throughout for all non-TLC scale chromatographic separations using silica gel 60 (less than 0.063 mm). Melting points were determined using a Koefler-Hotstage microscope apparatus. Decomposition points (decomp.) were determined using a DSC with samples hermetically sealed in aluminium pans under an argon atmosphere, using heating rates of 5 ºC/min. Solvents used for recrystallization are indicated after the melting point. Inflections in the UV spectra are identified by the abbreviation "inf". IR spectra were recorded using a Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w respectively. ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively. Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. DEPT135 or APT NMR studies identified quaternary and tertiary carbons, which are indicated by (s) and (d) notations, respectively. 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 GCMS with direct inlet probe. Tetracyanoethylene (TCNE)[59] and the *N*′-arylbenzamidines **11a-i**,[30] were prepared according to literature procedures.

4.2 Reaction of *N′*-arylbenzamidines with tetracyanoethylene (TCNE)

4.2.1 N′-*Phenyl*-N-*(1,2,2-tricyanovinyl)benzamidine (**12a**) (Typical Procedure, see Table 1).*

To a stirred solution of tetracyanoethylene (128 mg, 1 mmol) in dry THF (5 mL), at *ca.* 20 °C and protected with $CaCl_2$ drying tube was added a solution of *N′*-phenyl-benzamidine (**11a**) (196 mg, 1 mmol) in dry THF (5 mL). The mixture was then left to stir at *ca*. 20 °C for 2 h, after which time the reaction was complete (by TLC), and the solvent was evaporated under reduced pressure (at < 25 °C). The residue was then dissolved in Et_2O (2 mL) and after cooling to 0 °C, *n*-pentane (40 mL) was added and triturated to form the precipitated *title compound* **12a** (288.7 mg, 97%) as colorless plates, mp (DSC) onset 135.7 °C, peak max. 139.1 °C, decomp. onset 140.8 °C peak max. 141.0 °C (from *n*-pentane/THF); (found: C, 72.61; H, 3.66; N, 23.45. $C_{18}H_{11}N_5$ requires C, 72.72; H, 3.73; N, 23.56%); R_f 0.51 (DCM/Et_2O, 95:05); λ_{max}(DCM)/nm 241 (log ε 4.29), 280 inf (3.74); ν_{max}/cm^{-1} 3258m (NH), 3064w (Ar CH), 2826w, 2201w (C≡N), 1692s, 1670w, 1651w, 1603m, 1593m, 1562s, 1557s, 1493m, 1454w, 1445m, 1375m, 1323m, 1315m, 1310m, 1285m, 1263m, 1184w, 1159w, 1126s, 1071m, 1039w, 1030m, 1007m, 1001w, 941w, 935w, 918m, 910m, 881m, 847w, 814w, 783s, 729m; δ_H(500 MHz; $CDCl_3$) 8.04 (1H, br s, N*H*), 7.54-7.50 (3H, m, Ar *H*), 7.49-7.46 (3H, m, Ar *H*), 7.32 (2H, dd, *J* 8.0, 8.0, Ar *H*), 7.17 (2H, br s, Ar *H*); δ_C(125 MHz; $CDCl_3$) 168.5 (s), 161.8 (s), 132.84 (s), 132.81 (d), 130.8 (d), 130.4 (d), 129.3 (d), 128.6 (d), 127.8 (d), 126.4 (s), 112.5 (s, *C*≡N), 108.4 (s, *C*≡N), 108.0 (s, *C*≡N), 66.9 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 299 (MH^++1, 1%), 298 (MH^+, 8), 295, (3), 282 (100), 261 (3), 260 (7), 259 (8), 180 (18).

4.2.2 N′-*(4-Methoxyphenyl)*-N-*(1,2,2-tricyanovinyl)benzamidine (**12b**)*

Similar treatment of TCNE (128 mg, 1 mmol) with *N*′-(4-methoxyphenyl)benzamidine (**11b**) (226 mg, 1 mmol) gave the *title compound* **12b** (319.3 mg, 98%) as colorless plates, mp 68.8–69.5 °C (from *n*-pentane/THF); (found: C, 69.62; H, 4.18; N, 21.40. $C_{19}H_{13}N_5O$ requires C, 69.71; H, 4.00; N, 21.39%); R_f 0.56 (DCM/Et_2O, 95:05); λ_{max}(DCM)/nm 237 (log ε 4.51), 275 inf (3.96); ν_{max}/cm^{-1} 3269m (NH), 3063w (Ar CH), 2899w, 2843w, 2226w (C≡N), 1695w, 1684w, 1653w, 1636w, 1607w, 1593w, 1568w, 1539w, 1512s, 1466w, 1447w, 1420w, 1387w, 1321m, 1312m, 1302m, 1254s, 1180w, 1171w, 1125m, 1065w, 1028w, 910w, 841m, 812w, 799w, 775w, 746w; δ_H(500 MHz; $CDCl_3$) NH resonance missing, 7.50-7.48 (3H, m, Ar *H*), 7.33 (2H, dd, *J* 8.0, 8.0, Ar *H*), 7.08 (2H, br s, Ar *H*), 6.99 (2H, d, *J* 8.0, Ar *H*), 3.85 (3H, s, OC*H*$_3$); δ_C(125 MHz; $CDCl_3$) 168.7 (s), 162.4 (s), 160.7 (s), 132.7 (d), 129.3 (d), 129.2 (d), 128.6 (d), 126.5 (s), 125.0 (s), 116.0 (d), 112.5 (s, *C*≡N), 108.5 (s, *C*≡N), 108.0 (s, *C*≡N), 66.7 [s, *C*$(CN)_2$], 55.6 (q, O*C*H$_3$); *m*/*z* (MALDI-TOF) 331 (MH^++2, 17%), 331 (MH^++1, 3), 328 (MH^+, 2), 312 (8), 227 (29), 211 (12), 210 (100), 181 (13), 71 (8).

4.2.3 N'-*(*p-*Tolyl)*-N-*(1,2,2-tricyanovinyl)benzamidine (**12c**)*

Similar treatment of TCNE (128 mg, 1 mmol) with *N*′-(p-tolyl)benzamidine (**11c**) (210 mg, 1 mmol) gave the *title compound* **12c** (309.3 mg, 99%) as colorless plates, mp (DSC) onset 149.4 °C, peak max. 151.0 °C, decomp. onset 152.2 °C peak max. 153.6 °C (from *n*-pentane/THF); (found: C, 73.33; H, 4.25; N, 22.58. $C_{19}H_{13}N_5$ requires C, 73.30; H, 4.21; N, 22.49%); R_f 0.59 (DCM/Et_2O, 95:05); λ_{max}(DCM)/nm 239 (log ε 4.31), 277 inf (3.80); ν_{max}/cm^{-1} 3252m (NH), 2808w, 2517w, 2199w (C≡N), 1694m, 1682m, 1601m, 1591m, 1560s, 1510m, 1497w, 1470w, 1447m,

1385m, 1379m, 1323s, 1315m, 1296s, 1265m, 1213w, 1179w, 1128s, 1072m, 1065m, 1040w, 1030m, 1022w, 1007m, 980w, 966w, 945w, 933w, 912m, 880m, 845w, 830m, 810m, 806w, 798w, 781m, 746m; δ_H(500 MHz; $CDCl_3$) 8.00 (1H, s, N*H*), 7.50-7.46 (3H, m, Ar *H*), 7.34-7.29 (4H, m, Ar *H*), 7.03 (2H, br s, Ar *H*), 2.42 (3H, s, CH_3); δ_C(125 MHz; $CDCl_3$) 168.5 (s), 162.1 (s), 140.8 (s), 132.8 (d), 131.4 (d), 130.1 (s), 129.3 (d), 128.6 (d), 127.5 (d), 126.5 (s), 112.5 (s, *C*≡N), 108.4 (s, *C*≡N), 108.0 (s, *C*≡N), 66.8 [s, *C*$(CN)_2$], 21.3 (q, *C*H_3); *m*/*z* (MALDI-TOF) 312 (MH^+, 4%), 296 (7), 275 (3), 247 (4), 194 (100), 105 (3), 91 (9).

4.2.4 N'-*(4-Fluorophenyl)*-N-*(1,2,2-tricyanovinyl)benzamidine (**12d**)*

Similar treatment of TCNE (128 mg, 1 mmol) with *N'*-(4-fluorophenyl)benzamidine (**11d**) (214 mg, 1 mmol) gave the *title compound* **12d** (299.6 mg, 95%) as colorless plates, mp (DSC) onset 146.0°C, peak max. 148.2 °C, decomp. onset 149.1 °C peak max. 150.4 °C (from *n*-pentane/THF); (found: C, 68.36; H, 3.33; N, 22.19. $C_{18}H_{10}FN_5$ requires C, 68.57; H, 3.20; N, 22.21%); R_f 0.49 (DCM/Et_2O, 95:05); λ_{max}(DCM)/nm 244 (log ε 4.23), 276 inf (3.76); ν_{max}/cm^{-1} 3258m (NH), 2814w, 2521w, 2203w (C≡N), 1697m, 1686m, 1605m, 1593m, 1562m, 1508s, 1447m, 1418w, 1379m, 1323m, 1314m, 1292m, 1287m, 1265w, 1238m, 1223m, 1184w, 1155m, 1126s, 1096w, 1071m, 1042w, 1030m, 1008m, 982w, 943w, 933w, 916m, 883m, 849m, 841m, 822w, 802w, 783m, 750m; δ_H(500 MHz; $CDCl_3$) 8.02 (1H, br s, N*H*), 7.51 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.46 (2H, d, *J* 8.5, Ar *H*), 7.35 (2H, dd, *J* 8.0, 8.0, Ar *H*), 7.21-7.19 (4H, m, Ar *H*); δ_C(125 MHz; $CDCl_3$) 168.5 (s), 163.1 (s, $^1J_{CF}$ 251.5, *C*F), 161.8 (s), 133.0 (d), 129.9 (d, $^3J_{CF}$ 8.9, *C*HCHCF), 129.2 (d), 128.8 (d), 126.2 (s), 118.1 (d, $^2J_{CF}$ 22.4, *C*HCF), 112.3 (s, *C*≡N), 108.3 (s, *C*≡N), 108.0 (s, *C*≡N), 68.0 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 316 (MH^+, 3%), 300 (5), 198 (100), 105 (4).

4.2.5 N'-*(4-Chlorophenyl)*-N-*(1,2,2-tricyanovinyl)benzamidine (**12e**)*

Similar treatment of TCNE (154 mg, 1.2 mmol) with *N'*-(4-chlorophenyl)benzamidine (**11e**) (231 mg, 1 mmol) gave the *title compound* **12e** (314.6 mg, 95%) as colorless plates, mp (DSC) onset 146.8 °C, peak max. 148.4 °C, decomp. onset 150.3 °C peak max. 151.9 °C (from *n*-pentane/THF); (found: C, 64.97; H, 2.93; N, 21.17. $C_{18}H_{10}ClN_5$ requires C, 65.17; H, 3.04; N, 21.11%); R_f 0.41 (DCM/Et_2O, 95:05); λ_{max}(DCM)/nm 242 (log ε 4.33), 277 inf (3.81); ν_{max}/cm^{-1} 3254w (NH), 2525w, 2201w (C≡N), 1692m, 1603m, 1593m, 1562m, 1493s, 1447m, 1408w, 1383w, 1323m, 1304m, 1294m, 1277w, 1265w, 1188w, 1128m, 1094m, 1071w, 1030w, 1016m, 945w, 939w, 930w, 912m, 880w, 837m, 822w, 806w, 781m, 760w, 739w; δ_H(500 MHz; $CDCl_3$) 8.05 (1H, s, N*H*), 7.54-7.49 (3H, m, Ar *H*), 7.46 (2H, d, *J* 8.5, Ar *H*), 7.36 (2H, dd, *J* 7.8, 7.8, Ar *H*), 7.11 (2H, br s, Ar *H*); δ_C(125 MHz; $CDCl_3$) 168.3 (s), 161.5 (s), 136.6 (s), 133.0 (d), 131.3 (s), 131.1 (d), 129.2 (d), 129.1 (d), 128.8 (d), 126.1 (s), 112.3 (s, *C*≡N), 108.3 (s, *C*≡N), 107.9 (s, *C*≡N), 66.9 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 334 (MH^++2, 3%), 332 (MH^+, 1), 318 (12), 316 (55), 294 (34), 231 (30), 216 (29), 214 (100).

4.2.6 N'-*(3,4-Dichlorophenyl)*-N-*(1,2,2-tricyanovinyl)benzamidine (**12f**)*

Similar treatment of TCNE (154 mg, 1.2 mmol) with *N'*-(3,4-dichlorophenyl)benzamidine (**11f**) (265 mg, 1 mmol) gave the *title compound* **12f** (335.1 mg, 92%) as colorless plates, mp (DSC) onset 151.5 °C, peak max. 155.5 °C, decomp. onset 157.0 °C peak max. 158.1 °C (from *n*-pentane/THF); (found: C, 58.83; H, 2.59; N, 19.21. $C_{18}H_9Cl_2N_5$ requires C, 59.04; H, 2.48; N, 19.12%); R_f 0.46 (DCM/Et_2O, 95:05); λ_{max}(DCM)/nm 244 (log ε 4.67), 278 inf (4.13); ν_{max}/cm^{-1} 3254m (NH), 2795w, 2533w, 2259w and 2197w (C≡N), 1703w, 1688s, 1605m, 1593m, 1564m,

1497w, 1474s, 1447w, 1406w, 1393w, 1370w, 1327m, 1304s, 1277m, 1242w, 1128s, 1086w, 1076w, 1065m, 1036m, 1011w, 982w, 957w, 932w, 912m, 887w, 874m, 847w, 829m, 818w, 797m, 781s, 745m; δ_H(500 MHz; $CDCl_3$) 8.12 (1H, br s, N*H*), 7.58 (1H, d, *J* 8.5 Ar *H*), 7.55 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.47 (2H, d, *J* 7.5, Ar *H*), 7.38 (2H, dd, *J* 7.8, 7.8, Ar *H*), 7.33 (1H, br s, Ar *H*), 6.99 (1H, br s, Ar *H*); δ_C(125 MHz; $CDCl_3$) 167.8 (s), 160.8 (s), 135.4 (s), 135.2 (s), 133.2 (d), 132.6 (d), 132.0 (s), 129.5 (d), 129.2 (d), 129.0 (d), 127.1 (d), 125.8 (s), 112.1 (s, *C*≡N), 108.2 (s, *C*≡N), 107.9 (s, *C*≡N), 67.2 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 368 (MH^++2, 3%), 366 (MH^+, 2), 350 (8), 329 (4), 303 (2), 250 (65), 248 (100), 207 (8), 199 (9), 181 (7), 127 (8), 111 (22), 109 (4), 105 (15), 97 (5), 88 (13), 77 (2).

