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Synthesis and Aggregation Properties of Two- and Three-Armed Nitrogen-Rich Chelate Ligands: Novel Bis(*N*-acylamidines), Tris(*N*-acylamidines) and Bis(triazapentadienes) with Flexible or Rigid Spacers[‡]

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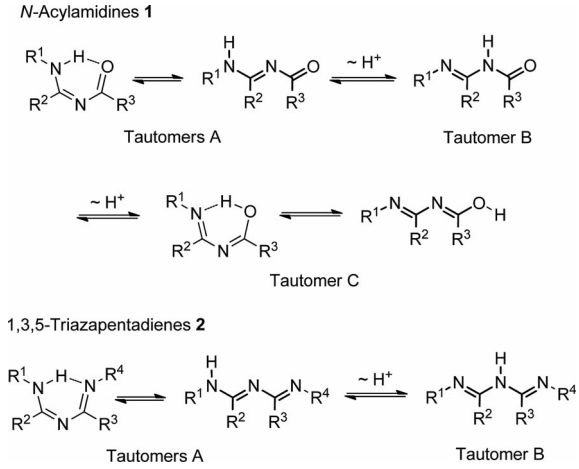
Two- and three-armed ligands, like bis(*N*-acylamidines) **7** and **9**, tris(*N*-acylamidines) **8** and bis(1,3,5-triazapenta-1,3-dienes) **10** with different spacers between the ligand moieties, have been easily prepared in moderate-to-good yields starting from diamines, triamines or dicarboxylic acid derivatives. Thus, the reaction of diamines and triamines with *N*-acylimidates **3** led to bis(*N*-acylamidines) **7** and tris(*N*-acylamidines) **8**, respectively, linked through the amino group. Ligands **9**, interconnected through the carbonyl groups, were obtained starting from dicarboxylic acid dichlorides and amidines. Bis(triazapentadienes) **10**, linked through carbon atoms, were synthesized from a diamide, which was converted into a bis(*N*-imidoylimidate) **17** followed by reactions with deprotonated amines. These compounds show variable aggregation behaviour in the solid state as a result of intra- and intermolecular hydrogen bonding. All compounds were thoroughly characterized including by X-ray diffraction.

Introduction

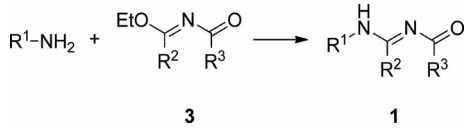
The development of novel ligands suitable for metal coordination to construct metallamacrocycles or the respective cavities is one of many challenges for chemists in the field of supramolecular chemistry. *N*-Acylamidines[1,2] **1** and 1,3,5-triazapenta-1,3-dienes[3] **2** are effective nitrogen-rich mono- or bidentate ligands for metal-ion coordination (Scheme 1). Compared with β-imino ketones[4] or β-diimines,[5] the nitrogen atom at the 3-position alters the electronic structures considerably so that conjugation over all five atoms is observed, even in the neutral form. Furthermore, this central nitrogen atom may also act as a ligand site for metal complexation.

Primary and secondary *N*-acylamidines **1** as well as 1,3,5-triazapentadienes **2** are subject to tautomerism in which a proton might be positioned at the amino group (tautomer A), at the central nitrogen atom (tautomer B) or at the oxygen atom (tautomer C; Scheme 1). A detailed discussion of this tautomerism was recently published by Wigbers et al.[6] For 1,3,5-triazapentadienes **2**,[7] two tautomers may be formulated. With respect to stability and to possible metal–ion coordination, the U forms with intramolecular hydrogen bonding are of special interest.

The synthesis of *N*-acylamidines **1** was first described by Pinner in 1889 by reaction of benzamidine hydrochloride and benzoic acid anhydride.[8] The treatment of *N*-acylimidates **3** with amines is another useful pathway for the synthesis of *N*-acylamidines **1** (Scheme 2).[6]



Scheme 1. *N*-Acylamidines **1** and 1,3,5-triazapentadienes **2** and their different tautomers.



