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Synthesis, Structures, and Aggregation Properties of *N*-Acylamidines[‡]

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Dedicated to Prof. Dr. Paul von Ragué Schleyer on the occasion of his 80th birthday

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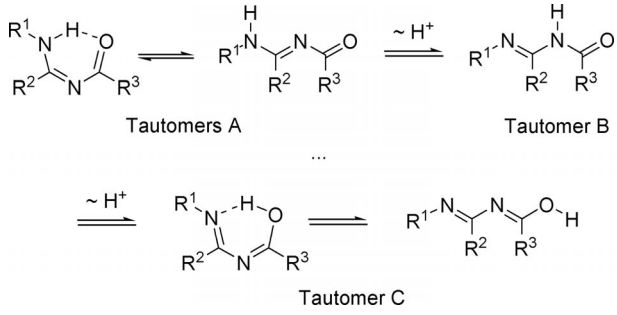
N-Acylamidines **1a–q**, which are important ligands for metal ion complexation, were easily prepared either by acylation of amidines **2** or by treatment of *N*-acylimidates **3** with amines. Additionally, the reaction of amidinium salts with aroyl halides in the presence of sodium hydroxide gave the aryl derivatives **1r–1ad** and three azobenzene derivatives **1ae–1ag**. The respective substitution pattern of these novel derivatives was selected with respect to possible steric and electronic effects in coordination reactions as well as with regard to the aggregation properties. *N*-Acylamidines **1** may exist as three types of tautomers, which were examined in solution by NMR spectroscopic analysis and by quantum chemical DFT and SCS-MP2-calculations for single molecules in the gas phase. Internal rotations require activation energies between 3–17 (C–N) and 15–27 (C=N) kcal/mol. Due to their excellent ability to form intra- and intermolecular hydrogen bonds, these molecules show very variable aggregation behavior in the solid state (X-ray analysis) as well as on surfaces, depending on the substitution pattern. Thus, dimeric (**1c**, **1d**, and **1u**) and tetrameric (**1f**) aggregates with strong NH···OC hydrogen bonding, as well as polymeric chain structures (**1x** and **1z**) were observed in the solid state. Furthermore, a dimer **1k** involving only the amidine subunits, rather than the carbonyl function, was found. Monolayers of molecules **1u** and **1ab** physisorbed at the liquid/HOPG (high orientated pyrolytic graphite) interface in 1-phenyloctane solution were examined by Scanning Tunneling Microscopy (STM).

Introduction

In coordination chemistry of metal ions and Lewis acids, *N*-acylamidines **1** and their anions are valuable nitrogen- and oxygen-containing monodentate or bidentate ligands (Scheme 1).[1–6] Structurally, they resemble the better-known β-iminoketones (β-ketoiminates).[7] However, the additional nitrogen atom in the 3-position strongly influences the electronic structure and allows extended conjugation over all five carbon, nitrogen and oxygen atoms of the parent species, even in the neutral form. Consequently, these ligands are able to generate robust complexes, for example, of transition metals and ions. Some of them show high activities in cross-coupling reactions based on good thermal stability and low loadings.[8–10]



Scheme 1. Tautomers and conformers of primary (R^1 = H) and secondary *N*-acylamidines **1**.

One may expect the formation of three different tautomeric forms of *N*-acylamidines **1** (Scheme 1): tautomer A, with an *N*-acylimine subunit, tautomer B, being an amide derivative, and tautomer C with its imidate substructure. All of the tautomers are subject to extensive conformational and configurational isomerism, and all may be involved in intermolecular hydrogen bonding; some of them may also involve intramolecular hydrogen bonding (see below). Besides the synthesis of such compounds with novel substitution patterns, a careful evaluation of their structural properties in the solid state (X-ray spectroscopic analysis), in

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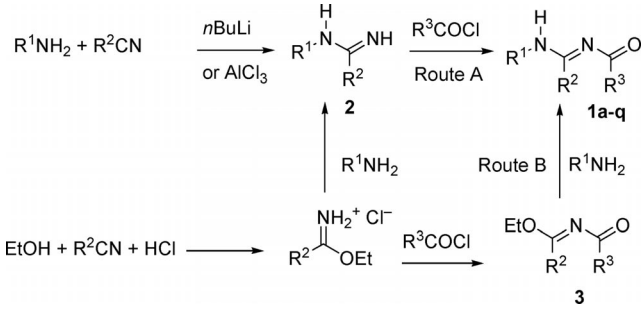
monolayers (scanning tunneling microscopy, STM), in solution (NMR spectroscopic analysis), and in the gas phase (quantum chemical calculations) is the subject of this study.

The synthesis of the first *N*-acylamidines, reported in 1889 by A. Pinner, involved the reaction of benzamidine hydrochloride with benzoic acid anhydride.[11] More recently, additional synthetic pathways for the synthesis of primary (without substituent at a nitrogen atom), secondary (one substituent at one of the nitrogen atoms) and tertiary *N*-acylamidines have been studied in our laboratory.[12,13] A principal synthetic pathway is based on the reaction of carboxylic acyl chlorides with amidines[14,15] **2** as published by Katritzky and co-workers (see Scheme 2).[16]



Scheme 2. Preparation of the secondary *N*-acylamidines **1a**–**q**.

Secondary *N*-acylamidines provoked interest in our group as ligands for catalytically active Pd complexes,[12] whereas primary *N*-acylamidines carrying alkoxyphenyl and azophenyl substituents attracted our attention because of their aggregation properties on surfaces.[17]

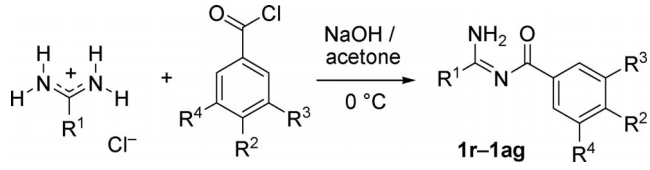
Results and Discussion

In a first series of experiments, a library of secondary *N*-acylamidines **1** with aliphatic and aromatic substituents was prepared either by acylation of amidines **2** with acyl chlorides or, in the case of **1f**, from the reaction of ethyl *N*-acylimidate **3** with a primary amine. Amidines **2** were synthesized from nitriles and primary amines, in the case of aliphatic nitriles the reaction proceeded best in the presence of aluminum chloride, whereas for aromatic amidines the use of lithiated amines was superior. For *N*-acylimidate **3**, a route through the corresponding Pinner salt was applied. These alternative pathways allow a relatively free and independent choice of the respective substituents: R^1, introduced by the choice of the primary amine; R^2, stemming from the nitrile, and R^3, from the acyl chloride. The substituents may either be aliphatic or aromatic, and can carry various electronically and sterically effective groups. Thus, we were able to synthesize one derivative **1a** with three aliphatic groups of varying steric demand, several with three aromatic substituents (**1b**–**h**), others with two aliphatic and one aromatic moiety (**1i**–**l**), and derivatives with one aliphatic and two aromatic residues (**1m**–**r**) (see Scheme 2 and Table 1).

Table 1. Substitution patterns and yields of the *N*-monosubstituted *N*-acylamidines **1a**–**q**.

	R^1	R^2	R^3	Route	Yield [%]
1a	*n*Bu	*t*Bu	*t*Bu	A	58
1b	Mes	Ph	Mes	A	45
1c	Mes	Ph	4-$MeOC_6H_4$	A	73
1d	4-$MeOC_6H_4$	Ph	4-$MeOC_6H_4$	A	39
1e	4-$MeOC_6H_4$	Ph	4-$CF_3C_6H_4$	A	9
1f	4-$CF_3C_6H_4$	Ph	4-$CF_3C_6H_4$	B	42
1g	3,5-Xyl	Ph	4-Tol	A	80
1h	Mes	4-Tol	4-Tol	A	61
1i	*n*Bu	*t*Bu	4-Tol	A	73
1j	Mes	Et	*n*Pr	A	74
1k	Ph	*t*Bu	$CH(Ph)_2$	A	30
1l	*n*Bu	Ph	4-Tol	A	91
1m	Ph	*t*Bu	4-Tol	A	17
1n	Ph	Ph	*t*Bu	A	89
1o	2,6-Xyl	Ph	*t*Bu	A	96
1p	Mes	4-Tol	*t*Bu	A	92
1q	2,6-(*i*Pr)$_2$$C_6H_3$	Ph	*t*Bu	A	66

In another series of experiments, several new primary *N*-acylamidines **1r**–**1ag** were prepared by acylation of the respective amidinium salts in the presence of sodium hydroxide using acetone as solvent at 0 °C (Scheme 3 and Table 2).[16] The substitution patterns of compounds **1r**–**1ad** were selected with regard to possible molecular aggregation phenomena by dispersion interaction, which is caused by extended alkoxy moieties in the *para*-position of the aromatic group (see below). Furthermore, three red azo compounds **1ae**–**1ag** were synthesized for evaluation of their optical properties. As expected for azobenzene derivatives, they show UV absorption near 446 nm.



Scheme 3. Preparation of the primary *N*-acylamidines **1r**–**1ag**.

Table 2. Substitution patterns and yields of the primary *N*-acylamidines **1r**–**1ag**.

	R^1	R^2	R^3	R^4	Yield [%]
1r	Ph	*n*BuO	H	H	78
1s	Ph	*n*HexO	H	H	72
1t	Ph	*n*OctO	H	H	83
1u	Ph	*n*-hexadecyl-O	H	H	12
1v	*t*Bu	*n*BuO	H	H	59
1w	*t*Bu	*n*HexO	H	H	86
1x	*t*Bu	*n*OctO	H	H	66
1y	Me	*n*BuO	H	H	52
1z	Me	*n*HexO	H	H	21
1aa	Me	*n*OctO	H	H	26[a]
1ab	Me	*n*HexadecO	H	H	54
1ac	Ph	*n*DecO	*n*DecO	H	33
1ad	Ph	*n*HexO	*n*HexO	*n*HexO	55
1ae	Ph	–N=N–Ph	H	H	91
1af	*t*Bu	–N=N–Ph	H	H	52
1ag	Me	–N=N–Ph	H	H	45

[a] Purity: 90%.

Tautomerism

It is known that *N*-acylamidines **1** are subject to tautomerism in both the solid state and in solution; the two main tautomers A and B shown in Scheme 1. For the gas phase, we performed quantum chemical calculations on all the tautomers of the parent compound $C_2H_4N_2O$ [SCS-MP2/B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p)] using the GAUSSIAN 03 suite of programs including frequency calculations.[18,19] All the tautomers may adopt many different conformations and configurations based on three principal types, namely W-, U- and sickle-shapes, with low to medium barriers for bond rotation. All tautomers A, B, and C may take part in intermolecular hydrogen bonding, but the U-shaped forms of tautomer A and C additionally offer the possibility of intramolecular hydrogen bonding. One of the structures of the tautomeric form B is predicted to be lowest in energy (see Figure 1 for the lowest energy species and the Supporting Information for all 28 possible conformers and configurational isomers). The best structure of type A is 3.4 kcal/mol higher in energy (Sickle-shape) with a second, chelate-type isomer (U-shape) very close in energy, whereas the best form of tautomer C, in spite of the intramolecular hydrogen bond, is higher in energy by approximately 10 kcal/mol. The structure of the predominant conformation/configuration depends on the steric and electronic properties and also on the overall dipole moment. Thus, amide tautomers with structures of type B are preferred over *N*-acylimine tautomers of type A, which, in turn, are much better in energy than the imidate structures of type C tautomers. Internal rotations were also studied by localization of the corresponding transition states: for tautomers A, rotation about the C=N bond requires about 15 kcal/mol, and rotation about the C–N bond approximately 3 kcal/mol. For tautomers B and C, barriers for NC=NH rotation of 23–27 kcal/mol, for NC–N rotation of 4–10 kcal/mol, and for OC–N (amide bond) of 9–17 kcal/mol were calculated. Thus, as expected, facile rotations about amidine type C–N bonds and higher barriers for amide-type bonds are typical for the dynamic behavior of these species.

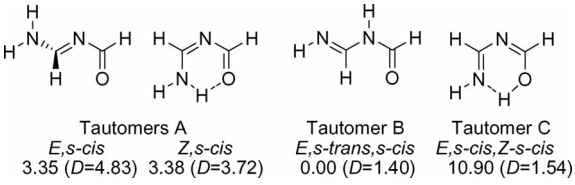


Figure 1. Calculated best structures for tautomers of type A, B, and C in the gas phase for the parent compound **1** ($R^1 = R^2 = R^3$ = H). Relative energies E_{rel} [kcal/mol] and dipole moments *D* [Debye]. SCS-MP2-B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) + ZPE.

For the substituted examples studied here, the nature of the particular substituents, crystal packing effects, and the solvent, are also quite important. In the majority of the examples described in the literature,[16] as well as in our studies, tautomer A was found to be predominant. However, in the course of our investigations we also prepared some examples that exist in both solution and the solid state in the tautomeric form B (see below).

Structures in the Solid State and in Solution

Several X-ray diffraction structures of *N*-acylamidines **1** revealed that both types of tautomers A and B are present in the solid state. Compounds **1c** and **1d** (Figure 2) are examples of type A tautomers ("U shape") with strong intramolecular hydrogen bonds. Typical N–H···O distances of 1.97 Å for **1c**, and 1.80 Å for **1d** (N···O distances of 2.63 Å for **1c** and 2.61 Å for **1d**; sum of the van-der-Waals radii:[20] H + O 2.74 Å, N + O 3.14 Å). The angles around the bridging hydrogen atom are 134.4° (**1c**) and 126.6° (**1d**), respectively. The N–C–N–C–O moieties are almost planar, with dihedral angles less than 2.4°.

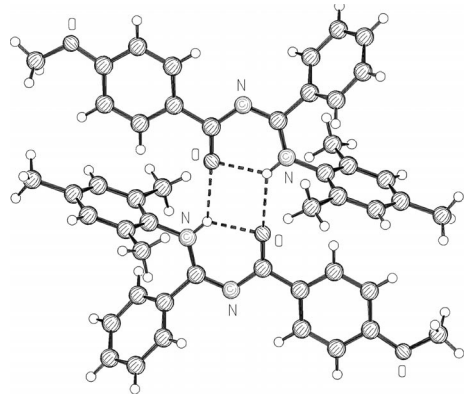


Figure 2. Molecular structure of the homodimer of **1c** in the solid state. NH–O distances, intra: 1.97 Å, inter: 2.37 Å.

Additionally, some of the compounds, for example **1c** and **1d**, are able to form homodimers using the same system of hydrogen bonding in a bifurcated way, so that each binding proton is surrounded by three heteroatoms (N and O). Possibly because of the steric bulk, the intermolecular hydrogen bonds are long (**1c**: 2.37 Å, **1d**: 2.53 Å).

For the parent *N*-acylamidine $C_2H_4N_2O$, the calculated heat of dimerization for this type of dimer amounts to approximately 8 kcal/mol (Figure 3); SCS-MP2/6-311+G(D,P +ZPE) resp. 9 kcal/mol (DFT-B97-D/TZVP,[21] a method including dispersion correction) with respect to the monomer of the same structural type. The calculated NH–O-distances indicate similar bond strengths for the intra- and intermolecular hydrogen bonding.

For the trifluoromethyl compound **1f** (Figure 4), a superstructure consisting of four "head-to-tail"-oriented *N*-acylamidines is formed by hydrogen bonding in the solid state, resembling a slightly distorted rectangle (Figures 5 and 6). A closer look at the crystalline ensemble shows that in this orientation a system of parallel channels is formed. Interestingly, a close neighborhood of fluorine atoms in one molecule and hydrogen atoms of adjacent molecules seems to contribute to the overall stabilization of the system.

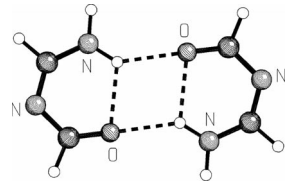


Figure 3. Calculated structure of the hydrogen bonded dimer of tautomer A of the parent compound of *N*-acylamidines **1**. Dimerisation energy: 7.94 kcal/mol [SCS-MP2/6-311+G(d,p) +ZPE] with respect to the corresponding monomer (see Figure 1, second structure from left). Calculated NH–O distances: intra: 2.109 Å, inter, 2.073 Å.

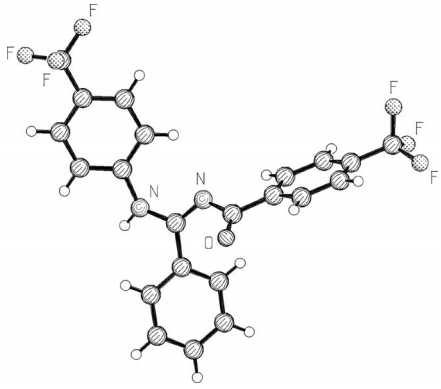


Figure 4. Molecular structure of a single molecule of **1f** in the solid state.

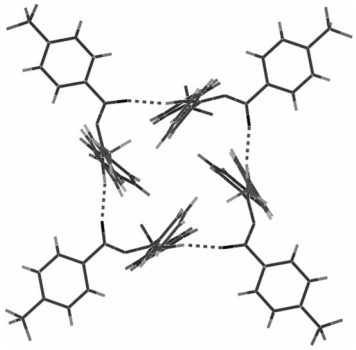


Figure 5. Molecular structure of the tetrameric aggregate of **1f** in the solid state. The hydrogen bonds (dotted lines) are 1.95 Å in length.

Derivative **1j** presents an example of the formation of tautomer B, which crystallizes in the sickle-type structure (Figure 7). The dihedral angles of –2.2° (OCNC) and 161.7° (CNCN) indicate a slight twisting of the molecule. Again, intermolecular hydrogen bonding is realized, resulting in the formation of homodimers, in this case, of the amidine subunits, whereas acyl moieties are not involved in hydrogen bonding. Here, N–H···N interactions with distances of 2.12 Å, N···N distances of 3.03 Å, and 2.97 Å (sum of vander-Waals radii:[20] HN 2.80 Å, NN 3.20 Å) between the amino groups of one molecule and the imino function of the other, lead to the formation of antiparallel orientated ensembles (Figure 7). In this example, the angles around the bridging hydrogen atoms are 169.1° and 170.3°, which are

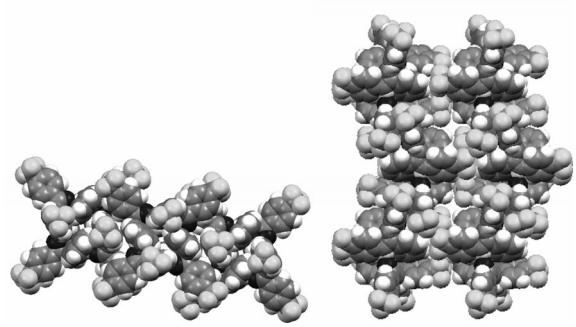


Figure 6. Molecular arrangement of the tetrameric subunits of **1f** in the crystal lattice (fluorine atoms in light-grey, hydrogen atoms in white). (Left) linear substructure; (right) two-dimension packing.

close to the ideal linear orientation. In this respect, this dimeric structure resembles a dimer of a 1-unsubstituted 1,3-diazabutadiene, which was recently observed in the solid state in our laboratory.[22]

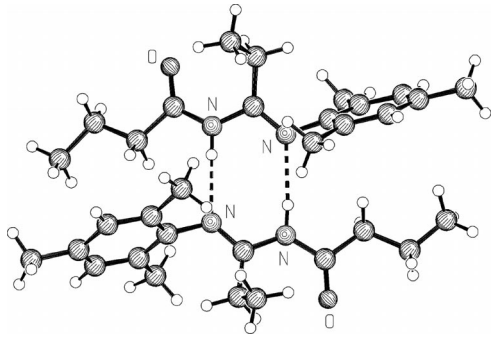


Figure 7. Molecular structure of the homodimer of **1j** in the solid state.