4.2.7 N'-*(4-Bromophenyl)*-N-*(1,2,2-tricyanovinyl)benzamidine (**12g**)*

Similar treatment of TCNE (154 mg, 1.2 mmol) with *N'*-(4-bromophenyl)benzamidine (**11g**) (275 mg, 1 mmol) gave the *title compound* **12g** (346.0 mg, 92%) as colorless plates, mp 85.2–86.6 °C (from *n*-pentane/THF); (found: C, 57.39; H, 2.72; N, 18.62. $C_{18}H_{10}BrN_5$ requires C, 57.47; H, 2.68; N, 18.62%); R_f 0.54 (DCM/Et_2O, 95:05); λ_{max}(DCM)/nm 242 (log ε 4.48), 279 inf (3.87); ν_{max}/cm^{-1} 3277w (NH), 3099w and 3063w (Ar CH), 2974w, 2899w, 2255w and 2201w (C≡N), 1692m, 1653w, 1609m, 1595m, 1568m, 1489s, 1449m, 1402w, 1379m, 1311s, 1296m, 1273w, 1249w, 1202w, 1182w, 1125s, 1072s, 1030w, 1013s, 937w, 910m, 837s, 808w, 794w, 777s, 750m; δ_H(500 MHz; $CDCl_3$) 8.05 (1H, br s, N*H*), 7.64 (2H, d, *J* 8.0 Ar *H*), 7.52 (1H, dd, *J* 7.3, 7.3, Ar *H*), 7.46 (2H, d, *J* 8.5, Ar *H*), 7.36 (2H, dd, *J* 7.8, 7.8, Ar *H*), 7.04 (2H, d, *J* 5.5, Ar *H*); δ_C(125 MHz; $CDCl_3$) 168.3 (s), 161.4 (s), 134.1 (d), 133.0 (d), 131.8 (s), 129.3 (d), 129.2 (d), 128.8 (d), 126.1 (s), 124.6 (s), 112.3 (s, *C*≡N), 108.3 (s, *C*≡N), 107.9 (s, *C*≡N), 66.9 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 378

(MH$^+$+2, 2%), 376 (MH$^+$, 1), 362 (4), 360 (5), 312 (2), 260 (90), 258 (100), 181 (26), 111 (3), 71 (27).

4.2.8 N'-*(4-Iodophenyl)*-N-*(1,2,2-tricyanovinyl)benzamidine (**12h**)*

Similar treatment of TCNE (154 mg, 1.2 mmol) with *N'*-(4-iodophenyl)benzamidine (**11h**) (322 mg, 1 mmol) gave the *title compound* **12h** (366.0 mg, 87%) as colorless plates, mp 89.5–91.2 °C (from *n*-pentane/THF); (found: C, 51.22; H, 2.31; N, 16.68. $C_{18}H_{10}IN_5$ requires C, 51.08; H, 2.38; N, 16.55%); R_f 0.59 (DCM/Et_2O, 95:05); λ_{max}(DCM)/nm 246 (log ε 4.51), 278 inf (3.94); ν_{max}/cm^{-1} 3273w (NH), 3067w (Ar CH), 2964w, 2903w, 2255w and 2201w (C≡N), 1692m, 1609m, 1593m, 1566m, 1493m, 1487s, 1449m, 1398w, 1375m, 1319s, 1312s, 1250w, 1182w, 1125s, 1067m, 1028w, 1009s, 937w, 910m, 849m, 835m, 777m, 748m; δ_H(500 MHz; $CDCl_3$) 8.06 (1H, br s, N*H*), 7.84 (2H, d, *J* 8.0, Ar *H*), 7.52 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.46 (2H, d, *J* 8.5, Ar *H*), 7.36 (2H, dd, *J* 7.8, 7.8, Ar *H*), 6.90 (2H, d, *J* 5.5, Ar *H*); δ_C(125 MHz; $CDCl_3$) 168.3 (s), 161.4 (s), 140.1 (d), 133.0 (d), 132.6 (s), 129.4 (d), 129.2 (d), 128.8 (d), 126.1 (s), 112.3 (s, *C*≡N), 108.3 (s, *C*≡N), 107.9 (s, *C*≡N), 96.3 (s), 66.9 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 426 (MH$^+$+2, 1%), 424 (MH$^+$, 2), 408 (2), 387 (2), 386 (2), 323 (55), 307 (10), 306 (100), 180 (30), 179 (11), 105 (9).

4.2.9 N'-*(4-Nitrophenyl)*-N-*(1,2,2-tricyanovinyl)benzamidine (**12i**)*

Similar treatment of TCNE (154 mg, 1.2 mmol) with *N'*-(4-nitrophenyl)benzamidine (**11i**) (241 mg, 1 mmol) gave the *title compound* **12i** (301.0 mg, 88%) as colorless plates, mp (DSC) onset 149.9 °C, peak max. 152.9 °C, decomp. onset 155.1 °C peak max. 156.1 °C (from *n*-pentane/THF); (found: C, 62.97; H, 2.84; N, 24.55. $C_{18}H_{10}N_6O_2$ requires C, 63.16; H, 2.94; N, 24.55%); R_f 0.64 (DCM/Et_2O, 95:05);

λ_{max}(DCM)/nm 248 (log ε 4.29), 282 inf (4.03); ν_{max}/cm^{-1} 3296w (NH), 3119w and 3082w (Ar CH), 2808w, 2627w, 2260w and 2201w (C≡N), 1757w, 1692m, 1612m, 1593m, 1574m, 1524s, 1497m, 1474w, 1449w, 1420w, 1387m, 1348s, 1321m, 1312m, 1292w, 1234w, 1184w, 1176w, 1144m, 1132m, 1109w, 1074w, 1028w, 1011w, 1001w, 939w, 926w, 912m, 856m, 837m, 822w, 771m, 754m, 741w; δ_H(500 MHz; $CDCl_3$) NH resonance missing, 8.35 (2H, d, *J* 8.5, Ar *H*), 7.55 (1H, dd, *J* 7.3, 7.3 Ar *H*), 7.43 (2H, d, *J* 8.5, Ar *H*), 7.39-7.35 (4H, m, Ar *H*); δ_C(125 MHz; $CDCl_3$) one C (s) peak missing 149.0 (s), 148.1 (s), 138.5 (s), 133.3 (d), 129.1 (d), 129.0 (d), 128.7 (d), 125.9 (d), 125.8 (s), 112.0 (s, *C*≡N), 108.1 (s, *C*≡N), 107.8 (s, *C*≡N), 68.0 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 344 (MH^++1, 1%), 343 (MH^+, 2), 340 (5), 327 (100), 304 (41), 242 (11), 225 (99), 179 (48).

4.3 Conversion of *N*-Aryl-*N*-(1,2,2-tricyanovinyl)benzamidines into 2-[5-imino-1-aryl-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitriles

*4.3.1 2-[5-Imino-1,2-diphenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile **(13a)** (Typical Procedure, see Table 2).*

A stirred solution of *N*′-phenyl-*N*-(1,2,2-tricyanovinyl)benzamidine (**12a**) (29.7 mg, 0.1 mmol) in dry acetonitrile (1 mL) was heated at *ca*. 82 °C for 3 h and chromatography (DCM) of the residue gave the *title compound* **13a** (26.2 mg, 88%) as yellow prisms, mp (DSC) onset 195.6 °C, peak max. 201.3 °C, decomp. onset 205.2 °C peak max. 207.9 °C (from *n*-pentane/THF, 90:10); (found: C, 72.61; H, 3.66; N, 23.45. $C_{18}H_{11}N_5$ requires C, 72.72; H, 3.73; N, 23.56%); R_f 0.48 (DCM); λ_{max}(DCM)/nm 235 (log ε 3.62), 265 (3.36), 331 (4.24), 440 (4.31); ν_{max}/cm^{-1} 3237w (NH), 3063w and 3051w (Ar CH), 2234w and 2214w (C≡N), 1655w, 1609w, 1597w, 1578w, 1503m, 1493m, 1466s, 1441m, 1416s, 1331s, 1317m, 1275m, 1221m, 1196w,

1182w, 1163w, 1121m, 1072w, 1032w, 1000w, 980w, 941w, 872m, 843w, 781m; δ_H(500 MHz; $CDCl_3$) 10.39 (1H, s, N*H*), 9.26 (1H, s, N*H*), 7.71 (2H, d, *J* 7.5, Ar *H*), 7.67 (2H, d, *J* 7.5, Ar *H*), 7.64-7.62 (3H, m, Ar *H*), 7.60-7.56 (2H, m, Ar *H*), 7.54-7.52 (3H, m, Ar *H*), 7.38-7.34 (4H, m, Ar *H*), 7.25-7.23 (2H, m, Ar *H*), 7.20-7.18 (2H, m, Ar *H*); δ_H[500 MHz; $CDCl_3$/HCl (g)] NH resonance missing, 7.69 (2H, d, *J* 8.5, Ar *H*), 7.59-7.56 (4H, m, Ar *H*), 7.36 (2H, dd, *J* 8.0, 8.0, Ar *H*), 7.23-7.21 (2H, m, Ar *H*); δ_H(500 MHz; DMSO-d_6) 10.47 (1H, s, N*H*), 7.63-7.54 (6H, m, Ar *H*), 7.45-7.42 (4H, m, Ar *H*); δ_C(125 MHz; $CDCl_3$) 171.4 (s), 168.7 (s), 165.0 (s), 160.8 (s), 158.4 (s), 157.3 (s), 134.8 (d), 134.6 (d), 133.9 (s), 132.5 (s), 131.23 (d), 131.20 (d), 131.0 (d), 130.9 (d), 130.1 (d), 130.0 (d), 128.89 (d), 128.85 (d), 128.1 (d), 128.0 (d), 125.8 (s), 125.6 (s), 113.0 (s, *C*≡N), 112.5 (s, *C*≡N), 112.3 (s, *C*≡N), 111.7 (s, *C*≡N), 72.1 [s, *C*$(CN)_2$], 70.5 [s, *C*$(CN)_2$]; δ_C(125 MHz; DMSO-d_6) 170.0 (s), 167.0 (s), 155.6 (s), 134.1 (d), 132.5 (s), 130.4 (d), 130.3 (d), 130.2 (d), 128.72 (d), 128.69 (d), 126.1 (s), 113.6 (s, *C*≡N), 112.9 (s, *C*≡N), 67.1 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 299 (MH^++1, 25%), 298 (MH^+, 100), 242 (2), 180 (4), 153 (70); *m*/*z* (EI) 297 (M^+, 58%), 296 (100), 271 (7), 244 (3), 194 (22), 180 (12), 167 (6), 153 (3), 118 (12), 104 (17), 91 (5), 77 (73), 65 (3), 51 (32).

*4.3.2 2-[5-Imino-1-(4-methoxyphenyl)-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]-malononitrile (**13b**)*

Similar treatment of *N′*-(4-methoxyphenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12b**) (32.7 mg, 0.1 mmol) gave the *title compound* **13b** (29.1 mg, 89%) as orange prisms, mp (DSC) onset 187.1 °C, peak max. 191.1 °C, decomp. onset 195.4 °C, peak max. 203.0 °C (from cyclohexane/DCE, 50:50); (found: C, 69.62; H, 3.90; N, 21.27. $C_{19}H_{13}N_5O$ requires C, 69.71; H, 4.00; N, 21.39%); R_f 0.38 (DCM); λ_{max}(DCM)/nm

233 (log ε 4.30), 267 (3.85), 276 inf (3.84), 283 inf (3.87), 319 (4.16), 378 inf (3.98), 447 (4.22); ν_{max}/cm^{-1} 3265w and 3232w (NH), 3069w (Ar CH), 2976 (CH_3), 2224w and 2208w (C≡N), 1653w, 1605w, 1595w, 1578w, 1514m, 1504w, 1468s, 1445m, 1423m, 1410m, 1337m, 1304w, 1273m, 1256m, 1217m, 1182w, 1171w, 1123m, 1076w, 1020w, 1001w, 982w, 912w, 854w, 845m, 810w, 781w, 766w; δ_H[500 MHz; $CDCl_3$/HCl (g)] NH resonance missing, 7.73 (2H, dd, *J* 8.5, 1.0, Ar *H*), 7.58 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.37 (2H, dd, *J* 8.0, 8.0, Ar *H*), 7.13 (2H, d, *J* 9.0, Ar *H*), 7.05 (2H, d, *J* 9.0, Ar *H*), 3.89 (3H, s, OC*H*$_3$); δ_H(500 MHz; DMSO-d_6) 10.41 (1H, s, N*H*), 7.64-7.59 (3H, m, Ar *H*), 7.45 (2H, dd, *J* 8.0, 8.0, Ar *H*), 7.36 (2H, d, *J* 9.0, Ar *H*), 7.12 (2H, d, *J* 8.5, Ar *H*), 3.82 (3H, s, OC*H*$_3$); δ_C(125 MHz; DMSO-d_6) 170.2 (s), 167.1 (s), 160.2 (s), 156.3 (s), 134.1 (d), 130.5 (d), 130.2 (d), 128.8 (d), 126.3 (s), 124.8 (s), 115.6 (d), 113.7 (s, *C*≡N), 113.1 (s, *C*≡N), 66.4 [s, *C*(CN)$_2$], 55.5 (q, O*C*H$_3$); *m*/*z* (MALDI-TOF) 329 (MH$^+$+1, 24%), 328 (MH$^+$, 100), 252 (17), 210 (8), 153 (2).

