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Reaction of α-iminomethylene amino esters with mono- and bidentate nucleophiles: a straightforward route to 2-amino-1*H*-5-imidazolones

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Abstract—The reaction between α-iminomethylene amino esters with different mono- and bidentate nucleophiles has been studied. It has been shown that the reactions with primary and secondary amines as monodentate nucleophiles afford 2-aminoimidazolones efficiently under very mild conditions. Judicious selection of the primary amines employed can modulate the regioselectivity. Analogous reactions employing bidentate nucleophiles (e.g. amidines) also afford imidazolyl derivatives. The formation of the latter is preferred over the formation of seven-membered heterocycles of the triazepinone type. The optimized methodology in solution described herein should be readily adaptable to use in the solid phase for the parallel synthesis of collections of 2-aminoimidazolone derivatives with a high degree of molecular diversity.

1. Introduction

2-Aminoimidazolones of type **1** (Fig. 1) represent an interesting pharmacophore that displays a wide variety of biological properties. Synthetic compounds containing this structural motif have been shown, for instance, to exert a potent hypoglycaemic[1–4] and hypotensive activity.[5] In addition, in the last few years, an increasingly important number of alkaloids isolated from marine organisms have been reported to bear the 2-aminoimidazolone moiety.[6] Examples of these include the discapamides, isolated from Caribbean *Agelas* sponges, of which some members show a potent antihistamine activity,[7] the hymenialdisines, isolated from various *Agelasidae* sponges and exhibiting potent activity against murine P388 lymphocytic leukaemia,[8] or leucettamine B and the mauritiamines, isolated from the marine sponges *Leucetta microraphis* and *Agelas mauritiana*, respectively, which show potent anti-inflammatory and antifouling activities.[9,10] For several of these alkaloids, their total synthesis has also been reported.[11–14]

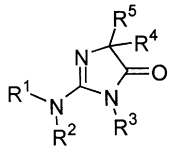

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Figure 1.

During the course of our ongoing studies dealing with the development of efficient methodologies that could readily be adapted for combinatorial and/or parallel synthesis, in solution and/or on solid supports, of relevant core structures with potential therapeutic interest,[15–18] we focused our attention on the 2-aminoimidazolone nucleus **1**. We wished to identify and to develop an efficient methodology that could afford collections of 2-aminoimidazolones of type **1** with a high degree of molecular diversity. This methodology should also be readily adaptable to use in the solid phase, taking full advantage of automated parallel synthesis systems. From the several methods available and described in the literature[19–23] for the synthesis of targets of type **1**, we needed to use a strategy that could employ readily available starting materials, and that in addition could be tethered to a solid support. Furthermore, this strategy should allow the introduction of a high degree of molecular diversity in each step by using easily available building blocks. Finally, the construction of the five-membered cyclic guanidines of type **1** should be performed in the last step through a cyclization process under mild conditions. This last requirement is of special significance when carried out on solid supports. Procedures for cyclization-assisted cleavage are largely

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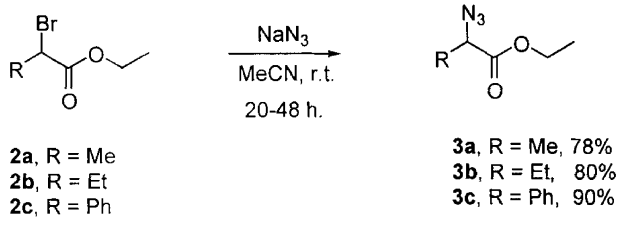
independent of the nature of the linker and offer several advantages. For example, only molecules that have gone through the whole reaction sequence necessary for the cyclization reaction will be cleaved, and even if single steps do not proceed quantitatively, the cyclization will nevertheless lead to pure products. In addition, the final products do not contain any residue or "memory" due to the solid support.[24]

Under the same premises, we recently disclosed the successful solid-phase synthesis of a library of 3*H*-quinazolinones.[15] This method, based on the formation of carbodiimide esters derived from anthranilic acid derivatives via an aza Wittig reaction, had previously been very well documented in the literature.[25,26] In fact, the use of iminophosphoranes as intermediates in organic synthesis have proven to be particularly useful for the preparation of different six-membered heterocyclic systems containing an endocyclic C=N double bond.[26–31] Surprisingly, however, the application in solution of similar methodologies for the synthesis of heterocycles in the five-membered series has been far less explored and little experimental data are available.[32–34] Therefore, based on this iminophosphorane chemistry and with the aim of establishing reliable reaction conditions in solution for the preparation of our targets of type **1**, which could eventually be adapted to the solid phase, we were prompted to pursue this study and the full details and scope are reported herein.



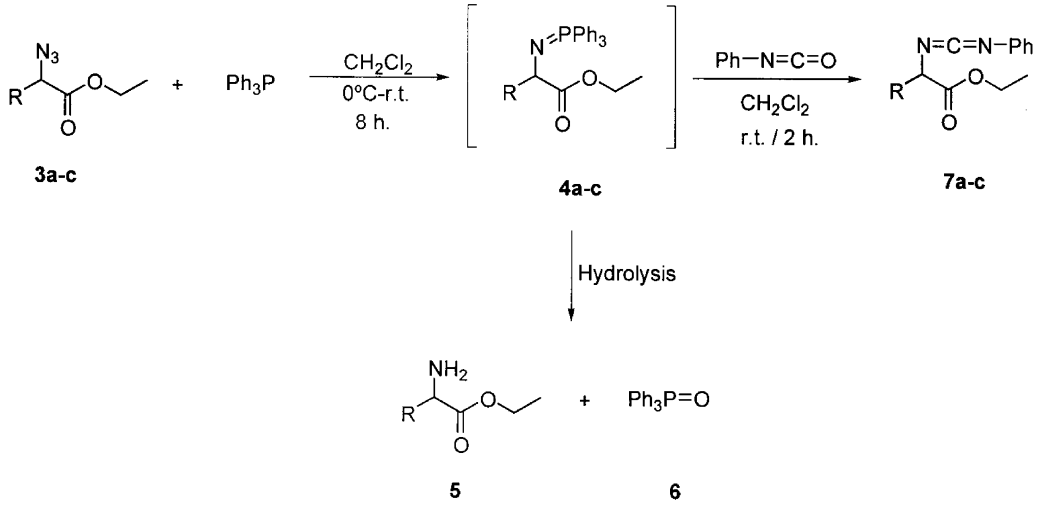
Scheme 1.

2. Results and discussion

2.1. Synthesis of α-iminomethylene amino esters 7a–c

Consistent with this goal, the readily available α-bromo esters **2a–c** were selected as starting materials. Their reaction with NaN_3 in MeCN at r.t. for 20–48 h, afforded after isolation by distillation under reduced pressure, the corresponding α-azido esters **3a–c** in good yields (78–90%) as shown in Scheme 1.

The subsequent Staudinger reaction of α-azido esters **3** with Ph_3P at 0°C in anhydrous CH_2Cl_2, led after 8 h to the corresponding iminophosphoranes **4**. Although the evolution of N_2 could be clearly detected in these reactions, and the disappearance of **3** could be properly monitored by TLC or GC, the iminophosphoranes **4** proved to be too labile to be isolated either by crystallization or by flash-chromatography. In all cases, only hydrolysed α-amino esters of type **5** together with phosphine oxide **6** could be isolated. In a second set of experiments, we moved directly toward the target carbodiimides **7** in a one-pot procedure simply by reacting *in situ* the previously formed imino-phosphoranes **4** with 1 equiv. of phenyl isocyanate in anhydrous CH_2Cl_2. After 2 h at r.t., total consumption of the starting materials was observed and the desired α-imino-methylene amino ester derivatives **7** were isolated in pure form and in good yields (56–75%, two steps, overall yield; see Scheme 2 and Table 1).



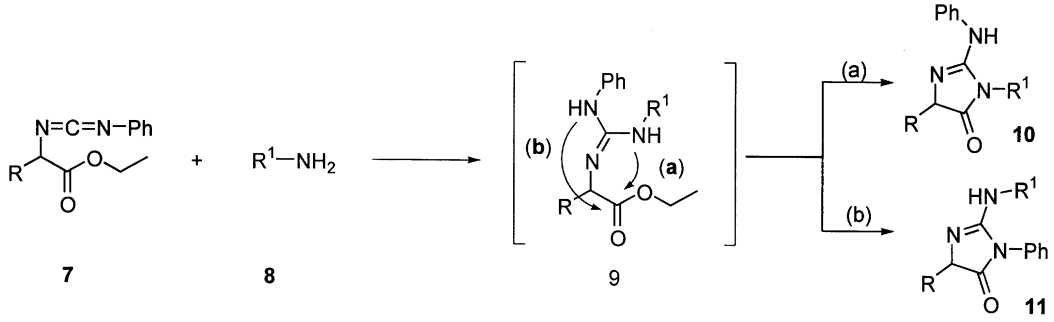
Scheme 2.

Table 1. Prepared α-iminomethylene amino esters **7a–c**

Entry	Compound	R	Yield (%)[a]	m.p. (°C):
1	**7a**	Me	65	Colourless oil
2	**7b**	Et	56	Colourless oil
3	**7c**	Ph	75	48–49

[a] Overall yields (two steps) for isolated pure products.

Having established a simple and reproducible procedure for the efficient generation of carbodiimides of type **7**, we then proceeded further by firstly investigating the reactivity of these types of substrates in the presence of monodentated nucleophiles (e.g. primary and secondary amines).



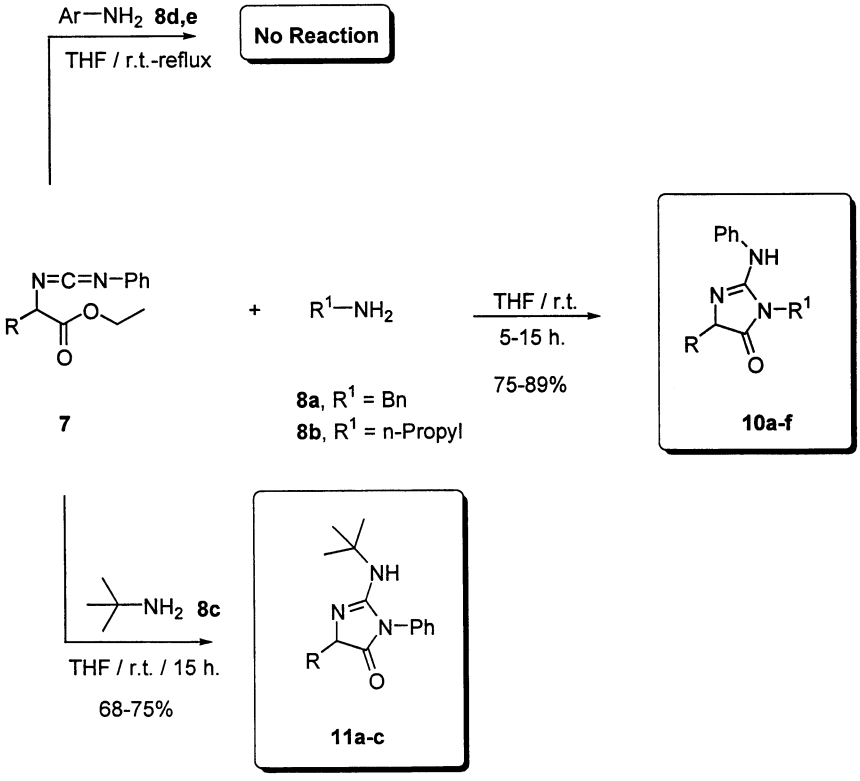
Scheme 3.

2.2. Reaction with monodentated primary amines

As can be seen in Scheme 3, the reaction between carbodiimides **7** and primary amines **8** should afford primarily guanidine intermediates of type **9**. From these intermediates **9**, the formation of two regioisomeric 2-aminoimidazolones (**10** and/or **11**) could in principle take place. 2-Aminoimidazolones of type **10** will be the resulting products after a subsequent nucleophilic attack from the intervening amine over the carbonyl ester (pathway a). Regioisomeric 2-aminoimidazolones of type **11** will be formed instead when the heterocyclization reaction is a result of the attack of the former carbodiimidic nitrogen atom (pathway b). The ratio of the formed imidazolones of type **10** and **11** will depend presumably on the electronic and/or the steric factors exerted by the two amine groups in intermediates of type **9**.

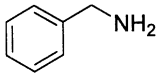
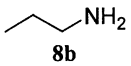
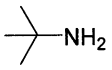
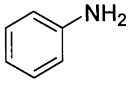
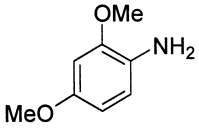
Accordingly, when primary amines like benzyl- and n-propyl amine (**8a** and **8b**, respectively) were allowed to react with carbodiimide esters **7a–c** in anhydrous THF at r.t. for a period of 5–15 h, regioselective cyclization with the formation of derivatives of type **10** took place and 2-phenylamino imidazolones **10a–f** were isolated in good yields (75–89%). However, the analogous reaction with t-butyl amine **8c** promoted the opposite regioselective cyclization affording exclusively 2-t-butylamino imidazolones **11a–c**, also in good yields (68–75%). However, when aniline **8d** and 2,4-dimethoxy aniline **8e** were employed as monodentate nucleophiles, no reaction occurred at r.t. and only the formation of decomposition products was observed when the reaction conditions were forced (Scheme 4 and Table 2).

These results indicate that in this type of transformation, regioselectivity toward the formation of **10** and/or **11** seems to be influenced not only by differences in the nucleophilic character of the two nitrogen atoms of the guanidine



Scheme 4.

Table 2. Synthesized 2-aminoimidazolones of type **10** and **11**

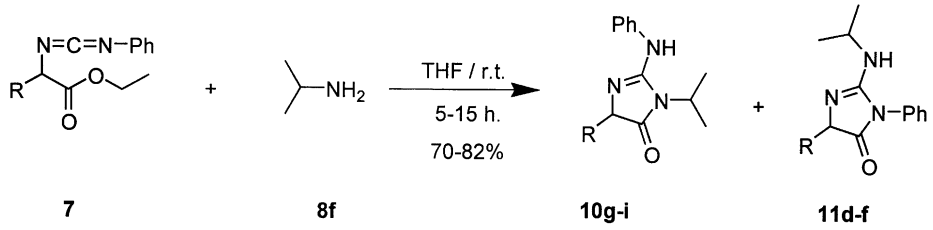
R^1–NH_2	Entry	R	Compound	Reaction time (h)	Yield (%)[a]	m.p. (°C):
 **8a**	i	Me	**10a**	6	86	Colourless oil
	ii	Et	**10b**	5	84	Colourless oil
	iii	Ph	**10c**	8	88	129–130
 **8b**	iv	Me	**10d**	15	76	Colourless oil
	v	Et	**10e**	15	75	Colourless oil
	vi	Ph	**10f**	12	89	$135–136_{dec.}$
 **8c**	vii	Me	**11a**	15	68	59–60
	viii	Et	**11b**	15	75	73–74
	ix	Ph	**11c**	15	72	$119–120_{dec.}$
 **8d**	x	Me	**NR**[b]	–	–	–
 **8e**	xi	Et	**NR**	–	–	–

[a] Yields of isolated pure products.
[b] No reaction.

intermediates of type **9**, but also by the steric factors involved. Thus, when nucleophilic, non-sterically hindered primary amines were used, 2-aminoimidazolones of type **10** were formed (entries i–vi in Table 2). However, when large steric restrictions are present in intermediates of type **9**, this effect predominates over any nucleophilic character and the opposite regioselectivity is obtained giving rise to the exclusive formation of 2-aminoimidazolones of type **11** (entries vii–ix in Table 2).