The different tautomers that are present in the crystalline materials, as shown from the X-ray data, also exhibit distinct IR spectra (recorded from the solids as KBr disks). Thus, two ranges were found for the C=O and C=N stretching vibrations. For the derivatives **1b**, **1j**, **1k**, and **1m**–**q**, these absorptions were found to be in the range of 1625 to 1715 cm^{-1}, which corresponds to tautomer B (compare Figure 7 for **1j**). In contrast, derivatives **1c**–**h**, which prefer to adopt the tautomeric structure A with direct, conjugative interaction of the C=N and the C=O moieties, show absorptions at lower energies between 1540 and 1625 cm^{-1}. Because, in each case, only one of the two ranges of absorptions was detected, the presence of mixtures of tautomers in the solid state can be excluded.

For the assignment of the tautomers in solution, a comparison of the ^{13}C NMR spectroscopic data of the mesityl derivatives **1b**, **1c**, **1h**, **1j**, and **1p** is indicative. Again, two groups with typical shifts in the range of *ipso*-mesityl, C=N and CO signals may be distinguished, corresponding to the two tautomers A and B (Table 3). For the derivatives **1c** and **1h**, we found relatively high-field signals for *ipso*-mesityl and low-field C=N and C=O signals, which is in agreement with the presence of tautomer A, whereas for **1b**, **1j**, and **1p** the *ipso*-mesityl signals at low field and the C=N and C=O

signals at high field indicate the presence of tautomer B. We conclude from these observations that, in the crystalline state as well as in solution, the same kind of tautomer is preferentially formed. Hence, lattice forces in the solid state do not exclusively determine the nature of the tautomer formed.

Table 3. ^{13}C NMR shifts of selected nuclei for some derivatives of **1**.

	^{13}C NMR: δ [ppm]			Tautomer in solution	Tautomer in solid state
	i-mesityl	CN	CO		
1c	133.6	167.7	179.7	A	A
1h	133.5	167.7	179.9	A	–
1b	142.3	151.2	167.8	B	B
1j	141.1	154.3	170.1	B	B
1p	142.5	152.1	175.6	B	–

In summary, it is difficult to predict the preferred tautomer simply by examining its substitution pattern. However, most of the fully aryl-substituted derivatives **1b**–**h** adopt the conformation of tautomer A, with the exception of **1b**. When R^1 and R^2 are aryl groups and R^3 is *tert*-butyl (**1n**–**q**), tautomer B is observed. All compounds with R^1 = alkyl (**1a**, **1i**, and **1l**) form tautomer A, independent of the nature of R^2 and R^3.

Compared to the ^{13}C NMR and IR data, we found that the ^1H NMR signals of the NH protons measured either in $CDCl_3$ or [D_6]dimethyl sulfoxide ([D_6]DMSO) were only of minor diagnostic value. Due to rapid exchange on the NMR time scale in $CDCl_3$, line-broadening of these signals (mostly between δ = 10 and 13 ppm) was observed; in [D_6]-DMSO, broad signals were also observed, generally at higher field (δ = 8–11 ppm) that were sometimes split into several signals of lower intensity.

Structures of the *N*-Unsubstituted *N*-Acylamidines in the Solid State

We were further able to obtain X-ray diffraction structures of the primary *N*-acylamidines **1u**, **1x**, **1z**, **1aa**, and **1ac**. In general, most of the molecular structures are close to planarity, with certain deviations observed for the derivatives **1u** and **1ac** (17 and 25°, respectively, for the C=N–C=O dihedral angle), which have aryl substituents as R^1. In all cases, tautomer A in its cyclic form with intramolecular hydrogen bonding is realized. The distances between the terminal oxygen and nitrogen atoms vary from 2.584–2.653 Å, all being significantly smaller than the sum of the van-der-Waals radii (see above).

As observed for **1c** and **1d**, in addition to the intramolecular hydrogen bond, **1u** also forms homodimers in the solid state; these are interconnected by additional intermolecular hydrogen bonds again involving the terminal oxygen and nitrogen atoms of the *N*-acylamidine subunits (Figure 8, a). The amine hydrogen atoms involved in hydrogen bonds are 1.918 and 2.220 Å away from the respective oxygen atoms. Intermolecular interactions of the long alkyl chains by dispersion seem to be the reason for the sheet-like aggregation of the molecules in the crystal lattice (Figure 8, b).

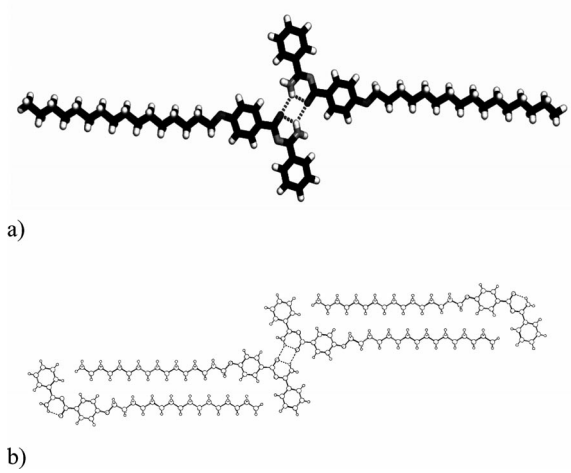


Figure 8. Molecular structure of the homodimer (a), and a sheet (b) of **1u** in the solid state.

Clearly, due to steric repulsion in compound **1ac**, the two alkyl groups attached to the R^2-substituent differ strongly in their spatial orientation (Figure 9). The decyloxy-substituent in the 4-position lies well within the plane of the rest of the molecule, whereas the decyloxy moiety in the 3-position is twisted by about 70° out of the plane of the molecule. In addition to the intramolecular hydrogen bond, **1ac** forms a complicated three-dimensional network involving hydrogen bonding of both NH_2 protons.

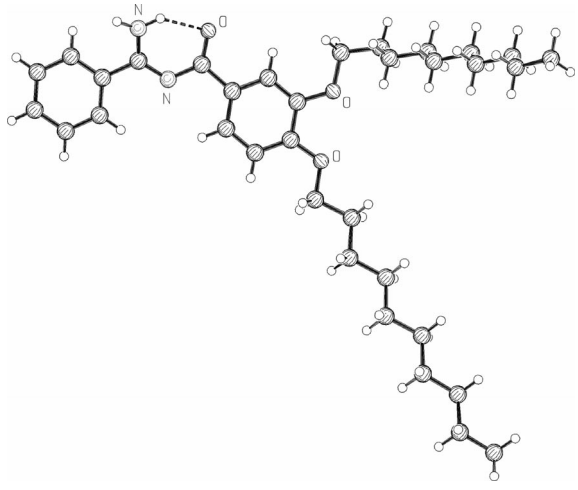


Figure 9. Molecular structure of a single molecule of **1ac** in the solid state.

The structural parameters of **1ac** obtained in this study bear some resemblance to the data reported by Hvoslef et al. for *N*-pivaloylpivalamidine.[23] Korbonits et al. reported on primary *N*-acylamidines, synthesized by hydrogenation of 1,2,4-oxadiazols.[24] They found a U-shape structure (type A) in one of the 2-aminobenzamidine derivatives in the solid state. Here, along with intermolecular hydrogen

bonding, an additional intramolecular hydrogen bond to the central nitrogen bond was observed with the 2-amino group acting as a hydrogen bridge donor.

Compounds **1x** and **1z** again show different superstructures (see Figure 10 for **1z**). In the latter case, in addition to the intramolecular chelate hydrogen bond, a polymeric fishbone-like, essentially planar orientation of the *N*-acylamidine molecules is found that is interconnected by hydrogen bonds. In **1x**, a similar pattern of hydrogen bonds is realized. The 4-(*n*-octyl)phenyl chains, however, are ordered in two planes tilted by approximately 60° with respect to each other.

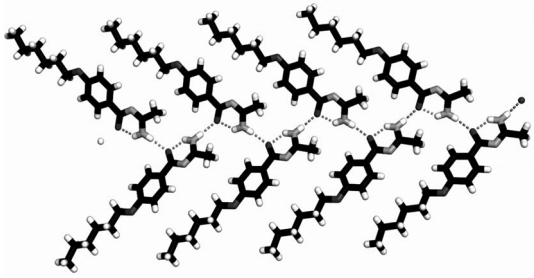


Figure 10. Molecular arrangement of **1z** in the solid state.

Similar orientation phenomena forming polymeric networks are also present in the solid-state structure of **1aa**. In this case, similar to **1z**, large polymeric sheets are formed in which the polar groups (NH_2, O) form continuous networks on one hand, whereas, on the other hand, the apolar alkyl groups also show a common aggregation behavior due to dispersion interactions. Surprisingly, small differences, for example, in the nature of the substituent R^1, generate quite different aggregation patterns.

STM Measurements

To understand the molecular interactions of *N*-acylamidines on surfaces (2D) compared to hydrogen bonding involving the terminal oxygen and nitrogen atoms of the *N*-acylamidine subunits in 3D, we also investigated the assembled structures of N-unsubstituted *N*-acylamidines at the liquid/high orientated pyrolytic graphite (HOPG) interface by means of Scanning Tunneling Microscopy (STM). Figure 11 (a) shows an STM image of a monolayer of molecule **1u** physisorbed at the liquid/graphite interface in 1-phenyloctane solution. In the STM image, the bright stripes correspond to the aromatic moieties of the molecules due to their high electron density; the dim areas correspond to the alkoxy substituents, in which alkyl chains are interdigitated. The length of an alkoxy chain (ΔL) is about (2.15 ± 0.1) nm, which compares well with the distance of 20.8 Å between the alkoxy oxygen atom and the terminal methyl group as measured by X-ray spectroscopic analysis. The angle (θ) between the direction of an alkyl chain and that of a bright row is about (108 ± 3)°, as indicated with white arrows. A comparable parameter is not present in the 3D X-ray structure. A 2D unit cell is shown in the image, and its lattice constants were determined to be a = (3.52 ± 0.1) nm, b = (0.94 ± 0.1) nm, and α = (71 ± 3)°. Within a bright stripe, two acylamidine and phenyl moieties originating from two adjacent molecules form a pair, and two adjacent pairs have a dislocation, as indicated with red bars. Based on the molecular structure seen in the single-crystal 3D experiment, this suggests that the two molecules of **1u** form a dimer from intermolecular hydrogen bonding. A model of the molecular alignment in the 2D structure is shown in Figure 11 (b), which is very similar to the structure of a sheet in 3D, as shown in Figure 8, satisfying the requirements of intermolecular interactions, hydrogen bonding and van-der-Waals interactions between the alkyl chains.

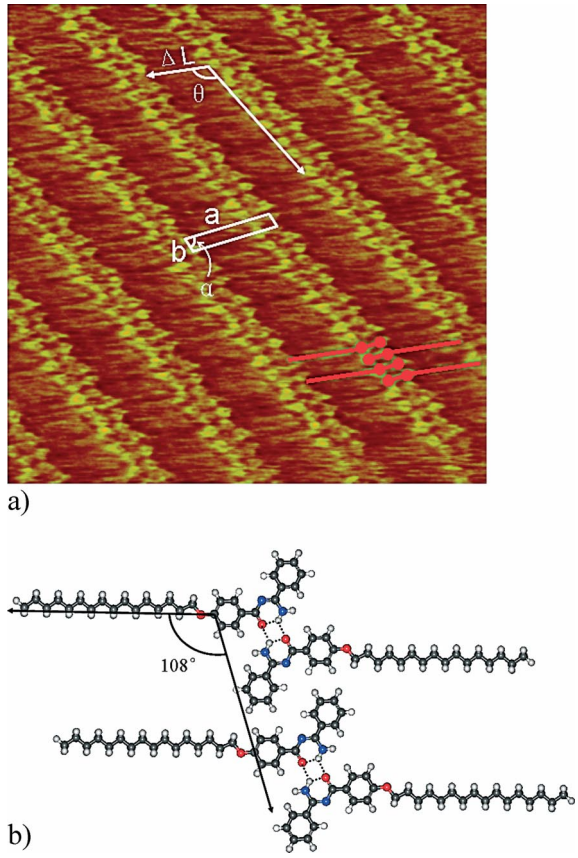


Figure 11. (a) STM image of compound **1u** on HOPG in phenyloctane (17.1 nm × 17.1 nm, U = –950 mV, I = 520 pA). (b) Proposed structural model, deduced from STM image.

For molecules of compound **1ab** adsorbed on graphite, we also observed striped structures, as shown in Figure 12 (a). The phenyl moieties of the molecules **1ab** form bright stripes, whereas the interdigitated alkoxy chains, with the same orientation, form the dim areas. The length of an alkoxy chain (ΔL) is about (2.05 ± 0.1) nm, and the angle (θ) between the direction of an alkyl chain and that of a bright stripe is about (124 ± 3)°, as indicated with white arrows. A 2D unit cell is shown in the image, and its lattice constants were determined to be a = (3.41 ± 0.1) nm, b = (1.13 ± 0.1) nm, and α = (63 ± 3)°. Examining each bright

stripe, we suggest that the phenyl moieties of molecule **1ab** are interlaced with each other, so that the acylamidine moieties of two adjacent molecules approach each other close enough, as indicated with red bars (Figure 12, a). Therefore, we consider that two adjacent molecules form a dimer by means of intermolecular hydrogen bonding and that the dimers construct stripes, as presented in Figure 12 (b). The 2D structure of **1ab** is different to the 3D structures of **1aa** and **1z**, the analogues of **1ab**, in which the polar groups (NH_2, O) form continuous networks with the alkyl chains having different orientations. The differences can be attributed to the many possible intermolecular hydrogen bonding and molecule–substrate interactions.

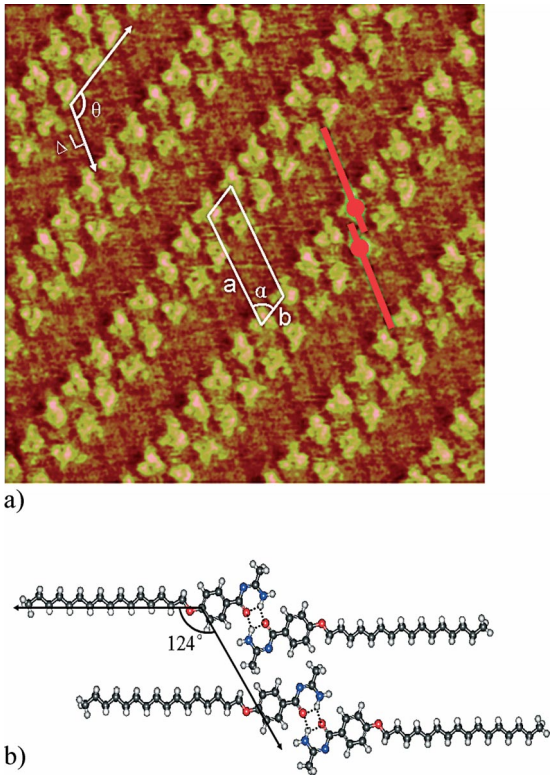


Figure 12. (a) STM image of compound **1ab** on HOPG in phenyloctane (15.0 nm × 15.0 nm, U = –524 mV, I = 300 pA). (b) Proposed structural model, deduced from the STM images.

In conclusion, molecules of *N*-unsubstituted *N*-acylamidines adsorbed at a liquid/graphite interface can form dimers by means of intermolecular hydrogen bonds, whereas dimeric basic units self-organize as ordered stripes with the same orientation as the alkyl chains.

Conclusions

In this study we have reported on the synthesis of 33 novel primary and secondary *N*-acylamidines **1** with quite varied substitution patterns incorporating many combinations of aliphatic and aromatic substituents. This class of compound shows versatile aggregation behavior, which was studied by spectroscopic, crystallographic, and STM methods. The formation of homodimers and tetramers, as well as higher aggregates in solution, in the solid state, and on surfaces due to hydrogen bonding is typical for such compounds. High-level quantum chemical calculations for the parent $C_2H_4N_2O$ compound **1** support and quantify the experimental findings. We will report on the coordination chemistry of the *N*-acylamidines **1** and on the catalytic properties of the resulting complexes in a separate paper.

Experimental Section

Materials and Methods: IR spectra were recorded with a Nicolet 5DXC spectrometer (KBr pellets). ^{1}H NMR spectra were recorded with Bruker WM 300 (300.13 MHz) or Bruker AMX 400 (400.13 MHz) spectrometers, with tetramethylsilane as internal reference. ^{13}C NMR were recorded with Bruker WM 300 (75.47 MHz) or Bruker AMX 400 (100.61 MHz) spectrometers with solvent as internal reference. CHN elemental analyses were recorded with an Elementar Vario El III. All solvents were rigorously dried by standard methods. When necessary, the experiments were carried out with complete exclusion of moisture (argon, septum/syringe technique) in glassware that had been thoroughly dried by repeated heating under argon and subsequent evacuation.

The corresponding amidines were prepared either from the respective lithiated amines (using *n*-butyllithium as base) and the respective nitriles,[25] or by reaction of amines with nitriles in the presence of aluminum chloride.[14]

Scanning Tunneling Microscopy: STM investigations were performed with a commercial multimode Nanoscope III scanning tunneling microscope (Digital Instrument Co., Santa Barbara, CA) with mechanically cut Pt/Ir (90:10) tips at ambient temperature. The images shown were recorded in the constant-current mode. For measurements at the solution–substrate interface, a saturated solution of *N*-unsubstituted *N*-acylamidines was applied to a freshly cleaved surface of highly orientated pyrolytic graphite (HOPG; MaTeck GmbH). Measurement conditions are given in the corresponding Figure captions. Different tips and samples were used to check for reproducibility. Measurements obtained from STM images, including unit cell parameters, are corrected against the substrate lattice parameters obtained from HOPG images. Flattening of the images was carried out to compensate for tilting of the substrate and scan line artefacts, and a lowpass filtered transform was employed to remove scanning noise in the STM images.

Preparation of *N*-Acylamidines 1. General Procedure: To a solution of an amidine (10.0 mmol) in dichloromethane (10.0 mL) was added an excess of triethylamine (1.5 mL, 11.0 mmol). The mixture was stirred and cooled to 0 °C. A solution of acyl chloride (9.5 mmol) in dichloromethane (10.0 mL) was added dropwise to the reaction mixture using a dropping funnel. Then, the suspension was warmed to 10 °C over the course of 1.5 h and was subsequently washed with water (2 × 10.0 mL). The organic layer was dried with magnesium sulfate and the solvent was removed in vacuo to yield the crude product.

***N*-Pivaloyl-*N*′-(*n*-butyl)pivalamidine (1a):** From *N*-(*n*-butyl)pivalamidine (1.62 g, 10.0 mmol; prepared from lithiated *n*-butylamine and pivalonitrile according to Konokahara et al.[25]) and pivaloyl chloride (1.14 g, 9.5 mmol), colorless crystals (1.33 g, 5.5 mmol, 58%) were obtained after washing of the crude product with water.