*4.3.3 2-[5-Imino-2-phenyl-1-*p*-tolyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**13c**)*

Similar treatment of *N′*-(*p*-tolyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12c**) (31.1 mg, 0.1 mmol) gave the *title compound* ***13c*** (27.7 mg, 89%) as yellow needles, mp (DSC) onset 173.9 °C, peak max. 179.9 °C, decomp. onset 192.5 °C peak max. 202.7 °C (from *n*-pentane/THF, 90:10); (found: C, 73.16; H, 4.15; N, 22.33. $C_{19}H_{13}N_5$ requires C, 73.30; H, 4.21; N, 22.49%); R_f 0.57 (DCM); λ_{max}(DCM)/nm 237 (log ε 4.07), 267 (3.89), 327 (4.22), 445 (4.29); ν_{max}/cm^{-1} 3227m (NH), 3065w and 3042w (Ar CH), 2230w and 2214w (C≡N), 1651w, 1607w, 1591w, 1578w, 1518m, 1503w, 1466s, 1439m, 1418s, 1331s, 1318w, 1300w, 1277m, 1221m, 1194w, 1182w, 1159w,

1121m, 1082w, 1070w, 1034w, 979w, 947w, 905w, 885m, 820m, 785m, 760w; δ_H[500 MHz; $CDCl_3$/HCl (g)] NH resonance missing, 7.72 (2H, d, *J* 7.5, Ar *H*), 7.58 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.38-7.35 (4H, m, Ar *H*), 7.09 (2H, d, *J* 8.0, Ar *H*), 2.46 (3H, s, CH_3); δ_H(500 MHz; DMSO-d_6) 10.41 (1*H*, s, N*H*), 7.62 (1*H*, dd, *J* 7.5, 7.5, Ar *H*), 7.58 (2H, d, *J* 8.0, Ar *H*), 7.44 (2H, dd, *J* 8.0, 7.5, Ar *H*), 7.39 (2H, d, *J* 8.0, Ar *H*), 7.30 (2H, d, *J* 8.0, Ar *H*), 2.40 (3H, s, CH_3); δ_C(125 MHz; DMSO-d_6) 170.1 (s), 167.0 (s), 155.9 (s), 139.9 (s), 134.1 (d), 130.9 (d), 130.4 (d), 129.8 (s), 128.7 (d), 128.5 (d), 126.2 (s), 113.7 (s, *C*≡N), 113.0 (s, *C*≡N), 66.7 [s, $C(CN)_2$], 20.8 (q, *C*H_3); *m*/*z* (MALDI-TOF) 313 (MH^++1, 11%), 312 (MH^+, 100).

*4.3.4 2-[1-(4-Fluorophenyl)-5-imino-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]-malononitrile (**13d**)*

Similar treatment of *N′*-(4-fluorophenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12d**) (31.5 mg, 0.1 mmol) gave the *title compound* **13d** (28.0 mg, 89%) as yellow needles, mp (DSC) onset 192.7 °C, peak max. 197.6 °C, decomp. onset 201.1 °C peak max. 210.1 °C (from *n*-pentane/THF, 90:10); (found: C, 68.46; H, 3.33; N, 22.16. $C_{18}H_{10}FN_5$ requires C, 68.57; H, 3.20; N, 22.21%); R_f 0.50 (DCM); λ_{max}(DCM)/nm 238 (log ε 3.73), 265 (2.70), 331 (4.18), 440 (4.25); ν_{max}/cm^{-1} 3235m (NH), 3073w (Ar CH), 2232w and 2216w (C≡N), 1653w, 1609w, 1580w, 1512s, 1466s, 1445s, 1418s, 1331s, 1315w, 1300w, 1277m, 1236m, 1221s, 1194w, 1184w, 1167w, 1155w, 1121m, 1099w, 1080w, 1074w, 1032w, 1001w, 984m, 964w, 945w, 874m, 841m, 820w, 814w, 779m, 756w; δ_H[500 MHz; $CDCl_3$/HCl (g)] NH resonance missing, 7.69 (2H, d, *J* 8.0, Ar *H*), 7.60 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.39 (2H, dd, *J* 8.0, 8.0, Ar *H*), 7.27-7.21 (4H, m, Ar *H*); δ_H(500 MHz; DMSO-d_6) 11.02 (1H, s, N*H*), 8.05 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.98 (2H, d, *J* 8.0, Ar *H*), 7.94-97 (2H, m, Ar *H*), 7.89-7.84 (4H, m,

Ar *H*); δ_C(125 MHz; DMSO-d_6) 170.0 (s), 167.0 (s), 162.6 (s, $^1J_{CF}$ 245.0, *C*F), 155.6 (s), 134.1 (d), 131.4 (d, $^3J_{CF}$ 8.8, *C*HCHCF), 130.4 (d), 128.84 (s), 128.77 (d), 126.1 (s), 117.3 (d, $^2J_{CF}$ 23.8, *C*HCF), 113.6 (s, *C*≡N), 112.9 (s, *C*≡N), 66.7 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 317 (MH^++1, 13%), 316 (MH^+, 100), 252 (2), 198 (3), 105 (2).

*4.3.5 2-[1-(4-Chlorophenyl)-5-imino-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]-malononitrile (**13e**)*

Similar treatment of *N'*-(4-chlorophenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12e**) (33.2 mg, 0.1 mmol) gave the *title compound* **13e** (28.9 mg, 87%) as yellow needles, mp (DSC) onset 188.6 °C, peak max. 193.5 °C, decomp. onset 198.2 °C peak max. 201.5 °C (from *n*-pentane/THF, 50:50); (found: C, 65.16; H, 2.99; N, 20.94. $C_{18}H_{10}ClN_5$ requires C, 65.17; H, 3.04; N, 21.11%); R_f 0.55 (DCM); λ_{max}(DCM)/nm 230 (log ε 4.11), 267 (3.69), 332 (4.12), 440 (4.23); ν_{max}/cm^{-1} 3231m (NH), 3061w (Ar CH), 2230w and 2218w (C≡N), 1651w, 1609w, 1591w, 1578w, 1503m, 1495s, 1466s, 1443s, 1414s, 1329s, 1315w, 1302w, 1277m, 1223s, 1194w, 1182w, 1123m, 1094m, 1082w, 1074w, 1032w, 1020w, 980w, 947w, 878m, 835m, 822w, 781m, 754w; δ_H[500 MHz; $CDCl_3$/HCl (g)] NH resonance missing, 7.69 (2H, d, *J* 7.5, Ar *H*), 7.61 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.53 (2H, d, *J* 7.5, Ar *H*), 7.40 (2H, dd, *J* 8.0, 8.0, Ar *H*), 7.17 (2H, d, *J* 8.5, Ar *H*); δ_H(500 MHz; DMSO-d_6) 10.67 (1H, s, N*H*), 7.67-7.62 (3H, m, Ar *H*), 7.56 (2H, d, *J* 8.0, Ar *H*), 7.48-7.46 (4H, m, Ar *H*); δ_C(125 MHz; DMSO-d_6) 169.9 (s), 167.0 (s), 155.2 (s), 134.8 (s), 134.1 (d), 131.5 (s), 130.8 (d), 130.4 (d), 130.3 (d), 128.8 (d), 126.0 (s), 113.5 (s, *C*≡N), 112.9 (s, *C*≡N), 66.8 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 334 (MH^++2, 25%), 333 (MH^++1, 9), 332 (MH^+, 100), 214 (3), 153 (2).

*4.3.6 2-[1-(3,4-Dichlorophenyl)-5-imino-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]-malononitrile (**13f**)*

Similar treatment of *N′*-(3,4-dichlorophenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12f**) (36.6 mg, 0.1 mmol) gave the *title compound* **13f** (31.7 mg, 87%) as orange needles, mp (DSC) onset 114.5 °C, peak max. 115.5 °C (from *n*-pentane/THF, 50:50); (found: C, 50.51; H, 2.53; N, 15.51. $C_{18}H_9Cl_2N_5.CH_2Cl_2$ requires C, 50.58; H, 2.46; N, 15.52%); R_f 0.60 (DCM); λ_{max}(DCM)/nm 230 (log ε 4.11), 242 inf (4.00), 267 inf (3.68), 333 (4.12), 436 (4.24); ν_{max}/cm^{-1} 3316w (NH), 3096w and 3076w (Ar CH), 2224w (C≡N), 1647w, 1589w, 1578w, 1566w, 1497m, 1477s, 1464s, 1435s, 1414s, 1385m, 1335m, 1315w, 1298w, 1278m, 1271m, 1250w, 1234w, 1229w, 1219w, 1196w, 1182w, 1161w, 1134m, 1113w, 1101w, 1057m, 1036w, 1001w, 991w, 949w, 885w, 851m, 826m, 808w, 783m, 766m; δ_H[500 MHz; $CDCl_3$/HCl (g)] NH resonance missing, 7.71 (2H, d, *J* 7.0, Ar *H*), 7.64 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.60 (1H, br s, Ar *H*), 7.44 (2H, dd, *J* 8.0, 8.0, Ar *H*), 7.40 (1H, br s, Ar *H*), 7.06 (1H, dd, *J* 8.5, 2.0, Ar *H*); δ_H(500 MHz; DMSO-d_6) 10.87 (1H, s, N*H*), 7.87-7.85 (2H, m, Ar *H*), 7.65 (1H, dd, *J* 7.3, 7.3, Ar *H*), 7.59 (2H, d, *J* 7.5, Ar *H*), 7.49 (2H, dd, 7.8, 7.8, Ar *H*), 7.45 (1H, dd, *J* 8.5, 2.0, Ar *H*), 5.75 (2H, s, C*H*$_2$Cl$_2$); δ_C(125 MHz; DMSO-d_6) 169.7 (s), 166.8 (s), 154.7 (s), 134.2 (d), 133.1 (s), 132.6 (s), 132.5 (s), 132.1 (d), 131.2 (d), 130.3 (d), 129.5 (d), 128.9 (d), 125.9 (s), 113.4 (s, *C*≡N), 112.8 (s, *C*≡N), 67.0 [s, *C*(CN)$_2$], 54.8 (*C*H$_2$Cl$_2$); *m*/*z* (MALDI TOF) 370 (MH$^+$+4, 5%), 369 (MH$^+$+3, 11), 368 (MH$^+$+2, 52), 367 (MH$^+$+1, 16), 366 (MH$^+$, 100), 316 (16), 252 (4), 242 (7).

*4.3.7 2-[1-(4-Bromophenyl)-5-imino-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]-malononitrile (**13g**)*

Similar treatment of *N*′-(4-bromophenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12g**) (37.6 mg, 0.1 mmol) gave the *title compound* **13g** (32.0 mg, 85 %) as yellow needles, mp (DSC) onset 166.1 °C, peak max. 170.5 °C, decomp. onset 172.7 °C peak max. 173.0 °C (from *n*-pentane/THF, 90:10); (found: C, 57.31; H, 2.64; N, 18.55. $C_{18}H_{10}BrN_5$ requires C, 57.47; H, 2.68; N, 18.62%); R_f 0.56 (DCM); λ_{max}(DCM)/nm 232 (log ε 4.27), 267 inf (3.81), 332 (4.17), 440 (4.28); ν_{max}/cm^{-1} 3233m (NH), 3063w (Ar CH), 2228w and 2218w (C≡N), 1649w, 1607w, 1591w, 1578w, 1493s, 1466s, 1439s, 1414s, 1404s, 1329s, 1314m, 1300m, 1277m, 1223m, 1192w, 1180m, 1121m, 1103w, 1080w, 1069w, 1032w, 1016w, 980w, 947w, 878m, 833m, 822w, 783m, 760w; δ_H[500 MHz; $CDCl_3$/HCl (g)] NH resonance missing, 7.69 (4H, d, *J* 7.5, Ar *H*), 7.61 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.41 (2H, dd, 8.0, 8.0, Ar *H*), 7.10 (2H, d, *J* 8.0, Ar *H*); δ_H(500 MHz; DMSO-d_6) 10.67 (1H, s, N*H*), 7.80 (2H, d, *J* 8.0, Ar *H*), 7.68 (1H, dd, *J* 7.0, 7.0, Ar *H*), 7.56 (2H, d, *J* 7.5, Ar *H*), 7.47 (2H, dd, *J* 7.5, 7.5, Ar *H*), 7.39 (2H, d, *J* 8.5, Ar *H*); δ_C(125 MHz; DMSO-d_6) 170.0 (s), 167.0 (s), 155.2 (s), 134.1 (d), 133.4 (d), 132.0 (s), 131.1 (d), 130.4 (d), 128.9 (d), 126.1 (s), 123.6 (s), 113.6 (s, *C*≡N), 113.0 (s, *C*≡N), 66.8 [s, *C*(CN)$_2$]; *m*/*z* (MALDI TOF) 379 (MH$^+$+3, 13%), 378 (MH$^+$+2, 90), 377 (MH$^+$+1, 8), 376 (MH$^+$, 100), 260 (12), 252 (18).

*4.3.8 2-[1-(4-Iodophenyl)-5-imino-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malono-nitrile (**13h**)*

Similar treatment of *N*′-(4-Iodophenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12h**) (42.3 mg, 0.1 mmol) gave the *title compound* **13h** (35.6 mg, 84%) as orange plates, mp (DSC) onset 172 °C, peak max. 176 °C, onset 185 °C decomp. 207 °C (from *n*-

pentane/THF, 90:10); (found: C, 50.92; H, 2.34; N, 16.49. $C_{18}H_{10}IN_5$ requires C, 51.08; H, 2.38; N, 16.55%); R_f 0.59 (DCM); λ_{max}(DCM)/nm 243 (log ε 4.65), 324 (4.43), 441 (4.54); ν_{max}/cm^{-1} 3316w (NH), 3084w and 3032w (Ar CH), 2222w (C≡N), 1641w, 1607w, 1589w, 1576w, 1501m, 1491m, 1468s, 1441s, 1416s, 1398m, 1335m, 1312w, 1298w, 1267m, 1244w, 1225w, 1196w, 1180w, 1161w, 1130m, 1103w, 1067m, 1055w, 1028w, 1011w, 1001w, 989w, 979w, 941w, 831m, 824m, 783w, 764m; δ_H[500 MHz; $CDCl_3$/HCl (g)] NH resonance missing, 7.88 (2H, d, *J* 8.5, Ar *H*), 7.70 (2H, d, *J* 7.5, Ar *H*), 7.61 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.41 (2H, dd, *J* 8.0, 8.0, Ar *H*), 6.96 (2H, d, *J* 8.5, Ar *H*); δ_H(500 MHz; DMSO-d_6) 10.66 (1H, s, N*H*), 7.95 (2H, d, *J* 8.5, Ar *H*), 7.63 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.56 (2H, d, *J* 7.5, Ar *H*), 7.47 (2H, dd, *J* 7.8, 7.8, Ar *H*), 7.22 (2H, d, *J* 8.5, Ar *H*); δ_C(125 MHz; DMSO-d_6) 169.9 (s), 167.0 (s), 155.1 (s), 139.2 (d), 134.1 (d), 131.9 (s), 130.9 (d), 130.3 (d), 128.8 (d), 126.1 (s), 113.6 (s, *C*≡N), 112.9 (s, *C*≡N), 97.2 (s), 66.8 [s, *C*$(CN)_2$]; *m*/*z* (MALDI TOF) 425 (MH^++1, 15%), 424 (MH^+, 100), 153 (4).