Using these arguments, it should also be possible to find mixtures of **10g–i** and **11d–f** in different ratios (Scheme 5 and Table 3).

The structure of regioisomeric 2-aminoimidazolones of type **10** and **11** could be unambiguously established with the help of X-ray crystal structure analyses. Initially, we attempted to obtain crystals of adequate quality from **11c** by slow evaporation of a CH_2Cl_2 solution at r.t. Surprisingly, however, and presumably as a consequence of the slow crystallization process, **11c** dimerized into **12** as found afterwards from the subsequent X-ray diffraction analysis



7 8f 10g-i 11d-f

Scheme 5.

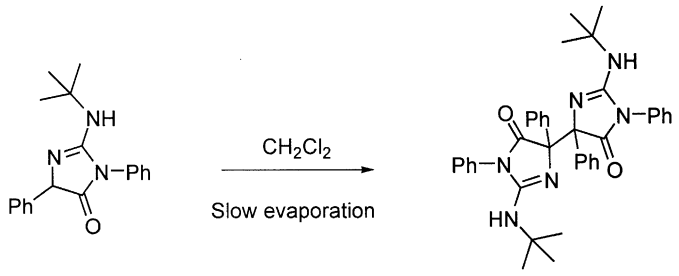
cases in which neither the nucleophilicity of the two guanidinic nitrogen atoms, nor the steric demand imposed in intermediates of type **9**, clearly predominate, and that mixtures of regioisomeric 2-aminoimidazolones **10** and **11** should then be obtained.

Indeed, this was effectively the case when isopropyl amine **8f** was employed as the monodentate nucleophile. In this case, despite the nucleophilic power of the aliphatic nitrogen atom, the steric effect exerted by the isopropyl group in intermediates of type **9** allowed the formation of

Table 3. Synthesized 2-aminoimidazolones from **7a–c** and **8f**

R	Entry	Compound	Reaction time (h)	Yield (%)[a]	m.p. (°C):
Me	1	**10g**	15	65	90–91
	2	**11d**	15	15	118–119
Et	3	**10h**	15	35	91–92
	4	**11e**	15	35	120–121
Ph	5	**10i**	15	70	$154–155_{dec.}$
	6	**11f**[b]	15	–	–

[a] Yields of isolated pure products.
[b] Compound detected by TLC but decomposes during the purification process.



11c **12**

Figure 2. Dimerization of **11c** during crystallization.

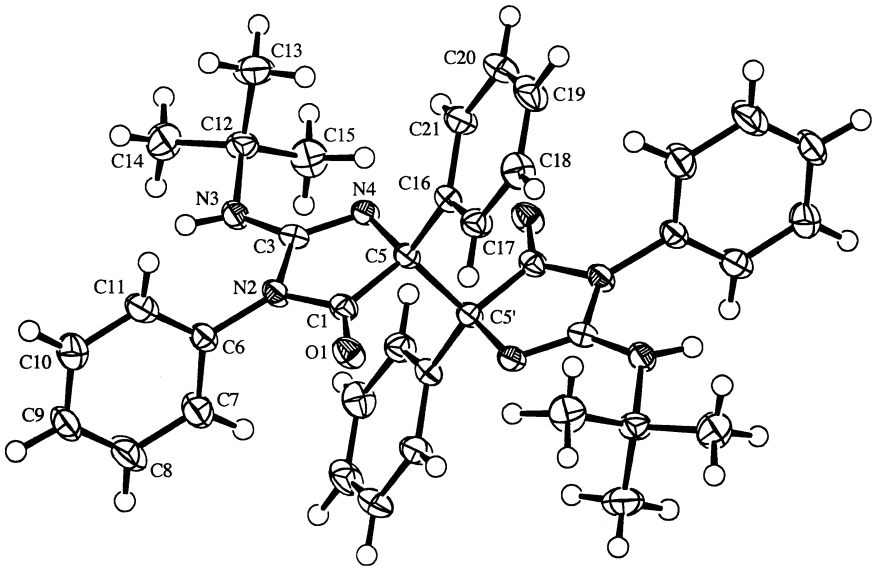


Figure 3. Ortep plot of the molecular structure of **12** with 50% probability ellipsoids.[35]

(Figs. 2 and 3). The dimerization mechanism to **12**, probably involving a radical and/or oxidation pathway was not fully investigated at this stage.

Although the crystal obtained did not correspond to the expected **11c**, the structure of the dimer **12** accounted for the mentioned regioselectivity. In addition, we were able to obtain crystals of **10g** and **11e** that were of adequate quality and these were also used for X-ray crystal structure analyses, which confirmed the proposed structures and regioselectivity (Figs. 4 and 5). Subsequent correlation of the spectroscopic data allowed for consistent structural elucidation of all synthesized 2-aminoimidazolones of types **10** and **11**.

Interestingly, as can be seen in Fig. 4, compound **10g** crystallized in another tautomeric form (**10g′**) with the C=N double bond *exo* to the five-membered ring, and the ring N-atom being the protonated amine group (Fig. 6).

Therefore, as has been shown, the reaction between α-iminomethylene amino esters of type **7** and amines **8** can lead under mild conditions via guanidine intermediates of type **9** (Scheme 3) to different regioisomeric imidazolones of type **10** and/or **11** depending

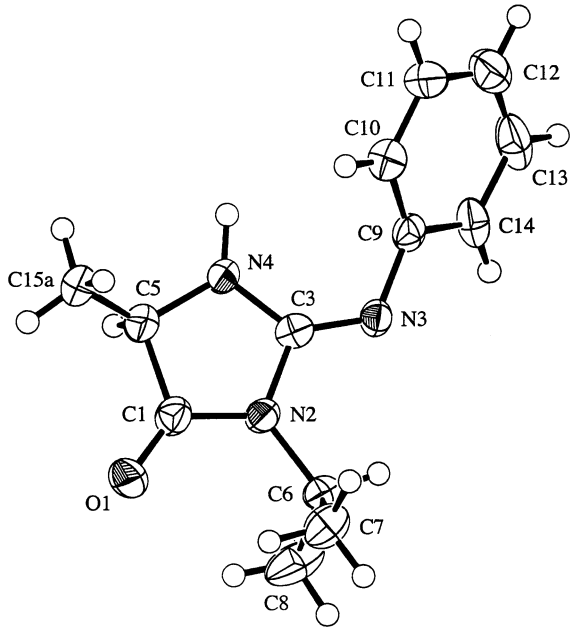


Figure 4. Ortep plot of the molecular structure of **10g′** with 50% probability ellipsoids.[35] Bond length of C(3)—N(3)=1.270 (4) Å (corresponding to a C=N double bond). Bond length of C(3)—N(4)=1.363 (4) Å (corresponding to a C—N single bond).

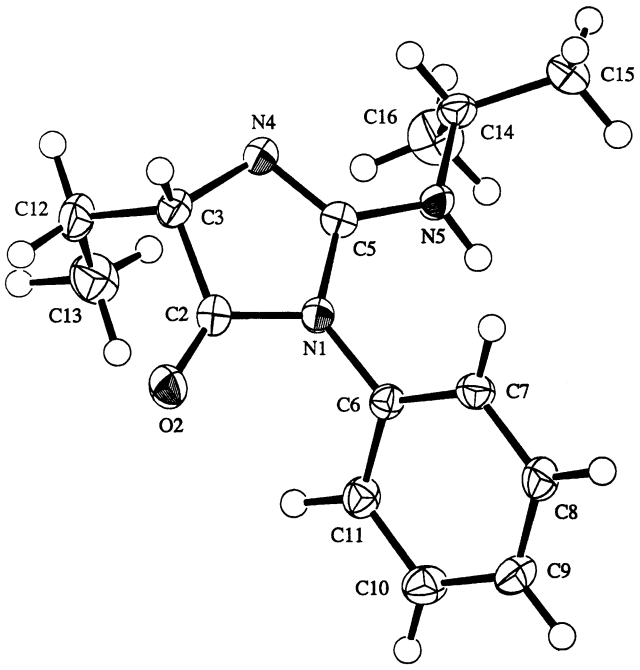


Figure 5. Ortep plot of the molecular structure of **11e** with 50% probability ellipsoids.[35]

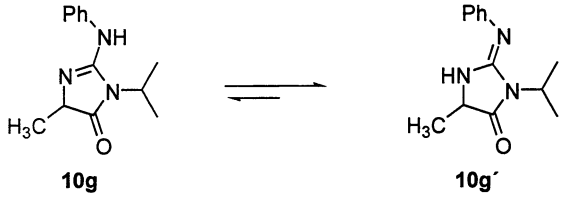


Figure 6.

on the nature of the primary amine employed, although it is possible to predict to some extent the kind of derivative obtained.

2.3. Reaction with monodentate secondary amines

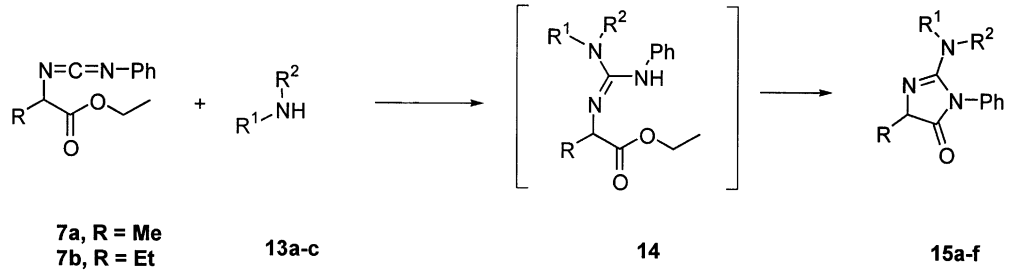
A much simpler picture should be expected, however, when the same type of reaction is carried out employing secondary amines as monodentate nucleophiles. In these cases, only one mode of cyclization is available, which is independent of the steric requirements imposed by the intervening amine.

Effectively, when a solution of carbodiimides **7a–b** in anhydrous THF were allowed to react with different secondary amines of type **13** for a period of 15–18 h, the corresponding 2-amino imidazolones of type **15** were isolated in excellent yields (79–98%, Scheme 6 and Table 4).

Special mention should be made of the reaction involving the carbodiimide ester **7c**. Its reaction with secondary amines **13a–c** proceeded as usual but the final products were rather unstable. They could not be isolated by flash-chromatography due to fast decomposition, and only **15h** could be isolated in 79% yield by crystallization from CH_2Cl_2:ether:n-pentane. 2-Aminoimidazolones **15g** and **15i**, when subjected to the same crystallization work-up dimerized into **16** and **17**, respectively, and were isolated in 75–77% yields (Scheme 7).

2.4. Reaction with bidentate amidines

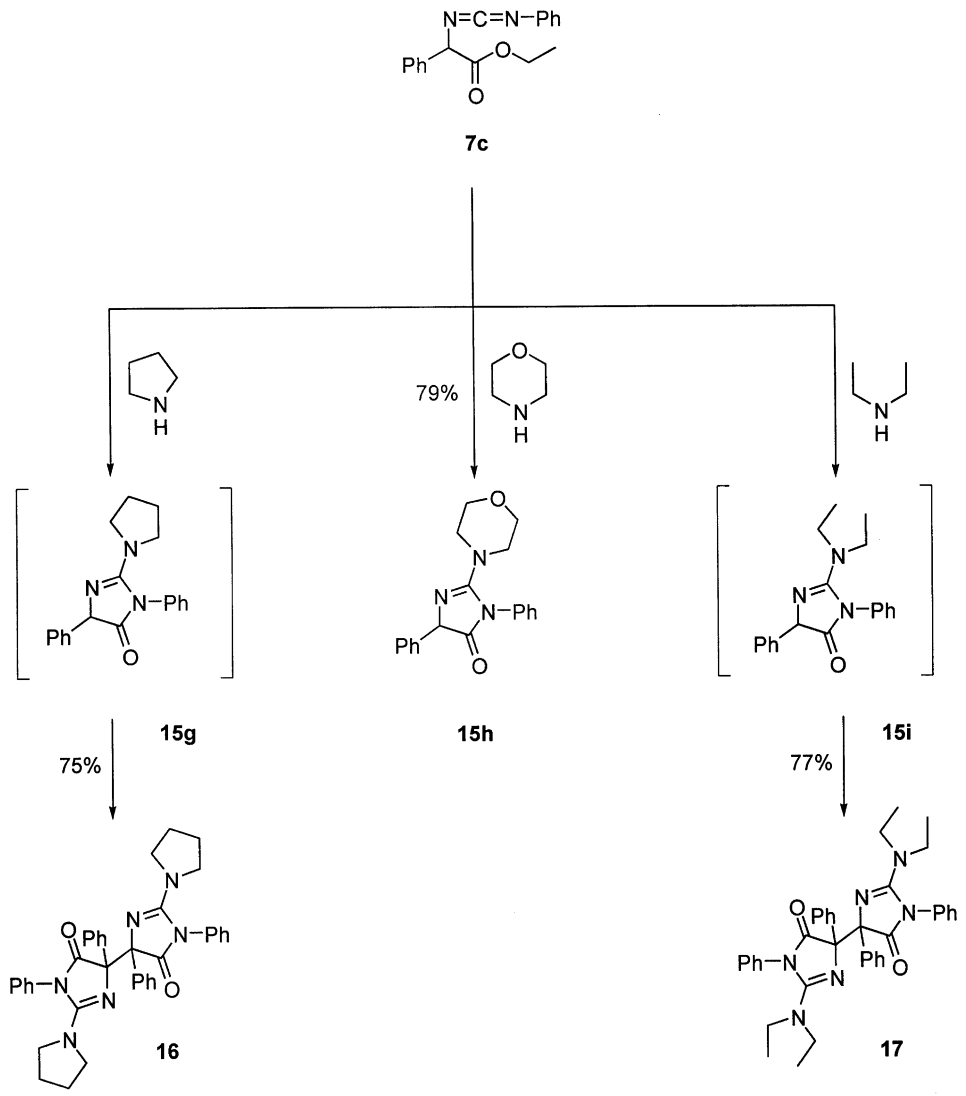
Having established the general behaviour of α-imino-methylene amino esters of type **7** in the presence of



Scheme 6.

Table 4. Synthesized imidazolones **15a–f**

R^1R^2NH	Entry	R	Reaction time (h)	Compound	Yield (%)	m.p. (°C):
NH	1	Me	15	**15a**	88	63–64
13a	2	Et	15	**15b**	98	Colourless oil
O NH	3	Me	18	**15c**	80	96–97
13b	4	Et	18	**15d**	79	Colourless oil
NH	5	Me	18	**15e**	92	Colourless oil
13c	6	Et	18	**15f**	96	Colourless oil



Scheme 7.