This material was used without further purification for the metal ion complexation experiments;[12] m.p. 138 °C. IR (KBr): $\tilde{\nu}$ = 3400 (vs, NH), 3294 (m, NH), 3204 (s, ν-$CH_{arom.}$), 2960 (s), 2928 (s), 2869 (m), 2770 (w, ν-CH_{aliph}), 1655 (vs, C=O/C=N), 1624 (vs, C=O/C=N), 1543 (s), 1485 (s), 1458 (s), 1410 (m), 1379 (m), 1225 (s), 1111 (m), 737 (m), 621 (m) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.93 (t, ^3J = 7.3 Hz, 3 H, CH_2CH_3), 1.19 [s, 9 H, COC(CH_3)$_3$], 1.24 [s, 9 H, C(CH_3)$_3$], 1.36 (m, 2 H, CH_2CH_3), 1.53 (m, 2 H, $CH_2CH_2CH_3$), 3.04 (br., 2 H, NCH_2), 5.20 (br., NH) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.6 (CH_2CH_3), 20.0 (CH_2CH_3), 28.2 [C(CH_3)$_3$], 28.5 [C(CH_3)$_3$], 31.0 ($CH_2CH_2CH_3$), 38.5 [C(CH_3)$_3$], 40.8 [C(CH_3)$_3$], 43.2 (NCH_2), 165.3 (C=N), 187.1 (C=O) ppm. MS (70 eV): *m/z* (%) = 240 (5) $[M]^+$, 225 (2) [M^+ – CH_3], 211 (2) [M^+ – C_2H_5], 183 (100) [M^+ – C_4H_9], 157 (4) [M^+ – C_4H_9CO + 2 H], 139 (3), 127 (4), 110 (3), 84 (7) $[C_4H_9CNH]^+$, 72 (5) $[C_4H_9NH]^+$, 57 (50) $[C_4H_9]^+$.

2,4,6-Trimethyl-*N*-[phenyl(2,4,6-trimethylphenylamino)methylene]-benzamide (1b): Synthesized from 2,4,6-trimethylbenzoyl chloride (1.73 g, 9.5 mmol) and *N*-(2,4,6-trimethylphenyl)benzamidine[26] (2.38 g, 10.0 mmol). Purification by column chromatography (TBME/*n*-pentane, 1:10 + 10% triethylamine); yield 1.64 g (4.3 mmol, 45%); pale yellow crystals; m.p. 148 °C. IR (KBr): $\tilde{\nu}$ = 3445 (m, NH), 3213 (m, NH), 3059 (m, ν-$CH_{arom.}$), 2959 (m), 2918 (m), 2858 (m), 2733 (w, ν-$CH_{aliph.}$), 1655 (s, C=O/C=N), 1628 (vs, C=O/C=N), 1611 (s), 1491 (s), 1477 (s), 1448 (s, C=$C_{arom.}$), 1267 (s), 1209 (s), 1175 (m), 1107 (m), 1034 (w), 1020 (m), 932 (vw), 851 (m), 762 (m), 689 (m, δ-$CH_{arom.}$) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.10 (s, 6 H, *o*-CH_3R^1), 2.19 (s, 6 H, *o*-CH_3R^3), 2.22 (s, 3 H, *p*-CH_3R^1), 2.23 (s, 3 H, *p*-CH_3R^3), 6.77 (s, 2 H, *m*-$CH_{arom.}R^3$), 6.84 (s, 2 H, *m*-$CH_{arom.}R^1$), 7.45–7.53 (m, 3 H, *m*,*p*-$CH_{arom.}R^2$), 7.88 (dd, ^3J = 7.7, ^4J = 1.7 Hz, 2 H, *o*-$CH_{arom.}R^2$), 12.90 (br., N*H*) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 17.9 (*o*-CH_3R^1), 19.2 (*o*-CH_3R^3), 20.7 (*p*-CH_3R^3),21.0 (*p*-CH_3R^1), 126.4 (*o*-$C_{arom.}R^1$), 128.0 (*o*-$CH_{arom.}R^2$), 128.1 (*m*-$CH_{arom.}R^2$), 128.5 (*m*-$CH_{arom.}R^3$), 129.1 (*m*-$CH_{arom.}R^1$), 130.5 (*p*-$CH_{arom.}R^2$), 133.2 (*p*-$C_{arom.}R^1$), 133.3 (*i*-$C_{arom.}R^3$), 134.3 (*o*-$C_{arom.}R^3$), 135.4 (*i*-$C_{arom.}$-R^2), 139.2 (*p*-$C_{arom.}R^3$), 142.3 (*i*-$C_{arom.}R^1$), 151.2 (*C*N), 167.8 (*C*O) ppm. MS (70 eV): *m/z* (%) = 384 (37) $[M]^+$, 369 (8) [M – CH_3]$^+$, 341 (2), 265 (1) [M – Mes]$^+$, 250 (7) [OC(Mes)NC(Ph)]$^+$, 221 (11), 147 (100) [MesCO]$^+$, 119 (28) [Mes]$^+$, 91 (7), 77 (2) $[Ph]^+$. $C_{26}H_{28}N_2O$ (384.52): calcd. C 81.21, H 7.34, N 7.29; found C 80.82, H 7.21, N 7.65.

X-ray Crystal Structure Analysis of 1b:[27,28] Formula $C_{26}H_{28}N_2O$, M = 384.50, colorless crystal, 0.25 × 0.20 × 0.10 mm, a = 11.188(1), b = 12.427(1), c = 16.875(1) Å, α = 93.55(1), β = 106.58(1), γ = 100.27(1)°, V = 2196.7(3) Å^3, ρ_{calc} = 1.163 gcm^{-3}, μ = 0.547 mm^{-1}, empirical absorption correction (0.875≤ T ≤0.947), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 22510 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 $Å^{-1}$, 7506 independent (R_{int} = 0.039) and 6545 observed reflections [$I \geq 2\sigma(I)$], 543 refined parameters, R = 0.046, wR^2 = 0.122, max. (min.) residual electron density 0.18 (–0.14) e·$Å^{-3}$. Hydrogen atoms at N3 from difference Fourier map, others calculated and refined as riding atoms, two almost identical molecules in the asymmetric unit.

4-Methoxy-*N*-[phenyl(2,4,6-trimethylphenylamino)methylene]benzamide (1c): Synthesized from 4-methoxybenzoyl chloride (1.62 g, 9.5 mmol) and *N*-(2,4,6-trimethylphenyl)benzamidine[26] (2.38 g, 10.0 mmol). Purification by washing with *n*-pentane and recrystallization from *n*-pentane; yield 2.58 g (6.9 mmol, 73%); colorless crystals; m.p. 178 °C. IR (KBr): $\tilde{\nu}$ = 3439 (m, NH), 3144 (m, NH), 3074 (m), 3022 (m, ν-$CH_{arom.}$), 2970 (m), 2945 (m), 2856 (m, ν-$CH_{aliph.}$), 2837 (m, OCH_3), 1923 (vw), 1805 (vw), 1609 (s), 1587 (vs, C=O/C=N), 1553 (vs, C=O/C=N), 1506 (s, C=$C_{arom.}$), 1441 (s), 1416 (s), 1327 (vs), 1254 (vs), 1198 (s), 1151 (vs), 1070 (m), 1022 (s), 810 (s), 772 (m), 698 (m, δ-$CH_{arom.}$) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.14 (s, 6 H, *o*-CH_3R^1), 2.23 (s, 3 H, *p*-CH_3R^1), 3.86 (s, 3 H, CH_3O), 6.80 (s, 2 H, *m*-$CH_{arom.}R^1$), 6.95 (d, ^3J = 8.7 Hz, 2 H, *m*-$CH_{arom.}R^3$), 7.23 (t, ^3J = 7.5 Hz, 2 H, *m*-$CH_{arom.}R^2$), 7.35 (t, ^3J = 7.5 Hz, 1 H, *p*-$CH_{arom.}R^2$), 7.55 (d, ^3J = 7.6 Hz, 2 H, *o*-$CH_{arom.}R^2$), 8.36 (d, ^3J = 8.2 Hz, 2 H, *o*-$CH_{arom.}R^3$), 11.23 (br., N*H*) ppm. ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 18.5 (*o*-CH_3R^1), 20.9 (*p*-CH_3R^1), 55.4 (OCH_3), 113.3 (*m*-$CH_{arom.}R^3$), 127.0 (*o*-$C_{arom.}R^1$), 127.8 (*m*-$CH_{arom.}R^2$), 129.0 (*o*-$CH_{arom.}R^2$), 129.2 (*m*-$CH_{arom.}R^1$), 130.2 (*i*-$C_{arom.}R^3$), 130.8 (*p*-$CH_{arom.}R^2$), 131.6 (*o*-$CH_{arom.}R^3$), 133.6 (*i*-$C_{arom.}R^1$), 135.2 (*i*-$C_{arom.}R^2$), 136.9 (*p*-$C_{arom.}$-R^1), 162.9 (*p*-$C_{arom.}R^3$), 167.7 (*C*N), 179.7 (*C*O) ppm. MS (70 eV): *m/z* (%) = 372 (21) $[M]^+$, 269 (2), 237 (2) [M – CO(PhOMe)]$^+$, 221 (30), 135 (100) [MeOPhCO]$^+$, 104 (5), 92 (5), 77 (12) $[Ph]^+$, 43 (2) $[NHCO]^+$. $C_{24}H_{24}N_2O_2$ (372.46): calcd. C 77.39, H 6.49, N 7.52; found C 77.22, H 6.58, N 7.43.

X-ray Crystal Structure Analysis of 1c:[27,28] Formula $C_{24}H_{24}N_2O_2$, M = 372.745, colorless crystal, 0.40 × 0.25 × 0.15 mm, a = 13.778(1), b = 9.289(1), c = 16.823(2) Å, β = 111.07(1)°, V = 2009.1(4) Å^3, ρ_{calc} = 1.231 gcm^{-3}, μ = 0.623 mm^{-1}, empirical absorption correction (0.789≤ T ≤0.912), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, $\omega/2\theta$ scans, 8254 reflections collected (+h, ±k, ±l), [(sinθ)/λ] = 0.62 $Å^{-1}$, 4092 independent (R_{int} = 0.045) and 2972 observed reflections [$I \geq 2\sigma(I)$], 261 refined parameters, R = 0.040, wR^2 = 0.123, max. (min.) residual electron density 0.22 (–0.18) e·$Å^{-3}$. Hydrogen atom at N5 from difference Fourier map, others calculated and refined as riding atoms.

4-Methoxy-*N*-[(4-methoxyphenylamino)phenylmethylene]benzamide (1d): Synthesized from 4-methoxybenzoyl chloride (1.62 g, 9.5 mmol) and *N*-(4-methoxyphenyl)benzamidine[15] (2.26 g, 10.0 mmol). Purification by column chromatography (acetone/*n*-Pentane, 1:3 + 5% triethylamine); yield 1.32 g (3.7 mmol, 39%); colorless crystals; m.p. 199 °C. IR (KBr): $\tilde{\nu}$ = 3437 (s, NH), 3059 (m), 3007 (m, ν-$CH_{arom.}$), 2945 (m), 2831 (m, OCH_3), 2052 (vw), 1902 (vw), 1603 (vs, C=$C_{arom.}$), 1589 (vs, C=O/C=N), 1555 (vs, C=O/C=N), 1512 (vs, C=$C_{arom.}$), 1441 (s), 1429 (s), 1331 (vs), 1250 (vs), 1202 (s), 1184 (s), 1167 (vs), 1070 (m), 1032 (s), 829 (m), 810 (m), 787 (m), 696 (m, δ-$CH_{arom.}$) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 3.73 (s, 3 H, CH_3OR^1), 3.85 (s, 3 H, CH_3OR^3), 6.73 (d, ^3J = 8.9 Hz, 2 H, *o*-$CH_{arom.}R^1$), 6.93 (d, ^3J = 8.9 Hz, 4 H, *m*-$CH_{arom.}R^1$, *m*-$CH_{arom.}R^3$), 7.29 (t, ^3J = 7.5 Hz, 2 H, *m*-$CH_{arom.}R^2$), 7.38 (t, ^3J = 7.4 Hz, 1 H, *p*-$CH_{arom.}R^2$), 7.59 (d, ^3J = 7.4 Hz, 2 H, *o*-$CH_{arom.}R^2$), 8.30 (d, ^3J = 8.6 Hz, 2 H, *o*-$CH_{arom.}R^3$), 12.44 (br., N*H*) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 55.3 (2·CH_3O), 113.3 (*m*-$CH_{arom.}R^3$), 114.2 (*o*-$CH_{arom.}R^1$), 122.7 (*i*-$C_{arom.}R^1$), 125.2 (*m*-$CH_{arom.}R^1$), 128.1 (*m*-$CH_{arom.}R^2$), 129.5 (*o*-$CH_{arom.}R^2$), 130.1 (*i*-$C_{arom.}R^3$), 130.6 (*p*-$CH_{arom.}R^2$), 131.6 (*o*-$CH_{arom.}R^3$), 134.7 (*i*-$C_{arom.}R^2$), 157.4 (*p*-$C_{arom.}R^1$), 162.9 (*p*-$C_{arom.}R^3$), 165.0 (*C*N), 179.1 (*C*O) ppm. MS (70 eV): *m/z* (%) = 360 (20) $[M]^+$, 257 (11) [OC(PhOMe)NH(PhOMe)]$^+$, 135 (100) [MeOPhCO]$^+$, 107 (6) [MeOPh]$^+$, 77 (9) $[Ph]^+$, 43 (5) $[NHCO]^+$. $C_{22}H_{20}N_2O_3$ (360.41): calcd. C 73.32, H 5.59, N 7.77; found C 73.04, H 5.45, N 7.70.

X-ray Crystal Structure Analysis of 1d:[27,28] Formula $C_{22}H_{20}N_2O_3$, M = 360.40, colorless crystal, 0.40 × 0.05 × 0.05 mm, a = 14.189(1), b = 5.706(1), c = 22.694(1) Å, β = 92.86(1)°, V = 1835.1(4) Å^3, ρ_{calc} = 1.304 gcm^{-3}, μ = 0.708 mm^{-1}, empirical absorption correction (0.765≤ T ≤0.966), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 8769 reflections

collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.59 Å^{-1}, 2705 independent (R_{int} = 0.058) and 1431 observed reflections [$I \geq 2\sigma(I)$], 250 refined parameters, R = 0.050, wR^2 = 0.117, max. (min.) residual electron density 0.22 (–0.27) e·Å^{-3}. Hydrogen atom at N5 from difference Fourier map, others calculated and refined as riding atoms.

***N*-[(4-Methoxyphenylamino)phenylmethylene]-4-(trifluoromethyl)-benzamide (1e):** Synthesized from 4-trifluoromethylbenzoyl chloride (1.98 g, 9.5 mmol) and *N*-(4-methoxyphenyl)benzamidine[15] (2.26 g, 10.0 mmol). Purification by kugelrohr distillation (208 °C, 2×10^{-2} mbar); yield 345 mg (0.9 mmol, 9%); yellow viscous oil/solid; m.p. 53 °C. IR (KBr): $\tilde{\nu}$ = 3276 (m, NH), 3065 (m, ν-CH$_{arom.}$), 2957 (m), 2936 (m), 2910 (w), 2837 (m, CH$_3$O), 1944 (vw), 1813 (vw, C=C$_{arom.}$), 1611 (vs, C=O/C=N), 1593 (vs, C=C$_{arom.}$), 1557 (vs, C=O/C=N), 1510 (vs, C=C$_{arom.}$), 1443 (s), 1410 (s), 1321 (vs), 1250 (vs), 1169 (vs), 1126 (vs, CF$_3$), 1069 (vs), 1034 (s), 1016 (s), 901 (m), 829 (s), 777 (s), 694 (s, δ-CH$_{arom.}$) cm^{-1}. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 3.76 (s, 3 H, C*H*$_3$O), 6.77 (d, ^3J = 8.8 Hz, 2 H, *o*-C*H*$_{arom.}$R^1), 6.96 (d, ^3J = 7.3 Hz, 2 H, *m*-C*H*$_{arom.}$R^1), 7.33 (t, ^3J = 7.7 Hz, 2 H, *m*-C*H*$_{arom.}$R^2), 7.42 (t, ^3J = 7.2 Hz, 1 H, *p*-C*H*$_{arom.}$R^2), 7.60 (d, ^3J = 7.3 Hz, 2 H, *o*-C*H*$_{arom.}$R^2), 7.70 (d, ^3J = 8.3 Hz, 2 H, *m*-C*H*$_{arom.}$R^3), 8.43 (d, ^3J = 7.7 Hz, 2 H, *o*-C*H*$_{arom.}$R^3), 12.92 (br., N*H*) ppm. ^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 55.4 (*C*H$_3$O), 114.4 (*o*-*C*H$_{arom.}$R^1), 122.7 (*i*-*C*$_{arom.}$R^1), 123.4 (q, ^1J = 229.8 Hz, *C*F$_3$), 125.0 (q, ^3J = 3.7 Hz, *m*-*C*H$_{arom.}$R^3), 125.4 (*m*-*C*H$_{arom.}$R^1), 128.3 (*m*-*C*H$_{arom.}$R^2), 129.6 (*o*-*C*H$_{arom.}$R^2), 129.9 (*o*-*C*H$_{arom.}$R^3), 131.0 (*p*-*C*H$_{arom.}$R^2), 133.3 (q, ^2J = 32.2 Hz, *p*-*C*$_{arom.}$R^3), 134.3 (*i*-*C*$_{arom.}$R^2), 140.6 (*i*-*C*$_{arom.}$R^3), 157.8 (*p*-*C*$_{arom.}$R^1), 166.6 (*C*N), 178.1 (*C*O) ppm. MS (70 eV): *m*/*z* (%) = 398 (22) [M]$^+$, 295 (29) [OC(PhCF$_3$)NH(PhOMe)]$^+$, 210 (13) [(MeO-Ph)NCPh]$^+$, 173 (100) [CF$_3$PhCO]$^+$, 145 (27), 105 (44) [PhCO]$^+$, 77 (11) [Ph]$^+$. C$_{22}$H$_{17}$F$_3$N$_2$O$_2$ (398.38): calcd. C 66.33, H 4.30, N 7.03; found C 65.84, H 4.17, N 6.77.