*4.3.9 2-[5-Imino-1-(4-nitrophenyl)-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malono-nitrile (**13i**)*

Similar treatment of *N′*-(4-nitrophenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12i**) (34.2 mg, 0.1 mmol) gave the *title compound* **13i** (31.5 mg, 92%) as yellow plates, mp (DSC) onset 209 °C, peak max. 214 °C, decomp. onset 219.4 °C, peak max. 224.2 °C (from *n*-pentane/DCE, 90:10); (found: C, 63.03; H, 2.99; N, 24.51. $C_{18}H_{10}N_6O_2$ requires C, 63.16; H, 2.94; N, 24.55%); R_f 0.35 (DCM); λ_{max}(DCM)/nm 229 (log ε 4.12), 264 (4.09), 325 (4.23), 433 (4.25); ν_{max}/cm^{-1} 3285w (NH), 3115w and 3084w (Ar CH), 2224w and 2216w (C≡N), 1663w, 1611w, 1591w, 1574w, 1520m, 1497m, 1468s, 1439m, 1416w, 1391m, 1348s, 1331w, 1315w, 1298w, 1275w, 1209m,

1186w, 1177w, 1113w, 1103w, 1061m, 1024w, 1013w, 1001w, 980w, 934w, 864m, 853m, 835m, 789m, 773w; δ_H[500 MHz; $CDCl_3$/HCl (g)] 8.43-8.37 (2H, m, Ar *H*), 7.69-7.61 (3H, m, Ar *H*), 7.46-7.43 (4H, m, Ar *H*); δ_H(500 MHz; DMSO-d_6) 10.80 (1H, s, N*H*), 8.43 (2H, d, *J* 8.0, Ar *H*), 7.70 (2H, d, *J* 8.5 Ar *H*), 7.64 (1H, dd, *J* 6.8, 6.8, Ar *H*), 7.55 (2H, d, *J* 6.5, Ar *H*), 7.46 (2H, dd, *J* 7.3, 7.3, Ar *H*); δ_C(125 MHz; DMSO-d_6) 169.8 (s), 166.9 (s), 154.4 (s), 147.9 (s), 138.4 (s), 134.1 (d), 130.44 (d), 130.38 (d), 129.1 (d), 128.9 (d), 125.8 (s), 125.5 (d), 113.4 (s, *C*≡N), 112.8 (s, *C*≡N), 66.9 [s, *C*$(CN)_2$]; *m*/*z* (MALDI TOF) 344 (MH^++1, 27%), 343 (MH^+, 100), 252 (90), 225 (18), 153 (8), 105 (53).

4.4 Conversion of *N*-Aryl-*N*-(1,2,2-tricyanovinyl)benzamidines into (*Z*)-2-[2-phenyl-4-(arylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitriles

*4.4.1 (Z)-2-[2-Phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (**14a**)*

A solution of *N*′-phenyl-*N*-(1,2,2-tricyanovinyl)benzamidine (**12a**) (29.7 mg, 0.1 mmol) in MeOH (1 mL) left to stir at *ca*. 65 °C for 1 h and chromatography of the residue (DCM/Et_2O, 95:05) gave the *title compound* **14a** (27.5 mg, 92%), as orange fibres, mp (DSC) decomp. onset 254.9 °C, peak max. 256.7 °C (from cyclohexane/DCE, 50:50); (found: C, 72.82; H, 3.54; N, 23.43. $C_{18}H_{11}N_5$ requires C, 72.72; H, 3.73; N, 23.56%); R_f 0.71 (DCM/Et_2O, 95:05); λ_{max}(pyridine)/nm 345 (4.28), 365 inf (4.16), 390 inf (3.96), 414 inf (3.88), 505 inf (4.05), 542 (4.28), 582 (4.30) λ_{max}(DCM)/nm 229 (log ε 4.10), 259 inf (4.01), 267 inf (4.04), 286 inf (4.12), 323 (4.26), 424 (4.28), 452 (4.26), 483 inf (4.17), 556 inf (3.17), 598 inf (3.03); λ_{max}(acetone)/nm 333 (log ε 4.27), 426 inf (4.20), 456 (4.24), 484 inf (4.18), 539 inf (3.67), 580 (3.58); λ_{max}(DMF)/nm 271 inf (log ε 4.30), 282 (4.33), 292 inf (4.32), 308

inf (4.24), 331 (4.28), 344 (4.31), 365 inf (4.21), 387 inf (4.00), 414 inf (3.86), 501 inf (4.06), 539 (4.33), 579 (4.37); λ_{max}(DMSO)/nm 272 inf (log ε 4.29), 283 (4.31), 293 inf (4.30), 308 inf (4.23), 332 inf (4.28), 346 (4.31), 365 inf (4.02), 389 inf (4.02), 415 inf (3.91), 503 inf (4.08), 538 (4.33), 578 (4.34); ν_{max}/cm^{-1} 3196w (NH), 3047w (Ar CH), 2230m and 2220w (C≡N), 1641m, 1601m, 1582m, 1570m, 1530s, 1491w, 1458m, 1418w, 1335w, 1319m, 1308m, 1294m, 1285s, 1225m, 1204m, 1180m, 1171m, 1155w, 1078w, 1065m, 1024w, 999w, 966m, 932w, 922m, 849m, 785m, 773s; δ_H(500 MHz; DMSO-d_6) 12.62 (1H, s, N*H*), 8.32 (2H, d, *J* 7.5, Ar *H*), 7.77 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.63 (2H, dd, *J* 7.8, 7.8, Ar *H*), 7.49 (2H, dd, *J* 7.5, 7.5, Ar *H*), 7.45 (2H, br s, Ar *H*), 7.31 (1H, d, *J* 7.3, Ar *H*); δ_C(125 MHz; DMSO-d_6) five carbon resonances missing possibly owing to prototautomerism 146.7 (s), 135.5 (d), 130.5 (d), 129.7 (d), 129.6 (d), 126.6 (s), 114.6 (s, *C*≡N), 114.1 (s, *C*≡N); *m/z* (EI) 297 (M$^+$, 100%), 296 (62), 271 (22), 194 (48), 180 (5), 167 (12), 135 (5), 118 (25), 104 (71), 103 (67), 91 (7), 77 (78), 63 (6), 51 (26); *m*/*z* (MALDI-TOF) 299 (MH$^+$+1, 17%), 298 (MH$^+$, 100%), 153 (1).

*4.4.2 (Z)-2-{4-[(4-Methoxyphenyl)imino]-2-phenyl-1*H*-imidazol-5(4*H*)ylidene}-malononitrile* (***14b***)

Similar treatment of *N′*-(4-methoxyphenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12b**) (32.7 mg, 0.1 mmol) gave the *title compound* **14b** (30.0 mg, 91%), as red fibres, mp (DSC) decomp. onset 258.5 °C, peak max. 260.3 °C (from cyclohexane/DCE, 50:50); (found: C, 69.72; H, 3.95; N, 21.30. $C_{19}H_{13}N_5O$ requires C, 69.71; H, 4.00; N, 21.39%); R_f 0.63 (DCM/Et_2O, 95:05); λ_{max}(DMF)/nm 281 inf (log ε 4.28), 290 (4.27), 300 (4.27), 341 inf (4.15), 403 (4.06), 427 (4.04), 481 inf (3.92), 503 inf (4.11), 540 (4.34), 583 (4.39); ν_{max}/cm^{-1} 3202w (NH), 2843w (CH_3), 2224m and 2212w (C≡N),

1641m, 1611w, 1599m, 1582m,1566s, 1520s, 1491m, 1454m, 1443w, 1427w, 1333w, 1312m, 1300m, 1290m, 1254s, 1242m, 1196w, 1182w, 1167m, 1159s, 1148s, 1061w, 1024s, 970w, 922s, 843s, 806w, 785m, 764w; δ_H(500 MHz; DMSO-d_6) 13.04 (1H, br s, N*H*), 8.32 (2H, d, *J* 7.5, Ar *H*), 7.76-7.73 (3H, m, Ar *H*), 7.62 (2H, dd, *J* 7.5, 7.5, Ar *H*), 7.06 (2H, d, *J* 8.5, Ar *H*), 3.83 (3H, s, OCH_3); δ_C(125 MHz; DMSO-d_6) five carbon resonances missing possibly owing to prototautomerism 159.7 (s), 139.1 (s), 134.4 (d), 129.5 (d), 129.0 (d), 126.2 (s), 114.6 (d), 114.2 (s, *C*≡N), 113.8 (s, *C*≡N), 55.4 (q, O*C*H$_3$); *m*/*z* (MALDI-TOF) 329 (MH^++1, 23%), 328 (MH^+, 100), 327 (M^+, 16).

*4.4.3 (Z)-2-[2-Phenyl-4-(*p*-tolylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (**14c**)*

Similar treatment of *N′*-(*p*-tolyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12c**) (31.1 mg, 0.1 mmol) gave the *title compound* **14c** (29.1 mg, 94%), as orange fibres, mp (DSC) decomp. onset 271.4 °C, peak max. 272.0 °C (from cyclohexane/DCE, 50:50); (found: C, 73.28; H, 4.17; N, 22.58. $C_{19}H_{13}N_5$ requires C, 73.30; H, 4.21; N, 22.49%); R_f 0.76 (DCM/Et_2O, 95:05); λ_{max}(DMF)/nm 275 inf (log ε 4.45), 286 (4.47), 295 inf (4.47), 311 inf (4.42), 338 (4.420), 369 inf (4.28), 394 (4.20), 420 (4.18), 469 inf (4.12), 504 (4.31), 538 (4.44), 581 (4.47); ν_{max}/cm^{-1} 3211w (NH), 3055w and 3030w (Ar CH), 2226m and 2216w (C≡N), 1643s, 1612m, 1601m, 1584s, 1572s, 1526s, 1489m, 1456s, 1416w, 1331w, 1312s, 1296s, 1284s, 1231m, 1194m, 1173s, 1101w, 1076w, 1061w, 1032w, 1014w, 1001w, 970w, 955w, 922m, 856w, 827s, 806w, 785s, 766w; δ_H(500 MHz; DMSO-d_6) 12.88 (1H, s, N*H*), 8.32 (2H, d, *J* 7.0, Ar *H*), 7.77 (1H, d, *J* 7.5, 7.5, Ar *H*), 7.63 (2H, dd, *J* 7.8, 7.8, Ar *H*), 7.45 (2H, br s, Ar *H*), 7.30 (2H, d, *J* 8.5, Ar *H*), 2.37 (3H, s, CH_3); δ_C(125 MHz; DMSO-d_6) six carbon resonances missing

possibly owing to prototautomerism 143.5 (s), 134.8 (d), 129.8 (d), 129.7 (d), 129.0 (d), 126.0 (s), 114.1 (s, *C*≡N), 113.5 (s, *C*≡N), 20.8 (q, *C*H_3); *m*/*z* (MALDI-TOF) 313 (MH^++1, 25%), 312 (MH^+, 100), 153 (2).

*4.4.4 (Z)-2-{4-[(4-Fluorophenyl)imino]-2-phenyl-1*H*-imidazol-5(4*H*)-ylidene}-malononitrile (**14d**)*

Similar treatment of *N'*-(4-fluorophenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12d**) (31.5 mg, 0.1 mmol) gave the *title compound* **14d** (27.8 mg, 88%) , as orange fibres, mp (DSC) onset 267.4 °C, peak max. 267.7 °C, decomp. onset 268.7 °C, peak max. 271.2 °C (from cyclohexane/DCE, 50:50); (found: C, 68.56; H, 3.27; N, 22.15. $C_{18}H_{10}FN_5$ requires C, 68.57; H, 3.20; N, 22.21%); R_f 0.65 (DCM/Et_2O, 95:05); λ_{max}(DMF)/nm 275 inf (log ε 4.44), 282 (4.46), 292 inf (4.44), 307 inf (4.37), 339 (4.40), 363 inf (4.33), 387 inf (4.18), 412 inf (4.09), 465 inf (3.96), 501 inf (4.19), 537 (4.41), 578 (4.47); ν_{max}/cm^{-1} 3229w (NH), 3053w (Ar CH), 2226m and 2210w (C≡N), 1647m, 1601m, 1570s, 1530s, 1487m, 1456m, 1414w, 1335w, 1314m, 1298m, 1287s, 1233s, 1213m, 1194m, 1167w, 1159m, 1146m, 1096w, 1061m, 1028w, 1010w, 1001w, 982w, 968w, 951m, 933w, 920m, 903w, 860w, 843s, 814m, 785m, 777m; δ_H(500 MHz; DMSO-d_6) 12.87 (1H, br s, N*H*), 8.32 (2H, d, *J* 7.5, Ar *H*), 7.78 (1H, dd, *J* 7.3, 7.3, Ar *H*), 7.64 (3H, dd, *J* 7.5, 7.5, Ar *H*), 7.52 (1H, br s, Ar *H*), 7.32 (2H, dd, *J* 8.5, 8.5, Ar *H*); δ_C(125 MHz; DMSO-d_6) five carbon resonances missing possibly owing to prototautomerism 163.3 (d, $^1J_{CF}$ 84.6, *C*F), 161.0 (d, $^2J_{CF}$ 246.3, *C*F), 142.5 (s), 134.9 (d), 129.8 (d), 129.0 (d), 125.9 (s), 116.0 (d, $^3J_{CF}$ 22.5, *C*HCF), 113.9 (s, *C*≡N), 113.4 (s, *C*≡N); *m*/*z* (MALDI-TOF) 317 (MH^++1, 27%), 316 (MH^+, 100), 153 (3).