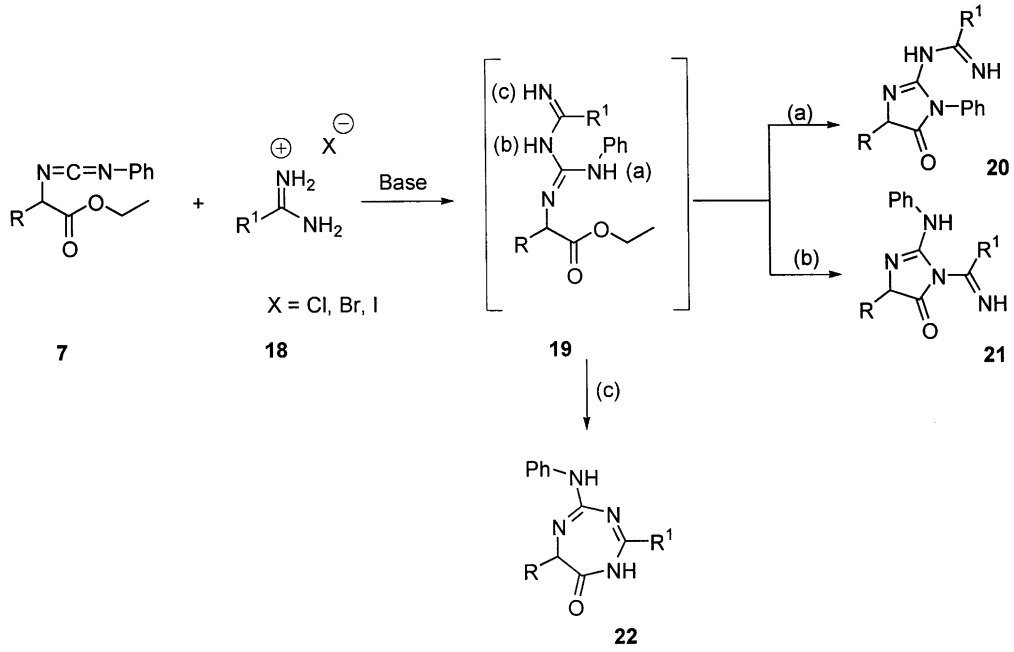
monodentate nucleophiles (primary and secondary amines), we wished to study further their synthetic potential. In particular, we were interested in examining their reactivity with bidentate nucleophiles of the amidine type.

α-Iminomethylene amino esters **7** can be catalogued as 1,4-bis-acceptor building blocks (or 1,4-dielectrophiles), and amidines **18** can be catalogued as 1,3-bis-donor building blocks (or 1,3-dinucleophiles). Therefore, the combination of both **7** and **18**, could lead via guanidine intermediates of type **19**, not only to imidazolones of general structure **20** (pathway a) or **21** (pathway b) but also to seven-membered heterocycles of the triazepinone type **22** (pathway c) (Scheme 8).

With the aim of disclosing the general trend followed in this type of reaction, several easily available amidines **18a–d** were selected and their reactions with carbodiimide esters **7a–c** were studied. We found that when a solution of the corresponding carbodiimides **7a–c** in anhydrous MeCN was treated with amidines **18a–d** in the presence of 2 equiv. of solid K_2CO_3 at r.t., the exclusive formation of 2-amino imidazolones of type **20** took place. No traces of imidazolones of the general type **21** or triazepinones of type **22** were detected. These derivatives **20**, could be isolated in pure form and in generally good yields (48–78%) after a simple chromatographic filtration, except those derived from carbodiimide **7c**, which proved to be too unstable and decomposed rapidly. However, for this particular case, by slightly changing the reaction conditions (DIPEA as a base in MeCN), it was possible to isolate **20i** and **20j**, although in low yields (35% and 20%, respectively; see Scheme 9 and Table 5).

The structural elucidation of imidazolones of type **20** was accomplished on the basis of the usual spectroscopic methods. As shown in Fig. 7, it is also possible to write other tautomeric forms (**20′** and **20″**) of the involved exocyclic guanidine moiety.

The data obtained from the ^{1}H-NMR spectra taken in $CDCl_3$ or DMSO-d_6 solutions of the synthesized **20a–j**, did not provide enough evidence for the preferred tautomeric form. The presence of two distinct D_2O exchangeable protons revealed the presence of two different NH groups,

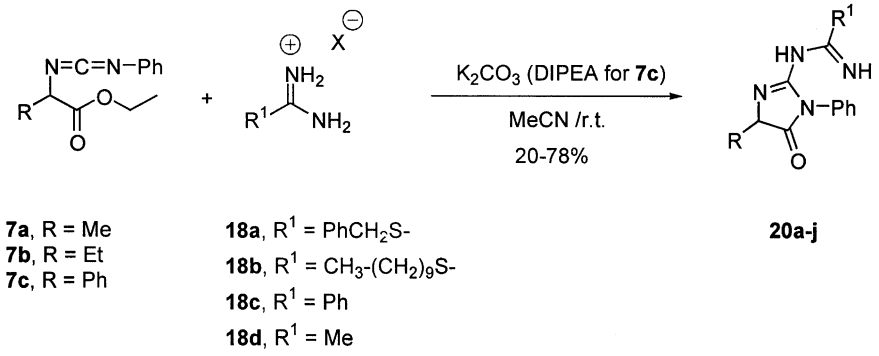


Scheme 8.

but since the two hydrogen atoms of **20′** could be placed in distinctly different environments due to the flat structure of its imidate moiety, none of the above-represented tautomers should *a priori* be neglected. In order to obtain more data about this point, **20e** was subjected to an X-ray crystal structure analysis, which showed that the preferred tautomeric form in the solid state corresponds with that represented by the general formula **20′** as shown in Figs. 7 and 8.

3. Conclusions

In summary, we have shown that 1,4-bis-aceptor α-iminomethylene amino esters of type **7**, easily available from α-bromo esters **2**, are good synthetic precursors for the preparation of imidazolyl derivatives. Their reactions with monodentate nucleophiles furnish under very mild conditions and in good yields collections of 2-aminoimidazolones of the type **10** and/or **11**. The regioselection



Scheme 9.

Table 5. Prepared 2-aminoimidazolones **20a–j**

R	R^1	Entry	Base	Reaction Time (h)	Compound	Yield (%)	m.p. (°C):
Me	$PhCH_2S$	1	K_2CO_3	6	**20a**	69	143–144
	$CH_3(CH_2)_9S$	2	K_2CO_3	18	**20b**	65	68–69
	Ph	3	K_2CO_3	18	**20c**	48	132–133
	Me	4	K_2CO_3	15	**20d**	68	151–152
Et	$PhCH_2S$	5	K_2CO_3	8	**20e**	75	144–145
	$CH_3(CH_2)_9S$	6	K_2CO_3	18	**20f**	78	73–74
	Ph	7	K_2CO_3	20	**20g**	56	139–140
	Me	8	K_2CO_3	8	**20h**	65	160–161
Ph	$CH_3(CH_2)_9S$	9	DIPEA	6	**20i**	35	$113–114_{dec.}$
	Me	10	DIPEA	15	**20j**	20	$165–166_{dec.}$

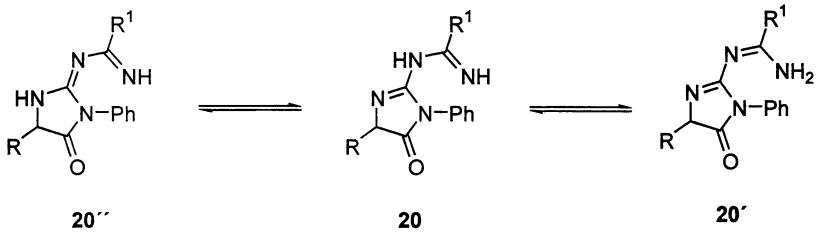


Figure 7.

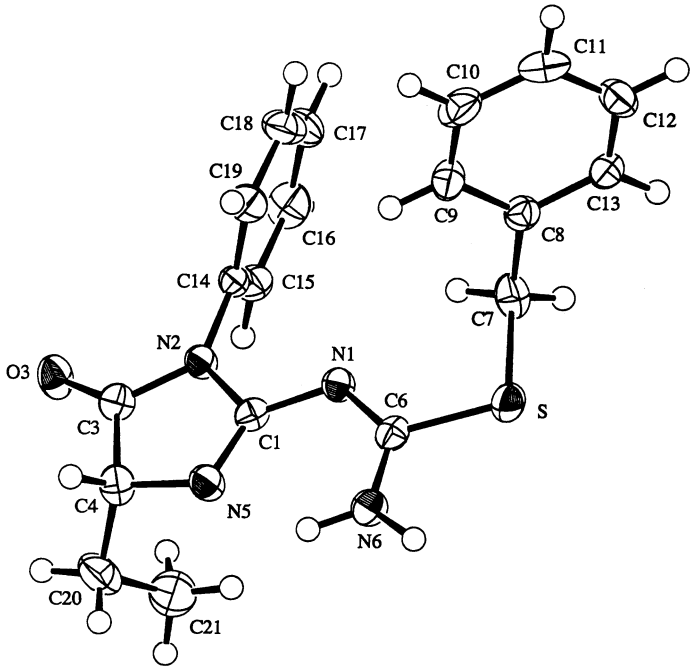


Figure 8. Ortep plot of the molecular structure of **20e′** with 50% probability ellipsoids.[35]

issue concerning the use of primary amines as nucleophiles can be modulated by the judicious selection of their electronic and/or the steric properties. Thus, when nucleophilic, non-sterically hindered primary amines are used, exclusive regioselective transformation toward derivatives of type **10** can be obtained. In turn, nucleophilic amines bearing groups with a large steric demand will promote the opposite regioselection, giving rise to 2-aminoimidazolones of type **11**. By using secondary amines as monodentate nucleophiles, only 2-aminoimidazolones of type **11** will be formed, without any dependence on steric factors. The structures of the 2-aminoimidazolones of type **10** and **11** were established unambiguously from the X-ray crystal structure analyses of some representatives and a correlation of their spectroscopic data with all other synthesized derivatives.

Finally, when bidentate nucleophiles like amidines **18a–d** were allowed to react with carbodiimide esters **7a–c** at r.t. imidazolyl derivatives of type **20** were formed in a highly regioselective manner. Despite the nucleophilic character of the nitrogen atoms in intermediates of type **19**, the formation of the five-membered heterocycles **20** was largely preferred over the seven-membered derivatives of type **22**.

The methodology presented herein should be readily adaptable to the solid phase. The coupling of easily available α-bromo acids (of which a good number is already commercially available) to hydroxymethyl polystyrene resin should provide the first synthetic precursor in analogy to **2a–c**. Following an analogous synthetic sequence, the reaction of polymer-bound carbodiimide esters with different secondary amines and amidines should lead in a highly regioselective manner to collections of imidazolones via a cyclization-assisted cleavage with the concomitant release from the solid support. Preliminary experiments along this line have been performed successfully and the results will be published in due course.

4. Experimental

4.1. General

All commercially available chemicals were used as purchased. MeCN was dried over activated molecular sieves (4 Å). THF was dried over Na/benzophenone prior to use. All reactions were run under a positive pressure of dry N_2. Melting points (capillary tube) were measured with an

Electrothermal digital melting point apparatus IA 9100 and are uncorrected. IR spectra were recorded on a Mattson-Galaxy Satellite FT-IR. ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Brucker DPX200 Advance instrument with TMS as internal standard. MS spectra were recorded on a VG Quattro instrument in the positive ionization FAB mode, using 3-NBA or 1-thioglycerol as the matrix. Elemental analyses were performed on an apparatus from Thermo instruments, model EA1110-CHNS. Analytical TLC was performed on precoated TLC plates, silica gel 60 F_{254} (Merck). Flash-chromatography purifications were performed on silica gel 60 (230–400 mesh, Merck).

4.2. Synthesis of α-azidoesters 3a–c. General procedure

To a suspension at r.t. of sodium azide (2.92 g, 45 mmol, 2.5 equiv.) in 72 mL of dry MeCN, the corresponding α-bromo esters **2a–c** (18 mmol, 1 equiv.) were added. The reaction mixture, under N_2, was stirred at r.t. for 20–48 h. The reaction mixture was filtered over a celite pad, the organic solvent eliminated under reduced pressure and the residue distilled bulb to bulb *in vacuo*.

4.2.1. Ethyl 2-azidopropanoate (3a). According to the general procedure described above, the reaction between **2a** and sodium azide afforded 2.0 g (78%) of **3a** as a colourless oil. B.p.: 50–52°C (0.1 Torr); ^{1}H NMR ($CDCl_3$): δ 1.29 (t, 3H, J=7 Hz, CH_3), 1.48 (d, 3H, J=7.1 Hz, CH_3), 3.9 (q, 1H, J=7.1 Hz), 4.25 (q, 2H, J=7 Hz, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 14.51 (q, CH_3CH_2), 17.13 (q, CH_3CH), 57.74 (d,CH), 62.19 (t, OCH_2CH$_3$), 171.38 (s, CO). IR (film) ν 2981, 2933, 2881, 2120, 1744, 1450, 1381, 1334, 1299, 1258, 1197, 1094, 1019, 901, 850 cm^{-1}. MS (FAB$^+$) *m/e*: 144 ([M+1]$^+$, 100). Anal. Calc. for $C_5H_9N_3O_2$ (143.14): C 41.95%, H 6.34%, N 29.36. Found: C 42.23%, H 6.21%, N 29.07%.

4.2.2. Ethyl 2-azidobutanoate (3b). According to the general procedure described above, the reaction between **2b** and sodium azide afforded 2.26 g (80%) of **3b** as a colourless oil. B.p.: 60–65°C (0.1 Torr). ^{1}H NMR ($CDCl_3$): δ 0.99 (t, 3H, J=7.4 Hz, CH_3), 1.29 (t, 3H, J=7.2 Hz, CH_3), 1.70–1.90 (m, 2H, CH_2), 3.75 (dd, 1H, J=7.7 Hz, J'=5.6 Hz, CH), 4.28 (q, 2H, J=7.2 Hz, OCH_2CH$_3$). ^{13}C NMR ($CDCl_3$): δ 9.97 (q, CH_3), 13.95 (q, CH_3), 24.68 (t, CH_2), 61.47 (d, CH), 63.14 (t, OCH_2), 170.29 (s, CO). IR (film) ν 2979, 2938, 2882, 2108, 1743, 1461, 1370, 1333, 1293, 1259, 1193, 1117, 1096, 1023, 899 cm^{-1}. MS (FAB$^+$) *m/e*: 158 ([M+1]$^+$, 100). Anal. Calc. for $C_6H_{11}N_3O_2$ (157.17): C 45.85%, H 7.05%, N 26.74. Found: C 45.62%, H 7.22%, N 26.49%.

4.2.3. Ethyl 2-azido-2-phenylacetate (3c). According to the general procedure described above, the reaction between **2c** and sodium azide afforded 3.32 g (90%) of **3c** as a colourless oil. B.p.: 80–82°C (0.1 Torr). ^{1}H NMR ($CDCl_3$): δ 1.29 (t, 3H, J=7.2 Hz, CH_3), 4.15 (q, 2H, J=7.2 Hz, OCH_2), 4.99 (s, 1H, CH), 7.44 (s, 5H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 13.91 (q, CH_3), 62.03 (d, CH), 65.22 (t, OCH_2), 127.52 (d, 2CH$_{arom.}$), 128.96 (d, 2CH$_{arom.}$), 129.12 (d, CH$_{arom.}$), 133.90 (s, $C_{arom.}$), 169.0 (s, CO). IR (film) ν 3064, 6036, 2980, 2938, 2910, 2106, 1743, 1496, 1454, 1391, 1370, 1335, 1300, 1257, 1197, 1178, 1096, 1026, 913, 878, 842, 779, 730, 702 cm^{-1}. MS (FAB$^+$) *m/e*: 206 ([M+1]$^+$, 6), 205 (M$^+$, 1), 178 (44), 164 (14), 163 (27), 137 (27), 136 (15), 135 (16), 132 (15), 107 (22), 106 (26), 105 (23), 104 (100). Anal. Calc. for $C_{10}H_{11}N_3O_2$ (205.21): C 58.53%, H 5.40%, N 20.48. Found: C 58.34%, H 5.19%, N 20.74%.