***N*-{Phenyl[4-(trifluoromethyl)phenylamino]methylene}-4-(trifluoromethyl)benzamide (1f):** A mixture of 4-(trifluoromethyl)aniline (1.61 g, 10.0 mmol) and *N*-(ethoxyphenylmethylene)-4-(trifluoromethyl)benzamide (from ethyl benzimidate hydrochloride and 4-(trifluormethyl)benzoyl chloride according to Kupfer et al.[29]; 3.21 g, 10.0 mmol) was stirred for 3 h at 60 °C. The excess of amine was removed by distillation, to give the crude product, which remained as a highly viscous oil that crystallized after 2 d. The compound was purified by washing the solid with diethyl ether and subsequent recrystallisation from ethanol or by column chromatography (ethanol/*n*-pentane, 1:7 + 10% triethylamine); yield 1.85 g (4.2 mmol, 42%); colorless crystals; m.p. 186 °C. IR (KBr): $\tilde{\nu}$ = 3433 (m, NH), 3269 (s, NH), 3204 (s), 3125 (m), 3076 (m, ν-CH$_{arom.}$), 2988 (w), 2928 (w), 1917 (vw), 1809 (vw, C=C$_{arom.}$), 1624 (vs, C=O/C=N), 1591 (vs), 1578 (vs, C=C$_{arom.}$), 1539 (vs, C=O/C=N), 1412 (vs), 1377 (s), 1325 (vs), 1271 (vs), 1236 (s), 1167 (vs), 1124 (vs, CF$_3$), 1065 (vs), 1016 (s), 899 (m), 849 (s), 775 (s), 758 (s), 698 (s, δ-CH$_{arom.}$) cm^{-1}. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 7.23 (d, ^3J = 7.7 Hz, 2 H, *o*-C*H*$_{arom.}$R^1), 7.36 (t, ^3J = 7.6 Hz, 2 H, *m*-C*H*$_{arom.}$R^2), 7.46 (t, ^3J = 7.4 Hz, 1 H, *p*-C*H*$_{arom.}$R^2), 7.51 (d, ^3J = 8.5 Hz, 2 H, *m*-C*H*$_{arom.}$R^1), 7.54 (d, ^3J = 7.4 Hz, 2 H, *o*-C*H*$_{arom.}$R^2), 7.70 (d, ^3J = 8.2 Hz, 2 H, *m*-C*H*$_{arom.}$R^3), 8.35 (d, ^3J = 7.9 Hz, 2 H, *o*-C*H*$_{arom.}$R^3), 11.45 (br., N*H*) ppm. ^{13}C NMR (100.61 MHz, CDCl$_3$): δ = 122.8 (*o*-*C*H$_{arom.}$R^1), 123.8 (q, ^1J = 280.5 Hz, *C*F$_3$R^1), 125.2 (q, ^3J = 3.7 Hz, *m*-*C*H$_{arom.}$R^3), 126.3 (q, ^3J = 3.6 Hz, *m*-*C*H$_{arom.}$R^1), 127.8 (q, ^2J = 32.5 Hz, *p*-*C*$_{arom.}$R^1), 128.7 (*m*-*C*H$_{arom.}$R^2), 129.0 (*o*-*C*H$_{arom.}$R^2), 129.9 (*o*-*C*H$_{arom.}$R^3), 131.6 (*p*-*C*H$_{arom.}$R^2), 133.7 (*i*-*C*$_{arom.}$R^2), 133.8 (^2J = 32.5 Hz, *p*-*C*$_{arom.}$R^3), 139.6 (*i*-*C*$_{arom.}$R^3), 141.5 (*i*-*C*$_{arom.}$R^1), 164.2 (*C*N), 177.6 (*C*O) ppm; signal of *C*F$_3$R^3 partially under the signal of *C*F$_3$R^1. MS (70 eV): *m*/*z* (%) = 436 (23) [M]$^+$, 417 (2), 382 (1), 333 (8), 291 (2) [M – CF$_3$Ph]$^+$, 248 (7), 173 (100) [CF$_3$PhCO]$^+$, 145 (22) [CF$_3$-Ph]$^+$, 104 (9) [C$_6$H$_4$CO]$^+$. C$_{22}$H$_{14}$F$_6$N$_2$O (436.35): calcd. C 60.56, H 3.23, N 6.42; found C 60.69, H 3.20, N 6.34.

X-ray Crystal Structure Analysis of 1f:[27,28] Formula C$_{22}$H$_{14}$F$_6$N$_2$O, M = 436.35, colorless crystal, 0.40 × 0.30 × 0.20 mm, a = 23.767(1), c = 14.412(1) Å, V = 8140.9(7) Å^3, ρ_{calc} = 1.424 g cm^{-3}, μ = 1.106 mm^{-1}, empirical absorption correction ($0.666 \leq T \leq 0.809$), Z = 16, tetragonal, space group $I4_1/a$ (No. 88), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 15794 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 3577 independent (R_{int} = 0.034) and 3065 observed reflections [$I \geq 2\sigma(I)$], 340 refined parameters, R = 0.051, wR^2 = 0.134, max. (min.) residual electron density 0.14 (–0.21) e·Å^{-3}. Hydrogen atom at N5 from difference Fourier map, others calculated and refined as riding atoms, both CF$_3$-groups are considerably disordered, refined with split position using geometrical and thermal restraints.

***N*-[(2,6-Dimethylphenylamino)phenylmethylene]-4-methylbenzamide (1g):** Synthesized from 4-methylbenzoyl chloride (1.47 g, 9.5 mmol) and *N*-(2,6-dimethylphenyl)benzamidine[30] (2.24 g, 10.0 mmol). Purification by kugelrohr distillation (190 °C, 3.7×10^{-2} mbar); yield 2.61 g (7.6 mmol, 80%); slight-green viscous oil/solid; m.p. 58 °C. IR (KBr): $\tilde{\nu}$ = 3395 (s, NH), 3267 (s, NH), 3061 (m), 3028 (s, ν-CH$_{arom.}$), 2951 (m), 2920 (s), 2856 (m, ν-CH$_{aliph.}$), 1925 (vw), 1803 (vw, C=C$_{arom.}$), 1638 (s), 1597 (vs, C=O/C=N), 1551 (vs, C=O/C=N), 1474 (vs, C=C$_{arom.}$), 1445 (s), 1414 (s), 1321 (vs), 1277 (vs), 1173 (s), 1067 (s), 1018 (s), 922 (m), 901 (m), 839 (m), 768 (s), 694 (s, δ-CH$_{arom.}$) cm^{-1}. ^{1}H NMR (400.14 MHz, CDCl$_3$): δ = 2.17 (s, 6 H, *o*-C*H*$_3$R^1), 2.41 (s, 3 H, *p*-C*H*$_3$R^3), 6.98 (d, ^3J = 7.5 Hz, 2 H, *m*-C*H*$_{arom.}$R^1), 7.07–7.09 (m, 1 H, *p*-C*H*$_{arom.}$R^1), 7.20–7.25 (m, 4 H, *m*-C*H*$_{arom.}$R^2, *m*-C*H*$_{arom.}$R^3), 7.34 (t, ^3J = 7.3 Hz, 1 H, *p*-C*H*$_{arom.}$R^2), 7.55 (d, ^3J = 7.5 Hz, 2 H, *o*-C*H*$_{arom.}$R^2), 8.29 (br., 2 H, *o*-C*H*$_{arom.}$R^3), 13.08 (br., N*H*) ppm. ^{13}C NMR (100.63 MHz, CDCl$_3$): δ = 18.6 (*o*-*C*H$_3$R^1), 21.6 (*p*-*C*H$_3$R^3), 124.0 (*p*-*C*H$_{arom.}$R^1), 127.2 (*o*-*C*$_{arom.}$R^1), 127.8 (*m*-*C*H$_{arom.}$R^2), 128.5 (*m*-*C*H$_{arom.}$R^1), 128.8 (*m*-*C*H$_{arom.}$R^3), 129.0 (*o*-*C*H$_{arom.}$R^2), 129.6 (*o*-*C*H$_{arom.}$R^3), 131.0 (*p*-*C*H$_{arom.}$R^2), 133.7 (*i*-*C*$_{arom.}$R^1), 134.8 (*i*-*C*$_{arom.}$R^3), 135.0 (*i*-*C*$_{arom.}$R^2), 142.5 (*p*-*C*$_{arom.}$R^3), 167.4 (*C*N), 179.9 (*C*O) ppm. MS (70 eV): *m*/*z* (%) = 342 (28) [M]$^+$, 251 (1) [M Tol]$^+$, 239 (4), 223 (4) [M – COTol]$^+$, 207 (50), 119 (100) [TolCO]$^+$, 91 (42) [Tol]$^+$, 77 (9) [Ph]$^+$. C$_{23}$H$_{22}$N$_2$O (342.44): calcd. C 80.67, H 6.48, N 8.18; found C 80.27, H 6.40, N 7.60.

4-Methyl-*N*-[*p*-tolyl(2,4,6-trimethylphenylamino)methylene]benzamide (1h): Synthesized from 4-methylbenzoyl chloride (1.47 g, 9.5 mmol) and 4-methyl-*N*-(2,4,6-trimethylphenyl)benzamidine[26] (2.52 g, 10.0 mmol). Purification by kugelrohr distillation (189 °C, 2.0×10^{-2} mbar); yield 2.13 g (5.7 mmol, 61%); yellow viscous oil/solid; m.p. 136 °C. IR (KBr): $\tilde{\nu}$ = 3437 (s, NH), 3069 (m), 3024 (s, ν-CH$_{arom.}$), 2953 (s), 2920 (s), 2860 (s), 2735 (m, ν-CH$_{aliph.}$), 1933 (vw), 1813 (vw, C=C$_{arom.}$), 1638 (m), 1611 (vs), 1585 (vs, C=O/C=N), 1545 (vs, C=O/C=N), 1410 (vs), 1317 (vs), 1202 (s), 1153 (s), 1069 (s), 1016 (s), 907 (m), 860 (m), 789 (s), 698 (m, δ-CH$_{arom.}$) cm^{-1}. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 2.14 (s, 6 H, *o*-C*H*$_3$R^1), 2.24 (s, 3 H, *p*-C*H*$_3$R^1), 2.30 (s, 3 H, *p*-C*H*$_3$R^2), 2.41 (s, 3 H, *p*-C*H*$_3$R^3), 6.80 (s, 2 H, *m*-C*H*$_{arom.}$R^1), 7.03 (d, ^3J = 8.0 Hz, 2 H, *m*-C*H*$_{arom.}$R^2), 7.24 (d, ^3J = 7.9 Hz, 2 H, *m*-C*H*$_{arom.}$R^3), 7.47 (d, ^3J = 8.2 Hz, 2 H, *o*-C*H*$_{arom.}$R^2), 8.28 (d, ^3J = 7.4 Hz, 2 H, *o*-C*H*$_{arom.}$R^3), 11.20 (br., N*H*) ppm. ^{13}C NMR (100.63 MHz, CDCl$_3$): δ = 18.5 (*o*-*C*H$_3$R^1), 20.9 (*p*-*C*H$_3$R^1), 21.4 (*p*-*C*H$_3$R^2), 21.6 (*p*-*C*H$_3$R^3), 127.0 (*o*-*C*$_{arom.}$R^1), 128.5 (*m*-*C*H$_{arom.}$R^2), 128.7 (*m*-*C*H$_{arom.}$R^3), 129.0 (*o*-*C*H$_{arom.}$R^2), 129.2 (*m*-*C*H$_{arom.}$R^1), 129.6 (*o*-*C*H$_{arom.}$R^3), 132.2 (*i*-*C*$_{arom.}$R^2), 133.5 (*i*-*C*$_{arom.}$R^1), 135.1 (*i*-

$C_{arom.}R^3$), 136.9 (p-$C_{arom.}R^1$), 141.4 (p-$C_{arom.}R^2$), 142.3 (p-$C_{arom.}R^3$), 167.7 (*C*N), 179.9 (*C*O) ppm. MS (70 eV): *m*/*z* (%) = 370 (35) $[M]^+$, 235 (46), 221 (4), 134 (5), 119 (100) $[TolCO]^+$, 91 (36) $[PhCH_2]^+$, 65 (5) $[C_5H_5]^+$. $C_{25}H_{26}N_2O$ (370.49): calcd. C 81.05, H 7.07, N 7.56; found C 80.95, H 7.01, N 7.38.

***N*-(4-Methylbenzoyl)-*N*′-(*n*-butyl)pivalamidine (1i):** Synthesized from *N*-(*n*-butyl)pivalamidine (1.56 g, 10.0 mmol) and 4-methoxybenzoyl chloride (1.47 g, 9.5 mmol); yield 1.89 g (6.9 mmol, 73%); colorless solid; m.p. 87 °C. IR (KBr): $\tilde{\nu}$ = 3431 (br., NH), 3267 (br., NH), 3101 (m, $CH_{arom.}$), 2959 (s, $CH_{aliph.}$), 2928 (s, $CH_{aliph.}$), 2872 (m, $CH_{aliph.}$), 1597 (vs, C=O/C=N), 1570 (vs, C=O/C=N), 1553 (vs, $C{=}C_{arom.}$), 1531 (vs), 1506 (s), 1458 (s), 1437 (s), 1389 (vs), 1362 (s), 1362 (s), 1304 (m), 1279 (s), 1231 (m), 1204 (m), 1173 (m), 1111 (m), 945 (w), 849 (m), 789 (m), 746 (m), 727 (m), 708 (m), 685 (s) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 7.3 Hz, 3 H, CH_2CH_3), 1.30 [s, 9 H, $C(CH_3)_3$], 1.31 (m, 2 H, CH_2CH_3), 1.50 (m, 2 H, $CH_2CH_2CH_3$), 2.38 [s, 3 H, $Ph(CH_3)$], 3.13 (br., 2 H, NCH_2), 5.50 (br., NH), 7.20 (m, 2 H, $CH_{arom.}$), 7.92 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.6 (CH_2CH_3), 19.9 (CH_2CH_3), 28.5 [$C(CH_3)_3$], 31.0 ($CH_2CH_2CH_3$), 39.0 [$C(CH_3)_3$], 43.3 (NCH_2), 128.5, 129.1 (*o*-, *m*-$CH_{arom.}$), 134.4 (*i*-$C_{arom.}$), 141.3 (*i*-$C_{arom.}$), 166.7 (C=N), 173.4 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 274 (27) $[M]^+$, 245 (6) $[M^+ - C_2H_5]$, 217 (23) $[M^+ - C_4H_9]$, 203 (6), 183 (10) $[M^+ - PhCH_3]$, 161 (4), 139 (12), 119 (100) $[CH_3PhCO]^+$, 110 (15), 91 (36) $[PhCH_3]^+$, 72 (30) $[C_4H_9NH]^+$, 57 (17) $[C_4H_9]^+$. $C_{17}H_{26}N_2O$ (274.20): calcd. C 74.41, H 9.55, N 10.21; found C 74.10, H 9.44, N 10.06.

***N*-[1-(2,4,6-Trimethylphenylamino)propylidene]butyramide (1j):** Synthesized from butyric acid (1.01 g, 9.5 mmol) and *N*-(2,4,6-trimethylphenyl)propionamidine[31] (1.90 g, 10.0 mmol), and purified by kugelrohr distillation (112 °C, 5×10^{-3} mbar); yield 1.82 g (7.0 mmol, 74%); colorless solid; m.p. 82 °C. IR (KBr): $\tilde{\nu}$ = 3437 (m, NH), 3229 (m), 3171 (m, NH), 3117 (m), 2961 (s), 2937 (s), 2876 (m), 2735 (w, $CH_{aliph.}$), 1715 (vs, C=O/C=N), 1655 (vs, C=O/C=N), 1510 (s), 1475 (s, $C{=}C_{arom.}$), 1466 (m), 1431 (m, δ-CH_2), 1377 (s, δ-CH_3), 1335 (s), 1242 (s), 1221 (m), 1177 (s), 1151 (m), 854 (m), 748 (w, δ-$CH_{arom.}$) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.79 (t, ^3J = 7.1 Hz, 3 H, $CH_3CH_2CH_2$), 0.99 (t, ^3J = 7.5 Hz, 3 H, CH_3CH_2), 1.45–1.56 (m, 2 H, $CH_3CH_2CH_2$), 2.03 (br., 2 H, $CH_3CH_2CH_2$), 2.06 (s, 6 H, *o*-CH_3R^1), 2.27 [s (br.), 3 H, *p*-CH_3R^1], 2.45 (br., 2 H, CH_3CH_2), 6.87 [s (br.), 2 H, *m*-$CH_{arom.}$], 9.68 (br., N*H*), 12.43 (br., N*H*) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 10.8 (CH_3CH_2), 13.3 ($CH_3CH_2CH_2$), 17.5 (*o*-CH_3R^1), 18.4 ($CH_3CH_2CH_2$), 20.7 (*p*-CH_3R^1), 23.9 (CH_3CH_2), 39.3 ($CH_3CH_2CH_2$), 127.3 (*o*-$C_{arom.}$), 128.8 (*m*-$CH_{arom.}$), 132.8 (*p*-$C_{arom.}$), 141.1 (*i*-$C_{arom.}$), 154.3 (*C*N), 170.1 (*C*O) ppm. MS (70 eV): *m*/*z* (%) = 260 (81) $[M]^+$, 245 (25) $[M - CH_3]^+$, 217 (18) [M – *n*Pr]$^+$, 205 (16) [OC(*n*Pr)NH(Mes)]$^+$, 174 (100) $[MesNCEt]^+$, 161 (37), 120 (21) $[Mes]^+$, 71 (23) $[nPrCO]^+$, 43 (45) $[nPr]^+$. $C_{16}H_{24}N_2O$ (260.37): calcd. C 73.81, H 9.29, N 10.76; found C 74.05, H 9.26, N 10.44.

X-ray Crystal Structure Analysis of 1j:[27,28] Formula $C_{16}H_{24}N_2O$, M = 260.37, colorless crystal, 0.30 × 0.25 × 0.20 mm, a = 10.1936(2), b = 24.6608(7), c = 13.0369(2) Å, β = 99.911(1)°, V = 3228.34(12) $Å^3$, ρ_{calc} = 1.071 gcm^{-3}, μ = 0.067 mm^{-1}, empirical absorption correction ($0.980 \leq T \leq 0.987$), Z = 8, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 198(2) K, ω and ϕ scans, 20315 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.66 $Å^{-1}$, 7681 independent (R_{int} = 0.055) and 4109 observed reflections [$I \geq 2\sigma(I)$], 369 refined parameters, R = 0.071, wR^2 = 0.210, max. (min.) residual electron density 0.86 (–0.32) e·$Å^{-3}$. Hydrogen atoms calculated and refined as riding atoms, propyl group in molecules B disordered, refined with split positions using geometrical and thermal restraints, two almost identical molecules in the asymmetric unit.

***N*-(2,2-Dimethyl-1-phenylaminopropylidene)-2,2-diphenylacetamide (1k):** Synthesized from diphenylacetyl chloride (2.19 g, 9.5 mmol) and 2,2-dimethyl-*N*-phenylpropionamidine[32] (1.76 g, 10.0 mmol). Purification by column chromatography (acetone/*n*-pentane, 1:5 + 5% triethylamine); yield 1.05 g (2.8 mmol, 30%); colorless solid; m.p. 139–148 °C. IR (KBr): $\tilde{\nu}$ = 3433 (m, NH), 3304 (s), 3252 (s, NH), 3061 (m), 3032 (m, *v*-$CH_{arom.}$), 2976 (s), 2932 (m), 2905 (w), 2870 (w, *v*-$CH_{aliph.}$), 1948 (vw), 1882 (vw), 1811 (vw, $C{=}C_{arom.}$), 1678 (vs, C=O/C=N), 1643 (vs, C=O/C=N), 1595 (s, $C{=}C_{arom.}$), 1493 (vs), 1448 (s), 1366 (m), 1236 (m), 1205 (s), 1169 (m), 1105 (s), 1030 (m), 976 (w), 802 (w), 756 (s), 731 (s), 698 (vs, δ-$CH_{arom.}$) cm^{-1}. ^1H NMR (400.14 MHz, $CDCl_3$): δ = 1.15 [s, 9 H, $C(CH_3)_3$], 4.78 (s, 1 H, $CHPh_2$), 6.74 (td, ^3J = 8.4, ^4J = 1.1 Hz, 2 H, *o*-$CH_{arom.}R^1$), 6.88–6.90 (m, 4 H, *o*-$CH_{arom.}R^3$), 7.07 (tt, ^3J = 7.1, ^4J = 1.1 Hz, 1 H, *p*-$CH_{arom.}R^1$), 7.21–7.28 (m, 8 H, *m*-$CH_{arom.}R^1$, *m*,*p*-$CH_{arom.}R^3$) ppm. ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 27.4 [$C(CH_3)_3$], 39.4 [$C(CH_3)_3$], 59.3 ($CHPh_2$), 119.6 (*o*-$CH_{arom.}R^1$), 123.3 (*p*-$CH_{arom.}R^1$), 127.4 (*p*-$CH_{arom.}R^3$), 128.7 (*m*-$CH_{arom.}R^1$), 2 × 128.8 (*o*,*m*-$CH_{arom.}R^3$), 138.6 (*i*-$C_{arom.}R^3$), 149.3 (*i*-$C_{arom.}R^1$), 157.9 (*C*N), 168.4 (*C*O) ppm. MS (70 eV): *m*/*z* (%) = 370 (76) $[M]^+$, 203 (24) $[M - CHPh_2]^+$, 194 (100) $[Ph_2CCO]^+$, 175 (60) $[M - COCHPh_2]^+$, 167 (72), 160 (78) $[PhNCtBu]^+$, 118 (12), 104 (59) $[PhNCH]^+$, 93 (37) $[PhNH_2]^+$, 57 (28) $[C_4H_9]^+$. $C_{25}H_{26}N_2O$ (370.20): calcd. C 81.05, H 7.07, N 7.56; found C 80.82, H 7.06, N 7.37.