*4.4.5 (Z)-2-{4-[(4-Chlorophenyl)imino]-2-phenyl-1*H*-imidazol-5(4*H*)-ylidene}-malononitrile (**14e**)*

Similar treatment of *N′*-(4-chlorophenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12e**) (33.2 mg, 0.1 mmol) gave the *title compound* **14e** (28.6 mg, 86%), as orange fibres, mp (DSC) onset 269.0 °C, peak max 269.5 °C, decomp. onset 270.1 °C, peak max. 271.9 °C (from cyclohexane/DCE, 50:50); (found: C, 65.24; H, 3.15; N, 21.01. $C_{18}H_{10}ClN_5$ requires C, 65.17; H, 3.04; N, 21.11%); R_f 0.71 (DCM/Et_2O, 95:05); λ_{max}(DMF)/nm 277 inf (log ε 4.43), 286 inf (4.46), 296 (4.46), 310 inf (4.42), 339 (4.42), 366 inf (4.32), 393 (4.18), 418 (4.12), 471 inf (4.01), 507 inf (4.23), 544 (4.43), 585 (4.46); ν_{max}/cm^{-1} 3208w (NH), 3048w (Ar CH), 2228m and 2218w (C≡N), 1641m, 1607m, 1595m, 1582m, 1568s, 1526s, 1493w, 1477m, 1456m, 1416w, 1312s, 1300s, 1290s, 1275w, 1236m, 1205w, 1190m, 1169m, 1092s, 1061w, 1030w, 1009m, 1001w, 972m, 955w, 922m, 839s, 802w, 785s, 756w; δ_H(500 MHz; DMSO-d_6) 12.69 (1H, br s, N*H*), 8.32 (2H, d, *J* 7.5, Ar *H*), 7.79 (1H, dd, *J* 7.3, 7.3, Ar *H*), 7.65 (2H, dd, *J* 7.8, 7.8, Ar *H*), 7.55 (2H, d, *J* 8.0, Ar *H*), 7.46 (2H, br s, Ar *H*); δ_C(125 MHz; DMSO-d_6) six carbon resonances missing possibly owing to prototautomerism 145.1 (s), 135.0 (d), 129.9 (d), 129.1 (d), 129.01 (d), 126.5 (s), 114.0 (s, *C*≡N), 113.4 (s, *C*≡N); *m*/*z* (MALDI-TOF) 335 (MH^++3, 7%), 334 (MH^++2, 39), 333 (MH^++1, 20), 332 (MH^+, 100).

*4.4.6 (Z)-2-{4-[(3,4-Dichlorophenyl)imino]-2-phenyl-1*H*-imidazol-5(4*H*)ylidene}-malononitrile (**14f**)*

Similar treatment of *N′*-(3,4-dichlorophenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12f**) (36.6 mg, 0.1 mmol) gave the *title compound* **14f** (32.9 mg, 90%), as red fibres, mp (DSC) onset 267.2 °C, peak max 269.1 °C, decomp. onset 270.5 °C, peak max.

274.8 °C (from cyclohexane/DCE, 50:50); (found: C, 59.19; H, 2.50; N, 19.20. $C_{18}H_9Cl_2N_5$ requires C, 59.04; H, 2.48; N, 19.12%); R_f 0.67 (DCM/Et_2O, 95:05); λ_{max}(DMF)/nm 285 inf (log ε 4.38), 296 (4.39), 310 (4.34), 348 (4.32), 369 inf (4.25), 393 (4.11), 419 inf (3.99), 476 inf (3.82), 510 inf (4.37), 548 (4.37), 591 (4.41); ν_{max}/cm^{-1} 3198w (NH), 3049w (Ar CH), 2234m and 2218w (C≡N), 1647m, 1605m, 1564s, 1528s, 1493m, 1454s, 1416w, 1383w, 1333w, 1312s, 1296s, 1271w, 1254w, 1219s, 1192m, 1161w, 1124m, 1063w, 1024s, 1001w, 970m, 924s, 901m, 891s, 829m, 816w, 779m; δ_H(500 MHz; DMSO-d_6) 12.72 (1H, br s, N*H*), 8.29 (3H, d, *J* 7.5, Ar *H*), 7.79 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.72 (1H, d, Ar *H*), 7.65 (2H, dd, *J* 7.5, 7.5, Ar *H*), 7.34 (2H, br s, Ar *H*); δ_C(125 MHz; DMSO-d_6) seven peaks missing possibly owing to prototautomerism 171.7 (s), 146.4 (s), 135.2 (d), 131.5 (s), 131.0 (d), 129.9 (d), 129.1 (d), 126.0 (s), 113.8 (s, *C*≡N), 113.2 (s, *C*≡N); *m*/*z* (MALDI-TOF) 370 (MH^++4, 1%), 369 (MH^++3, 1), 368 (MH^++2, 12), 367 (MH^++1, 3), 366 (MH^+, 23), 271 (2), 153 (100).

*4.4.7 (Z)-2-{4-[(4-Bromophenyl)imino]-2-phenyl-1*H*-imidazol-5(4*H*)-ylidene}malononitrile (**14g**)*

Similar treatment of *N*′-(4-bromophenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12g**) (37.6 mg, 0.1 mmol) gave the *title compound* **14g** (32.8 mg, 87%), as orange fibres, mp (DSC) onset 278.1 °C, peak max 278.4 °C, decomp. onset 279.0 °C, peak max. 281.7 °C (from cyclohexane/DCE, 50:50); (found: C, 57.40; H, 2.73; N, 18.75. $C_{18}H_{10}BrN_5$ requires C, 57.47; H, 2.68; N, 18.62%); R_f 0.72 (DCM/Et_2O, 95:05); λ_{max}(DMF)/nm 287 inf (log ε 4.39), 296 (4.40), 310 (4.35), 347 (4.34), 366 inf (4.26), 394 inf (4.10), 417 inf (3.98), 476 inf (3.80), 508 inf (4.15), 545 (4.41), 586 (4.44); ν_{max}/cm^{-1} 3208w (NH), 3044w (Ar CH), 2228m and 2218w (C≡N), 1643m, 1605m,

1593m, 1581w, 1566s, 1526s, 1493w, 1474m, 1456m, 1416w, 1312s, 1300s, 1290s, 1271w, 1234m, 1200w, 1169s, 1028w, 1007m, 970w, 922m, 835s, 785s, 756w; δ_H(500 MHz; DMSO-d_6) 12.68 (1H, br s, N*H*), 8.31 (2H, d, *J* 7.5 Ar *H*), 7.78 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.68-7.63 (4H, m, Ar *H*), 7.35 (2H, br s, Ar *H*); δ_C(125 MHz; DMSO-d_6) six carbon resonances missing possibly owing to prototautomerism 145.5 (s), 135.1 (d), 132.1 (d), 129.9 (d), 129.1 (d), 126.0 (s), 113.9 (s, *C*≡N), 113.4 (s, *C*≡N); *m*/*z* (MALDI-TOF) 379 (MH^++3, 9%), 378 (MH^++2, 58), 377 (MH^++1, 10), 376 (MH^+, 100), 260 (47), 258 (90), 153 (30), 105 (17).

*4.4.8 (Z)-2-{4-[(4-Iodophenyl)imino]-2-phenyl-1*H*-imidazol-5(4*H*)-ylidene}-malononitrile (**14h**)*

Similar treatment of *N′*-(4-iodophenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12h**) (37.6 mg, 0.1 mmol) gave the *title compound* **14h** (35.9 mg, 85%), as orange fibres, mp (DSC) onset 281.4 °C, peak max 282.5 °C, decomp. onset 283.2 °C, peak max. 284.8 °C (from cyclohexane/DCE, 50:50); (found: C, 51.17; H, 2.46; N, 16.46. $C_{18}H_{10}IN_5$ requires C, 51.08; H, 2.38; N, 16.55%); R_f 0.74 (DCM/Et_2O, 95:05); λ_{max}(DMF)/nm 290 (log ε 4.39), 312 (3.35), 344 (4.33), 395 inf (4.07), 421 inf (3.95), 482 inf (3.80), 509 inf (4.12), 546 (4.39), 587 (4.42); ν_{max}/cm^{-1} 3202w (NH), 3046w (Ar CH), 2230m and 2220w (C≡N), 1643m, 1607m, 1593m, 1582w, 1562s, 1526s, 1493m, 1474m, 1455s, 1416w, 1335w, 1312s, 1300s, 1290s, 1269w, 1234m, 1221w, 1200m, 1171m, 1055m, 1028w, 1003s, 970m, 920m, 849w, 831s, 800w, 787s; δ_H(500 MHz; DMSO-d_6) 12.59 (1H, br s, N*H*), 8.31 (2H, d, *J* 7.5, Ar *H*), 7.83 (2H, d, *J* 8.5, Ar *H*), 7.78 (2H, dd, *J* 7.5, 7.5, Ar *H*), 7.64 (2H, dd, *J* 7.8, 7.8, Ar *H*), 7.20 (2H, br s, Ar *H*); δ_C(125 MHz; DMSO-d_6) six carbon resonances missing possibly owing to prototautomerism 145.9 (s), 137.9 (d), 135.1 (d), 129.9 (d), 129.1 (d), 125.9 (s), 113.9

(s, *C*≡N), 113.4 (s, *C*≡N), *m*/*z* (MALDI-TOF) 426 (MH^++2, 3%), 425 (MH^++1, 18), 424 (MH^+, 100), 252 (3).

*4.4.9 (Z)-2-{4-[(4-Nitrophenyl)imino]-2-phenyl-1*H*-imidazol-5(4*H*)-ylidene}-malononitrile (**14i**)*

Similar treatment of *N*′-(4-nitrophenyl)-*N*-(1,2,2-tricyanovinyl)benzamidine (**12i**) (34.2 mg, 0.1 mmol) gave the *title compound* **14i** (31.9 mg, 93%), as red fibres, mp (DSC) onset 299.3 °C, peak max 299.9 °C, decomp. onset 300.5 °C, peak max. 303.4 °C (from *n*-pentane/DCE, 50:50); (found: C, 63.26; H, 3.04; N, 24.54. $C_{18}H_{10}N_6O_2$ requires C, 63.16; H, 2.94; N, 24.55%); R_f 0.40 (DCM/Et_2O, 95:05); λ_{max}(DMF)/nm 353 (log ε 4.92), 524 inf (4.27), 567 (4.50), 612 (4.44); ν_{max}/cm^{-1} 3244w (NH), 3103w (Ar CH), 2232w and 2222w (C≡N), 1649w, 1609w, 1599w, 1589w, 1535s, 1514m, 1493w, 1481w, 1456m, 1414w, 1344s, 1333m, 1319m, 1298m, 1288s, 1236w, 1202w, 1188w, 1157w, 1107w, 1061w, 1026w, 1001w, 972w, 922w, 862s, 835w, 800w, 785w, 762w; δ_H(500 MHz; DMSO-d_6) 12.56 (1H, br s, N*H*), 8.33 (2H, d, *J* 8.5, Ar *H*), 8.29 (2H, d, *J* 7.5, Ar *H*), 7.79 (1H, dd, *J* 7.0, 7.0, Ar H), 7.64 (2H, dd, *J* 7.0, 7.0, Ar H), 7.47 (2H, br s, Ar *H*); δ_C(125 MHz; DMSO-d_6) five carbon resonances missing possibly owing to prototautomerism 152.8 (s), 144.7 (s), 135.4 (d), 130.0 (d), 129.2 (d), 125.9 (s), 124.9 (d), 113.7 (s, *C*≡N), 113.2 (s, *C*≡N), 67.0 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 344 (MH^++1, 16%), 343 (MH^+, 52), 226 (6), 172 (6), 153 (100), 116 (5).

4.5 Methylation of (*Z*)-2-[2-Phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (14a)

To a stirred solution of (*Z*)-2-[2-phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (**14a**) (29.7 mg, 0.1 mmol) in dry THF (1 mL) at *ca.* 20 °C was added NaH (4.8 mg, 0.2 mmol) and dimethyl sulfate (19 μL, 0.2 mmol). The mixture was heated at *ca*. 66 °C for 3 h and then allowed to cool to *ca.* 20 °C. Removal of the volatiles followed by chromatography (DCM/*n*-hexane, 70:30) of the residue gave *(Z)-2-[1-methyl-2-phenyl-4-(phenylimino)-1*H-*imidazol-5(4*H*)-ylidene]malononitrile* (**16**) (27.3 mg, 88%) as orange needles, mp (DSC) onset 216.1 °C, peak max. 216.8 °C, decomp. onset 241.8 °C, peak max. 259.1 °C (from cyclohexane/DCE, 80:20); (found: C, 73.17; H, 4.22; N, 22.36. $C_{19}H_{13}N_5$ requires C, 73.30; H, 4.21; N, 22.49%); R_f 0.47 (DCM/*n*-hexane, 70:30); λ_{max}(pyridine)/nm 325 (log ε 4.10), 404 inf (3.90), 431 inf (4.06), 461 (4.20), 488 (4.21); λ_{max}(DCM)/nm 281 (log ε 4.18), 319 (4.11), 401 inf (3.99), 427 (4.14), 457 (4.27), 483 (4.28); λ_{max}(acetone)/nm 332 (log ε 4.06), 401 inf (3.96), 427 inf (4.14), 454 (4.27), 480 (4.21); λ_{max}(DMF)/nm 277 (log ε 4.14), 322 (4.12), 404 inf (3.95), 431 inf (4.13), 460 (4.27), 485 (4.26); λ_{max}(DMSO)/nm 278 (log ε 4.13), 327 (4.11), 405 inf (3.92), 433 inf (4.09), 463 (4.22), 490 (4.22), 580 (2.94);; ; ν_{max}/cm^{-1} 3074w (Ar CH), 2949w (CH_3), 2218w (C≡N), 1636w, 1595m, 1580w, 1570m, 1524s, 1489m, 1460w, 1445m, 1437w, 1369w, 1325s, 1306s, 1290m, 1232m, 1198w, 1182m, 1161w, 1074w, 1061s, 1041w, 1024w, 1001w, 966w, 932w, 924w, 866w, 847m, 841m, 812w, 779s, 771s; δ_H(500 MHz; DMSO-d_6) 7.86 (2H, d, *J* 7.5, Ar *H*), 7.75-7.70 (3H, m, Ar *H*), 7.65 (2H, dd, *J* 7.8, 7.8, Ar *H*), 7.48 (2H, dd, *J* 7.8, 7.8, Ar *H*), 7.34 (1H, dd, *J* 7.3, 7.3, Ar *H*), 3.65 (3H, s, C*H*$_3$); δ_C(125 MHz; DMSO-d_6) 171.4 (s), 158.5 (s), 156.6 (s), 145.5 (s), 132.9 (d), 129.7 (d), 129.0 (d), 128.9 (d), 128.5 (d), 126.2 (d), 126.1 (s), 113.9 (s, *C*≡N),