4.3. Synthesis of α-iminomethylene amino ester derivatives 7a–c. General procedure

To a cooled (0°C) solution of 10 mmol (1 equiv.) of the corresponding α-azido esters **3a–c** in 30 mL of dry CH_2Cl_2, 10 mL (10 mmol, 1 equiv.) of a 1 M solution of Ph_3P in dry CH_2Cl_2 were added dropwise. A vigorous N_2 gas evolved immediately. The reaction mixture was stirred under a positive pressure of dry Ar from 0°C to r.t. for 8 h. Then 1.09 mL (10 mmol, 1 equiv.) of phenylisocyanate were added, and the new reaction mixture stirred at r.t. under Ar for an additional 2 h. The solvent was eliminated under reduced pressure and the resulting residue purified by flash-chromatography (n-hexane:AcOEt) to afford pure **7a–c**.

4.3.1. Ethyl 2-phenyliminomethyleneaminopropanoate (7a). According to the general procedure described above, the reaction between **3a** and phenyl isocyanate afforded 0.86 g (65%) of **7a** as a colourless oil. ^{1}H NMR ($CDCl_3$): δ 1.3 (t, 3H, J=7.2 Hz, CH_3), 1.59 (d, 3H, J=7.0 Hz, CH_3), 4.18 (q, 1H, J=7.0 Hz, CH), 4.21 (q, 2H, J=7.2 Hz, OCH_2), 7.35–7.15 (m, 5H, $H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 14.02 (q, CH_3), 20.24 (q, CH_3), 55.05 (d, CH), 61.84 (t, OCH_2), 123.91 (d, 2CH$_{arom.}$), 124.94 (d, CH$_{arom.}$), 129.18 (d, 2CH$_{arom.}$), 137.31 (s, $C_{arom.}$), 139.43 (s, —N=*C*=N—), 171.82 (s, CO). IR (film) ν 3063, 2988, 2942, 2890, 2130, 1739, 1593, 1502, 1450, 1375, 1293, 1257, 1205, 1158, 1097, 1075, 1018, 899, 871, 850, 757, 690 cm^{-1}. MS (FAB$^+$) *m/e*: 219 ([M+1]$^+$, 20), 218 (M$^+$, 9), 191 (10), 146 (11), 145 (100), 120(10), 119 (13). Anal. Calc. for $C_{12}H_{14}N_2O_2$ (218.25): C 66.04%, H 6.47%, N 12.84. Found: C 65.77%, H 6.67%, N 12.55%.

4.3.2. Ethyl 2-phenyliminomethyleneaminobutanoate (7b). According to the general procedure described above, the reaction between **3b** and phenyl isocyanate afforded 0.94 g (50%) of **7b** as a colourless oil. ^{1}H NMR ($CDCl_3$): δ 0.97 (t, 3H, J=7.2 Hz, CH_3CH$_2$), 1.19 (t, 3H, J=7.1 Hz, CH_3), 1.75–1.90 (m, 2H, CH_3CH_2), 3.99 (dd, 1H, J=6.95 Hz, J'=5.3 Hz, CH), 4.18 (q, 2H, J=7.1 Hz, OCH_2), 7.0–7.25 (m, 5H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 9.95 (q, CH_3), 14.13 (q, CH_3), 27.53 (t, CH_2), 60.80 (t, OCH_2), 61.81 (d, CH), 123.98 (d, 2CH$_{arom.}$), 124.87 (d, CH$_{arom.}$), 125.83 (s, $C_{arom.}$), 129.25 (d, 2CH$_{arom.}$), 139.68 (s, —N=*C*=N—), 171.29 (s, CO). IR (film) ν 3063, 2974, 2933, 2878, 2140, 1737, 1593, 1457, 1368, 1342, 1293, 1251, 1204, 1183, 1156, 1103, 1082, 1018, 934, 850, 758, 688 cm^{-1}. MS (FAB$^+$) *m/e*: 233 ([M+1]$^+$, 39), 232 (M$^+$, 12), 205 (21), 194 (17), 172 (16), 160 (11), 159 (100), 144 (24), 120 (12), 119 (17). Anal. Calc. for $C_{13}H_{16}N_2O_2$ (232.28): C 67.22%, H 6.94%, N 12.06. Found: C 67.01%, H 6.75%, N 12.21%.

4.3.3. Ethyl 2-phenyl-2-phenyliminomethyleneamino-acetate (7c). According to the general procedure described

above, the reaction between **3c** and phenyl isocyanate afforded 2.10 g (75%) of **7c** as a colourless solid. M.p.: 48–49°C. ^{1}H NMR ($CDCl_3$): δ 1.03 (t, 3H, J=7.1 Hz, CH_3), 4.15 (q, 2H, OCH_2), 4.97 (s, 1H, CH), 7.05–7.35 (m, 10H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 9.95 (q, CH$_3$), 62.75 (t, OCH$_2$), 63.54 (d, CH), 124.63 (d, 2CH$_{arom.}$), 125.59 (d, CH$_{arom.}$), 127.47 (d, 2CH$_{arom.}$), 129.15 (d, CH$_{arom.}$), 129.33 (d, 2CH$_{arom.}$), 129.74 (d, 2CH$_{arom.}$), 136.49 (s, $C_{arom.}$), 137.76 (s, $C_{arom.}$), 139.16 (s, —N=C=N—), 170.11 (s, CO). IR (KBr) ν 3063, 3030, 2984, 2938, 2896, 2129, 2105, 1734, 1592, 1502, 1440, 1377, 1327, 1307, 1204, 1174, 1154, 1075, 1023, 969, 934, 857, 835, 754, 723, 694 cm^{-1}. MS (FAB$^+$) *m/e*: 281 ([M+1]$^+$, 37), 280 (M$^+$, 8), 207 (28), 164 (12), 163 (100), 135 (7). Anal. Calc. for $C_{17}H_{16}N_2O_2$ (280.32): C 72.84%, H 5.75%, N 9.99. Found: C 73.07%, H 5.94%, N 9.78%.

4.4. Synthesis of 2-amino imidazolones derivatives of type 10, 11, 15, 16 and 17. General procedure

To a solution of 2 mmol (1 equiv.) of the corresponding carbodiimides **7a–c** in 6 mL of dry THF, 2.2 mmol (1.1 equiv.) of the corresponding amines **8a–f** were added at r.t. The reaction mixture was stirred at r.t. under Ar for the time specified in Tables 2–4. After completion of the reaction (TLC and/or GC monitoring), the solvent was removed under reduced pressure and the resulting residue was purified by flash-chromatography (n-hexane:AcOEt) and dried under high vacuum.

4.4.1. 2-Anilino-1-benzyl-4-methyl-4,5-dihydro-1*H*-5-imidazolone (10a). According to the general procedure described above, the reaction between **7a** and benzyl amine **8a** afforded 0.48 g (86%) of **10a** as a colourless oil. ^{1}H NMR ($CDCl_3$): δ 0.79 (d, 3H, J=6.9 Hz, CH_3), 4.02 (q, 1H, J=6.9 Hz, CH), 4.86 (s, 2H, PhCH_2), 4.94 (s, br., 1H, NH), 7.0–7.55 (m, 10H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 18.01 (q, CH$_3$), 42.45 (t, PhCH$_2$), 53.24 (d, CH), 122.29 (d, 2CH$_{arom.}$), 123.09 (d, CH$_{arom.}$), 127.55 (d, CH$_{arom.}$), 128.38 (d, 2CH$_{arom.}$), 128.57 (d, 2CH$_{arom.}$), 129.34 (d, 2CH$_{arom.}$), 136.41 (s, $C_{arom.}$), 147.43 (s, C(2)), 149.08 (s, $C_{arom.}$), 174.13 (s, CO). IR (film) ν 3335, 3063, 3023, 2977, 2930, 1742, 1676, 1592, 1545, 1490, 1441, 1418, 1391, 1367, 1322, 1278, 1237, 1197, 1131, 110, 1075, 990, 835, 758, 744, 730, 697 cm^{-1}. MS (FAB$^+$) *m/e*: 280 ([M+1]$^+$, 100), 279 (M$^+$, 25), 207 (30), 165 (20), 149 (31), 147 (39), 145 (54), 119 (78), 109 (93), 105 (98). Anal. Calc. for $C_{17}H_{17}N_3O$ (279.34): C 73.10%, H 6.13%, N 15.04. Found: C 73.07%, H 5.96%, N 15.32%.

4.4.2. 2-Anilino-1-benzyl-4-ethyl-4,5-dihydro-1*H*-5-imidazolone (10b). According to the general procedure described above, the reaction between **7b** and benzyl amine **8a** afforded 0.49 g (84%) of **10b** as a colourless oil. ^{1}H NMR ($CDCl_3$): δ 0.79 (t, 3H, J=7.4 Hz, CH_3), 1.65–1.70 (m, 2H, CH_2), 3.85 (t, 1H, J=5.7 Hz, CH), 4.69 (s, br., 1H, NH), 4.76 (s, 2H, PhCH_2), 6.90–7.45 (m, 10H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 8.55 (q, CH$_3$), 25.24 (t, CH$_3$$CH_2$), 42.49 (t, Ph$CH_2$), 58.36 (d, CH), 122.31 (d, 2CH$_{arom.}$), 123.10 (d, CH$_{arom.}$), 127.57 (d, CH$_{arom.}$), 128.39 (d, 2CH$_{arom.}$), 128.65 (d, 2CH$_{arom.}$), 129.45 (d, 2CH$_{arom.}$), 133.51 (s, $C_{arom.}$), 147.66 (s, C(2)), 149.44 (s, $C_{arom.}$), 173.39 (s, CO). IR (film) ν 3343, 3063, 3029, 2967, 2926, 2878, 1744, 1682, 1593, 1491, 1443, 1416, 1368, 1320, 1236, 1194, 1131, 1103, 1068, 1025, 934, 906, 842, 772, 723, 695 cm^{-1}. MS (FAB$^+$) *m/e*: 294 ([M+1]$^+$, 100), 293 (M$^+$, 28), 154 (16), 137 (14), 136 (17), 123 (10), 119 (18), 109 (17), 107 (16), 105 (17). Anal. Calc. for $C_{18}H_{19}N_3O$ (293.36): C 73.69%, H 6.53%, N 14.32. Found: C 73.91%, H 6.67%, N 14.03%.

4.4.3. 2-Anilino-1-benzyl-4-phenyl-4,5-dihydro-1*H*-5-imidazolone (10c). According to the general procedure described above, the reaction between **7c** and benzyl amine **8a** afforded after recrystallization from CCl_4 0.59 g (88%) of **10c** as a colourless solid. M.p.: 129–130°C. ^{1}H NMR ($CDCl_3$): δ 4.75 (d, 1H, J=14.2 Hz, PhCH_2), 4.83 (s, 1H, CH), 4.87 (d, 1H, J=14.2 Hz, PhCH'_2), 5.04 (s, br., 1H, NH), 6.95–7.50 (m, 15H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 42.80 (t, PhCH$_2$), 61.16 (d, CH), 122.48 (d, 2CH$_{arom.}$), 123.89 (d, CH$_{arom.}$), 126.49 (d, 2CH$_{arom.}$), 127.65 (d, CH$_{arom.}$), 128.42 (d, 2CH$_{arom.}$), 128.69 (d, 2CH$_{arom.}$), 128.81 (d, 2CH$_{arom.}$), 128.96 (d, 2CH$_{arom.}$), 129.54 (d, CH$_{arom.}$), 135.60 (s, $C_{arom.}$), 136.31 (s, $C_{arom.}$), 147.28 (s, C(2)), 149.01 (s, $C_{arom.}$), 171.63 (s, CO). IR (KBr) ν 3388, 3057, 3036, 2917, 2868, 1750, 1670, 1591, 1491, 1451, 1435, 1412, 1361, 1335, 1307, 1278, 1264, 1229, 1187, 10632, 941, 899, 774, 728, 695 cm^{-1}. MS (FAB$^+$) *m/e*: 342 ([M+1]$^+$, 19), 341 (M$^+$, 74), 340 (11), 313 (14), 312 (17), 209.(10), 208 (13), 207 (49), 117 (11), 106 (100), 104 (13), 91 (52), 77 (37), 65 (18), 51 (12). Anal. Calc. for $C_{22}H_{19}N_3O$ (341.41): C 77.40%, H 5.61%, N 12.31. Found: C 77.61%, H 5.76%, N 12.03%.

4.4.4. 2-Anilino-4-methyl-1-propyl-4,5-dihydro-1*H*-5-imidazolone (10d). According to the general procedure described above, the reaction between **7a** and n-propyl amine **8b** afforded 0.35 g (76%) of **10d** as a colourless oil. ^{1}H NMR ($CDCl_3$): δ 0.97 (t, 3H, J=7.4 Hz, CH_3), 1.35 (d, 3H, J=6.9 Hz, CH_3), 1.74 (sext., 2H, J=7.4 Hz, CH_2), 3.62 (t, 2H, J=7.2 Hz, NCH_2), 3.95 (q, 1H, J=6.9 Hz, H_4), 4.55 (s, br., 1H, NH), 6.95–7.35 (m, 5H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 11.12 (q, CH$_3$), 18.07 (q, CH$_3$), 20.94 (t, CH$_2$), 40.60 (t, NCH$_2$), 53.06 (d, CH), 122.31 (d, 2CH$_{arom.}$), 123.02 (d, CH$_{arom.}$), 129.30 (d, 2CH$_{arom.}$), 147.55 (s, C(2)), 149.57 (s, $C_{arom.}$), 174.45 (s, CO). IR (KBr) ν 3329, 3057, 3022, 2964, 2933, 2877, 1735, 1675, 1592, 1490, 1454, 1446, 1422, 1372, 1321, 1278, 1229, 1210, 1132, 1089, 1046, 1025, 835, 793, 751, 730, 698 cm^{-1}. MS (FAB$^+$) *m/e*: 232 ([M+1]$^+$, 100), 231 (M$^+$, 23), 230 (14), 161 (13), 145 (22), 123 (18), 121 (16), 119 (41), 109 (38), 107 (26), 105 (32). Anal. Calc. for $C_{13}H_{17}N_3O$ (231.29): C 67.51%, H 7.41%, N 18.17. Found: C 67.67%, H 7.51%, N 17.93%.