***N*-(4-Methylbenzoyl)-*N*′-(*n*-butyl)benzamidin (1l):** Synthesized from *N*-(*n*-butyl)benzamidine[33] (1.76 g, 10.0 mmol) and 4-methylbenzoyl chloride (1.47 g, 9.5 mmol), and purified by kugelrohr distillation (180 °C, 0.004 hPa); yield 2.54 g (8.6 mmol, 91%); light-yellow viscous oil; b.p. 180 °C (0.004 hPa); m.p. 87 °C. IR (KBr): $\tilde{\nu}$ = 3447 (br., NH), 3261 (br., NH), 3094 (s, $CH_{arom.}$), 3063 (s, $CH_{arom.}$), 3034 (s, $CH_{arom.}$), 2961 (s, $CH_{aliph.}$), 2930 (s, $CH_{aliph.}$), 2870 (s, $CH_{aliph.}$), 1610 (s, C=O/C=N), 1589 (s, C=O/C=N), 1562 (vs, $C{=}C_{arom.}$), 1502 (m), 1493 (m), 1462 (m), 1441 (m), 1385 (m), 1312 (m), 1285 (m), 1163 (w), 1088 (w), 1020 (vw), 922 (vw), 893 (w), 881 (w), 841 (w), 793 (w), 766 (w), 744 (w), 696 (m) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 0.90 (br., 3 H, CH_2CH_3), 1.38 (br., 2 H, CH_2CH_3), 1.60 (br., 2 H, $CH_2CH_2CH_3$), 2.38 [s, 3 H, $Ph(CH_3)$], 3.41 (br., 2 H, NCH_2), 5.43 (br., NH), 7.18–8.15 (m, 9 H, $CH_{arom.}$), 11.68 (br., NH) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.5 (CH_2CH_3), 19.7 (CH_2CH_3), 21.5 ($PhCH_3$), 32.4 ($CH_2CH_2CH_3$), 45.3 (NCH_2), 128.3, 128.6, 129.4 (*o*-, *m*-$CH_{arom.}$), 130.4 (*p*-$CH_{arom.}$), 134.7 (*i*-$C_{arom.}$), 135.1 (*i*-$C_{arom.}$), 141.9 (*i*-$C_{arom.}$), 161.9 (C=N), 180.0 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 294 (60) $[M]^+$, 251 (22) $[M^+ - C_3H_7]$, 237 (23) $[M^+ - C_4H_9]$, 203 (18) $[M^+ - PhCH_3]$, 175 (4) $[M^+ - COPhCH_3]$, 159 (10), 130 (13). 119 (100) $[CH_3PhCO]^+$, 104 (34) $[PhCNH]^+$, 91 (39) $[CH_3Ph]^+$, 72 (26) $[C_4H_9NH]^+$. $C_{19}H_{22}N_2O$ (294.39): calcd. C 77.52, H 7.53, N 9.52; found C 77.29, H 7.54, N 9.52.

***N*-[2,2-Dimethyl-1-(phenylamino)propylidene]-4-methylbenzamide (1m):** Synthesized from 4-methylbenzoyl chloride (1.47 g, 9.5 mmol) and 2,2-dimethyl-*N*-phenylpropionamidine[32] (1.76 g, 10.0 mmol). Purification by kugelrohr distillation (148 °C, 6×10^{-3} mbar); yield 0.47 g (1.6 mmol, 17%); colorless solid; m.p. 152 °C. IR (KBr): $\tilde{\nu}$ = 3373 (vs, NH), 3061 (m), 3034 (m, *v*-$CH_{arom.}$), 2963 (s), 2928 (s), 2909 (s), 2866 (m, *v*-$CH_{aliph.}$), 1944 (vw), 1873 (vw), 1803 (vw, $C{=}C_{arom.}$), 1672 (vs, C=O/C=N), 1639 (vs, C=O/C=N), 1612 (s), 1593 (s), 1520 (s, $C{=}C_{arom.}$), 1475 (vs), 1443 (vs), 1364 (m), 1261 (s), 1198 (s), 1132 (s), 1090 (s), 1020 (m),

910 (m), 841 (s), 824 (m), 752 (vs), 698 (s, δ-$CH_{arom.}$) cm^{-1}. ^1H NMR (400.14 MHz, $CDCl_3$): δ = 1.38 [s, 9 H, $C(CH_3)_3$], 2.37 (s, 3 H, *p*-CH_3R^3), 7.06–7.11 (m, 1 H, *p*-$CH_{arom.}R^1$), 7.15 (d, ^3J = 8.1 Hz, 2 H, *m*-$CH_{arom.}R^3$), 7.21 (d, ^3J = 7.3 Hz, 2 H, *o*,*m*-$CH_{arom.}R^1$), 7.29 (d, ^3J = 7.5 Hz, 2 H, *o*,*m*-$CH_{arom.}R^1$), 7.78 (d, ^3J = 8.1 Hz, 2 H, *o*-$CH_{arom.}R^3$) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 21.5 (*p*-CH_3R^3), 28.8 [$C(CH_3)_3$], 40.2 [$C(CH_3)_3$], 122.9 (*o*,*m*-$CH_{arom.}R^1$), 125.1 (*p*-$CH_{arom.}R^1$), 128.6 (*m*-$CH_{arom.}R^3$), 128.8 (*o*,*m*-$CH_{arom.}R^1$), 129.1 (*o*-$CH_{arom.}R^3$), 133.7 (*i*-$C_{arom.}R^3$), 141.9 (*p*-$C_{arom.}R^3$), 149.0 (*i*-$C_{arom.}R^1$), 161.5 (*C*N), 174.6 (*C*O) ppm. MS (70 eV): *m*/*z* (%) = 294 (20) $[M]^+$, 279 (5) $[M - CH_3]^+$, 211 (5), 119 (100) $[TolCO]^+$, 91 (31) $[Tol]^+$, 57 (5) $[C_4H_9]^+$. $C_{19}H_{22}N_2O$ (294.39): calcd. C 77.52, H 7.53, N 9.52; found C 77.51, H 7.36, N 9.30.

2,2-Dimethyl-*N*-(phenylphenylaminomethylene)propionamide (1n): Synthesized from pivaloyl chloride (1.15 g, 9.5 mmol) and *N*-phenylbenzamidine[32] (1.96 g, 10.0 mmol), and purified by kugelrohr distillation (190 °C, 4.0×10^{-3} mbar). The compound was isolated as a mixture of tautomers; yield 2.36 g (8.4 mmol, 89%); pale yellow viscous oil, which began to crystallize after two weeks; m.p. 90 °C. IR (KBr): $\tilde{\nu}$ = 3466 (br., NH), 3234 (br. NH), 3088 (m, $CH_{arom.}$), 3059 (m, $CH_{arom.}$), 3028 (m, $CH_{arom.}$), 2993 (m), 2974 (s), 2957 (s), 2934 (m), 2870 (m, $CH_{aliph.}$), 1664 (vs, C=O/C=N), 1630 (vs, C=O/C=N), 1593 (vs), 1578 (s), 1504 (vs), 1477 (vs, C=$C_{arom.}$), 1448 (s), 1402 (s), 1373 (m), 1313 (s), 1294 (vs), 1279 (s), 1215 (s), 1175 (vs), 1072 (s), 1024 (m), 951 (m), 920 (m), 843 (m), 808 (m), 766 (s), 750 (vs), 694 (vs, δ-$CH_{arom.}$) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.06 [s, 4.9 H, $C(CH_3)_3$], 1.28 [s, 4.1 H, $C(CH_3)_3$], 6.91–7.49 (m, 9 H, $CH_{arom.}$), 7.70–7.74 (m, 1 H, $CH_{arom.}$), 9.30 (br., 1 H, N*H*) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 27.0 [$C(CH_3)_3$], 27.6 [$C(CH_3)_3$], 39.8 [$C(CH_3)_3$], 120.1 (*o*-$CH_{arom.}R^1$), 122.8, 124.0, 128.1, 128.8, 129.2, 129.6, 130.4, 130.8 ($CH_{arom.}$), 135.2 (*i*-$C_{arom.}R^2$), 148.1 (*i*-$C_{arom.}R^1$), 152.4 (*C*N), 176.2 (*C*O) ppm. MS (70 eV): *m*/*z* (%) = 280 (11) $[M]^+$, 265 (3), 237 (2), 223 (100) $[M - C_4H_9]^+$, 196 (15), 195 (33) $[M - COtBu]^+$, 180 (31) $[PhCNPh]^+$, 127 (4), 119 (5), 104 (29) $[PhCNH]^+$, 93 (37) $[PhNH_2]^+$, 92 (17) $[PhNH]^+$, 77 (59) $[Ph]^+$, 57 (81) $[C_4H_9]^+$. $C_{18}H_{20}N_2O$ (280.36): calcd. C 77.11, H 7.19, N 9.99; found C 77.12, H 6.97, N 10.58.

***N*-[(2,6-Dimethylphenylamino)phenylmethylene]-2,2-dimethylpropionamide (1o):** Synthesized from pivaloyl chloride (1.15 g, 9.5 mmol) and *N*-(2,6-dimethylphenyl)benzamidine[30] (2.24 g, 10.0 mmol). Purification by kugelrohr distillation (150 °C, 3.0×10^{-2} mbar). The compound was isolated as a mixture of tautomers; yield 2.81 g (9.1 mmol, 96%); pale yellow viscous oil; m.p. 67 °C. IR (KBr): $\tilde{\nu}$ = 3402 (s, NH), 3354 (vs, NH), 3065 (m), 3055 (m), 3026 (m, *v*-$CH_{arom.}$), 2964 (s), 2922 (s), 2866 (m, *v*-$CH_{aliph.}$), 1954 (vw, C=$C_{arom.}$), 1686 (vs, C=O/C=N), 1626 (vs, C=O/C=N), 1593 (s), 1578 (s, C=$C_{arom.}$), 1477 (vs), 1288 (s), 1250 (s), 1213 (s), 1200 (s), 1163 (s), 1151 (vs), 1096 (s), 1026 (m), 843 (m), 781 (s), 766 (vs), 690 (vs, δ-$CH_{arom.}$) cm^{-1}. ^1H NMR (400.14 MHz, $CDCl_3$): δ = 0.98 [s, 7 H, $C(CH_3)_3$], 1.33 [s, 2 H, $C(CH_3)_3$], 2.11 (s, 6 H, *o*-CH_3R^1), 6.97 (t, ^3J = 7.4 Hz, 1 H, *p*-$CH_{arom.}R^1$), 7.10 (d, ^3J = 7.5 Hz, 2 H, *m*-$CH_{arom.}R^1$), 7.38–7.49 (m, 3 H, *m*,*p*-$CH_{arom.}R^2$), 7.75 (d, ^3J = 7.7 Hz, 2 H, *o*-$CH_{arom.}R^2$) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 17.6 (*o*-CH_3R^1), 26.9 [$C(CH_3)_3$], 27.7 [$C(CH_3)_3$], 39.8 [$C(CH_3)_3$], 124.0 (*p*-$CH_{arom.}R^1$), 127.0 (*o*-$C_{arom.}R^1$), 127.9 (*m*-$CH_{arom.}R^1$), 128.0 (*o*,*m*-$CH_{arom.}R^2$), 128.4 (*m*-$CH_{arom.}R^1$), 130.6 (*p*-$CH_{arom.}R^2$), 134.9 (*i*-$C_{arom.}R^2$), 145.1 (*i*-$C_{arom.}R^1$), 152.1 (*C*N), 175.6 (*C*O) ppm. MS (70 eV): *m*/*z* (%) = 308 (60) $[M]^+$, 265 (2), 251 (100) $[M - C_4H_9]^+$, 207 (82), 193 (7), 147 (3), 121 (16) $[XylNH_2]^+$, 104 (27), 77 (20) $[Ph]^+$, 57 (47) $[C_4H_9]^+$. $C_{20}H_{24}N_2O$ (308.42): calcd. C 77.89, H 7.84, N 9.08; found C 77.86, H 7.65, N 9.14.

2,2-Dimethyl-*N*-[*p*-tolyl-(2,4,6-trimethylphenylamino)methylene]propionamide (1p): Synthesized from pivaloyl chloride (1.15 g, 9.5 mmol) and 4-methyl-*N*-(2,4,6-trimethylphenyl)benzamidine[34] (2.52 g, 10.0 mmol). Purification by kugelrohr distillation (147 °C, 1.7×10^{-2} mbar). The compound was isolated as a mixture of tautomers; yield 2.93 g (8.7 mmol, 92%); yellow viscous oil; m.p. 83 °C. IR (KBr): $\tilde{\nu}$ = 3408 (vs, NH), 3061 (m), 3015 (m, *v*-$CH_{arom.}$), 2980 (s), 2961 (s), 2934 (s), 2918 (s), 2868 (s, *v*-$CH_{aliph.}$), 1923 (vw, C=$C_{arom.}$), 1699 (vs, C=O/C=N), 1632 (vs, C=O/C=N), 1572 (m), 1514 (m, C=$C_{arom.}$), 1477 (vs), 1315 (s), 1215 (s), 1161 (s), 1020 (w), 935 (w), 864 (m), 799 (m, δ-$CH_{arom.}$) cm^{-1}. ^1H NMR (400.14 MHz, $CDCl_3$): δ = 0.99 [s, 6 H, $C(CH_3)_3$], 1.32 [s, 3 H, $C(CH_3)_3$], 2.06 (s, 6 H, *o*-CH_3R^1), 2.27 (s, 3 H, *p*-CH_3R^1), 2.39 (s, 3 H, *p*-CH_3R^2), 6.90 (s, 2 H, *m*-$CH_{arom.}R^1$), 7.23 (d, ^3J = 7.4 Hz, 2 H, *m*-$CH_{arom.}R^2$), 7.63 (d, ^3J = 7.7 Hz, 2 H, *o*-$CH_{arom.}R^2$), 12.29 (br., N*H*) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 17.6 (*o*-CH_3R^1), 20.7 (*p*-CH_3R^1), 21.4 (*p*-CH_3R^2), 26.9 [$C(CH_3)_3$], 39.8 [$C(CH_3)_3$], 126.8 (*o*-$C_{arom.}R^1$), 127.9 (*o*-$CH_{arom.}R^2$), 128.7 (*m*-$CH_{arom.}R^2$), 129.1 (*m*-$CH_{arom.}R^1$), 132.2 (*i*-$C_{arom.}R^2$), 133.1 (*p*-$C_{arom.}R^1$), 140.7 (*p*-$C_{arom.}R^2$), 142.5 (*i*-$C_{arom.}R^1$), 152.1 (*C*N), 175.6 (*C*O) ppm. MS (70 eV): *m*/*z* (%) = 336 (53) $[M]^+$, 321 (6) $[M - CH_3]^+$, 279 (100) $[M - C_4H_9]^+$, 235 (54), 221 (9), 135 (13) $[MesNH_2]^+$, 118 (21) $[TolCNH]^+$, 91 (13) $[Tol]^+$, 57 (31) $[C_4H_9]^+$. $C_{22}H_{28}N_2O$ (336.47): calcd. C 78.53, H 8.39, N 8.33; found C 78.33, H 8.27, N 8.37.

***N*-[(2,6-Diisopropylphenylamino)phenylmethylene]-2,2-dimethylpropionamide (1q):** Synthesized from pivaloyl chloride (1.15 g, 9.5 mmol) and *N*-(2,6-diisopropylphenyl)benzamidine[35] (2.80 g, 10.0 mmol), and purified by recrystallization from diethyl ether. The compound was isolated as a mixture of tautomers; yield 2.27 g (6.2 mmol, 66%); colorless crystals; m.p. 127 °C. IR (KBr): $\tilde{\nu}$ = 3410 (s, NH), 3393 (s, NH), 3354 (s, NH), 3063 (m, *v*-$CH_{arom.}$), 2963 (vs), 2928 (s), 2868 (s, *v*-$CH_{aliph.}$), 1919 (vw, C=$C_{arom.}$), 1695 (vs, C=O/C=N), 1630 (vs, C=O/C=N), 1580 (s, C=$C_{arom.}$), 1479 (s), 1454 (vs), 1362 (m), 1317 (s), 1302 (s), 1244 (m), 1194 (s), 1157 (s), 937 (m), 787 (s), 764 (s), 746 (s), 694 (s, δ-$CH_{arom.}$) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 0.96 [s, 8.5 H, $C(CH_3)_3$], 1.18 [d, ^3J = 1.0 Hz, 6 H, $(CH_3)_2CH$], 1.20 [d, ^3J = 1.1 Hz, 6 H, $(CH_3)_2CH$], 1.35 [s, 0.5 H, $C(CH_3)_3$], 2.90 [sep., ^3J = 6.9 Hz, 2 H, $(CHCH_3)_2$], 7.04–7.23 (m, 3 H, $CH_{arom.}R^1$), 7.41–7.51 (m, 3 H, *m*,*p*-$CH_{arom.}R^2$), 7.69–7.73 (m, 2 H, *o*-$CH_{arom.}R^2$) ppm. ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 23.1 [$CH(CH_3)_2$], 23.4 [$CH(CH_3)_2$], 27.0 [$C(CH_3)_3$], 28.2 [$CH(CH_3)_2$], 39.8 [$C(CH_3)_3$], 123.7 (*m*-$CH_{arom.}R^1$), 124.7 (*p*-$CH_{arom.}R^1$), 127.9, 128.1 (*o*,*m*-$CH_{arom.}R^2$), 130.4 (*p*-$CH_{arom.}R^2$), 135.0 (*i*-$C_{arom.}R^2$), 137.6 (*o*-$C_{arom.}R^1$), 142.8 (*i*-$C_{arom.}R^1$), 151.9 (*C*N), 175.5 (*C*O), 194.4 (*C*O) ppm. MS (70 eV): *m*/*z* (%) = 364 (76) $[M]^+$, 321 (9) $[M - iPr]^+$, 307 (54) $[M - C_4H_9]^+$, 263 (61) $[M - OC(tBu)NH_2]^+$, 248 (74), 235 (100) $[M - COtBu - iPr - 1]^+$, 220 (12) $[M - OC(tBu)NH_2 - iPr]^+$, 175 (11), 160 (6), 127 (11), 104 (11) $[PhCNH]^+$, 57 (47) $[C_4H_9]^+$. $C_{24}H_{32}N_2O$ (364.53): calcd. C 79.08, H 8.85, N 7.68; found C 79.09, H 8.76, N 7.62.