Scheme 2. Synthesis of *N*-acylamidines **1** reported by Wigbers et al.[6]

[‡] Unsaturated Hetero Chains, XX. Part XIX: Ref.[2]

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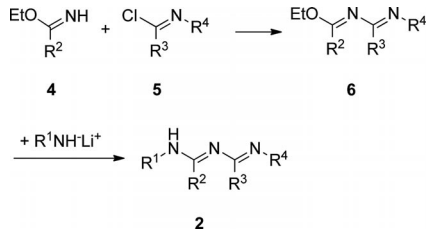
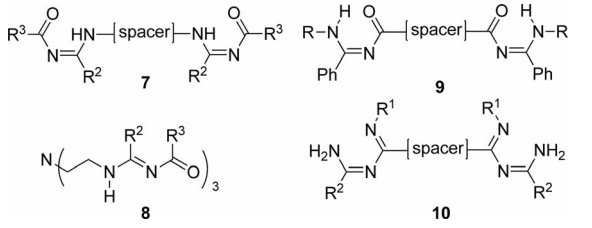
An analogous reaction for the preparation of tertiary and quaternary 1,3,5-triazapenta-1,3-dienes **2** was investigated by Häger et al. (Scheme 3).[9] Starting from imidates **4**, which were treated with imidoyl chlorides **5** to give *N*-imidoyl imidates **6**, it was possible to generate triazapentadienes **2**. Another method was described by Ley and Müller in 1907 based on the reaction of *N*-imidoyl halides **5** with amidines.[10] Additional reaction pathways for the synthesis of 1,3,5-triazapenta-1,3-dienes **2** have been described by Cooper, Partridge and Short.[11]



Scheme 3. Synthesis of tertiary 1,3,5-triazapenta-1,3-dienes **2** by Häger et al.[9]

The use of two- and three-armed ligands with flexible or inflexible spacer groups between two or more ligand moieties for manifold metal coordination is a current topic of interest in the field of supramolecular chemistry.[12] To extend our research from ligands with one chelating coordination site like *N*-acylamidines **1** and triazapentadienes **2**, we started to investigate the suitable synthesis of *N*- and *C*-linked bis(*N*-acylamidines) **7** and **9**, tris(*N*-acylamidines) **8** and *C*-linked bis(triazapentadienes) **10** (Scheme 4).



Scheme 4. *N*- and *C*-linked bis(*N*-acylamidines) **7** and **9**, tris(*N*-acylamidines) **8** and bis(triazapentadienes) **10**.

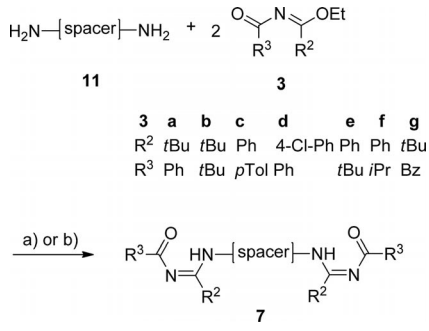
In this context, bis(triazapentadienes) and oligomers with small spacer molecules have been reported by Greving and co-workers[13] and poly(triazapentadienes) have been described in a patent by Dorfman et al.[14] Similar compounds, such as bis(*N*-acylthioureas),[15,16] bis(*N*-acylguanidines)[17,18] and bis(*N*-acylisoureas),[19,20] have also been described in the literature. In 2010 we reported a method for the synthesis of bis(*N*-acylamidines) **9** linked through carbonyl moieties using *N*-acylbenzotriazoles as acylation agents.[21] In this paper we report our results on the preparation of bis(*N*-acylamidines) **9**, *N*-linked bis(*N*-acylamidines) **7**, tris(*N*-acylamidines) **8** and *C*-linked bis(triazapentadienes) **10**. On the one hand we will demonstrate how procedures for the synthesis of mono-*N*-acylamidines and triazapentadienes were adjusted for the synthesis of such ligands with two and three chelating moieties and on the other hand we reveal that the novel derivatives form interesting assemblies in the solid state as a result of hydrogen bonding.