4.4.5. 2-Anilino-4-ethyl-1-propyl-4,5-dihydro-1*H*-5-imidazolone (10e). According to the general procedure described above, the reaction between **7b** and n-propyl amine **8b** afforded 0.38 g (75%) of **10e** as a colourless oil. ^{1}H NMR ($CDCl_3$): δ 0.8 (t, 3H, J=7.5 Hz, CH_3), 0.89 (t, 3H, J=7.4 Hz, CH_3), 1.60–1.75 (m, 4H, 2CH_2), 3.56 (t, 2H, J=7.2 Hz, NCH_2), 3.85 (t, 1H, J=5.6 Hz, CH), 4.60 (s, br., 1H, NH), 6.85–7.30 (m, 5H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 8.41 (q, CH$_3$), 11.21 (q, CH$_3$), 21.02 (t, CH$_2$), 25.12 (t, CH$_2$), 40.65 (t, NCH$_2$), 58.18 (d, CH), 122.34 (d, 2CH$_{arom.}$), 123.04 (d, CH$_{arom.}$), 129.40 (d, 2CH$_{arom.}$), 147.74 (s, C(2)), 149.98 (s, $C_{arom.}$), 173.67 (s, CO). IR (KBr) ν 3297, 3072,

3051, 2972, 2952, 2932, 2873, 1713, 1681, 1588, 1488, 1452, 1415, 1374, 1321, 1213, 1125, 1101, 1063, 848, 772, 745, 696 cm^{-1}. MS (FAB^+) *m/e*: 246 ($[M+1]^+$, 100), 245 (M^+, 20), 207 (10), 159 (12), 147 (32), 145 (10). Anal. Calc. for $C_{14}H_{19}N_3O$ (245.32): C 68.54%, H 7.81%, N 17.13%. Found: C 68.26%, H 7.94%, N 16.92%.

4.4.6. 2-Anilino-4-phenyl-1-propyl-4,5-dihydro-1*H*-5-imidazolone (10f). According to the general procedure described above, the reaction between **7c** and n-propyl amine **8b** afforded 0.52 g (89%) of **10f** as a colourless solid. M.p.: 135–136°C_{dec}. ^1H NMR (DMSO-d_6): δ 0.86 (t, 3H, *J*=7.4 Hz, CH_3), 1.65 (sext., 2H, *J*=7.4 Hz, CH_2), 3.5 (t, 2H, *J*=6.9Hz, NCH_2), 5.07 (d, 1H, *J*=2 Hz, C*H*), 6.90–7.40 (m, 10$H_{arom.}$), 7.75 (d, 1H, *J*=2 Hz, N*H*). ^{13}C NMR (DMSO-d_6): δ 11.05 (q, *C*H_3), 20.59 (t, *C*H_2), 40.05 (t, N*C*H_2), 60.51 (*C*H), 121.98 (d, *C*$H_{arom.}$), 122.48 (d, *C*$H_{arom.}$), 126.74 (d, *C*$H_{arom.}$), 127.99 (d, *C*$H_{arom.}$), 128.47 (d, *C*$H_{arom.}$), 128.93 (d, *C*$H_{arom.}$), 137.23 (s, $C_{arom.}$), 147.99 (s, $C_{arom.}$), 149.26 (s, *C*(2)), 172.15 (s, *C*O). IR (KBr) ν 3290, 3044, 3022, 2959, 2931, 2875, 1725, 1683, 1665, 1589, 1489, 1452, 1420, 1368, 1335, 1300, 1236, 1208, 1159, 1112, 1060, 1004, 899, 850, 779, 744, 698 cm^{-1}. MS (FAB^+) *m/e*: 294 ($[M+1]^+$, 16), 293 (M^+, 68), 264 (10), 252 (13), 251 (59), 250 (37), 236 (13), 222 (24), 207 (11), 183 (15), 182 (100), 176 (58), 175 (38), 146 (11), 145 (13), 131 (14), 119 (21), 118 (44), 107 (10), 106 (92), 104 (32), 93 (10), 92 (10), 91 (38), 83 (12), 81 (11), 78 (13), 77 (74), 69 (23), 57 (22), 55 (20), 51 (25). Anal. Calc. for $C_{18}H_{19}N_3O$ (293.36): C 73.69%, H 6.53%, N 14.32%. Found: C 73.44%, H 6.71%, N 14.05%.

4.4.7. 2-(*tert*-Butylamino)-4-methyl-1-phenyl-4,5-dihydro-1*H*-5-imidazolone (11a). According to the general procedure described above, the reaction between **7a** and *tert*-butylamine **8c** afforded 0.33 g (68%) of **11a** as a colourless solid. M.p.: 59–60°C. ^1H NMR ($CDCl_3$): δ 1.39 (s, 9H, 3CH_3), 1.48 (d, 3H, *J*=7.4 Hz, CH_3), 3.72 (s, br., 1H, N*H*), 4.22 (q, 1H, *J*=7.4 Hz, C*H*), 7.20–7.50 (m, 5$H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 18.25 (q, *C*H_3), 28.73 (q, 3*C*H_3), 51.57 (s, $C_{t\text{-}bu}$), 62.27 (d, *C*H), 127.27 (d, 2*C*$H_{arom.}$), 128.83 (d, *C*$H_{arom.}$), 129.91 (d, 2*C*$H_{arom.}$), 132.23 (s, $C_{arom.}$), 151.20 (s, *C*(2)), 181.52 (s, *C*O). IR (KBr) ν 3424, 3063, 2959, 2927, 2869, 1734, 1652, 1595f, 1457, 1364, 1304, 1221, 1182, 1132, 763, 738, 695 cm^{-1}. MS (FAB^+) *m/e*: 246 ($[M+1]^+$, 100), 245 (M^+, 8), 192 (19), 191(13), 190 (71), 189 (16), 188 (32), 136 (18), 133 (62). Anal. Calc. for $C_{14}H_{19}N_3O$ (245.32): C 68.54%, H 7.81%, N 17.13%. Found: C 68.25%, H 7.91%, N 16.97%.

4.4.8. 2-(*tert*-Butylamino)-4-ethyl-1-phenyl-4,5-dihydro-1*H*-5-imidazolone (11b). According to the general procedure described above, the reaction between **7b** and *tert*-butylamine **8c** afforded 0.38 g (75%) of **11b** as a colourless solid. M.p.: 73–74°C. ^1H NMR ($CDCl_3$): δ 1.01 (t, 3H, *J*=7.3 Hz, CH_3), 1.42 (s, 9H, 3CH_3), 1.90–1.95 (m, 2H, CH_2), 3.73 (s, br., 1H, N*H*), 4.23 (t, 1H, *J*=5.3 Hz, H_4), 7.20–7.55 (m, 5$H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 8.51 (q, *C*H_3), 25.47 (t, *C*H_2), 29.06 (q, 3*C*H_3), 51.62 (s, $C_{t\text{-}bu}$), 67.20 (d, *C*H), 127.34 (d, 2*C*$H_{arom.}$), 128.68 (d, *C*$H_{arom.}$), 129.94 (d, 2*C*$H_{arom.}$), 132.35 (s, $C_{arom.}$), 151.55 (s, *C*(2)), 180.96 (s, *C*O). IR (KBr) ν 3353, 2974, 2961, 2929, 2869, 1724, 1653, 1596, 1523, 1493, 1458, 1398, 1365, 1305, 1287, 1222, 1180, 1135, 1068, 990, 927, 793, 765, 735, 706, 681 cm^{-1}. MS (FAB^+) *m/e*: 260 ($[M+1]^+$, 100), 259 (M^+, 11), 204 (51), 202 (24). Anal. Calc. for $C_{15}H_{21}N_3O$ (259.35): C 69.47%, H 8.16%, N 16.20%. Found: C 69.25%, H 8.01%, N 16.47%.

4.4.9. 2-(*tert*-Butylamino)-1,4-diphenyl-4,5-dihydro-1*H*-5-imidazolone (11c). According to the general procedure described above, the reaction between **7c** and *tert*-butylamine **8c** afforded 0.44 g (72%) of **11c** as a colourless solid. M.p.: 119–120°C_{dec}. ^1H NMR ($CDCl_3$): δ 1.32 (s, 9H, 3CH_3), 3.72 (s, br., 1H, N*H*), 5.12 (s, 1H, C*H*), 7.05–7.40 (m, 10$H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 29.40 (q, 3*C*H_3), 52.38 (s, $C_{t\text{-}bu}$), 69.95 (d, *C*H), 127.29 (d, 2*C*$H_{arom.}$), 127.89 (d, 2*C*$H_{arom.}$), 128.05 (d, *C*$H_{arom.}$), 128.88 (d, 2*C*$H_{arom.}$), 129.45 (d, *C*$H_{arom.}$), 130.46 (d, 2*C*$H_{arom.}$), 132.73 (s, $C_{arom.}$), 138.28 (s, $C_{arom.}$), 152.94 (s, *C*(2)), 179.13 (s, *C*O). IR (KBr) ν 3382, 3058, 3029, 2980, 2961, 2924, 1739, 1636, 1596, 1513, 1496, 1451, 1393, 1355, 1295, 120, 1159, 1103, 1025, 927, 751, 704, 690 cm^{-1}. MS (FAB^+) *m/e*: 308 ($[M+1]^+$, 10), 307 (M^+, 16), 252 (20), 251 (20), 222 (23), 159 (36), 132 (33), 131 (36), 119 (77), 118 (40), 85 (26), 83 (40), 81 (26), 77 (65), 73 (24), 71 (38), 69 (52), 67 (25), 60 (22), 57 (100), 56 (31), 55 (73), 51 (26). Anal. Calc. for $C_{19}H_{21}N_3O$ (307.39): C 74.24%, H 6.89%, N 13.67%. Found: C 74.14%, H 7.06%, N 13.54%. Spectroscopic data for **12**: ^1H NMR ($CDCl_3$): δ 1.47 (s, 18H, 6CH_3), 6.65 (s, br., 2H, 2N*H*), 7.15–7.45 (m, 16$H_{arom.}$), 7.55–7.65 (m, 2$H_{arom.}$), 8.1–8.2 (m, 2$H_{arom.}$). M.p.: 149–151°C_{dec}.

4.4.10. 2-Anilino-1-isopropyl-4-methyl-4,5-dihydro-1*H*-5-imidazolone (10g) and 2-isopropyl-amino-4-methyl-1-phenyl-4,5-dihydro-1*H*-5-imidazolone (11d). According to the general procedure described above, the reaction between **7a** and isopropyl amine **8f** afforded 0.31 g (67%) of **10g** as a colourless solid. M.p.: 90–91°C_{dec}, and 0.07 g (15%) of **11d** as a colourless solid. M.p.: 118–119°C. Spectroscopic data for **10g**: ^1H NMR ($CDCl_3$): δ 1.35 (d, 3H, *J*=6.8 Hz, CH_3), 1.51 (d, 3H, *J*=7 Hz, CH_3), 1.55 (d, 3H, *J*=7 Hz, CH_3), 3.91 (q, 1H, *J*=6.8 Hz, C*H*), 4.58 (m, 1H, *J*=7 Hz, NC*H*(CH_3)$_2$), 4.69 (s, br., 1H, N*H*), 7.0–7.40 (m, 5$H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 18.14 (q, CH_3), 19.22 (q, 2CH_3), 44.17 (d, NCH(CH_3)$_2$), 57.70 (d, CH), 122.29 (d, 2$CH_{arom.}$), 122.96 (d, $CH_{arom.}$), 129.38 (d, 2$CH_{arom.}$), 147.84 (s, C(2)), 149.32 (s, $C_{arom.}$), 174.35 (s, CO). IR (KBr) ν 3343, 3077, 2917, 2931, 2890, 1743, 1679, 1590, 1487, 1425, 1387, 1324, 1222, 1137, 1041 cm^{-1}. MS (FAB^+) *m/e*: 232 ($[M+1]^+$, 100), 231 (M^+, 25), 218 (5), 204 (5), 190 (9), 189 (6), 188 (5). Anal. Calc. for $C_{13}H_{17}N_3O$ (231.29): C 67.51%, H 7.41%, N 18.17%. Found: C 67.32%, H 7.25%, N 17.99%. Spectroscopic data for **11d**: ^1H NMR ($CDCl_3$): δ 1.12 (d, 6H, *J*=6.4 Hz, 2CH_3), 1.41 (d, 3H, *J*=7.4 Hz, CH_3), 3.62 (s, br., 1H, N*H*), 4.01 (m, 1H, *J*=6.4 Hz, NC*H*(CH_3)$_2$), 4.11 (q, 1H, *J*=7.4 Hz, C*H*), 7.15–7.50 (m, 5$H_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 17.17 (q, *C*H_3), 22.68 (q, *C*H_3), 22.85 (q, *C*H_3), 43.41 (d, NCH(CH_3)$_2$), 62.00 (d, *C*H), 127.21 (d, 2*C*$H_{arom.}$), 128.92 (d, *C*$H_{arom.}$), 130.0 (d, 2*C*$H_{arom.}$), 132.12 (s, $C_{arom.}$), 152.73 (s, *C*(2)), 181.87 (s, *C*O). IR (KBr) ν 3344, 3069, 3043, 2966, 2926, 2864, 1724, 1646, 1593, 1520, 1453, 1370, 1344, 1322, 1279, 1239, 1159, 1126, 1068, 957, 844, 767, 735, 706, 690 cm^{-1}. MS (FAB^+) *m/e*: 232 ($[M+1]^+$, 89), 231 (M^+, 6), 178 (18),

165 (10), 154 (16), 149 (22), 145 (13), 137 (12), 136 (20), 133 (100), 131 (15), 123 (13), 121 (16), 119 (40), 115 (20), 109 (27), 107 (30), 105 (38). Anal. Calc. for $C_{13}H_{17}N_3O$ (231.29): C 67.51%, H 7.41%, N 18.17%. Found: C 67.22%, H 7.66%, N 17.96%.

4.4.11. 2-Anilino-4-ethyl-1-isopropyl-4,5-dihydro-1*H*-5-imidazolone (10h) and 4-ethyl-2-isopropylamino-1-phenyl-4,5-dihydro-1*H*-5-imidazolone (11e). According to the general procedure described above, the reaction between **7b** and isopropyl amine **8f** afforded 0.17 g (35%) of **10h** as a colourless solid. M.p.: 91–92°C, and 0.17 g (35%) of **11e** as a colourless solid. M.p.: 120–121°C. Spectroscopic data for **10h**: ^{1}H NMR ($CDCl_3$): δ 0.92 (t, 3H, J=7.4 Hz, CH_3), 1.52 (d, 3H, J=6.9 Hz, CH_3), 1.53 (d, 3H, J=6.9 Hz, CH_3), 1.70–1.85 (m, 2H, CH_2), 3.86 (t, 1H, J=5.2 Hz, CH), 4.59 (m, 1H, J=6.9 Hz, NCH(CH_3)$_2$), 4.66 (s, br., 1H, NH), 6.95–7.40 (m, 5H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 8.13 (q, CH$_3$), 19.17 (q, CH$_3$), 19.29 (q, CH$_3$), 25.62 (t, CH$_2$), 44.19 (d, NCH(CH$_3$)$_2$), 57.62 (d, CH), 122.28 (d, 2CH$_{arom.}$), 122.90 (d, CH$_{arom.}$), 129.41 (d, 2CH$_{arom.}$), 147.99 (s, C(2)), 149.71 (s, $C_{arom.}$), 173.57 (s, CO). IR (KBr) ν 3338, 2968, 2926, 2877, 2853, 1725, 1677, 1590, 1487, 1458, 1428, 1385, 1331, 1246, 1218, 1123, 1080, 934, 874, 720, 691 cm^{-1}. MS (FAB$^+$) *m/e*: 246 ([M+1]$^+$, 100), 245 (M$^+$, 32), 204 (22), 202 (20), 159 (18). Anal. Calc. for $C_{14}H_{19}N_3O$ (245.32): C 68.54%, H 7.81%, N 17.13%. Found: C 68.41%, H 7.92%, N 16.87%. Spectroscopic data for **11e**: ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H, J=7.3 Hz, CH_3), 1.11 (d, 3H, J=6.3 Hz, CH_3), 1.12 (d, 3H, J=6.3 Hz, CH_3), 1.80–2.0 (m, 2H, CH_2), 3.62 (s, br., 1H, NH), 4.02 (m, 1H, J=6.3 Hz, NCH(CH_3)$_2$), 4.11 (t, 1H, J=5.3 Hz, CH), 7.10–7.50 (m, 5H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 8.61 (q, CH$_3$), 22.67 (q, CH$_3$), 22.81 (q, CH$_3$), 25.40 (t, CH$_2$), 43.40 (d, NCH(CH$_3$)$_2$), 66.89 (d, CH), 127.21 (d, 2CH$_{arom.}$), 128.89 (d, CH$_{arom.}$), 129.96 (d, 2CH$_{arom.}$), 132.11 (s, $C_{arom.}$), 151.95 (s, C(2)), 181.17 (s, CO). IR (KBr) ν 3336, 3050, 2965, 2920, 2875, 2853, 1728, 1640, 1595, 1524, 1497, 1454, 1371, 1341, 1328, 1293, 1264, 1215, 1155, 1130, 1104, 1068, 983, 765, 737, 716, 695 cm^{-1}. MS (FAB$^+$) *m/e*: 246 ([M+1]$^+$, 100), 245 (M$^+$, 5), 133 (19), 119 (25). Anal. Calc. for $C_{14}H_{19}N_3O$ (245.32): C 68.54%, H 7.81%, N 17.13%. Found: C 68.26%, H 7.94%, N 16.99%.