X-ray Crystal Structure Analysis of 1q:[27,28] Formula $C_{24}H_{32}N_2O$, M = 364.52, colorless crystal, $0.30 \times 0.30 \times 0.20$ mm, a = 11.590(1), b = 13.321(1), c = 16.715(1) Å, α = 99.29(1), β = 100.21(1), γ = 114.64(1)°, V = 2117.1(3) $Å^3$, ρ_{calc} = 1.087 $g\,cm^{-3}$, μ = 0.508 mm^{-1}, empirical absorption correction ($0.863 \leq T \leq 0.905$), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 34464 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.60 $Å^{-1}$, 7795 independent (R_{int} = 0.035) and 7104 observed reflections [$I \geq 2\sigma(I)$], 557 refined parameters, R = 0.057, wR^2 = 0.155, max. (min.) residual electron density 0.50 (–0.31) $e \cdot Å^{-3}$. Hydrogen atoms at N3 from difference Fourier map, others calculated and refined as riding atoms, *tert*-butyl groups are considerably disor-

dered, refined with split positions using geometrical restraints, two almost identical molecules in the asymmetric unit.

General Procedure for the Synthesis of *N*-Acylamidines 1r–x: At 0 °C, amidine hydrochloride (1 equiv.) was suspended in acetone (20 mL) and treated with aqueous NaOH (2 N, 2.5 equiv.). After 5 min of stirring, acyl chloride (1 equiv.), dissolved in acetone (10 mL), was added slowly. After 1.5 h stirring at 0 °C, the solvent was removed in vacuo as completely as possible. The residue was treated with water (100 mL), and the mixture was extracted with chloroform (3 × 50 mL). After removal of the chloroform in vacuo from the organic phase, the remaining residue was purified by column chromatography.

***N*-[4-(*n*-Butyloxy)benzoyl]benzamidine (1r):** Synthesized from 4-(*n*-butyloxy)benzoyl chloride[36] (0.328 g, 1.54 mmol), benzamidine hydrochloride (0.291 g, 1.54 mmol) and NaOH (2 N, 1.93 mL). Purified by column chromatography (ethyl acetate/petroleum ether, 5:1); yield 0.355 g (78%); colorless amorphous solid; R_f = 0.58 (ethyl acetate/petroleum ether, 1:1); m.p. 86–87 °C. IR (KBr): $\tilde{\nu}$ = 3321 (br. m, NH), 3184 (br. m, NH), 3070 (w), 3031 (w, $CH_{arom.}$), 2959 (m), 2934 (m), 2872 (m), 2841 (sh, CH_{alk}), 1622 (sh), 1595 (s), 1580 (m), 1560 (m), 1553 (sh), 1508 (s), 1475 (s), 1468 (sh), 1443 (s), 1389 (m), 1331 (s), 1292 (m), 1252 (s), 1227 (sh), 1173 (m), 1159 (sh), 1148 (m), 1103 (m), 1069 (m), 1028 (m), 1007 (m), 1001 (m), 970 (m), 957 (sh), 854 (m), 820 (sh), 810 (m), 783 (s), 770 (m), 704 (sh), 698 (m), 669 (m), 658 (m), 633 (m), 579 (m), 546 (m), 509 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.41–1.57 (m, 2 H, CH_2), 1.68–1.83 (m, 2 H, CH_2), 4.00 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 6.91 (m, 2 H, *m*-$CH_{arom.}$, CO), 7.43 (m, 2 H, *m*-$CH_{arom.}$), 7.52 (m, 1 H, *p*-$CH_{arom.}$), 7.98 (m, 2 H, *o*-$CH_{arom.}$), 8.32 (m, 2 H, *o*-$CH_{arom.}$, CO), 10.4 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 (CH_3), 19.1, 31.2 (CH_2), 67.8 (OCH_2), 113.7 (*m*-$CH_{arom.}$, CO), 127.3, 128.6 ($CH_{arom.}$), 130.3 (*p*-C_{ipso}, CO), 131.6, 132.0 ($CH_{arom.}$), 135.3 (C_{ipso}), 162.4 (*p*-C_{ipso}, CO), 166.1 ($C_{quat.}$, C=N), 179.9 ($C_{quat.}$, C=O) ppm. MS (70 eV): *m*/*z* (%) = 296 (42) $[M]^+$, 295 (25) $[M^+ - 1]$, 239 (3) $[M^+ - C_4H_9]$, 177 (100) $[C_4H_9OC_6H_4CO]^+$, 147 (7) $[H_2NC(Ph)NCO]^+$, 121 (99) $[HO - C_6H_4CO]^+$, 104 (16) $[C_6H_4CO]^+$, 103 (6) $[PhCN]^+$, 93 (18) $[C_6H_4OH]^+$, 92 (5), 77 (9) $[C_6H_5]^+$, 65 (15), 57 (6) $[C_4H_9]^+$. $C_{18}H_{20}N_2O_2$ (296.37): calcd. C 72.95, H 6.80, N 9.45; found C 73.10, H 6.82, H 9.46.

***N*-[4-(*n*-Hexyloxy)benzoyl]benzamidine (1s):** Synthesized from 4-(*n*-hexyloxy)benzoyl chloride[36] (0.481 g, 2.00 mmol), benzamidine hydrochloride (0.378 g, 2.00 mmol), and NaOH (2 N, 2.50 mL). Purified by column chromatography (ethyl acetate/petroleum ether, 5:1); yield 0.467 g (72%); colorless solid; R_f = 0.61 (ethyl acetate/petroleum ether, 1:1); m.p. 89–90 °C. IR (KBr): $\tilde{\nu}$ = 3325 (br. m, NH), 3186 (br. m, NH), 3070 (w), 3032 (w, $CH_{arom.}$), 2955 (s), 2930 (s), 2872 (m), 2858 (m, CH_{alk}), 1622 (sh), 1597 (s), 1582 (m), 1560 (s), 1508 (s), 1475 (s), 1443 (s), 1333 (s), 1319 (sh), 1292 (m), 1252 (s), 1229 (sh), 1175 (m), 1159 (m), 1150 (s), 1126 (m), 1001 (m), 938 (m), 928 (sh), 891 (m), 851 (m), 843 (sh), 812 (m), 783 (s), 702 (m), 696 (m), 675 (m), 669 (m), 660 (m), 635 (m), 579 (m), 542 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87–0.96 (m, 3 H, CH_3), 1.27–1.55 (m, 6 H, CH_2), 1.74–1.87 (m, 2 H, CH_2), 4.02 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 6.50 (br. s, 1 H, NH), 6.93 (m, 2 H, *m*-$CH_{arom.}$, CO), 7.49 (m, 2 H, *m*-$CH_{arom.}$), 7.57 (m, 1 H, *p*-$CH_{arom.}$), 8.03 (m, 2 H, *o*-$CH_{arom.}$), 8.33 (m, 2 H, *o*-*CH*$_{arom.}$, CO), 10.60 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 22.5, 25.7, 29.1, 31.5 (CH_2), 68.1 (OCH_2), 113.8 (*m*-$CH_{arom.}$, CO), 127.3, 128.7 ($CH_{arom.}$), 130.3 (C_{ipso}, C=O), 131.7, 132.1 ($CH_{arom.}$), 135.4 (C_{ipso}), 162.5 (*p*-$C_{arom.}$, CO), 166.1 ($C_{quat.}$, C=N), 180.1 ($C_{quat.}$, C=O) ppm. MS (70 eV): *m*/*z* (%) = 324 (39) $[M]^+$, 323 (27) $[M^+ - 1]$, 239 (6) $[M^+ - C_6H_{13}]$, 205 (73) $[H_{13}C_6OC_6H_4CO]^+$, 147 (7) $[H_2NC(Ph)NCO]^+$, 138 (5), 137 (7), 121 (100) $[HOC_6H_4CO]^+$, 120 (6), 104 (9) $[C_6H_4CO]^+$, 103 (9) $[PhCN]^+$, 99 (12), 97 (6), 93 (10) $[C_6H_4OH]^+$, 85 (6) $[C_6H_{13}]^+$, 83 (9), 77 (4) $[C_6H_5]^+$, 71 (9) $[C_5H_{11}]^+$, 70 (7), 69 (10), 65 (7), 58 (6), 57 (18) $[C_4H_9]^+$, 56 (7), 55 (13). $C_{20}H_{24}N_2O_2$ (324.42): calcd. C 74.05, H 7.46, N 8.63; found C 73.89, H 7.57, N 8.53.

***N*-[4-(*n*-Octyloxy)benzoyl]benzamidine (1t):** Synthesized from 4-(*n*-octyloxy)benzoyl chloride[37] (0.537 g, 2.00 mmol), benzamidine hydrochloride (0.378 g, 2.00 mmol), and NaOH (2 N, 2.50 mL). Purified by column chromatography (ethyl acetate, 5:1); yield 0.584 g (83%); colorless solid; R_f = 0.66 (ethyl acetate/petroleum ether, 1:1); m.p. 76 °C. IR (KBr): $\tilde{\nu}$ = 3337 (br. m, NH), 3198 (br. m, NH), 3080 (w), 3053 (w, $CH_{arom.}$), 2955 (s), 2937 (s), 2924 (m), 2872 (m), 2854 (m, CH_{alk}), 1609 (sh), 1591 (s), 1562 (m), 1514 (s), 1501 (s), 1473 (m), 1359 (m), 1333 (sh), 1321 (s), 1294 (m), 1285 (m), 1259 (sh), 1252 (s), 1175 (m), 1151 (m), 1040 (m), 1030 (m), 997 (m), 865 (m), 852 (m), 725 (m), 698 (m), 653 (m), 634 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85–0.93 (m, 3 H, CH_3), 1.22–1.54 (m, 10 H, CH_2), 1.74–1.87 (m, 2 H, CH_2), 4.02 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 6.7 (br. s, 1 H, NH), 6.92 (m, 2 H, *m*-$CH_{arom.}$, CO), 7.45–7.60 (m, 3 H, *m*-/*p*-$CH_{arom.}$), 8.02 (m, 2 H, *o*-$CH_{arom.}$), 8.33 (m, 2 H, *o*-$CH_{arom.}$, CO), 10.56 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6, 26.0, 29.2, 29.3, 31.7 (CH_2), 68.1 (OCH_2), 113.8 (*m*-$CH_{arom.}$, CO), 127.4, 128.7 ($CH_{arom.}$), 130.3 (C_{ipso}, C=O), 131.7, 132.1 ($CH_{arom.}$), 135.3 (C_{ipso}), 162.5 (*p*-$C_{arom.}$, CO), 166.1 ($C_{quat.}$, C=N), 180.0 ($C_{quat.}$, C=O) ppm. MS (70 eV): *m*/*z* (%) = 352 (48) $[M]^+$, 351 (34) $[M^+ - 1]$, 324 (3) $[M^+ - C_2H_4]$, 239 (6), 233 (85) $[H_{17}C_8OC_6H_4CO]^+$, 147 (9) $[H_2NC(Ph)NCO]^+$, 138 (5), 137 (7) $[HOC_6H_4CONH_2]^+$, 121 (100) $[HOC_6H_4CO]^+$, 120 (5), 104 (12) $[C_6H_4CO]^+$, 103 (12) $[PhCN]^+$, 93 (11) $[C_6H_4OH]^+$, 77 (6) $[C_6H_5]^+$, 76 (5), 71 (6) $[C_5H_{11}]^+$, 69 (6), 65 (7), 57 (14) $[C_4H_9]^+$, 55 (10). $C_{22}H_{28}N_2O_2$ (352.48): calcd. C 74.97, H 8.01, N 7.95; found C 74.76, H 8.17, N 7.93.

***N*-[4-(*n*-Hexadecyloxy)benzoyl]benzamidine (1u):** Synthesized from 4-(*n*-hexadecyloxy)benzoyl chloride (0.552 g, 1.45 mmol), benzamidine hydrochloride (0.274 g, 1.45 mmol), and NaOH (2 N, 1.80 mL). Purified by column chromatography (ethyl acetate, 10:1); yield 0.080 g (12%); colorless solid; R_f = 0.70 (ethyl acetate/petroleum ether, 1:1); m.p. 78–79 °C. IR (KBr): $\tilde{\nu}$ = 3458 (br. m, NH), 3252 (br. m, NH), 3069 (w), 3059 (w), 3030 (w, $CH_{arom.}$), 2955 (m), 2939 (s), 2916 (s), 2860 (sh), 2851 (s, CH_{alk}), 2766 (w), 1630 (s), 1603 (s), 1566 (s), 1508 (s), 1472 (s), 1445 (s), 1416 (s), 1391 (m), 1313 (s), 1298 (s), 1290 (sh), 1246 (s), 1180 (sh), 1171 (s), 1161 (sh), 1146 (s), 1099 (m), 1026 (m), 999 (m), 881 (m), 847 (m), 820 (m), 800 (m), 783 (s), 770 (m), 719 (m), 700 (m), 694 (m), 675 (m), 662 (m), 575 (m), 548 (m), 530 (m), 511 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.81–0.95 (m, 3 H, CH_3), 1.17–1.55 (m, 26 H, CH_2), 1.73–1.87 (m, 2 H, CH_2), 4.01 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 6.67 (br. s, 1 H, NH), 6.94 (m, 2 H, *m*-$CH_{arom.}$, CO), 7.47 (m, 2 H, *m*-$CH_{arom.}$), 7.55 (m, 1 H, *p*-$CH_{arom.}$), 8.02 (m, 2 H, *o*-$CH_{arom.}$, CO), 8.33 (m, 2 H, *o*-$CH_{arom.}$), 10.51 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.7, 26.0, 29.2, 29.3, 29.4, 29.6, 29.7, 31.9 (CH_2), 68.1 (OCH_2), 113.8 (*m*-$CH_{arom.}$, CO), 127.3, 128.7 ($CH_{arom.}$), 130.3 (C_{ipso}, CO), 131.7, 132.1 ($CH_{arom.}$), 135.4 (C_{ipso}), 162.5 (*p*-$C_{arom.}$, CO), 166.0 ($C_{quat.}$, C=N), 180.0 ($C_{quat.}$, C=O) ppm. MS (70 eV): *m*/*z* (%) = 464 (40) $[M]^+$, 463 (16) $[M^+ - 1]$, 435 (4) $[M^+ - C_2H_5]$, 421 (3) $[M^+ - C_3H_7]$, 407 (3) $[M^+ - C_4H_9]$, 365 (3) $[M^+ - C_7H_{15}]$, 361 (7), 346 (14), 345 (47) $[H_{33}C_{16}OC_6H_4CO]^+$, 253 (20) $[M^+ - C_{15}H_{31}]$, 241 (6), 240 (29) $[M^+ - C_{16}H_{32}]$, 147 (13) $[H_2NC(Ph)NCO]^+$, 138 (13), 137 (19) $[HOC_6H_4CONH_2]^+$, 121 (100) $[HOC_6H_4CO]^+$, 120 (10), 104 (19) $[C_6H_4CO]^+$, 103 (75) $[PhCN]^+$, 99 (22) $[C_7H_{11}]^+$, 97 (7), 93 (7), 85 (10) $[C_6H_{13}]^+$, 83 (13),

81 (7), 77 (12) $[C_6H_5]^+$, 76 (25), 75 (9), 71 (21) $[C_5H_{11}]^+$, 70 (9), 69 (20), 57 (52) $[C_4H_9]^+$, 56 (13), 55 (33), 51 (9), 50 (11). $C_{30}H_{44}N_2O_2$ (464.69): calcd. C 77.54, H 9.54, N 6.03; found C 77.33, H 9.58, N 6.03.

X-ray Crystal Structure Analysis of 1u:[27,28] Formula $C_{30}H_{44}N_2O_2$, M = 464.67, colorless crystal, 0.35 × 0.20 × 0.10 mm, a = 44.009(3), b = 5.483(1), c = 23.630(2) Å, β = 107.72(1)°, V = 5431.4(12) Å^3, ρ_{calc} = 1.137 g cm^{-3}, μ = 0.542 mm^{-1}, empirical absorption correction ($0.833 \leq T \leq 0.948$), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 1.54178 Å, T = 223(2) K, $\omega/2\theta$ scans, 5685 reflections collected ($-h$, $+k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.62 Å^{-1}, 5534 independent (R_{int} = 0.024) and 4093 observed reflections [$I \geq 2\sigma(I)$], 315 refined parameters, R = 0.042, wR^2 = 0.139, max. (min.) residual electron density 0.18 (–0.19) e·Å^{-3}. Hydrogen atoms at N5 from difference Fourier map, others calculated and refined as riding atoms.

***N*-[4-(*n*-Butyloxy)benzoyl]pivalamidine (1v):** Synthesized from 4-(*n*-butyloxy)benzoyl chloride[36] (0.393 g, 1.85 mmol), pivalamidine hydrochloride (0.252 g, 1.85 mmol), and NaOH (2 N, 2.30 mL). Purified by column chromatography (ethyl acetate, 5:1); yield 0.300 g (59%, 93% purity); colorless solid; R_f = 0.62 (ethyl acetate/petroleum ether, 1:1); m.p. 95 °C. IR (KBr): $\tilde{\nu}$ = 3362 (m, NH), 3238 (w, NH), 3074 (w, $CH_{arom.}$), 2961 (m), 2932 (m), 2872 (m, CH_{alk}), 1622 (sh), 1603 (s), 1591 (s), 1560 (m), 1508 (s), 1475 (s), 1466 (s), 1366 (m), 1333 (sh), 1319 (s), 1290 (s), 1250 (s), 1229 (sh), 1165 (s), 1146 (m), 1132 (m), 1117 (m), 1067 (m), 1029 (m), 1004 (m), 972 (m), 874 (m), 856 (s), 851 (s), 821 (m), 806 (m), 744 (m), 696 (m), 638 (s), 540 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (m, 3 H, CH_3), 1.32 (s, 9 H, *t*Bu), 1.50 (m, 2 H, CH_2), 1.77 (m, 2 H, CH_2), 4.01 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 6.27 (br. s, 1 H, NH), 6.88 (m, 2 H, *m*-$CH_{arom.}$), 8.23 (m, 2 H, *o*-$CH_{arom.}$), 10.52 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_2CH_3), 22.5, 25.6 (CH_2), 28.0 [$C(CH_3)_3$], 31.5 (CH_2), 38.5 [$C(CH_3)_3$], 68.0 (OCH_2), 113.6 (*m*-$CH_{arom.}$), 130.6 (C_{ipso}, C=O), 131.6 (*o*-$CH_{arom.}$), 162.2 (*p*-$C_{arom.}$), 178.8, 179.9 ($C_{quat.}$, C=O, C=N) ppm. MS (70 eV): *m*/*z* (%) = 276 (38) $[M]^+$, 275 (5) $[M^+ - 1]$, 262 (8), 261 (42) $[M^+ - CH_3]$, 234 (5) $[M^+ - C_3H_6]$, 206 (6), 177 (100) $[H_9C_4OC_6H_4CO]^+$, 121 (96) $[HOC_6H_4CO]^+$, 99 (17) $[H_2NC(tBu)N]^+$, 97 (6), 93 (17) $[C_6H_4OH]^+$, 92 (7), 85 (5), 84 (5), 71 (8), 69 (10), 65 (17), 57 (36) $[C_4H_9]^+$, 56 (6), 55 (16).