Results and Discussion

Bis(*N*-acylamidines) 7 Linked Through Amino Groups

In our previous report we described the synthesis of bis(*N*-acylamidines) from dicarboxylic acid or dinitriles as commercially available starting materials.[21] This method was limited to the generation of bis(*N*-acylamidines) linked through the carbonyl groups of the amidine unit. To synthesize bis(*N*-acylamidines) **7**, linked through the amino groups, another procedure starting from diamines was required. Therefore the synthesis of *N*-acylamidines reported previously was adjusted to molecules with flexible or inflexible spacers separating the chelating subgroups.[6]

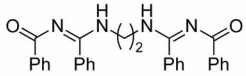
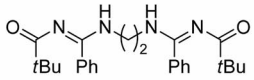
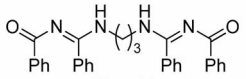
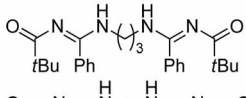
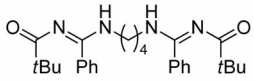
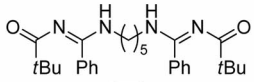
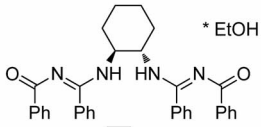
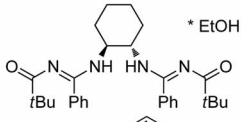
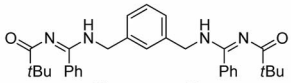
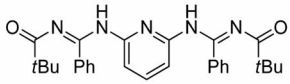
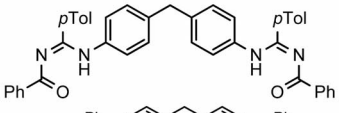
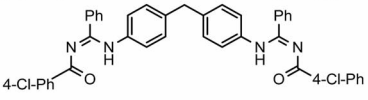
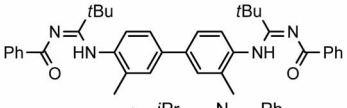
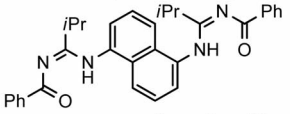
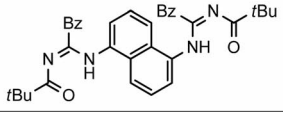
To prepare the novel *N*-linked bis(*N*-acylamidines) **7a**–**o**, 1 equiv. of a diamine **11** was treated with at least 2 equiv. of *N*-acylimidate **3** (Scheme 5). The reactions took place either in solvent-free conditions at 80–90 °C for 5 h or at reflux temperature in dioxane for 16 h. By these methods, 15 different bis(*N*-acylamidines) (**7a**–**o**) with flexible or sterically constrained spacer units were synthesized in moderate-to-good yields (Table 1).



Scheme 5. Synthesis of bis(*N*-acylamidines) **7** linked through the amino moiety. Reaction conditions: a) 80–90 °C, 5 h; b) dioxane, 101 °C, 16 h.

The choice of ligands and substituents was based on aspects of flexibility (**7a**–**f**) combined with variable steric bulk and electronic effects exerted by aliphatic and aryl groups. These patterns proved to be important for the structural, catalytic and supramolecular properties of various metal coordination compounds.[22] Two examples (**7g**,**h**) are based on the chiral diamine *trans*-1,2-diaminocyclohexane, which offers the possibility of asymmetric complexes. Compounds **7i**–**o** contain aromatic moieties with varying structural and electronic properties, **7j** with its pyridine-based spacer offers an additional site for coordination and hydrogen bonding. Compounds **7i**–**m** contain a central spacer group with limited flexibility and thus offer varying steric constraints but

Table 1. Bis(*N*-acylamidines) linked through the amino moiety.