4.4.12. 2-Anilino-1-isopropyl-4-phenyl-4,5-dihydro-1*H*-5-imidazolone (10i). According to the general procedure described above, the reaction between **7c** and isopropyl amine **8f** afforded 0.41 g (70%) of **10i** as a yellow solid. M.p.: 154–155°C$_{dec}$. ^{1}H NMR ($CDCl_3$): δ 1.55 (d, 3H, J=7 Hz, CH_3), 1.59 (d, 3H, J=7 Hz, CH_3), 4.66 (m, 1H, J=7Hz, NCH(CH_3)$_2$), 4.85 (s, 1H, CH), 5.07 (s, br. 1H, NH), 7.05–7.45 (m, 10H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 19.19 (q, CH$_3$), 19.3 (q, CH$_3$), 44.52 (d, NCH(CH$_3$)$_2$), 60.67 (d, CH), 122.25 (d, 2CH$_{arom.}$), 123.145 (d, CH$_{arom.}$), 126.41 (d, 2CH$_{arom.}$), 128.74 (d, CH$_{arom.}$), 128.99 (d, 2CH$_{arom.}$), 129.49 (d, 2CH$_{arom.}$), 133.16 (s, $C_{arom.}$), 147.72 (s, C(2)), 149.3 (s, $C_{arom.}$), 171.74 (s, CO). IR (KBr) ν 3325, 3064, 3029, 2980, 2938, 2875, 1746, 1674, 1644, 1590, 1574, 1492, 1455, 1421, 1389, 1368, 1343, 1287, 1209, 1124, 1103, 1075, 983, 906, 842, 729, 699 cm^{-1}. MS (FAB$^+$) *m/e*: 294 ([M+1]$^+$, 100), 293 (M$^+$, 63), 292 (40), 291 (43), 251(24), 250 (41), 248 (20), 182 (22), 176 (15), 172 (14), 93 (11), 91 (26), 77 (55), 76 (15), 65 (12), 51 (20). Anal. Calc. for $C_{18}H_{19}N_3O$ (293.36): C 73.69%, H 6.53%, N 14.32%. Found: C 73.51%, H 6.82%, N 14.15%.

4.4.13. 4-Methyl-1-phenyl-2-tetrahydro-1*H*-1-pyrrolyl-4,5-dihydro-1*H*-5-imidazolone (15a). According to the general procedure described above, the reaction between **7a** and pyrrolidine **13a** afforded 0.21 g (88%) of **15a** as a colourless solid. M.p.: 63–64°C. ^{1}H NMR ($CDCl_3$): δ 1.39 (d, 3H, J=7.4 Hz, CH_3), 1.60–1.75 (m, 4H), 3.0–3.05 (m, 4H), 4.14 (q, 1H, J=7.4 Hz, CH), 7.15–7.40 (m, 5H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 18.30 (q, CH$_3$), 25.15 (t, 2CH$_2$), 48.46 (t, 2CH$_2$), 61.71 (d, CH), 127.64 (d, 2CH$_{arom.}$), 128.29 (d, CH$_{arom.}$), 129.33 (d, 2CH$_{arom.}$), 134.90 (s, $C_{arom.}$), 156.2 (s, C(2)), 182.80 (s, CO). IR (KBr) ν 2966, 2929, 2872, 1740, 1616, 1490, 1418, 1329, 1251, 1176, 1130, 1078, 1027, 981, 885, 750, 699 cm^{-1}. MS (FAB$^+$) *m/e*: 244 ([M+1]$^+$, 100), 243 (M$^+$, 11), 320 (31), 205 (22), 189 (20), 137 (21), 136 (45), 107 (72), 105 (10). Anal. Calc. for $C_{14}H_{17}N_3O$ (243.30): C 69.11%, H 7.04%, N 17.27%. Found: C 69.15%, H 6.85%, N 17.01%.

4.4.14. 4-Ethyl-1-phenyl-2-tetrahydro-1*H*-1-pyrrolyl-4,5-dihydro-1*H*-5-imidazolone (15b). According to the general procedure described above, the reaction between **7b** and pyrrolidine **13a** afforded 0.25 g (98%) of **15b** as a colourless oil. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, J=7.4 Hz, CH$_3$), 1.60–1.80 (m, 4H), 1.80–1.95 (m, 2H, CH_2), 3.0–3.05 (m, 4H), 4.13 (t, 1H, J=5.5 Hz, CH), 7.15–7.40 (m, 5H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 8.74 (q, CH$_3$), 25.15 (t, 2CH$_2$), 25.56 (t, CH$_2$), 48.45 (t, 2CH$_2$), 66.73 (d, CH), 127.62 (d, 2CH$_{arom.}$), 128.25 (d, CH$_{arom.}$), 129.33 (d, 2CH$_{arom.}$), 134.97 (s, C_{arom}), 156.18 (s, C(2)), 182.81 (s, CO). IR (film) ν 3064, 3043, 2966, 2931, 2868, 1743, 1616, 1496, 1454, 1419, 1342, 1335, 1229, 1180, 1145, 906, 758, 716, 681 cm^{-1}. MS (FAB$^+$) *m/e*: 258 ([M+1]$^+$, 100), 257 (M$^+$, 17), 205 (32), 189 (23), 136 (29), 107 (15). Anal. Calc. for $C_{15}H_{19}N_3O$ (257.33): C 70.01%, H 7.44%, N 16.33%. Found: C 70.23%, H 7.25%, N 17.21%.

4.4.15. 4-Methyl-2-morpholine-1-phenyl-4,5-dihydro-1*H*-5-imidazolone (15c). According to the general procedure described above, the reaction between **7a** and morpholine **13b** afforded 0.20 g (80%) of **15c** as a colourless solid. M.p.: 95–97°C. ^{1}H NMR ($CDCl_3$): δ 1.49 (d, 3H, J=7.4 Hz, CH_3), 3.06 (t, 4H, J=4.8 Hz), 3.6 (t, 4H, J=4.8), 4.18 (q, 1H, J=7.4 Hz, CH), 7.30–7.50 (m, 5H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 17.74 (q, CH$_3$), 47.44 (t, 2CH$_2$), 62.08 (d, CH), 65.87 (t, 2CH$_2$), 125.81 (d, 2CH$_{arom.}$), 128.04 (d, CH$_{arom.}$), 129.38 (d, 2CH$_{arom.}$), 134.55 (s, $C_{arom.}$), 158.38 (s, C(2)), 182.40 (s, CO). IR (KBr) ν 3055, 2976, 2921, 2854, 1739, 1617, 1591, 1494, 1452, 1368, 1330, 1304, 1260, 1171, 1114f, 1008, 904, 868, 743, 698 cm^{-1}. MS (FAB$^+$) *m/e*: 260 ([M+1]$^+$, 100), 259 (M$^+$, 14), 258 (42), 207 (16), 206 (83), 205 (11), 149 (25), 147 (18), 145 (47), 133 (49), 131 (29), 119 (47), 117 (25), 115 (17), 111 (22), 109 (45), 107 (33), 105 (46), 104 (19). Anal. Calc. for $C_{14}H_{17}N_3O_2$ (259.30): C 64.85%, H 6.61%, N 16.21%. Found: C 64.66%, H 6.48%, N 16.49%.

4.4.16. 4-Ethyl-2-morpholine-1-phenyl-4,5-dihydro-1*H*-5-imidazolone (15d). According to the general procedure described above, the reaction between **7b** and morpholine

13b afforded 0.21 g (79%) of **15d** as a colourless oil. ^{1}H NMR ($CDCl_3$): δ 0.92 (t, 3H, J=7.4 Hz, CH_3), 1.70–2.05 (m, 2H, CH_2), 2.90–3.15 (m, 4H), 3.05–3.55 (m, 4H), 4.12 (t, 1H, J=5.5 Hz, CH), 7.20–7.45 (m, 5H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 8.79 (q, CH_3), 25.16 (t, CH_2), 47.49 (t, 2CH_2), 65.89 (t, 2CH_2), 67.09 (d, CH), 125.85 (d, 2$CH_{arom.}$), 128.04 (d, $CH_{arom.}$), 129.4 (d, 2$CH_{arom.}$), 134.51 (s, $C_{arom.}$), 158.74 (s, C(2)), 181.81 (s, CO). IR (film) ν 3062, 3038, 2963, 2923, 2854, 1745, 1626, 1596, 1497, 1455, 1407, 1334, 1303, 1260, 1182, 1160, 1119f, 1070, 1014, 900, 881, 752, 730, 711, 693 cm^{-1}. MS (FAB$^+$) *m/e*: 274 ([M+1]$^+$, 10), 273 (M$^+$, 9), 207 (19), 206 (100), 205 (12), 189 (11), 149 (17), 133 (20), 109 (38). Anal. Calc. for $C_{15}H_{19}N_3O_2$ (273.33): C 65.91%, H 7.01%, N 15.37%. Found: C 66.12%, H 6.85%, N 15.59%.

4.4.17. 2-Diethylamino-4-methyl-1-phenyl-4,5-dihydro-1*H*-5-imidazolone (15e). According to the general procedure described above, the reaction between **7a** and diethyl amine **13c** afforded 0.22 g (92%) of **15e** as a colourless oil. ^{1}H NMR ($CDCl_3$): δ 1.03 (t, 6H, J=7 Hz, 2CH_3), 1.53 (d, 3H, J=7.4 Hz, CH_3), 3.09 (q, 4H, J=7 Hz, 2NCH_2), 4.27 (q, 1H, J=7.4 Hz, CH), 7.30–7.55 (m, 5H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 12.34 (q, 2CH_3), 18.2 (q, CH_3), 42.86 (t, 2NCH_2), 61.88 (d, CH), 126.51 (d, 2$CH_{arom.}$), 128.06 (d, $CH_{arom.}$), 129.38 (d, 2$CH_{arom.}$), 135.16 (s, $C_{arom.}$), 157.92 (s, C(2)), 183.56 (s, CO). IR (film) ν 3063, 3036, 2973, 2931, 2871, 1742, 1621, 1537, 1495, 1450, 1415, 1378, 1333, 1277, 1179, 1115, 1076, 895, 781, 744, 698 cm^{-1}. MS (FAB$^+$) *m/e*: 246 ([M+1]$^+$, 52), 231 (M$^+$,22), 244 (64), 234 (10), 193(16), 192 (100), 175 (27), 119 (41). Anal. Calc. for $C_{14}H_{19}N_3O_2$ (245.32): C 68.54%, H 7.81%, N 17.13%. Found: C 68.26%, H 7.97%, N 17.01%.

4.4.18. 2-Diethylamino-4-ethyl-1-phenyl-4,5-dihydro-1*H*-5-imidazolone (15f). According to the general procedure described above, the reaction between **7b** and diethyl amine **13c** afforded 0.25 g (96%) of **15f** as a colourless oil. ^{1}H NMR ($CDCl_3$): δ 0.80–0.95 (m, 9H, 3CH_3), 1.80–1.95 (m, 2H, CH_2), 2.85–3.10 (m, 4H, 2NCH_2), 4.13 (t, 1H, J=5.4 Hz, CH), 7.15–7.45 (m, 5H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 8.56 (q, CH_3), 12.32 (q, 2CH_3), 25.22 (t, CH_2), 42.80 (t, 2NCH_2), 66.95 (d, CH), 126.38 (d, 2$CH_{arom.}$), 127.87 (d, $CH_{arom.}$), 129.26 (d, 2$CH_{arom.}$), 135.14 (s, $C_{arom.}$), 158.27 (s, C(2)), 182.55 (s, CO). IR (film) ν 3057, 3043, 2968, 2931, 2875, 1741, 1621, 1596, 1497, 1461, 1412, 1378, 1334, 1274, 1178, 1131, 1089, 1068, 1028, 984, 883, 782, 747, 694 cm^{-1}. MS (FAB$^+$) *m/e*: 260 ([M+1]$^+$, 20), 259 (M$^+$, 2), 193 (17), 192 (100), 183 (14), 119 (11), 100 (17). Anal. Calc. for $C_{15}H_{21}N_3O$ (259.35): C 69.47%, H 8.16%, N 16.20%. Found: C 69.60%, H 7.95%, N 16.38%.

4.4.19. 2-Morpholino-1,4-diphenyl-4,5-dihydro-1*H*-5-imidazolone (15h). According to the general procedure described above, the reaction between **7c** and morpholine **13b** afforded after crystallization of the residue with CH_2Cl_2:ether:n-pentane instead of the chromatographic purification, 0.25 g (79%) of **15h** as a colourless solid. M.p.: 138–139°C. ^{1}H NMR ($CDCl_3$): δ 3.05–3.10 (m, 4H), 3.55–3.60 (m, 4H), 5.19 (s, 1H, CH), 7.20–7.40 (m, 10H$_{arom.}$). ^{13}C NMR ($CDCl_3$): δ 47.54 (t, 2CH_2), 65.89 (t, 2CH_2), 69.03 (d, CH), 125.91 (d, 2$CH_{arom.}$), 126.81 (d, 2$CH_{arom.}$), 127.91 (d, $CH_{arom.}$), 128.18 (d, $CH_{arom.}$), 128.60 (d, 2$CH_{arom.}$), 129.45 (d, $CH_{arom.}$), 134.48 (s, $C_{arom.}$), 136.14 (s, $C_{arom.}$), 159.27 (s, C(2)), 179.60 (s, CO). IR (KBr) ν 3060, 2990, 2972, 2913, 2888, 2852, 1743, 1619, 1591, 1492, 1450, 1393, 1365, 1328, 1300, 1256, 1221, 1160, 1115, 1068, 1020, 895, 795, 756, 703, 697 cm^{-1}. MS (FAB$^+$) *m/e*: 322 ([M+1]$^+$, 100), 321 (M$^+$, 19), 320 (35), 206 (28), 189 (20), 154 (30), 138 (11), 137 (21), 136 (29), 107 (10), 104 (10). Anal. Calc. for $C_{20}H_{20}N_2O_2$ (320.39): C 79.48%, H 6.29%, N 8.74%. Found: C 79.19%, H 6.07%, N 8.99%.