113.5 (s, *C*≡N), 58.1 [s, *C*(CN)$_2$], 34.5 (q, *C*H$_3$); *m*/*z* (MALDI-TOF) 312 (MH$^+$, 7%), 153 (100). Further elution (DCM) gave *(Z)-2-[1-methyl-2-phenyl-5-(phenylimino)-1*H*-imidazol-4(5*H*)-ylidene]malononitrile* (**17**) (0.8 mg, 2%) as orange plates, mp (DSC) decomp. onset 213.2 ^{o}C, peak max. 215.4 ^{o}C (from *n*-pentane/DCM, 80:20); (found: C, 73.13; H, 4.16; N, 22.21. $C_{19}H_{13}N_5$ requires C, 73.30; H, 4.21; N, 22.49%); R_f 0.52 (DCM); λ_{max}(pyridine)/nm 332 (log ε 4.12), 445 (4.10), 488 inf (4.06), 527 inf (3.83); λ_{max}(DCM)/nm 230 (log ε 4.23), 267 (4.05), 322 (4.26), 336 inf (4.16), 436 (4.19), 496 inf (4.01); λ_{max}(acetone)/nm 333 (log ε 4.13), 447 (4.18), 482 inf (4.11); λ_{max}(DMF)/nm 267 (log ε 4.22), 324 (4.24), 340 inf (4.14), 449 (4.12), 486 inf (4.06); λ_{max}(DMSO)/nm 268 (log ε 4.16), 327 (4.24), 451 (4.00), 500 inf (3.99), 535 inf (3.89), 580 (3.68); ν_{max}/cm^{-1} 3082w and 3061w (Ar CH), 2830w (CH$_3$), 2218w (C≡N), 1659w, 1649w, 1607w, 1589w, 1576w, 1506m, 1470s, 1437s, 1387s, 1339m, 1296w, 1229m, 1196w, 1180w, 1097w, 1070w, 1051m, 1022w, 999w, 937w, 922m, 843m, 804w, 783w, 756m; δ_H(500 MHz; $CDCl_3$) 7.89 (2H, d, *J* 7.7, Ar *H*), 7.68 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.57 (2H, dd, *J* 7.8, 7.8, Ar *H*), 7.41 (2H, dd, *J* 8.0, 8.0, Ar *H*), 7.21 (1H, dd, *J* 7.3, 7.3, Ar *H*), 7.06 (1H, d, *J* 7.8, Ar *H*), 3.03 (3H, s, C*H*$_3$); δ_C(125 MHz; $CDCl_3$) one quaternary C (s) resonance missing 174.5 (s), 147.5 (s), 145.2 (s), 134.2 (d), 130.2 (d), 129.3 (d), 129.1 (d), 126.4 (s), 126.0 (d), 120.7 (d), 113.0 (s, *C*≡N), 112.5 (s, *C*≡N), 71.8 [s, *C*(CN)$_2$], 35.9 (q, *C*H$_3$); *m*/*z* (MALDI-TOF) 312 (MH$^+$, 22%), 290 (12), 289 (100), 205 (19), 178 (11), 118 (7).

4.6 Dimroth rearrangement of 2-[1-aryl-5-imino-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (13a) into (*Z*)-2-[4-(arylimino)-2-phenyl-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (14a)

*4.6.1 (Z)-2-[2-Phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (14a)* (Typical procedures, see Table 3)

Method A: A stirred solution of 2-[5-imino-1,2-diphenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**13a**) (1 g, 3.37 mmol) in MeOH (15 mL) was heated at *ca*. 67 ^{o}C for 1 h and then allowed to cool to *ca.* 20 ^{o}C. Addition of H_2O (30 mL) and filtration of the precipitate, gave the title compound **14a** (989.5 mg, 99%), as orange fibres, mp (DSC) onset 254.9 ^{o}C, decomp. 256.7 ^{o}C (from cyclohexane/DCE, 50:50), identical to that described above.

Method B*:* To a stirred solution of 2-[5-imino-1,2-diphenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**13a**) (1 g, 3.37 mmol) in dry DCM (15 mL) at *ca*. 20 ^{o}C, DBU (502 μL, 3.37 mmol) was added. The reaction mixture was then heated at *ca*. 40 ^{o}C for 4 h, protected from moisture with $CaCl_2$ drying tube. The reaction mixture was then extracted (5% HCl), washed (H_2O) and the organic fraction dried (Na_2SO_4). Removal of the volatiles followed by addition of MeOH (10 mL), H_2O (30 mL), and filtration of the precipitant, gave the title compound **14a** (912.4 mg, 91%) as orange fibres, mp (DSC) onset 254.9 ^{o}C, decomp. 256.7 ^{o}C (from cyclohexane/DCE, 50:50), identical to that described above.

4.7 Thermal behavior of 2-[5-imino-1,2-diphenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (13a)

Heating 2-[5-imino-1,2-diphenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**13**) at *ca*. 220 °C (Wood's metal bath) for 20 min under Ar atmosphere followed by chromatography (DCM) gave *2-phenyl-6-(phenylamino)pyrimidine-4,5-dicarbonitrile* (**22**) (3.4 mg, 11%) as yellow fibres, mp (DSC) onset 237.4 °C, peak max. 238.3 °C (from cyclohexane/DCE, 80:20); (found: C, 72.85; H, 3.67; N, 23.39. $C_{18}H_{11}N_5$ requires C, 72.72; H, 3.73; N, 23.56%); R_f 0.42 (DCM); λ_{max}(DCM)/nm 273 inf (log ε 4.59), 292 (4.64), 363 inf (3.76); ν_{max}/cm^{-1} 3298w (NH), 3163w, 3127w, 3065w (Ar CH), 2226w (C≡N), 1611m, 1574m, 1555s, 1495w, 1481w, 1460w, 1429m, 1385m, 1350w, 1290w, 1244w, 1196w, 1173w, 1155w, 1092w, 1070w, 1036w, 1028w, 1018w, 1001w, 937w, 908w, 841w, 806w, 766m; δ_H(500 MHz; $CDCl_3$), 8.37 (2H, d, *J* 7.5, Ar *H*), 7.65 (2H, d, *J* 8.0, Ar *H*), 7.58 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.50 (4H, dd, *J* 7.8, 7.8, Ar *H*), 7.45 (1H, br s, N*H*), 7.33 (1H, dd, *J* 7.5, 7.5, Ar *H*); δ_C(125 MHz; $CDCl_3$) 166.7 (s), 159.5 (s), 144.4 (s), 135.8 (s), 134.9 (s), 133.2 (d), 129.5 (d), 129.3 (d), 128.9 (d), 126.5 (d), 122.5 (d), 113.6 (*C*≡N), 112.5 (*C*≡N), 93.3 (s); *m*/*z* (MALDI-TOF) 299 (MH^++1, 21%), 298 (MH^+, 100%). Further elution (DCM/Et_2O, 95:05) gave (*Z*)-2-[2-phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (**14a**) (10.1 mg, 34%) as orange fibres, mp (DSC) decomp. onset 254.9 °C, peak. 256.7 °C (from cyclohexane/DCE, 50:50), identical to that described above, followed by traces of 2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15a**) as colorless fibres, mp (DSC) decomp. onset 304.7 °C, peak max. 305.1 °C (from cyclohexane/DCE, 50:50); identical to that described above.

4.8 Thermal behavior of (*Z*)-2-[2-phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylid-ene]malononitrile (14a)

*4.8.1 2-Phenyl-1*H-*imidazo[4,5-*b*]quinoline-9-carbonitrile (**15a**) (Typical procedure, see Table 4).*

An intimate mixture of (*Z*)-2-[2-phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (**14a**) (14.6 mg, 0.05 mmol) and diphenyl ether (1 mL) was heated at *ca*. 280 °C for 4 h. Chromatography (*n*-hexane/DCM, 50:50) of the reaction mixture gave recovered diphenyl ether (1 mL) and further elution (DCM/Et_2O, 90:10) gave the *title compound* **15a** (13.4 mg, 100%) as colorless fibres, mp (DSC) decomp. onset 304.7 °C, peak max. 305.1 °C; (from *n*-pentane/THF, 90:10); (found: C, 75.53; H, 3.62; N, 20.80. $C_{17}H_{10}N_4$ requires C, 75.54; H, 3.73; N, 20.73%); R_f 0.23 (DCM/Et_2O, 90:10); λ_{max}(EtOH)/nm 216 (log ε 4.77), 265 (4.68), 281 inf (4.39), 371 (4.71); ν_{max}/cm^{-1} 3073br&w and 3015br&w (Ar CH & NH), 2887w, 2710w, 2230w (C≡N), 1628m, 1616w, 1593w, 1526m, 1514w, 1481m, 1472m, 1460s, 1402s, 1333s, 1288m, 1240m, 1186w, 1163m, 1138w, 1072w, 1028w, 1001w, 939m, 928w, 880w, 862w, 843w, 787s, 762s; δ_H(500 MHz; TFA-*d*) N*H* deuterium exchanged, 8.42 (1H, d, *J* 8.5, Ar *H*), 8.22-8.20 (3H, m, Ar *H*), 8.11 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.97 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.78 (1H, dd, *J* 7.5, 7.5 Ar *H*), 7.63 (2H, dd, *J* 8.0, 8.0 Ar *H*); δ_C(125 MHz; TFA-*d*) 166.6 (s), 150.9 (s), 139.6 (s), 139.3 (d), 137.4 (d), 132.9 (d), 132.50 (d), 132.46 (s), 131.4 (d), 127.9 (d), 126.2 (s), 124.5 (s), 124.2 (d), 112.6 (s, *C*≡N), 109.2 (s); *m*/*z* (MALDI-TOF) 272 (MH^++1, 18%), 271 (MH^+, 100), 270 (M^+, 15).

*4.8.2 7-Methoxy-2-phenyl-1*H-*imidazo[4,5-*b*]quinoline-9-carbonitrile (**15b**)*

Similar treatment of (*Z*)-2-[4-(4-methoxyphenylimino)-2-phenyl-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (**14b**) (16.4 mg, 0.05 mmol) gave the *title compound* **15b** (14.9

mg, 99%) as pale yellow plates, mp (DSC) decomp. onset 309.3 °C, peak max. 309.5 °C; (from *n*-pentane/THF, 90:10); (found: C, 71.87; H, 3.97; N, 18.66. $C_{18}H_{12}N_4O$ requires C, 71.99; H, 4.03; N, 18.66%); R_f 0.23 (DCM/Et_2O, 90:10); λ_{max}(EtOH)/nm 226 (log ε 4.68), 253 inf (4.69), 271 (4.83), 372 (4.52), 402 inf (4.27); ν_{max}/cm^{-1} 3069br&w (Ar CH & NH), 2963w, 2920w and 2855w (CH_3), 2224w (C≡N), 1630m, 1601w, 1514m, 1472m, 1460s, 1433w, 1402w, 1336s, 1288w, 1261m, 1242s, 1211m, 1179m, 1148w, 1128w, 1070w, 1041m, 1028w, 997w, 986w, 939m, 849w, 822m, 804w, 783w, 766w; δ_H(500 MHz; TFA-*d*) N*H* deuterium exchanged, 8.27 (2H, d, *J* 8.0 Ar *H*), 8.19 (1H, d, *J* 9.5 Ar *H*), 7.89-7.84 (2H, m, Ar *H*), 7.76-7.72 (3H, m, Ar *H*), 4.11 (3H, s, C*H*$_3$); δ_C(125 MHz; TFA-*d*) one quaternary C (s) resonance missing 163.7 (s), 162.8 (s), 146.7 (s), 138.7 (d), 137.5 (s), 132.1 (d), 130.8 (s), 130.58 (d), 130.56 (d), 129.0 (s), 126.5 (d), 123.3 (s), 105.6 (s), 104.3 (d), 57.2 (q); *m*/*z* (MALDI-TOF) 302 (MH^++1, 12%), 301 (MH^+, 100), 300 (M^+, 37), 242 (16), 153 (34).

*4.8.3 7-Methyl-2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15c**)*

Similar treatment of (*Z*)-2-[2-phenyl-4-(*p*-tolylimino)-1*H*-imidazol-5(4*H*)-ylidene]-malononitrile (**14c**) (15.6 mg, 0.05 mmol) gave the *title compound* **15c** (14.8 mg, 99%) as pale yellow plates, mp (DSC) decomp. onset 322.8 °C, peak 323.8 °C; (from *n*-pentane/THF, 90:10); (found: C, 75.94; H, 4.26; N, 19.68. $C_{18}H_{12}N_4$ requires C, 76.04; H, 4.25; N, 19.71%); R_f 0.26 (DCM/Et_2O, 90:10); λ_{max}(EtOH)/nm 220 (log ε 4.68), 267 (4.58), 282 inf (4.30), 369 (4.60); ν_{max}/cm^{-1} 3063br&w and 3028br&w (Ar CH & NH), 2967w, 2912w, 2758w, 2224w (C≡N), 1632w, 1618w, 1591w, 1524w, 1514m, 1479s, 1460s, 1404m, 1396m, 1333s, 1288m, 1233m, 1213m, 1202w, 1184w, 1157w, 1148w, 1101w, 1069w, 1034w, 1022w, 974w, 934s, 893w, 868w, 826s,

808m, 779w, 768w; δ_H(500 MHz; TFA-*d*) N*H* deuterium exchanged, 8.23-8.20 (3H, m, Ar *H*), 8.14-8.09 (1H, m, Ar *H*), 8.01-7.96 (1H, m, Ar *H*), 7.80-7.6 (1H, m, Ar *H*), 7.66-7.63 (2H, m, Ar *H*), 2.64 (3H, t, *J* 9.0, C*H*$_3$); δ_C(125 MHz; TFA-*d*) 165.5 (s), 149.5 (s), 145.3 (s), 139.5 (d), 138.7 (d), 137.8 (s), 132.0 (d), 131.8 (s), 130.8 (d), 126.2 (s), 126.0 (d), 124.1 (s), 123.3 (d), 112.3 (s, *C*≡N), 107.8 (s), 21.8 (q); *m*/*z* (MALDI-TOF) 286 (MH^++1, 14%), 285 (MH^+, 100), 284 (M^+, 30).