***N*-[4-(*n*-Hexyloxy)benzoyl]pivalamidine (1w):** Synthesized from 4-(*n*-hexyloxy)benzoyl chloride[36] (0.303 g, 1.26 mmol), pivalamidine hydrochloride (0.172 g, 1.26 mmol), and NaOH (2 N, 1.6 mL). Purified by column chromatography (ethyl acetate, 5:1); yield 0.330 g (86%); colorless solid; R_f = 0.65 (ethyl acetate/petroleum ether, 1:1); m.p. 97–99 °C. IR (KBr): $\tilde{\nu}$ = 3335 (br. s, NH), 3184 (br. m, NH), 3057 (w, $CH_{arom.}$), 2991 (sh), 2976 (m), 2953 (s), 2937 (s), 2912 (sh), 2868 (m), 2856 (sh, CH_{alk}), 1622 (sh), 1605 (s), 1587 (s), 1558 (s), 1510 (s), 1493 (s), 1475 (s), 1466 (m), 1443 (m), 1396 (m), 1369 (m), 1358 (m), 1317 (s), 1290 (s), 1277 (sh), 1272 (s), 1227 (m), 1173 (s), 1128 (m), 1107 (m), 1061 (m), 1030 (s), 1007 (m), 989 (m), 895 (m), 860 (s), 827 (m), 820 (sh), 806 (m), 773 (m), 727 (m), 687 (m), 669 (sh), 640 (s), 633 (m), 546 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (m, 3 H, CH_3), 1.24–1.53 [m, 15 H, CH_2, $C(CH_3)_3$], 1.78 (m, 2 H, CH_2), 3.99 (t, ^3J = 6.7 Hz, 2 H, OCH_2), 6.31 (br. s, 1 H, NH), 6.88 (m, 2 H, *m*-$CH_{arom.}$), 8.23 (m, 2 H, *o*-$CH_{arom.}$), 10.50 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 22.5, 25.6 (CH_2), 28.0 [$C(CH_3)_3$], 29.1, 31.5 (CH_2), 38.5 [$C(CH_3)_3$], 68.0 (OCH_2), 113.6 (*m*-$CH_{arom.}$), 130.6 (C_{ipso}), 131.6 (*o*-$CH_{arom.}$), 162.2 (*p*-$C_{arom.}$), 178.8, 179.9 ($C_{quat.}$, C=N, C=O) ppm. MS (70 eV): *m*/*z* (%) = 304 (33) $[M]^+$, 303 (8) $[M^+ - 1]$, 290 (9), 289 (45) $[M^+ - CH_3]$, 262 (7), 234 (6), 206 (12), 205 (79) $[H_{13}C_6OC_6H_4CO]^+$, 137 (7) $[HOC_6H_4CONH_2]^+$, 127 (3) $[H_2NC(tBu)NCO]^+$, 121 (100) $[HOC_6H_4CO]^+$, 120 (7), 99 (18) $[H_2NC(tBu)N]^+$, 93 (13) $[C_6H_4OH]^+$, 92 (6), 85 (5), 84 (5), 69 (6), 65 (9), 57 (17) $[C_4H_9]^+$, 56 (4), 55 (12). $C_{18}H_{28}N_2O_2$ (304.43): calcd. C 71.01, H 9.27, N 9.20; found C 71.04, H 9.25, N 9.31.

***N*-[4-(*n*-Octyloxy)benzoyl]pivalamidine (1x):** Synthesized from 4-*n*-octyloxybenzoyl chloride[37] (0.331 g, 1.23 mmol), pivalamidine hydrochloride (0.168 g, 1.23 mmol), NaOH (2 N, 1.5 mL). Purified by column chromatography (ethyl acetate, 5:1); yield 0.270 g (66%); colorless solid; R_f = 0.66 (ethyl acetate/petroleum ether, 1:1); m.p. 66–67 °C. IR (KBr): $\tilde{\nu}$ = 3335 (br. s, NH), 3186 (br. m, NH), 3072 (w, $CH_{arom.}$), 2988 (sh), 2974 (m), 2953 (s), 2937 (s), 2922 (s), 2905 (sh), 2868 (m), 2853 (m), 1623 (sh), 1603 (s), 1589 (s), 1560 (s), 1508 (s), 1493 (s), 1474 (m), 1466 (sh), 1443 (sh), 1418 (w), 1394 (m), 1371 (m), 1329 (sh), 1317 (s), 1286 (s), 1254 (s), 1227 (m), 1207 (sh), 1167 (s), 1042 (m), 1036 (m), 1005 (sh), 999 (m), 860 (m), 854 (m), 822 (m), 814 (sh), 804 (sh), 723 (m), 689 (m), 669 (sh), 640 (m), 635 (m), 546 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (m, 3 H, CH_3), 1.21–1.53 [m, 19 H, CH_2, $C(CH_3)_3$], 1.78 (m, 2 H, CH_2), 3.99 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 6.26 (br. s, 1 H, NH), 6.88 (m, 2 H, *m*-$CH_{arom.}$), 8.23 (m, 2 H, *o*-$CH_{arom.}$), 10.47 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.58, 26.0 (CH_2), 28.0 [$C(CH_3)_3$], 29.2, 29.3, 31.7 (CH_2), 38.5 [$C(CH_3)_3$], 68.1 (OCH_2), 113.6 (*m*-$CH_{arom.}$), 130.7 (C_{ipso}), 131.6 (*o*-$CH_{arom.}$), 162.2 (*p*-$C_{arom.}$), 178.8, 179.9 ($C_{quat.}$, C=N, C=O) ppm. MS (70 eV): *m*/*z* (%) = 332 (42) $[M]^+$, 331 (8) $[M^+ - 1]$, 318 (7), 317 (41) $[M^+ - CH_3]$, 290 (4), 262 (3), 234 (11), 233 (63) $[H_{17}C_8OC_6H_4CO]^+$, 191 (4), 138 (4), 137 (6) $[HOC_6H_4CONH_2]^+$, 127 (5) $[H_2NC(tBu)NCO]^+$, 121 (100) $[HOC_6H_4CO]^+$, 120 (8), 104 (3), 99 (3) $[H_2NC(tBu)N]^+$, 97 (3), 93 (10) $[C_6H_4OH]^+$, 92 (4), 84 (4), 71 (6), 65 (7) $[C_5H_5]^+$, 57 (17) $[C_4H_9]^+$, 55 (8). $C_{20}H_{32}N_2O_2$ (332.49): calcd. C 72.25, H 9.70, N 8.43; C 72.27, H 9.67, N 8.54.

X-ray Crystal Structure Analysis of 1x:[27,28] Formula $C_{20}H_{32}N_2O_2$, M = 332.48, colorless crystal, 0.40 × 0.15 × 0.15 mm, a = 10.059(2), b = 8.570(1), c = 23.878(5) Å, β = 90.67(2)°, V = 2058.3(6) Å^3, ρ_{calc} = 1.073 g cm^{-3}, μ = 0.539 mm^{-1}, empirical absorption correction ($0.813 \leq T \leq 0.924$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, $\omega/2\theta$ scans, 4447 reflections collected ($-h$, $+k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.62 Å^{-1}, 4203 independent (R_{int} = 0.029) and 2340 observed reflections [$I \geq 2\sigma(I)$], 227 refined parameters, R = 0.051, wR^2 = 0.171, max. (min.) residual electron density 0.13 (–0.18) e·Å^{-3}. Hydrogen atoms at N5 from difference Fourier map, others calculated and refined as riding atoms.

General Procedure for the Synthesis of the *N*-Acylacetamidines 1y–1ab: At 0 °C, acetamidine hydrochloride (2 mmol) was suspended in acetone (30 mL). An exact amount of NaOH (2 N, 4.0 mmol, 2.0 mL) was added and the mixture was stirred for 1 min at 0 °C. Subsequently, acyl chloride (2 mmol) dissolved in acetone (5 mL), was added slowly. After 1.5 h stirring at 0 °C, the solvent was removed in vacuo as completely as possible. The residue was treated with water (100 mL), which was extracted with chloroform (3 × 50 mL). After removal of the chloroform in vacuo, the remaining residue was crystallized from chloroform/petroleum ether by diffusion.

***N*-[4-(*n*-Butyloxy)benzoyl]acetamidine (1y):** Synthesized from 4-(*n*-butyloxy)benzoyl chloride[36] (0.419 g, 1.97 mmol), acetamidine hydrochloride (0.186 g, 1.97 mmol), and NaOH (2 N, 0.98 mL); yield 0.240 g (52%); colorless solid; m.p. 103 °C. IR (KBr): $\tilde{\nu}$ = 3331 (br. m, NH), 3197 (br. m, NH), 3080 (w), 3062 (w, $CH_{arom.}$), 2956 (m), 2940 (m), 2928 (sh), 2920 (sh), 2873 (m), 2854 (w, CH_{alk}), 1617 (sh), 1603 (s), 1590 (s), 1559 (m), 1512 (s), 1497 (s), 1476 (m), 1462 (m), 1455 (sh), 1361 (m), 1328 (s), 1296 (m), 1270 (m), 1257 (s),

1179 (s), 1038 (m), 1004 (m), 868 (m), 855 (m), 654 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.98 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.49 (m, 2 H, CH_2), 1.78 (m, 2 H, CH_2), 2.18 (s, 3 H, CH_3, CH_3-amidine), 4.00 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 6.11 (br. s, 1 H, NH), 6.88 (m, 2 H, *m*-$CH_{arom.}$), 8.18 (m, 2 H, *o*-$CH_{arom.}$), 10.16 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 (CH_3), 19.2 (CH_2), 24.7 (CH_3, CH_3-amidine), 31.2 (CH_2), 67.8 (OCH_2), 113.8 (*m*-$CH_{arom.}$), 129.9 (C_{ipso}), 131.5 (*o*-$CH_{arom.}$), 162.4 (*p*-$C_{arom.}$), 169.3 ($C_{quat.}$, C=N), 179.6 ($C_{quat.}$, C=O) ppm. MS (70 eV): *m*/*z* (%) = 234 (37) $[M]^+$, 233 (12) $[M^+ - 1]$, 193 (5), 178 (8), 177 (75) $[H_9C_4OC_6H_4CO]^+$, 137 (5) $[HOC_6H_4CONH_2]^+$, 121 (100) $[HOC_6H_4CO]^+$, 108 (7), 103 (3), 93 (16) $[C_6H_4OH]^+$, 92 (8), 85 (6), 76 (5) $[C_6H_4]^+$, 65 (15) $[C_5H_5]^+$, 57 (10) $[H_2NC(CH_3)N^+, C_4H_9]^+$, 55 (4). $C_{13}H_{18}N_2O_2$ (234.39): calcd. C 66.64, H 7.74, N 11.96; found C 66.65, H 7.43, N 12.06.

If a surplus of NaOH was used or after chromatographic work up, the hydrolysis product *N*-acetyl-(4-*n*-butyloxy)benzamide was isolated. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 7.5 Hz, 3 H, CH_3), 1.42–1.57 (m, 2 H), 1.72–1.84 (m, 2 H, CH_2), 2.59 (s, 3 H, CH_3, Acetyl), 4.02 (t, ^3J = 6.4 Hz, 2 H, OCH_2), 6.94 (m, 2 H, *m*-$CH_{arom.}$), 7.87 (m, 2 H, *o*-$CH_{arom.}$), 9.23 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 (CH_3), 19.1 (CH_2), 25.4 (CH_3, Acetyl), 31.0, 68.0 (OCH_2), 114.5 (*m*-$CH_{arom.}$), 124.4 (C_{ipso}), 130.0 (o-$CH_{arom.}$), 163.2 (*p*-$C_{arom.}$), 165.2, 174.0 ($C_{quat.}$, C=O) ppm. MS (70 eV): *m*/*z* (%) = 235 (34) $[M]^+$, 179 (15) $[M^+ - C_4H_8]$, 177 (12) $[M^+ - HNCOCH_3]$, 137 (11), 121 (100) $[HOC_6H_4CO]^+$, 120 (9), 93 (15), 65 (21), 57 (15).

***N*-[4-(*n*-Hexyloxy)benzoyl]acetamidine (1z):** Synthesized from 4-(*n*-hexyloxy)benzoyl chloride[36] (0.722 g, 3.00 mmol), acetamidine hydrochloride (0.284 g, 3.00 mmol), and NaOH (2 N, 3.00 mL); yield 0.165 g (21%); colorless solid; m.p. 109 °C. IR (KBr): $\tilde{\nu}$ = 3315 (br. s, NH), 3182 (br. m, NH), 3084 (w, $CH_{arom.}$), 2957 (m), 2941 (m), 2932 (m), 2912 (m), 2872 (m), 2856 (m, CH_{alk}), 1620 (sh), 1603 (s), 1589 (s), 1560 (s), 1512 (s), 1493 (s), 1474 (s), 1396 (m), 1360 (m), 1321 (s), 1292 (s), 1275 (s), 1256 (s), 1173 (s), 1148 (m), 1107 (m), 1024 (m), 1011 (sh), 995 (m), 866 (m), 858 (m), 814 (m), 806 (m), 781 (m), 702 (m), 667 (sh), 653 (m), 635 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (m, 3 H, CH_3), 1.28–1.52 (m, 6 H, CH_2), 1.78 (m, 2 H, CH_2), 2.13 (s, 3 H, CH_3, CH_3-amidine), 3.99 (t, ^3J = 6.7 Hz, 2 H, OCH_2), 6.54 (br. s, 1 H, NH), 6.88 (m, 2 H, *m*-$CH_{arom.}$), 8.13 (m, 2 H, *o*-$CH_{arom.}$), 10.10 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 22.4 (CH_2), 24.5 (CH_3, CH_3-amidine), 25.5, 29.0, 31.4 (CH_2), 68.0 (OCH_2), 113.7 (*m*-$CH_{arom.}$), 129.8 (C_{ipso}), 131.4 (*o*-$CH_{arom.}$), 162.3 (*p*-$C_{arom.}$), 169.5 ($C_{quat.}$, C=N), 179.5 ($C_{quat.}$, C=O) ppm. MS (70 eV): *m*/*z* (%) = 262 (36) $[M]^+$, 261 (14) $[M^+ - 1]$, 221 (3), 206 (11), 205 (79) $[H_{13}C_6OC_6H_4CO]^+$, 177 (6), 149 (3), 138 (3), 137 (7), 121 (100) $[HOC_6H_4CO]^+$, 120 (6), 108 (9), 103 (3), 93 (12) $[C_6H_4OH]^+$, 92 (8), 85 (8), 65 (9) $[C_5H_5]^+$, 57 (3) $[H_2NC(CH_3)N^+, C_4H_9]^+$, 55 (6). $C_{15}H_{22}N_2O_2$ (262.35): calcd. C 68.67, H 8.45, N 10.68; found C 68.77, H 8.51, N 10.75.

X-ray Crystal Structure Analysis of 1z:[27,28] Formula $C_{15}H_{22}N_2O_2$, M = 262.35, colorless crystal, 0.50 × 0.30 × 0.15 mm, a = 14.338(1), b = 22.277(1), c = 9.411(1) Å, V = 3005.9(4) $Å^3$, ρ_{calc} = 1.159 $g\,cm^{-3}$, μ = 0.077 mm^{-1}, empirical absorption correction ($0.962 \leq T \leq 0.989$), Z = 8, orthorhombic, space group *Pccn* (No. 56), λ = 0.71073 Å, T = 198(2) K, ω and ϕ scans, 25662 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.71 $Å^{-1}$, 4407 independent (R_{int} = 0.041) and 3103 observed reflections [$I \geq 2\sigma(I)$], 180 refined parameters, R = 0.076, wR^2 = 0.240, max. (min.) residual electron density 0.67 (–0.37) e·$Å^{-3}$. Hydrogen atoms at N5 from difference Fourier map, others calculated and refined as riding atoms.

***N*-[4-(*n*-Octyloxy)benzoyl]acetamidine (1aa):** Synthesized from 4-(*n*-octyloxy)benzoyl chloride[37] (0.895 g, 3.33 mmol), acetamidine hydrochloride (0.315 g, 3.33 mmol) and NaOH (2 N, 3.33 mL); yield 0.251 g (26%, purity 92%); colorless solid. IR (KBr): $\tilde{\nu}$ = 3325 (br. s, NH), 3180 (br. m, NH), 3084 (w, $CH_{arom.}$), 2957 (m), 2941 (s), 2936 (m), 2918 (s), 2890 (sh), 2856 (m, CH_{alk}), 1604 (s), 1592 (s), 1560 (s), 1512 (m), 1493 (s), 1474 (s), 1393 (m), 1367 (m), 1321 (s), 1292 (s), 1275 (s), 1255 (s), 1173 (m), 1148 (m), 1107 (m), 1022 (m), 998 (m), 866 (m), 814 (m), 806 (m), 784 (m), 704 (m), 667 (m), 653 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (m, 3 H, CH_3), 1.20–1.52 (m, 10 H, CH_2), 1.78 (m, 2 H, CH_2), 2.14 (s, 3 H, CH_3, CH_3-amidine), 3.99 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 6.37 (br. s, 1 H, NH), 6.88 (m, 2 H, *m*-$CH_{arom.}$), 8.16 (m, 2 H, *o*-$CH_{arom.}$), 10.14 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.5 (CH_2), 24.6 (CH_3, CH_3-amidine), 25.9, 29.1, 29.2, 31.7 (CH_2), 68.1 (OCH_2), 113.8 (*m*-$CH_{arom.}$), 129.9 (C_{ipso}), 131.5 (*o*-$CH_{arom.}$), 162.4 (*p*-$C_{arom.}$), 169.4 ($C_{quat.}$, C=N), 179.6 ($C_{quat.}$, C=O) ppm. MS (70 eV): *m*/*z* (%) = 290 (41) $[M]^+$, 289 (18) $[M^+ - 1]$, 249 (3), 234 (14), 233 (74) $[H_{17}C_8OC_6H_4CO]^+$, 177 (9), 161 (3), 149 (3), 138 (4), 137 (7), 121 (100) $[HOC_6H_4CO]^+$, 120 (6), 104 (4), 93 (11) $[C_6H_4OH]^+$, 92 (7), 85 (11) $[C_6H_{13}]^+$, 71 (3) $[C_5H_{11}]^+$, 69 (6), 65 (8) $[C_5H_5]^+$, 57 (9) $[H_2NC(CH_3)N^+, C_4H_9]^+$, 55 (12).

X-ray Crystal Structure Analysis of 1aa:[27,28] Formula $C_{17}H_{26}N_2O_2$, M = 290.40, colorless crystal, 0.30 × 0.30 × 0.25 mm, a = 8.270(1), b = 9.160(1), c = 22.462(1) Å, β = 93.74(1)°, V = 1697.9(3) $Å^3$, ρ_{calc} = 1.136 $g\,cm^{-3}$, μ = 0.074 mm^{-1}, empirical absorption correction ($0.978 \leq T \leq 0.982$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198(2) K, ω and ϕ scans, 6990 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 $Å^{-1}$, 3993 independent (R_{int} = 0.029) and 2674 observed reflections [$I \geq 2\sigma(I)$], 198 refined parameters, R = 0.058, wR^2 = 0.144, max. (min.) residual electron density 0.21 (–0.19) e·$Å^{-3}$. Hydrogen atoms at N1 from difference Fourier map, others calculated and refined as riding atoms.