4.4.20. 4-(5-Oxo-1,4-diphenyl-2-tetrahydro-1*H*-1-pyrrolyl-4,5-dihydro-1*H*-4-imidazolyl)-1,4-diphenyl-2-tetrahydro-1*H*-1-pyrrolyl-4,5-dihydro-1*H*-5-imidazolone (16). According to the general procedure described above, the reaction between **7c** and pyrrolidine **13a** afforded after crystallization of the residue with CH_2Cl_2:ether:n-pentane instead of the chromatographic purification, 0.23 g (75%) of the dimer **16** as a colourless solid. M.p.: 171–172°C. ^{1}H NMR (DMSO-d_6): δ 1.85–1.80 (m, 8H), 3.15–3.30 (m, 8H), 6.55–7.35 (m, 20H$_{arom.}$). ^{13}C NMR (DMSO-d_6): δ 25.19 (t, 4CH_2), 48.69 (t, 4CH_2), 90.9 (s, 2C(4)), 126.47 (d, 4$CH_{arom.}$), 128.11 (d, 2$CH_{arom.}$), 128.17 (d, 4$CH_{arom.}$), 128.57 (d, 4$CH_{arom.}$), 128.88 (d, 2$CH_{arom.}$), 129.80 (d, 4$CH_{arom.}$), 135.54 (s, 2$C_{arom.}$), 141.74 (s, 2$C_{arom.}$), 155.98 (s, 2C(2)), 180.75 (s, 2CO). IR (KBr) ν 3056, 2971, 2868, 2824, 1766, 1609, 1578, 1488, 1450, 1434, 1350, 1311, 1225, 1193, 1169, 1126, 1065, 977, 909, 783, 753, 715, 692 cm^{-1}. MS (FAB$^+$) *m/e*: 608 (M$^+$, 10), 304 (5), 191 (29), 190 (100), 189 (13), 105 (18). Anal. Calc. for $C_{38}H_{36}N_6O_2$ (608.73): C 74.98%, H 5.96%, N 13.81%. Found: C 74.42%, H 6.17%, N 13.52%.

4.4.21. 2-Diethylamino-4-(2-diethylamino-1,4-diphenyl-5-oxo-4,5-dihydro-1*H*-4-imidazolyl)-1,4-diphenyl-4,5-dihydro-1*H*-5-imidazolone (17). According to the general procedure described above, the reaction between **7c** and diethylamine **13c** afforded after crystallization of the residue with CH_2Cl_2:ether:n-pentane instead of the chromatographic purification, 0.24 g (77%) of the dimer **17** as a colourless solid. M.p.: 159–160°C. ^{1}H NMR (DMSO-d_6): δ 1.08 (t, 12H, J=7.0 Hz, 4CH_3), 2.85–3.10 (q, 8H, J=7.0 Hz, 4NCH_2), 6.70–7.70 (m, 20H$_{arom.}$). ^{13}C NMR (DMSO-d_6): δ 12.32 (q, 4CH_3), 42.80 (t, 4NCH_2), 90.36 (s, 2C(4)), 126.38 (d, 4$CH_{arom.}$), 127.87 (d, 2$CH_{arom.}$), 129.26 (d, 4$CH_{arom.}$), 135.14 (s, 2$C_{arom.}$), 158.27 (s, 2C(2)), 182.55 (s, 2CO). IR (KBr) ν 3059, 2987, 2967, 2930, 2790, 1757, 1612f, 1578, 1493, 1444, 1424, 1330, 1278, 1231, 1185, 1111, 1062, 1000, 877, 786, 753, 706, 695 cm^{-1}. MS (FAB$^+$) *m/e*: 613 ([M+1]$^+$10), 612 (M$^+$, 5), 193 (19), 192 (100), 154 (17), 137 (13), 136 (19), 119 (11), 105 (17). Anal. Calc. for $C_{38}H_{40}N_6O_2$ (612.76): C 74.48%, H 6.58%, N 13.71%. Found: C 74.18%, H 6.36%, N 13.97%.

4.5. Synthesis of 4,5-dihydro-1*H*-5-imidazolones of general structure 20. General procedure

Method A: To a solution of the corresponding carbodiimides **7a–b** (1 mmol, 1 equiv.) in 3 mL of anhydrous MeCN, 1 mmol (1 equiv.) of the corresponding amidines **18a–d** (as hydrohalide salts; X=Br for **18a**, X=I for **18b** and X=Cl for **18c** and **18d**) followed by 1 mmol K_2CO_3

were added sequentially at r.t. The reaction mixture was stirred at r.t. under an Ar atmosphere for the time specified in Table 5. After completion of the reaction (TLC monitoring) the solvent was eliminated under reduced pressure and the resulting residue was partitioned with 25 mL of a 4:1 mixture of AcOEt:H_2O. The organic layer was separated and washed with 5 mL portions of brine (3×). The organic layer was dried over anhydrous $MgSO_4$, the solvent eliminated under reduced pressure and the resulting residue purified by flash-chromatography (n-hexane: AcOEt) and the pure products dried under high vacuum.

Method B: To a solution of the carbodiimide **7c** (1 mmol, 1 equiv.) in 3 mL of anhydrous MeCN, 1 mmol (1 equiv.) of amidines **18b** and **18d** were added followed by the addition of 1 mmol of DIPEA. After stirring at r.t. under Ar atmosphere for the time specified in Table 5, a solid precipitates, which was filtered and washed sequentially with MeCN, ether and n-pentane and dried under high vacuum.

4.5.1. 2-Benzylsulfanyl(imino)methylamino-1-phenyl-4-methyl-4,5-dihydro-1*H*-5-imidazolone (20a). According to the general procedure described above (Method A), the reaction between **7a** and **18a** afforded 0.23 g (69%) of **20a** as a colourless solid. M.p.: 143–144°C. ^{1}H NMR (DMSO-d_6): δ 1.18 (d, 3H, J=7.4 Hz, CH_3), 4.08 (s, 2H, CH_2S), 4.27 (q, 1H, J=7.4 Hz, CH), 6.80–7.45 (m, 10H$_{arom.}$), 9.01 (s, br., 1H, NH), 9.85 (s, br., 1H, NH). ^{13}C NMR ($CDCl_3$): δ 17.59 (q, CH$_3$), 34.82 (t, CH$_2$S), 62.31 (d, CH), 127.10 (d, CH$_{arom.}$), 127.44 (d, 2CH$_{arom.}$), 127.61 (d, CH$_{arom.}$), 128.32 (d, 2CH$_{arom.}$), 128.52 (d, 2CH$_{arom.}$), 128.62 (d, 2CH$_{arom.}$), 133.69 (s, $C_{arom.}$), 137.24 (s, $C_{arom.}$), 159.34 (s, C(2)), 168.04 (s, C=N), 181.31 (s, CO). IR (KBr) ν 3330, 3135, 3022, 2980, 2924, 2860, 1718, 1609, 1581, 1454, 1386, 1317, 1281, 1241, 1180, 1111, 1061, 962, 821, 751, 700 cm^{-1}. MS (FAB$^+$) *m/e*: 340 ([M+2]$^+$, 2), 339 ([M+1]$^+$, 4), 243 (19), 215 (96), 190 (8), 92 (9), 91 (100). Anal. Calc. for $C_{18}H_{18}N_4OS$ (338.43): C 63.88%, H 5.36%, N 16.56%. Found: C 63.61%, H 5.13%, N 16.30%.

4.5.2. 2-Decylsulfanyl(imino)methylamino-1-phenyl-4-methyl-4,5-dihydro-1*H*-5-imidazolone (20b). According to the general procedure described above (Method A), the reaction between **7a** and **18b** afforded 0.25 g (65%) of **20b** as a colourless solid. M.p.: 68–69°C. ^{1}H NMR (DMSO-d_6): δ 0.96 (t, 3H, J=6.2 Hz, CH_3), 1.15–1.40 (m, 16H, 8CH_2), 1.45 (d, 3H, J=7.4 Hz, CH_3), 2.7 (t, 2H, J=7.2 Hz, SCH_2), 4.36 (q, 1H, J=7.4 Hz, CH), 7.35–7.60 (m, 5H$_{arom.}$), 9.05 (s, br., 1H, NH), 9.89 (s, br., 1H, NH). ^{13}C NMR (DMSO-d_6): δ 13.97 (q, CH$_3$), 17.47 (q, CH$_3$), 22.13 (t, CH$_2$), 28.10 (t, CH$_2$), 28.55 (t, CH$_2$), 28.71 (t, CH$_2$), 28.94 (t, 3CH$_2$), 29.79 (t, CH$_2$), 33.32 (t, SCH$_2$), 61.69 (d, CH), 127.11 (d, CH$_{arom.}$), 127.53 (d, 2CH$_{arom.}$), 128.24 (d, 2CH$_{arom.}$), 134.01 (s, $C_{arom.}$), 158.93 (s, C(2)), 168.22 (s, C=N), 180.68 (s, CO). IR (KBr) ν 3359, 3219, 3156, 3064, 2959, 2919, 2850, 1707, 1617, 1587, 1510, 1488, 1454, 1385, 1319, 1278, 1236, 1186, 1114, 1060, 1011, 955, 892, 828, 751, 710, 690 cm^{-1}. MS (FAB$^+$) *m/e*: 390 ([M+2]$^+$, 25), 389 ([M+1]$^+$, 100), 388 (M$^+$, 10), 215 (69), 187 (21), 161 (20), 145 (32), 144 (28), 133 (53), 120(24), 119 (76), 117 (26), 115 (22), 114 (21), 109 (46), 107 (39), 105 (56). Anal. Calc. for $C_{21}H_{32}N_4OS$ (388.57): C 64.91%, H 8.30%, N 14.42%. Found: C 64.67%, H 8.46%, N 14.20%.

4.5.3. 2-Imino(phenyl)methylamino-1-phenyl-4-methyl-4,5-dihydro-1*H*-5-imidazolone (20c). According to the general procedure described above (Method A), the reaction between **7a** and **18c** afforded 0.13 g (48%) of **20c** as a colourless solid. M.p.: 132–133°C. ^{1}H NMR (DMSO-d_6): δ 1.52 (d, 3H, J=8.0 Hz, CH_3), 4.51 (q, 1H, J=8.0 Hz, CH), 7.40–7.90 (m, 10H$_{arom.}$), 9.29 (s, br., 1H, NH), 10.58 (s, br., 1H, NH). ^{13}C NMR (DMSO-d_6): δ 17.59 (q, CH$_3$), 61.87 (d, CH), 127.14 (d, CH$_{arom.}$), 127.35 (d, 2CH$_{arom.}$), 127.62 (d, 2CH$_{arom.}$), 128.41 (d, 2CH$_{arom.}$), 128.57 (d, 2CH$_{arom.}$), 131.82 (d, CH$_{arom.}$), 135.49 (d, $C_{arom.}$), 136.31 (d, $C_{arom.}$), 161.05 (s, C(2)), 164.96 (s, C(2)), 178.72 (s, CO). IR (KBr) ν 3341, 3058, 2980, 1718, 1644, 1592, 1560, 1522, 1482, 1444, 1391, 1325, 1285, 1179, 1157, 766, 692 cm^{-1}. MS (FAB$^+$) *m/e*: 293 ([M+1]$^+$, 100), 292 (M$^+$, 10), 291 (21), 190 (34), 154 (16), 149 (22), 146 (19), 145 (31), 136 (24), 133 (22), 131 (24), 123 (27), 120 (20), 119 (49), 111 (24), 109 (49), 107 (38), 105 (49), 104 (38). Anal. Calc. for $C_{17}H_{16}N_4O$ (292.13): C 69.85%, H 5.52%, N 19.17%. Found: C 70.12%, H 5.33%, N 18.90%.

4.5.4. 2-(1-Iminoethylamino)-1-phenyl-4-methyl-4,5-dihydro-1*H*-5-imidazolone (20d). According to the general procedure described above (Method A), the reaction between **7a** and **18d** afforded 0.13 g (55%) of **20d** as a colourless solid. M.p.: 151–152°C. ^{1}H NMR (DMSO-d_6): δ 1.36 (d, 3H, J=7.4 Hz, CH_3), 1.93 (s, 3H, CH_3), 4.25 (q, 1H, J=7.4 Hz, CH), 7.25–7.50 (m, 5H$_{arom.}$), 8.70 (s, br., 1H, NH), 9.92 (s, br., 1H, NH). ^{13}C NMR (DMSO-d_6): δ 18.72 (q, CH$_3$), 24.92 (q, CH$_3$), 61.58 (d, CH), 127.04 (d, CH$_{arom.}$), 128.37 (d, 2CH$_{arom.}$), 129.23 (d, 2CH$_{arom.}$), 138.21 (s, $C_{arom.}$), 160.70 (s, C(2)), 167.40 (s, C=N), 181.03 (s, CO). IR (KBr) ν 3273, 3106, 3061, 2984, 2931, 2864, 1747, 1706, 1676, 1646, 1554, 1516, 1491, 1422, 1309, 1225, 1186, 1141, 1099, 1053, 1018, 760, 694 cm^{-1}. MS (FAB$^+$) *m/e*: 231 ([M+1]$^+$, 100), 230 (M$^+$, 13), 229 (17), 190 (38), 149 (29), 145 (33), 136 (25), 133 (23), 123 (25), 121(25), 119 (54), 117 (20), 111 (28), 109 (49), 107 (39), 105 (49). Anal. Calc. for $C_{12}H_{14}N_4O$ (230.27): C 62.59%, H 6.13%, N 24.33%. Found: C 62.33%, H 6.34%, N 24.17%.

4.5.5. 2-Benzylsulfanyl(imino)methylamino-4-ethyl-1-phenyl-4,5-dihydro-1*H*-5-imidazolone (20e). According to the general procedure described above (Method A), the reaction between **7b** and **18a** afforded 0.26 g (75%) of **20e** as a colourless solid. M.p.: 144–145°C. ^{1}H NMR (DMSO-d_6): δ 0.93 (t, 3H, J=7.4 Hz, CH_3), 1.60–1.95 (m, 2H, CH_2), 3.96 (s, 2H, SCH_2), 4.22 (dd, 1H, J=6.8 Hz, J'=5.0 Hz, CH), 6.80–7.45 (m, 10H$_{arom.}$), 9.02 (s, br., 1H, NH), 9.90 (s, br., 1H, NH). ^{13}C NMR ($CDCl_3$): δ 9.6 (q, CH$_3$), 25.34 (t, CH$_2$), 34.87 (t, SCH$_2$), 67.51 (d, CH), 127.13 (d, CH$_{arom.}$), 127.46 (d, 2CH$_{arom.}$), 127.64 (d, CH$_{arom.}$), 128.34 (d, 2CH$_{arom.}$), 128.55 (d, 2CH$_{arom.}$), 128.65 (d, 2CH$_{arom.}$), 133.68 (s, $C_{arom.}$), 137.22 (s, $C_{arom.}$), 159.65 (s, C(2)), 168.12 (s, C=N), 180.50 (s, CO). IR (KBr) ν 3347, 3301, 3032, 2966, 2925, 2871, 1711, 1604, 1584, 1515, 1387, 1318, 1186, 1124 cm^{-1}. MS (FAB$^+$) *m/e*: 354 ([M+2]$^+$, 7), 353 ([M+1]$^+$, 32), 352 (M$^+$, 2), 257 (22), 230 (17), 229 (100), 204 (12), 91 (93). Anal. Calc. for $C_{19}H_{20}N_4OS$ (352.45): C 64.74%, H 5.72%, N 15.90%. Found: C 64.58%, H 5.93%, N 15.67%.