*4.8.4 7-Fluoro-2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15d**)*

Similar treatment of (*Z*)-2-[5-(4-fluorophenylimino)-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**14d**) (15.8 mg, 0.05 mmol) gave the *title compound* **15d** (14.3 mg, 99%) as pale yellow plates, mp (DSC) decomp. onset 338.5 °C, peak max. 339.1 °C; (from *n*-pentane/THF, 90:10); (found: C, 70.82; H, 3.10; N, 19.38. $C_{17}H_9FN_4$ requires C, 70.83; H, 3.15; N, 19.43%); R_f 0.34 (DCM/Et_2O, 90:10); λ_{max}(EtOH)/nm 218 (log ε 4.76), 266 (4.62), 279 inf (4.38), 366 (4.69); ν_{max}/cm^{-1} 3067br&w and 3010br&w (Ar CH & NH), 2903w, 2228w (C≡N), 1637m, 1597w, 1524m, 1477m, 1458s, 1406s, 1398m, 1333s, 1302w, 1281w, 1236s, 1207w, 1188w, 1157w, 1128w, 1097w, 1088w, 1070w, 1038w, 1028w, 1007w, 974w, 939m, 852m, 824w, 818w, 783m; δ_H(500 MHz; TFA-*d*) N*H* deuterium exchanged, 8.28 (1H, dd, $^3J_{HH}$ 9.5, $^4J_{HF}$ 4.5, Ar *H*), 8.25 (2H, d, *J* 7.5, Ar *H*), 8.05 (1H, dd, $^3J_{HF}$ 7.8, $^4J_{HH}$ 2.3, Ar *H*), 7.89-7.84 (2H, m, Ar *H*), 7.71 (2H, dd, *J* 8.0, 8.0, Ar *H*); δ_C(125 MHz; TFA-*d*) 165.9 (s), 163.6 (s, $^1J_{CF}$ 232.5, *C*F), 148.1 (s), 139.4 (s), 139.3 (d), 132.2 (d), 130.8 (d), 130.6 (s), 128.9 (d, $^3J_{CF}$ 10.0, *C*HCHCF), 127.9 (s, $^3J_{CF}$ 10.0, *C*CHCF), 126.7 (d, $^2J_{CF}$ 27.5, *C*HCF), 122.6 (s), 112.1 (s, *C*≡N), 111.1 (d, $^2J_{CF}$ 25.0, *C*HCF), 106.5 (s, $^3J_{CF}$ 6.3, *C*CHCF); *m*/*z* (MALDI-TOF) 290 (MH^++1, 12%), 289 (MH^+, 100), 288 (M^+, 21), 153 (4).

*4.8.5 7-Chloro-2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15e**)*

Similar treatment of (*Z*)-2-[5-(4-chlorophenylimino)-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**14e**) (16.7 mg, 0.05 mmol) gave the *title compound* **15e** (15 mg, 98%) as pale yellow plates, mp (DSC) decomp. onset 356.4 °C, peak max. 357.8 °C; (from *n*-pentane/THF, 90:10); (found: C, 66.93; H, 2.98; N, 18.26. $C_{17}H_9ClN_4$ requires C, 67.00; H, 2.98; N, 18.39%); R_f 0.38 (DCM/Et_2O, 90:10); λ_{max}(EtOH)/nm 206 (log ε 4.55), 226 (4.82), 235 inf (4.78), 272 (4.79), 283 inf (4.68), 369 (4.79), 385 inf (4.62), 414 inf (4.21); ν_{max}/cm^{-1} 3194br&w, 3156br&w and 3069br&w (Ar CH & NH), 2903w, 2708w, 2241w (C≡N), 1628m, 1603w, 1589w, 1529m, 1499m, 1476s, 1458s, 1443w, 1406s, 1391s, 1333s, 1317m, 1294m, 1277w, 1231m, 1202m, 1188m, 1157w, 1134w, 1125w, 1082w, 1026w, 1003w, 980w, 949m, 935w, 878w, 864w, 829s, 785m; δ_H(500 MHz; TFA-*d*) N*H* deuterium exchanged, 8.44 (1H, d, *J* 1.5, Ar *H*), 8.29 (2H, d, *J* 7.5, Ar *H*), 8.22 (1H, d, *J* 9.0, Ar *H*), 8.07 (1H, dd, *J* 9.0, 2.0 Ar *H*), 7.89 (1H, dd, *J* 7.5, 7.5 Ar *H*), 7.74 (2H, dd, *J* 8.0, 8.0 Ar *H*); δ_C(125 MHz; TFA-*d*) 164.0 (s), 148.8 (s), 140.4 (s), 140.2 (s), 139.4 (d), 137.3 (d), 132.2 (d), 130.97 (s), 130.94 (d), 127.1 (d), 126.9 (s), 125.9 (d), 122.9 (s), 112.0 (s, *C*≡N), 106.4 (s); *m*/*z* (MALDI-TOF) 307 (MH^++2, 33%), 306 (MH^++1, 18), 305 (MH^+, 100), 304 (M^+, 11).

*4.8.6 6,7-Dichloro-2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15f**) and 7,8-dichloro-2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15g**)*

Similar treatment of (*Z*)-2-[5-(3,4-dichlorophenylimino)-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**14f**) (18.3 mg, 0.05 mmol) gave *6,7-dichloro-2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile* (**15f**) (14.2 mg, 84%) as colorless needles mp (DSC) decomp. onset 323.6 °C, peak max. 324.4 °C; (from *n*-pentane/THF,

90:10); (found: C, 60.09; H, 2.29; N, 16.46. $C_{17}H_8Cl_2N_4$ requires C, 60.20; H, 2.38; N, 16.52%); R_f 0.63 (DCM/Et_2O, 90:10); λ_{max}(EtOH)/nm 205 (log ε 4.59), 231 inf (4.79), 244 (4.85), 277 (4.87), 290 inf (5.02), 367 inf (4.76), 376 (4.79), 389 inf (4.62), 422 inf (4.18); ν_{max}/cm^{-1} 3096br&w (Ar CH & NH), 2978w, 2879w, 2228w (C≡N), 1628m, 1587w, 1528m, 1474m, 1460s, 1439w, 1408m, 1389s, 1335m, 1313w, 1288m, 1242m, 1223m, 1204m, 1183w, 1119m, 1101w, 1070w, 1047s, 1028w, 986m, 941m, 928w, 876s, 841w, 816w, 787m, 764w; δ_H(500 MHz; TFA-*d*) N*H* deuterium exchanged, 8.51 (1H, s, Ar *H*), 8.38 (1H, s, Ar *H*), 8.25 (2H, d, *J* 7.5, Ar *H*), 7.88 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.72 (2H, dd, *J* 8.0, 8.0, Ar *H*); δ_C(125 MHz; TFA-*d*) 161.2 (s), 146.7 (s), 140.7 (s), 140.0 (s), 137.8 (d), 137.4 (s), 130.5 (d), 129.1 (d), 128.0 (s), 125.8 (d), 125.5 (d), 123.6 (s), 120.4 (s), 110.1 (s, *C*≡N), 104.0 (s); *m*/*z* (MALDI-TOF) 343 (MH^++4, 3%), 342 (MH^++3, 7), 341 (MH^++2, 54), 340 (MH^++1, 13), 339 (MH^+, 100), 338 (12), 219 (56). Further elution (DCM/Et_2O, 90:10) gave *7,8-dichloro-2-phenyl-1*H-*imidazo[4,5*-b*]quinoline-9-carbonitrile* (**15g**) (2.1 mg, 12 %) as colorless plates mp (DSC) decomp. onset 358.3 °C, peak max. 362.1 °C; (from *n*-pentane/THF, 90:10); (found: C, 60.28; H, 2.42; N, 16.34. $C_{17}H_8Cl_2N_4$ requires C, 60.20; H, 2.38; N, 16.52%); R_f 0.50 (DCM/Et_2O, 90:10); λ_{max}(EtOH)/nm 209 (log ε 4.87), 225 inf (4.73), 277 (4.39), 365 (3.94), 378 (3.94); ν_{max}/cm^{-1} 3173br&w (Ar CH & NH), 2234w (C≡N), 1624w, 1609w, 1574w, 1526m, 1479s, 1456s, 1435w, 1393s, 1375s, 1317m, 1300m, 1285w, 1194s, 1153m, 1103w, 1049w, 1038w, 1024w, 1001w, 986w, 947w, 924m, 881w, 824s, 814s, 781m, 752w; δ_H(500 MHz; TFA-*d*) N*H* deuterium exchanged, 8.41 (2H, d, *J* 8.0, Ar *H*), 8.19 (1H, d, *J* 9.0, Ar *H*), 8.12 (1H, d, *J* 9.5, Ar .*H*), 7.95 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.78 (2H, dd, *J* 7.8, 7.8, Ar *H*); δ_C(125 MHz; TFA-*d*) one quaternary C (s) resonance missing 163.2 (s), 147.2 (s), 145.1 (s), 140.1 (d), 139.8 (s), 136.8 (d), 133.3 (s), 132.6 (d), 131.5 (d), 130.8 (s),

128.0 (d), 125.0 (s), 122.1 (s), 104.6 (s); *m*/*z* (MALDI-TOF) 343 (MH^++4, 3%), 342 (MH^++3, 5), 341 (MH^++2, 64), 340 (MH^++1, 24), 339 (MH^+, 100), 338 (12), 219 (13).

*4.8.7 7-Bromo-2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15h**)*

Similar treatment of (*Z*)-2-[5-(4-bromophenylimino)-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**14h**) (18.8 mg, 0.05 mmol) gave the *title compound* **15h** (17.1 mg, 98%) as colorless plates, mp (DSC) decomp. onset 337.6 °C, peak max. 338.6 °C; (from *n*-pentane/THF, 90:10); (found: C, 58.35; H, 2.67; N, 15.96. $C_{17}H_9BrN_4$ requires C, 58.47; H, 2.60; N, 16.05%); R_f 0.43 (DCM/Et_2O, 90:10); λ_{max}(EtOH)/nm 229 inf (log ε 4.73), 235 (4.74), 273 (4.75), 283 inf (4.64), 369 (4.77), 412 inf (3.94); ν_{max}/cm^{-1} 3069br&w (Ar CH & NH), 2878w, 2735w, 2222w (C≡N), 1628m, 1599w, 1589w, 1529m, 1495m, 1476s, 1464s, 1406s, 1393s, 1333s, 1296m, 1234m, 1202m, 1188m, 1165w, 1132w, 1126w, 1105w, 1070w, 1040s, 972w, 935m, 918w, 874s, 858m, 818s, 781m; δ_H(500 MHz; TFA-*d*) N*H* deuterium exchanged, 8.61 (1H, s, Ar *H*), 8.27 (2H, d, *J* 8.0, Ar *H*), 8.18 (1H, d, *J* 9.5, Ar *H*), 8.11 (1H, d, *J* 9.0, Ar *H*), 7.87 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.72 (2H, dd, *J* 7.8, 7.8, Ar *H*); δ_C(125 MHz; TFA-*d*) one quaternary C (s) resonance missing 162.7 (s), 148.9 (s), 140.4 (s), 139.9 (d), 139.3 (d), 132.2 (d), 130.94 (s), 130.89 (d), 129.3 (d), 127.7 (s), 127.1 (s), 126.7 (d), 122.9 (s), 112.0 (s, *C*≡N), 106.3 (s); *m*/*z* (MALDI-TOF) 351 (MH^++2, 49%), 350 (MH^++1, 14), 349 (MH^+, 100), 312 (25), 270 (30), 246 (8), 219 (37), 105 (6).

*4.8.8 7-Iodo-2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15i**)*

Similar treatment of (*Z*)-2-[5-(4-iodophenylimino)-2-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**14i**) (15.8 mg, 0.05 mmol) gave the *title compound* **15i** (14.3 mg,

99%) as pale colorless needles, mp (DSC) decomp. onset 342.2 °C, peak max. max. 342.8 °C; (from *n*-pentane/THF, 90:10); (found: C, 51.50; H, 2.23; N, 14.05. $C_{17}H_9IN_4$ requires C, 51.54; H, 2.29; N, 14.14%); R_f 0.30 (DCM/Et_2O, 90:10); λ_{max}(EtOH)/nm 207 (log ε 4.62), 227 (4.84), 249 inf (4.67), 272 (4.82), 285 inf (4.64), 374 (4.81), 386 (4.64); ν_{max}/cm^{-1} 3098br&w (Ar CH & NH), 2911w, 2737w, 2224w (C≡N), 1697m, 1630m, 1597w, 1528m, 1490m, 1477s, 1460s, 1404s, 1391s, 1333s, 1315m, 1294m, 1233m, 1204m, 1194w, 1136w, 1103w, 1067w, 1028w, 1001w, 966w, 937s, 872m, 824s, 785s, 760m; δ_H(500 MHz; TFA-*d*) N*H* deuterium exchanged, 8.92 (1H, s, Ar *H*), 8.44 (1H, d, *J* 9.0, Ar *H*), 8.34 (2H, d, *J* 8.0, Ar *H*), 8.03 (1H, d, *J* 9.0, Ar *H*), 7.95 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.79 (2H, dd, *J* 7.8, 7.8, Ar *H*); δ_C(125 MHz; TFA-*d*) 164.6 (s), 149.1 (s), 145.5 (d), 140.4 (s), 139.3 (d), 136.0 (d), 132.2 (d), 131.0 (s), 130.9 (d), 127.2 (s), 125.9 (d), 123.1 (s), 112.1 (s, *C*≡N), 106.2 (s), 98.1 (s); *m*/*z* (MALDI-TOF) 398 (MH^++1, 8%), 397 (MH^+, 100), 270 (63), 246 (3), 219 (43), 105 (4).