***N*-[4-(*n*-Hexadecyloxy)benzoyl]acetamidine (1ab):** Synthesized from 4-(*n*-hexadecyloxy)benzoyl chloride (1.33 g, 3.48 mmol), acetamidine hydrochloride (0.329 g, 3.48 mmol), and NaOH (2 N, 3.48 mL); yield 0.751 g (54%); colorless needles; m.p. 83 °C. IR (KBr): $\tilde{\nu}$ = 3323 (br. s, NH), 3196 (br. m, NH), 3076 (w, $CH_{arom.}$), 2955 (m), 2935 (m), 2920 (m), 2872 (m), 2853 (m, CH_{alk}), 1622 (sh), 1599 (s), 1560 (m), 1510 (s), 1491 (s), 1473 (s), 1358 (m), 1327 (s), 1292 (s), 1256 (s), 1175 (s), 1153 (m), 1105 (m), 1041 (m), 1022 (m), 1001 (m), 976 (m), 868 (m), 853 (m), 802 (m), 783 (m), 771 (m), 720 (m), 700 (m), 667 (sh), 654 (m), 635 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (m, 3 H, CH_3), 1.18–1.54 (m, 26 H, CH_2), 1.73–1.84 (m, 2 H, CH_2), 2.18 (s, 3 H, CH_3, CH_3-amidine), 4.00 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 6.06 (br. s, 1 H, NH), 6.89 (m, 2 H, *m*-$CH_{arom.}$), 8.18 (m, 2 H, *o*-$CH_{arom.}$), 10.13 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6 (CH_2), 24.7 (CH_3, CH_3-amidine), 26.0, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9 (CH_2), 68.1 (OCH_2), 113.8 (*m*-$CH_{arom.}$), 129.8 (C_{ipso}), 131.5 (*o*-$CH_{arom.}$), 162.4 (*p*-$C_{arom.}$), 169.3 ($C_{quat.}$, C=N), 179.5 ($C_{quat.}$, C=O) ppm. MS (70 eV): *m*/*z* (%) = 402 (61) $[M]^+$, 401 (24) $[M^+ - 1]$, 362 (11), 361 (39) $[M^+ - CH_3CN]$, 346 (20), 345 (76) $[H_{33}C_{16}OC_6H_4CO]^+$, 191 (9), 178 (12) $[M^+ - C_{16}H_{32}]$, 177 (7), 150 (10), 138 (38), 137 (54) $[HOC_6H_4CONH_2]^+$, 127 (7) $[C_9H_{19}]^+$, 121 (100) $[HOC_6H_4CO]^+$, 120 (7), 113 (11) $[C_8H_{17}]^+$, 85 (14) $[C_6H_{13}^+, H_2NC(CH_3)NCO]^+$, 83 (9), 71 (14) $[C_5H_{11}]^+$, 69 (14), 57 (36), 55 (22). $C_{25}H_{42}N_2O_2$ (402.62): calcd. C 74.58, H 10.51, N 6.96; found C 74.49, H 10.20, N 6.86.

***N*-[3,4-Bis(*n*-decyloxy)benzoyl]benzamidine (1ac):** KOH (0.122 g, 2.17 mmol) was dissolved in a little water and treated with acetone

(20 mL). The solution was cooled to 0 °C, then benzamidine hydrochloride (0.412 g, 2.17 mmol) was added. Subsequently, 3,4-bis(*n*-decyloxy)benzoyl chloride (0.987 g, 2.17 mmol), dissolved in acetone (10 mL), was added dropwise and the solution was stirred for 1.5 h at 0 °C. Acetone was distilled off and the residue was treated with water (50 mL). The aqueous phase was extracted with chloroform (1 × 100 mL, 2 × 50 mL) and the solvent of the organic phase was removed in vacuo. The remaining substance was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 1:1); yield 0.383 g (33%); colorless plates; m.p. 85 °C. IR (KBr): $\tilde{\nu}$ = 3391 (m, NH), 3275 (m), 3194 (w), 3094 (w), 3075 (w), 3055 (w, $CH_{arom.}$), 2955 (s), 2920 (s), 2870 (s), 2851 (s, CH_{alk}), 1601 (s), 1562 (s), 1512 (s), 1485 (s), 1470 (sh), 1443 (m), 1424 (s), 1385 (m), 1319 (s), 1296 (s), 1278 (s), 1258 (sh), 1223 (s), 1181 (m), 1130 (sh), 1119 (s), 1022 (m), 988 (m), 953 (m), 880 (m), 872 (m), 829 (m), 795 (m), 779 (s), 756 (m), 721 (m), 698 (m), 664 (m), 594 (m), 563 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (m, 6 H, CH_3), 1.98–1.54 (m, 29 H, CH_2), 1.83 (m, 4 H, CH_2), 4.05, 4.08 (t, ^3J = 6.8 Hz, 2 H, OCH_2), 6.71 (s, br., 1 H, NH), 6.89 (d, ^3J = 8.6 Hz, 1 H, C-5), 7.46 (m, 2 H, *m*-$CH_{arom.}$, Ph), 7.53 (m, 1 H, *p*-$CH_{arom.}$, Ph), 7.88 (d, ^4J = 1.9 Hz, 1 H, C-2), 8.03 (m, 3 H, $CH_{arom.}$, *o*-Ph, C-6), 10.55 (s, br., 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6, 26.0, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9 (CH_2), 69.1, 69.3 (OCH_2), 112.1, 114.8 ($CH_{arom.}$, C-2, C-5), 124.0, 127.3, 128.7, 130.7 (C_{ipso}), 132.1, 135.4, 148.5, 152.8 (C-3, C-4), 166.0 ($C_{quat.}$, C=N), 180.1 ($C_{quat.}$, C=O) ppm. MS (70 eV): *m*/*z* (%) = 536 (11) $[M]^+$, 433 (9) $[M^+ – PhCN]$, 293 (4) $[M^+ – PhCN – C_{10}H_{20}]$, 171 (6), 154 (8), 153 (43), 149 (6), 137 (24), 136 (8), 128 (5), 124 (8), 121 (6), 104 (16), 103 (100) $[C_6H_3CO^+, PhCN]^+$, 86 (7), 85 (19), 83 (24), 81 (6), 77 (13) $[Ph]^+$, 76 (49), 75 (16), 74 (9), 73 (8), 71 (17), 70 (10), 69 (17), 67 (9), 63 (7), 62 (4), 60 (8), 57 (38) $[C_4H_9]^+$, 56 (10), 55 (30), 53 (7), 52 (12), 51 (22). $C_{34}H_{52}N_2O_3$ (536.79): calcd. C 76.08, H 9.76, N 5.22; found C 76.24, H 9.93, N 5.16.

X-ray Crystal Structure Analysis of 1ac:[27,28] Formula $C_{34}H_{52}N_2O_3$, M = 536.78, colorless crystal, 0.60 × 0.40 × 0.02 mm, a = 34.504(5), b = 9.707(1), c = 9.777(2) Å, β = 93.08(1)°, V = 3269.9(9) $Å^3$, ρ_{calc} = 1.090 $g\,cm^{-3}$, μ = 0.532 mm^{-1}, empirical absorption correction (0.741 ≤ T ≤ 0.989), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, $\omega/2\theta$ scans, 7087 reflections collected (±h, +k, +l), [(sinθ)/λ] = 0.62 $Å^{-1}$, 6662 independent (R_{int} = 0.045) and 3552 observed reflections [$I \geq 2\sigma(I)$], 360 refined parameters, R = 0.065, wR^2 = 0.217, max. (min.) residual electron density 0.39 (–0.25) e·$Å^{-3}$. Hydrogen atoms at N1 from difference Fourier map, others calculated and refined as riding atoms.

***N*-[3,4,5-Tris(*n*-hexyloxy)benzoyl]benzamidine (1ad):** Synthesized from 3,4,5-tris(*n*-hexyloxy)benzoyl chloride (0.500 g, 1.13 mmol), benzamidine hydrochloride (0.214 g, 1.13 mmol), and NaOH (50%, 0.090.8 g). Purified by column chromatography (petroleum ether/ethyl acetate, 5:1); yield 0.326 g (55%, purity of 90%); colorless oil; R_f = 0.21 (petroleum ether/ethyl acetate, 5:1). IR (Film): $\tilde{\nu}$ = 3380 (br. m, NH), 3193 (w, br, NH), 3067 (w, $CH_{arom.}$), 2955 (s), 2930 (s), 2870 (s), 2858 (s, CH_{alk}), 1618 (sh), 1607 (s), 1568 (s), 1508 (s), 1474 (s), 1445 (s), 1425 (s), 1394 (sh), 1381 (m), 1333 (s), 1269 (m), 1219 (m), 1138 (sh), 1128 (sh), 1111 (s), 1001 (w), 781 (m), 698 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (m, 9 H, CH_3), 1.28–1.41 (m, 12 H), 1.44–1.54 (m, 6 H), 1.72–1.87 (m, 6 H, CH_2), 4.04 (t, ^3J = 6.6 Hz, 2 H), 4.07 (t, ^3J = 6.6 Hz, 4 H), 6.70 (br. s, 1 H, NH), 7.44–7.51 (m, 2 H, *m*-$CH_{arom.}$), 7.52–7.58 (m, 1 H, *p*-$CH_{arom.}$), 7.64 (s, 2 H, $CH_{arom.}$), 7.98–8.04 (m, 2 H, *o*-$CH_{arom.}$), 10.66 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 14.0 (CH_3), 22.5, 22.6, 25.7, 25.8, 29.4, 30.3, 31.6, 31.7 (CH_2), 69.2, 73.5 (OCH_2), 108.5 ($CH_{arom.}$, *o*-CO), 127.3, 128.8 ($CH_{arom.}$), 132.2, 132.7, 135.3, 142.1, 152.6 (C_{ipso}, OR), 166.3 ($C_{quat.}$, C=N), 180.1 ($C_{quat.}$, C=O) ppm. MS (ESI): *m*/*z* (%) = 547 (9) $[M^+ + Na]$, 525 (100) $[M^+ + 1]$.

General Procedure for the Synthesis of *N*-(4-Phenylazobenzoyl)amidines 1ae-1ag: Amidine hydrochloride (1 mmol) was dissolved at 0 °C in a mixture of acetone (20 mL) and NaOH (2 N, 1 mL), then 4-phenylazobenzoyl chloride (1 mmol), dissolved in acetone (5 mL), was added slowly. After 2 h stirring at 0 °C, the solvent was removed in vacuo and the residue was treated with water (50 mL). This mixture was extracted with chloroform (3 × 50 mL) and the combined organic extracts were dried with magnesium sulfate, the solvent was removed in vacuo, and the residue was purified by column chromatography or crystallized from chloroform/petroleum ether by diffusion of the solvents.

***N*-(4-Phenylazobenzoyl)benzamidine (1ae):** Synthesized from 4-phenylazobenzoyl chloride[38] (0.489 g, 2.00 mmol) and benzamidine hydrochloride (0.378 g, 2.00 mmol), and purified by column chromatography (petroleum ether/ethyl acetate, 5:1); yield 0.593 g (91%); orange felted needles; R_f = 0.61 (petroleum ether/ethyl acetate); m.p. 160–161 °C. IR (KBr): $\tilde{\nu}$ = 3361 (br. m, NH), 3177 (w, br, NH), 3059 (w, $CH_{arom.}$), 1616 (sh), 1601 (s), 1556 (s), 1506 (s), 1474 (s), 1443 (s), 1333 (s), 1300 (sh), 1290 (m), 1221 (w), 1138 (m), 1126 (w), 783 (m), 700 (m), 689 (sh), 542 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.73 (br. s, 1 H, NH), 7.44–7.61 (m, 6 H, *m*-/*p*-$CH_{arom.}$), 7.92–8.00 (m, 4 H, $CH_{arom.}$), 8.02–8.07 (m, 2 H, $CH_{arom.}$), 8.52 (m, 2 H, *o*-$CH_{arom.}$, CO), 10.75 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 122.4, 123.0, 127.4, 128.9, 129.1, 130.7, 131.3, 132.4 ($CH_{arom.}$), 135.0 (C_{ipso}, C=N), 139.7 (C_{ipso}, C=O), 152.8, 154.7 (C_{ipso}, N=N), 166.9 ($C_{quat.}$, C=N), 179.7 ($C_{quat.}$, C=O) ppm. MS (70 eV): *m*/*z* (%) = 328 (79) $[M]^+$, 327 (4) $[M^+ – 1]$, 251 (3) $[M^+ – Ph]$, 225 (11), 224 (15), 223 (91) $[M^+ – PhN_2]$, 209 (18) $[Ph\text{-}N{=}N\text{-}C_6H_4\text{-}CO]^+$, 181 (5), 180 (8), 152 (10) $[C_6H_4\text{-}C_6H_4]^+$, 147 (12) $[H_2N\text{-}C(Ph)N\text{-}CO]^+$, 120 (11), 105 (28) $[PhN_2]^+$, 104 (54) $[C_6H_4CO]^+$, 103 (51) $[PhCN]^+$, 92 (7), 78 (10), 77 (100) $[C_6H_5]^+$, 76 (34), 75 (16), 69 (10), 65 (6), 57 (6), 55 (5), 51 (20) $[C_4H_3]^+$. UV (acetonitrile): λ_{max} [lg(ε/$M^{-1}\,cm^{-1}$)] = 447 (2.60), 331 (4.50), 225 (4.11) nm. $C_{20}H_{16}N_4O$ (328.37): calcd. C 73.15, H 4.91, N 17.06; found C 72.82, H 5.20, N 16.71.

***N*-(4-Phenylazobenzoyl)pivalamidine (1af):** Synthesized from 4-phenylazobenzoyl chloride[38] (0.734 g, 3.00 mmol), pivalamidine hydrochloride (0.410 g, 3.00 mmol), and purified by column chromatography (petroleum ether/ethyl acetate, 5:1); yield 0.480 g (52%); red solid; R_f = 0.66 (petroleum ether/ethyl acetate, 1:1); m.p. 128–129 °C. IR (KBr): $\tilde{\nu}$ = 3342 (m, br), 3190 (br. m, NH), 3072 (w), 3053 (w, $CH_{arom.}$), 2966 (m, CH_{alk}), 1626 (sh), 1616 (sh), 1593 (s), 1564 (s), 1493 (s), 1466 (m), 1458 (sh), 1373 (m), 1367 (m), 1325 (sh), 1313 (s), 1304 (sh), 1225 (w), 1148 (w), 1009 (w), 870 (w), 858 (w), 698 (w), 683 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.34 [s, 9 H, $C(CH_3)_3$], 6.43 (br. s, 1 H, NH), 7.42–7.55 (m, 3 H, *m*-/*p*-$CH_{arom.}$), 7.90–7.98 (m, 4 H, *o*-$CH_{arom.}$, N=N), 8.43 (d, 2 H, *o*-$CH_{arom.}$, CO), 10.68 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.0 (CH_3), 38.7 [$C(CH_3)_3$], 122.3, 123.0, 129.0, 130.5, 131.2 ($CH_{arom.}$), 140.0 (C_{ipso}, C=O), 152.7, 154.5 (C_{ipso}, N=N), 179.4, 179.9 ($C_{quat.}$, C=O, C=N) ppm. MS (70 eV): *m*/*z* (%) = 308 (20) $[M]^+$, 293 (10) $[M^+ – CH_3]$, 209 (26) $[Ph\text{-}N{=}N\text{-}C_6H_4\text{-}CO]^+$, 203 (27) $[M^+ – PhN_2]$, 188 (9), 152 (10) $[C_6H_4\text{-}C_6H_4]^+$, 146 (8), 127 (5), 105 (22) $[PhN_2]^+$, 104 (45) $[C_6H_4CO]^+$, 103 (14) $[PhCN]^+$, 92 (7), 84 (9), 78 (9), 77 (100) $[Ph]^+$, 76 (39), 75 (9), 58 (5), 57 (23) $[C_4H_9]^+$, 51 (28), 50 (9). UV (acetonitrile): λ_{max} [lg(ε/$M^{-1}\,cm^{-1}$)] = 447 (2.53), 329 (4.43), 230 (4.02) nm. $C_{18}H_{20}N_4O$ (308.38): calcd. C 70.11, H 6.54, N 18.17; found C 70.00, H 6.67, N 17.91.

***N*-(4-Phenylazobenzoyl)acetamidine (1ag):** Synthesized from 4-phenylazobenzoyl chloride[38] (0.734 g, 3.00 mmol) and acetamidine hydrochloride (0.284 g, 3.00 mmol); yield 0.360 g (45%); red needles; m.p. 126.5 °C. IR (KBr): $\tilde{\nu}$ = 3312 (br. m, NH), 3182 (br. m, NH), 3061 (w, $CH_{arom.}$), 2947 (m), 2847 (m, CH_{alk}), 1624 (sh), 1603 (s), 1570 (m), 1504 (s), 1491 (sh), 1466 (sh), 1404 (m), 1364 (m), 1325 (sh), 1308 (s), 1288 (sh), 864 (m), 777 (m), 698 (m), 679 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 3 H, CH_3), 6.22 (br. s, 1 H, NH), 7.47–7.57 (m, 3 H, *m*-/*p*-$CH_{arom.}$), 7.90–7.98 (m, 4 H, *o*-$CH_{arom.}$, N=N), 8.38 (m, 2 H, *o*-$CH_{arom.}$, CO), 10.37 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.8 (CH_3), 122.4, 123.0, 129.1. 130.5, 131.9 ($CH_{arom.}$), 139.4 (C_{ipso}, CO), 152.7, 154.6 (C_{ipso}, N=N), 170.4 ($C_{quat.}$, C=N), 179.3 ($C_{quat.}$, C=O) ppm. MS (70 eV): *m*/*z* (%) = 266 (74) $[M]^+$, 209 (16) [Ph-N=N-C_6H_4-CO]$^+$, 162 (10), 161 (86) [M^+ – PhN_2], 153 (5), 152 (10) [C_6H_4-C_6H_4]$^+$, 133 (5), 120 (6), 105 (27) $[PhN_2]^+$, 104 (26) $[C_6H_4CO]^+$, 103 (33) $[PhCN]^+$, 93 (5), 92 (15), 85 (16) $[H_2N\text{-}C(CH_3)=NCO]^+$, 78 (7), 77 (100) $[C_6H_5]^+$, 76 (33), 75 (15), 71 (6), 69 (7), 65 (6), 57 (12) $[H_2N\text{-}C(CH_3)=N]^+$, 56 (5), 55 (10), 51 (22). UV (acetonitrile): λ_{max} [lg(ε/$M^{-1}cm^{-1}$)] = 446 (2.43), 330 (4.47), 229 (4.01) nm. $C_{15}H_{14}N_4O$ (266.30): calcd. C 67.65, H 5.30, N 21.04; found C 67.41, H 5.58, N 20.72.

Supporting Information (see also the footnote on the first page of this article): Details of the quantum chemical calculations of all $C_2H_4N_2O$-*N*-acylamidine isomers (two tables and one figure).

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