4.5.6. 2-Decylsulfanyl(imino)methylamino-4-ethyl-1-phenyl-4,5-dihydro-1*H*-5-imidazolone (20f). According to the general procedure described above (Method A), the reaction between **7b** and **18b** afforded 0.31 g (78%) of **20f** as a colourless solid. M.p.: 73–74°C. ^{1}H NMR (DMSO-d_6): δ 0.95–1.40 (m, 22H, 2CH_3, 8CH2), 1.70–2.00 (m, 2H, CH_2), 2.75 (t, 2H, J=7.2 Hz, SCH_2), 4.32 (dd, 1H, J=6.8 Hz, J'=5 Hz, CH), 7.35–7.55 (m, 5H$_{arom.}$), 9.05 (s, br., 1H, NH), 9.96 (s, br., 1H, NH). ^{13}C NMR (DMSO): δ 9.37 (q, CH$_3$), 13.97 (q, CH$_3$), 22.13 (t, CH$_2$), 24.82 (t, CH$_2$), 28.10 (t, CH$_2$), 28.54 (t, CH$_2$), 28.72 (t, CH$_2$), 28.94 (t, 2CH$_2$), 29.79 (t, 2CH$_2$), 31.32 (t, CH$_2$S), 66.82 (d, CH), 127.11 (d, CH$_{arom.}$), 127.47 (t, 2CH$_{arom.}$), 128.27 (t, 2CH$_{arom.}$), 133.97 (s, $C_{arom.}$), 159.32 (s, C(2)), 168.29 (s, C=N), 179.89 (s, CO). IR (KBr) ν 3296, 3142, 2959, 2924, 2853, 1714, 1613, 1585, 1515, 1454, 1387, 1346, 1322, 1306, 1288, 1191, 1138, 1117, 1068, 1025, 990, 969, 835, 779, 751, 709, 695 cm^{-1} MS (FAB$^+$) *m/e*: 404 ([M+2]$^+$, 25), 403 ([M+1]$^+$, 100), 402 (M$^+$, 5), 229 (58), 204 (37), 201 (25), 161 (21), 145 (27), 144 (32), 133 (56), 131 (30), 129 (26), 128 (23), 121 (26), 120 (26), 119 (86), 117 (32), 115 (27), 109 (56), 107 (47), 105 (66). Anal. Calc. for $C_{22}H_{34}N_4OS$ (402.60): C 65.63%, H 8.51%, N 13.92%. Found: C 65.82%, H 8.39%, N 13.65%.

4.5.7. 2-Imino(phenyl)methylamino-4-ethyl-1-phenyl-4,5-dihydro-1*H*-5-imidazolone (20g). According to the general procedure described above (Method A), the reaction between **7b** and **18c** afforded 0.16 g (56%) of **20g** as a colourless solid. M.p.: 139–140°C. ^{1}H NMR (DMSO-d_6): δ 1.08 (t, 3H, J=7.4 Hz, CH_3), 1.80–2.10 (m, 2H, CH_2), 4.42 (dd, 1H, J=6.0 Hz, J'=4.0 Hz, CH), 7.50–7.95 (m, 10H$_{arom.}$), 9.29 (s, br., 1H, NH), 10.62 (s, br., 1H, NH). ^{13}C NMR (DMSO-d_6): δ 9.8 (q, CH$_3$), 25.27 (t,CH$_2$), 67.30 (d, CH), 127.14 (d, CH$_{arom.}$), 127.33 (d, 2CH$_{arom.}$), 127.42 (d, 2CH$_{arom.}$), 128.38 (d, 2CH$_{arom.}$), 128.41 (d, 2CH$_{arom.}$), 131.72 (d, CH$_{arom.}$), 134.09 (s, $C_{arom.}$), 134.33 (s, $C_{arom.}$), 161.64 (s, C(2)), 163.46 (s, C=N), 179.92 (s, CO). IR (KBr) ν 3342, 3142, 3050, 2952, 2931, 2875, 1705, 1633, 15993, 1572, 1524, 1497, 1447, 1385, 1345, 1319, 1308, 1190, 1155, 1053, 1025, 997, 842, 772, 730, 695 cm^{-1}. MS (FAB$^+$) *m/e*: 307 ([M+1]$^+$, 100), 306 (M$^+$, 12). Anal. Calc. for $C_{18}H_{18}N_4O$ (306.36): C 70.57%, H 5.92%, N 18.29%. Found: C 70.80%, H 5.77%, N 18.01%.

4.5.8. 2-(1-Iminoethylamino)-4-ethyl-1-phenyl-4,5-dihydro-1*H*-5-imidazolone (20h). According to the general procedure described above (Method A), the reaction between **7b** and **18c** afforded 0.17 g (65%) of **20h** as a colourless solid. M.p.: 160–161°C. ^{1}H NMR (DMSO-d_6): δ 0.94 (t, 3H, J=7.4 Hz, CH_3), 1.60–1.90 (m, 2H, CH_2), 1.94 (s, 3H, CH_3), 4.21 (t, 1H, J=6.4 Hz, CH), 7.20–7.45 (m, 5H$_{arom.}$), 8.69 (s, br., 1H, NH), 9.95 (s, br., 1H, NH). ^{13}C NMR (DMSO-d_6): δ 9.56 (q, CH$_3$), 24.37 (q, CH$_3$), 25.42 (t, CH$_2$), 67.65 (d, CH), 127.11 (d, 2CH$_{arom.}$), 127.21 (d, CH$_{arom.}$), 128.49 (d, 2CH$_{arom.}$), 133.73 (s, $C_{arom.}$), 161.69 (s, C(2)), 166.92 (s, C=N), 181.04 (s, CO). IR (KBr) ν 3369, 3140, 3064, 2963, 2931, 2876, 1709, 1629, 1578, 1532, 1503, 1456, 1422, 1382, 1322, 1279, 1255, 1190, 1125, 1101, 1074, 1029, 996, 746, 728, 695 cm^{-1}. MS (FAB$^+$) *m/e*: 245 ([M+1]$^+$, 23), 244 (M$^+$, 4), 233 (26), 205 (22), 204 (11), 195 (22), 194 (19), 186 (16), 159 (100), 132 (52). Anal. Calc. for $C_{13}H_{16}N_4O$ (244.29): C 63.91%, H 6.60%, N 22.93%. Found: C 64.17%, H 6.47%, N 23.14%.

4.5.9. 2-Decylsulfanyl(imino)methylamino-1,4-diphenyl-4,5-dihydro-1*H*-5-imidazolone (20i). According to the general procedure described above (Method B), the reaction between **7c** and **18b** afforded 0.17 g (35%) of **20i** as a colourless solid. M.p.: 113–114°C$_{dec.}$ ^{1}H NMR (DMSO-d_6): δ 0.90–1.60 (m, 19H, CH_3, 8CH2), 2.6 (t, 2H, J=8 Hz, SCH_2), 6.01 (s, 1H, CH), 6.70–8.15 (m, 10H$_{arom.}$), 9.21 (s, br., 1H, NH), 10.43 (s, br., 1H, NH). ^{13}C NMR (DMSO-d_6): δ 13.9 (q, CH$_3$), 22.061 (t, CH$_2$), 27.98 (t, CH$_2$), 28.50 (t, CH$_2$), 28.63 (t, CH$_2$), 28.88 (t, 2CH$_2$), 29.75 (t, 2CH$_2$), 31.32 (t, CH$_2$S), 76.71 (d, CH), 126.73 (d, CH$_{arom.}$), 127.20 (d, 2CH$_{arom.}$), 127.81 (d, 2CH$_{arom.}$), 128.075 (d, 2CH$_{arom.}$), 128.26 (d, 2CH$_{arom.}$), 128.99 (d, CH$_{arom.}$), 133.30 (s, $C_{arom.}$), 134.34 (s, $C_{arom.}$), 159.2 (s, C(2)), 169.25 (s, C=N), 176.59 (s, CO). IR (KBr) ν 3323, 3219, 3125, 3063, 2960, 2919, 2851, 1716, 1600, 1566, 1498, 1436, 1375, 1299, 1215, 1180, 1103, 1068, 1032, 835, 800, 744, 716, 695 cm^{-1}. MS (FAB$^+$) *m/e*: 452 ([M+2]$^+$, 17), 451 ([M+1]$^+$, 58), 450 (M$^+$, 38), 449 (78), 277 (17), 161 (27), 154 (33), 145 (16), 144 (53), 137 (21), 136 (43), 120 (18), 119 (100), 118 (19), 105 (33), 104 (41), 103 (21). Anal. Calc. for $C_{26}H_{34}N_4OS$ (450.64): C 69.30%, H 7.60%, N 12.43%. Found: C 69.00%, H 7.82%, N 12.73%.

4.5.10. 2-(1-Iminoethylamino)-1,4-diphenyl-4,5-dihydro-1*H*-5-imidazolone (20j). According to the general procedure described above (Method B), the reaction between **7c** and **18d** afforded 61 mg (20%) of **20j** as a colourless solid. M.p.: 165–166°C$_{dec.}$ ^{1}H NMR (DMSO-d_6): δ 2.04 (s, 3H, J=7.4 Hz, CH_3), 5.85 (s, 1H, CH), 6.85–7.85 (m, 10H$_{arom.}$), 9.32 (s, br., 1H, NH), 10.71 (s, br., 1H, NH). ^{13}C NMR (DMSO-d_6): δ 23.51 (q, CH$_3$), 76.68 (d, CH), 126.77 (d, CH$_{arom.}$), 127.25 (d, 2CH$_{arom.}$), 127.40 (d, 2CH$_{arom.}$), 127.86 (d, CH$_{arom.}$), 128.29 (d, 2CH$_{arom.}$), 128.41 (d, 2CH$_{arom.}$), 133.61 (s, $C_{arom.}$), 134.65 (s, $C_{arom.}$), 160.98 (s, C(2)), 168.43 (s, C=N), 177.02 (s, CO). IR (KBr) ν 3360, 3090, 1714, 1623, 1588, 1513, 1380, 1300, 1183, 995, 872, 747, 729, 693 cm^{-1}. MS (FAB$^+$) *m/e*: 293 ([M+1]$^+$, 12), 292 (M$^+$, 25), 172 (100). Anal. Calc. for $C_{17}H_{16}N_4O$ (292.34): C 69.85%, H 5.52%, N 19.17%. Found: C 70.13%, H 5.23%, N 18.88%.

4.6. X-ray crystallographic details. General procedure[36]

Rigaku AFC5R diffractometer, graphite-monochromated MoK_α radiation, λ=0.71073 Å, unit cell dimensions from 25 centred reflections, ω–2θ scans, intensities of 3 standards checked after every 150 reflections: no decay. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Structure solution by direct methods using SHELXS-86[37] and refined on F with weights of $w=[\sigma^2(F_o)+(0.005F_o)^2]^{-1}$ by full-matrix least-squares methods using TEXSAN.[38]

4.6.1. Crystallographic data for compound 10g′ (Fig. 4). $C_{13}H_{17}N_3O$, M_r=231.30, orthorhombic, space group $P2_12_12_1$, a=11.165(2), b=11.255(3), c=10.054(2) Å, V=1263.4(4) Å^3, Z=4, D_c=1.216 Mg m^{-3}, F(000)=496, T=190(1) K, μ(MoK_α)=0.0796 mm^{-1}, colourless prism,

dimensions: 0.22×0.25×0.45 mm, 2θ range 5°–55°, 2048 measured reflections of which 1673 were unique (R_{int}=0.029). The methyl substituent on the five-membered ring is disordered so that it lies both above and below the plane of the five-membered ring. Two positions were defined for this group with equal site occupation factors. Although the compound crystallizes in a chiral space group, this disorder indicates that the compound is racemic. All non-H atoms refined anisotropically, amine H-atom refined isotropically, all other H-atoms fixed in calculated positions. The refinement of 168 parameters using 1099 observed reflections with $I>2\sigma(I)$ gave R=0.0459, wR=0.0340, S=1.682, max. and min. $\Delta\rho$=0.17; −0.16 e Å^{-3}.

4.6.2. Crystallographic data for compound 11e (Fig. 5). $C_{14}H_{19}N_3O$, M_r=245.32, monoclinic, space group *Cc*, a=14.925(2), b=9.416(2), c=11.701(2) Å, β=124.977(6)°, V=1347.4(4) Å^3, Z=4, D_c=1.209 Mg m^{-3}, F(000)=528, T=173(1) K, μ(MoK_α)=0.0784 mm^{-1}, colourless prism, dimensions: 0.33×0.33×0.50 mm, 2θ range 5°– 60°, 2147 measured reflections of which 2030 were unique (R_{int}=0.022). All non-H atoms refined anisotropically, H-atoms refined isotropically. The refinement of 238 parameters using 1799 observed reflections with $I>2\sigma(I)$ gave R=0.0358, wR=0.0316, S=1.734, max. and min. $\Delta\rho$=0.23; −0.19 e Å^{-3}.

4.6.3. Crystallographic data for compound 12 (Fig. 3). $C_{38}H_{40}N_6O_2{\cdot}2CH_2Cl_2$, M_r=782.64, triclinic, space group *P*1̄, a=10.379(3), b=12.050(3), c=8.836(2) Å, α=107.71(2), β=89.97(3), γ=69.86(2)°, V=981.5(5) Å^3, Z=1, D_c=1.324 Mg m^{-3}, F(000)=410, T=173(1) K, μ(MoK_α)=0.344 mm^{-1}, colourless prism, dimensions: 0.30×0.33×0.40 mm, 2θ range 5°–55°, 4758 measured reflections of which 4511 were unique (R_{int}=0.016). The asymmetric unit contains one half of the molecule of **12**, which sits across a centre of inversion, plus one molecule of CH_2Cl_2. All non-H atoms refined anisotropically, H-atoms refined isotropically. The refinement of 323 parameters using 3303 observed reflections with $I>2\sigma(I)$ gave R=0.0465, wR=0.0417, S=2.395, max. and min. $\Delta\rho$=0.42; −0.30 e Å^{-3}.

4.6.4. Crystallographic data for compound 20e′ (Fig. 8). $C_{19}H_{20}N_4OS$, M_r=352.45, monoclinic, space group $P2_1/n$, a=13.221(2), b=10.043(3), c=13.999(2) Å, β=103.36(1)°, V=1808.6(6) Å^3, Z=4, D_c=1.294 Mg m^{-3}, F(000)=744, T=173(1) K, μ(MoK_α)=0.193 mm^{-1}, colourless plate, dimensions: 0.12×0.32×0.42 mm, 2θ range 5°–55°, 4575 measured reflections of which 4151 were unique (R_{int}=0.029). All non-H atoms refined anisotropically, H-atoms fixed in calculated positions. The refinement of 226 parameters using 2590 observed reflections with $I>2\sigma(I)$ gave R=0.0620, wR=0.0583, S=2.373, max. and min. $\Delta\rho$=0.83; −0.31 e Å^{-3}.

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