4.9 *N*-Methylation of 2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (15a)

To a stirred solution of 2-phenyl-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**15a**) (13.5 mg, 0.05 mmol) in dry THF (1 mL) at *ca.* 20 °C was added NaH (2.4 mg, 0.1 mmol) and dimethyl sulfate (9.5 μL, 0.1 mmol). The mixture was heated at *ca*. 66 °C for 26 h and then allowed to cool to *ca.* 20 °C. Removal of the volatiles followed by chromatography (DCM/Et_2O, 90:10) of the residue gave *3-methyl-2-phenyl-3*H-*imidazo[4,5-*b*]quinoline-9-carbonitrile* (**27**) (13.5 mg, 95%) as colorless needles, mp (DSC) onset 204.0 °C, peak max. 204.4 °C (from *n*-pentane/DCE, 70:30); (found: C, 75.90; H, 4.36; N, 19.69. $C_{18}H_{12}N_4$ requires C, 76.04; H, 4.25; N, 19.71%); R_f 0.68

(DCM/Et_2O, 90:10); λ_{max}(EtOH)/nm 217 (log ε 4.90), 263 (4.80), 357 (4.76); ν_{max}/cm^{-1} 3063w (Ar CH), 2995w, 2953w, 2922w and 2851w (CH_3), 2228w (C≡N), 1612w, 1584w, 1516w, 1484m, 1466s, 1447m, 1435m, 1396m, 1335s, 1286m, 1258w, 1232w, 1204w, 1182w, 1169m, 1157w, 1107w, 1076w, 1053w, 1022w, 945w, 930w, 860w, 849w, 795w, 779m, 764s; δ_H(500 MHz; TFA-*d*) 8.44 (1H, d, *J* 8.5, Ar *H*), 8.39 (1H, d, *J* 8.0, Ar *H*), 8.06 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.99-7.96 (3H, m, Ar *H*), 7.90 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.77 (2H, dd, *J* 8.0, 8.0, Ar *H*), 4.35 (3H, s, C*H*$_3$); δ_C(125 MHz; TFA-*d*) one quaternary C (s) resonance missing 158.6 (s), 146.6 (s), 144.4 (s), 136.1 (d), 132.9 (d), 131.1 (d), 130.4 (d), 129.7 (d), 129.5 (d), 125.8 (s), 124.6 (d), 123.6 (s), 120.1 (s), 102.5 (s), 31.4 (q, *C*H_3); *m*/*z* (MALDI-TOF) 286 (MH^++1, 11%), 285 (MH^+, 100), 284 (M^+, 93). Further elution (DCM/Et_2O, 90:10) gave *4-methyl-2-phenyl-4*H-*imidazo[4,5*-b*]quinoline-9-carbonitrile* (**28**) (1.1 mg, 1%) as yellow plates, mp (DSC) onset 254.9 °C, peak max. 255.6 °C (from *n*-pentane/DCE, 70:30); (found: C, 75.88; H, 4.29; N, 19.62. $C_{18}H_{12}N_4$ requires C, 76.04; H, 4.25; N, 19.71%); R_f 0.54 (DCM/Et_2O, 90:10); λ_{max}(EtOH)/nm 228 (log ε 4.71), 248 inf (4.42), 264 inf (4.31), 381 (4.67), 389 inf (4.59); ν_{max}/cm^{-1} 3069w (Ar CH), 2951w and 2922w (CH_3), 2222w (C≡N), 1624w, 1593m, 1578w, 1483m, 1454s, 1431s, 1412m, 1393w, 1369m, 1335m, 1308w, 1285m, 1256s, 1217m, 1171m, 1136w, 1105w, 1074m, 1066m, 1022w, 1011w, 935m, 856w, 797w, 760m; δ_H(500 MHz; TFA-*d*) 8.54 (1H, d, *J* 8.5, Ar *H*), 8.46 (2H, d, *J* 7.5, Ar *H*), 8.37 (1H, d, *J* 9.0, Ar *H*), 8.25 (1H, ddd, *J* 8.0, 8.0, 1.0, Ar *H*), 8.06 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.79 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.66 (2H, dd, *J* 7.8, 7.8 Ar *H*), 4.85 (3H, s, C*H*$_3$); δ_C(125 MHz; TFA-*d*) 169.3 (s), 156.0 (s), 138.4 (d), 138.0 (s), 137.2 (d), 134.7 (s), 131.8 (d), 131.7 (d), 131.6 (d), 128.8 (d), 126.7 (s), 125.2 (s), 119.2 (d), 112.8 (s, *C*≡N), 107.4 (s), 37.7 (q, *C*H_3); *m*/*z* (MALDI-TOF) 286 (MH^++1, 13%), 285 (MH^+, 100), 284 (M^+, 9).

4.10 Thermolysis of (*Z*)-2-[1-methyl-2-phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (16)

An intimate mixture of (*Z*)-2-[1-methyl-2-phenyl-4-(phenylimino)-1*H*-imidazol-5(4*H*)-ylidene]malononitrile (**16**) (14.2 mg, 0.05 mmol) and diphenyl ether (1 mL) was heated at *ca*. 250 °C for 4 h. Chromatography (*n*-hexane/DCM, 50:50) of the reaction mixture gave recovered diphenyl ether (1 mL) and further elution (DCM/Et_2O, 90:10) gave *1-methyl-2-phenyl-1*H-*imidazo[4,5-*b*]quinoline-9-carbonitrile* (**26**) (12.9 mg, 91%) as colorless prisms, mp (DSC) onset 226.4 °C, peak max. 227.3 °C; (from *n*-pentane/THF, 90:10); (found: C, 75.92; H, 4.35; N, 19.68. $C_{18}H_{12}N_4$ requires C, 76.04; H, 4.25; N, 19.71%); R_f 0.34 (DCM/Et_2O, 90:10); λ_{max}(EtOH)/nm 218 (log ε 4.92), 263 (4.83), 358 (4.77); ν_{max}/cm^{-1} 3086w (Ar CH), 2951w (CH_3), 2220w (C≡N), 1605w, 1524m, 1479m, 1462m, 1443m, 1400m, 1366s, 1337s, 1292m, 1246m, 1238m, 1211w, 1184w, 1163w, 1136w, 1078m, 1055w, 1047w, 1022w, 1015w, 984w, 962w, 943w, 932w, 881w, 870w, 860w, 798w, 793w, 785s, 773s; δ_H(500 MHz; TFA-*d*) 8.66 (1H, d, *J* 8.5, Ar *H*), 8.39 (1H, d, *J* 8.5, Ar *H*), 8.28 (1H, dd, *J* 7.9, 7.9, Ar *H*), 8.15 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.99 (2H, d, *J* 7.0, Ar *H*), 7.93 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.82 (2H, dd, *J* 8.0, 8.0, Ar *H*), 4.59 (3H, s, C*H*$_3$); δ_C(125 MHz; TFA-*d*) 167.3 (s), 148.7 (s), 141.2 (s), 137.7 (d), 137.5 (d), 133.1 (d), 132.2 (d), 132.0 (d), 131.8 (s), 127.7 (d), 126.9 (s), 125.1 (d), 123.9 (s), 112.3 (s, *C*≡N), 109.5 (s), 36.2 (q, *C*H$_3$); *m*/*z* (MALDI-TOF) 286 (MH^++1, 18%), 285 (MH^+, 100), 284 (M^+, 24), 283 (13), 118 (7), 105 (6).

4.11 Thermolysis of (*Z*)-2-(1-methyl-2-phenyl-5-(phenylimino)-1*H*-imidazol-4(5*H*)-ylidene)malononitrile (17)

An intimate mixture of (*Z*)-2-(1-methyl-2-phenyl-5-(phenylimino)-1*H*-imidazol-4(5*H*)-ylidene)malononitrile (**17**) (14.2 mg, 0.05 mmol) and diphenyl ether (1 mL) was heated at *ca*. 250 °C for 4 h. Chromatography (*n*-hexane/DCM, 50:50) of the reaction mixture gave recovered diphenyl ether (1 mL) and further elution (DCM/Et_2O, 90:10) gave *1-methyl-2-phenyl-1*H-*imidazo[4,5*-b*]quinoline-9-carbo-nitrile* (**27**) (14.4 mg, 93%) as colorless prisms, mp (DSC) onset 204.0 °C, peak max. 204.4 °C (from *n*-pentane/DCE, 70:30) identical to that described above.

4.12. X-ray crystallographic studies

Data were collected on an diffractometer, equipped with a CCD area detector utilizing Cu-Kα radiation (λ = 1.5418 Å) for compounds **13a** (CCDC-943799), **14a** (CCDC-943800) and **16** (CCDC-943801) while Mo-Kα radiation (λ = 0.71073 Å) was used for compound **22** (CCDC-943798). Suitable crystals were attached to glass fibers using paratone-N oil and transferred to a goniostat where they were cooled for data collection. Unit cell dimensions were determined and refined by using 2161 ($3.45 \leq \theta \leq 66.97^{o}$), 2247 ($3.33 \leq \theta \leq 71.89^{o}$), 2367 ($4.97 \leq \theta \leq 66.97^{o}$) and 2113 ($2.98 \leq \theta \leq 2$ 8.90^{o}) reflections for compounds **13a**, **14a**, **16** and **22**, respectively. Empirical absorption corrections (multi-scan based on symmetry-related measurements) were applied using CrysAlis RED software.[60] The structures were solved by direct method and refined on F^2 using full-matrix least squares using SHELXL97.[61] Software packages used: CrysAlis CCD[60] for data collection, CrysAlis RED[60] for cell refinement and data reduction, WINGX for geometric calculations,[62] and DIAMOND[63] for molecular graphics. The non-H atoms were treated anisotropically.

The hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms.

4.12.1. Crystal refinement data for compound ***13a****.* (yellow crystals): $C_{18}H_{11}N_5$, M = 297.32, *orthorhombic*, space group *P b c a*, a = 6.7212(5) Å, b = 16.922(2) Å, c = 25.652(3) Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 2917.5(5) Å^3, Z = 8, T = 100(2) K, ρ_{calcd} = 1.354 g cm^{-3}, $2\theta_{max}$ = 67. Refinement of 215 parameters on 2584 independent reflections out of 6039 measured reflections (R_{int} = 0.0374) led to R_1 = 0.0541 (I>2s(I)), wR_2 = 0.1703 (all data), and S = 1.082 with the largest difference peak and hole of 0.324 and -0.263 e^{-3}, respectively.

4.12.2. Crystal refinement data for compound ***14a****.* (orange crystals-rods): $C_{18}H_{11}N_5$, M = 297.32, *orthorhombic*, space group *P b c n*, a = 23.5138(7) Å, b = 13.2286(4) Å, c = 9.4729(3) Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 2946.59(16) Å^3, Z = 8, T = 100(2) K, ρ_{calcd} = 1.340 g cm^{-3}, $2\theta_{max}$ = 67. Refinement of 212 parameters on 2632 independent reflections out of 6161 measured reflections (R_{int}=0.0222) led to R_1 = 0.0359 (I>2s(I)), wR_2 = 0.0977 (all data), and S = 1.099 with the largest difference peak and hole of 0.211 and -0.186 e^{-3}, respectively.

4.12.3. Crystal refinement data for compound ***16****.* (orange crystals-rods): $C_{19}H_{13}N_5$, M = 311.34, *monoclinic*, space group *P 2/c*, a = 18.0008(18) Å, b = 12.1839(12) Å, c = 14.6705(19) Å, $\alpha = 90^o$, $\beta = 108.737(12)^o$, $\gamma = 90^o$, V = 3047.0(6) Å^3, Z = 8, T = 100(2) K, ρ_{calcd} = 1.357 g cm^{-3}, $2\theta_{max}$ = 67. Refinement of 217 parameters on 2688 independent reflections out of 5111 measured reflections (R_{int} = 0.0180) led to R_1 =

0.0538 (I>2s(I)), wR_2 = 0.1536 (all data), and S = 1.041 with the largest difference peak and hole of 0.394 and -0.296 e^{-3}, respectively.

4.12.4. Crystal refinement data for compound ***22****.* (green crystals): $C_{18}H_{11}N_5$, M = 297.32, *monoclinic*, space group $P\ 2_1/c$, a = 8.5353(6) Å, b = 14.8828(10) Å, c = 11.7854 (8) Å, $\alpha = 90^o$, β = 104.911(7)^o, $\gamma = 90^o$, V = 1446.68(17) Å^3, Z = 4, T = 100(2) K, ρ_{calcd} = 1.365 g cm^{-3}, $2\theta_{max}$ = 25. Refinement of 211 parameters on 2540 independent reflections out of 5481 measured reflections (R_{int} = 0.0290) led to R_1 = 0.0432 (I>2s(I)), wR_2 = 0.1153 (all data), and S = 1.066 with the largest difference peak and hole of 0.197 and -0.209 e^{-3}, respectively.

Crystallographic data for compounds **13a**, **14a**, **16** and **22** have been deposited with the Cambridge Crystallographic Data Centre with deposit numbers CCDC-943799, CCDC-943800, CCDC-943801 and CCDC-943798, respectively. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information: Copies of 1D ^{1}H and ^{13}C NMR spectra of all new compounds, 2D NOESY ^{1}H NMR spectra of compounds **17**, **26**, **27** and **28**, and UV/vis spectra of compounds **14a** (Fig. S3), **16** (Fig. S5) and **17** (Fig. S6). X-ray structures for compounds **13a** (Fig. S1), **14a** (Fig. S2), **16** (Fig. S4) and **22** (Fig. S7). Structure elucidation discussion for compounds **12a-15a** and **22**. This material is available free of charge *via* the Internet at http://pubs.acs.org/.

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