Product	Structure	Yield
7a		61 % [a]
7b		56 % [a]
7c	 * 0.5 EtOH	28 % [a]
7d		80 % [a]
7e		71 % [a]
7f		46 % [a]
7g	 * EtOH	53 % [a]
7h	 * EtOH	27 % [a]
7i		62 % [a]
7j		38 % [a]
7k		53 % [b]
7l		56 % [b]
7m		79 % [b]
7n		47 % [b]
7o		86 % [b]

[a] 80–90 °C, 5 h. [b] Dioxane, 101 °C, 16 h.

allow rotation about one or at most two single bonds. The last two compounds **7n** and **7o** restrict the relative positions of both chelating parts almost completely.

All the compounds are crystalline solids and are stable at room temperature. The conformation and configuration in the solid state of compounds **7a**, **7g** and **7j** were elucidated by single-crystal X-ray diffraction. In the solid state, **7a** and **7g** form one-dimensional networks (open-chain tautomer A, Scheme 1) interconnected by the intermolecular hydrogen bonding of both NH subunits to the carbonyl functions of two neighbouring molecules (**7a**: NH···O distance 1.94 Å, N···O distance 2.78 Å; **7g**: NH···O distance 2.06 Å, N···O distance 2.88 Å; sum of the van der Waals radii:[23] O + H 2.72 Å, N + O 3.07 Å; compare also Figure 4).

The molecular structure of compound **7j** is depicted in Figure 1. Interestingly, unsymmetrical intramolecular hydrogen bonds are formed exclusively between the amino protons and the nitrogen atom of the pyridine spacer unit (tautomer B, Scheme 1), whereas other bis(*N*-acylamidines) are characterized by the intermolecular hydrogen bonding of amino protons (see below, compare Figures 2 and 4). The NH···N distances are 1.98 and 2.21 Å (N···N distances: 2.71 and 2.82 Å; sum of the van der Waals radii:[23] N + H 2.75 Å, N + N 3.10 Å).

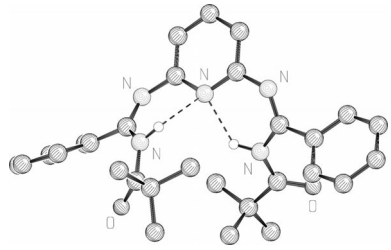


Figure 1. Molecular structure of **7j** as obtained by X-ray diffraction (hydrogen atoms have been omitted for clarity).

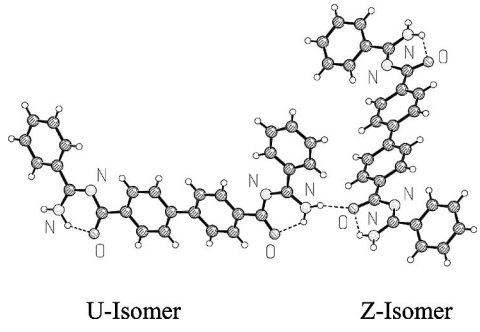
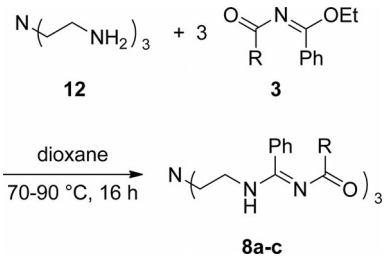


Figure 2. Part of the molecular assembly of **9c** (U and Z isomers) as obtained by X-ray diffraction.

Tris(*N*-acylamidines) 8

Three novel tris(*N*-acylamidines) **8a**–**c**, linked through the amino moiety, were synthesized under similar conditions using tris(2-aminoethyl)amine (**12**) and 3 equiv. of *N*-acylimidates **3** as starting materials. The reaction was carried out in dioxane at 70–90 °C for 16 h (Scheme 6 and Table 2).



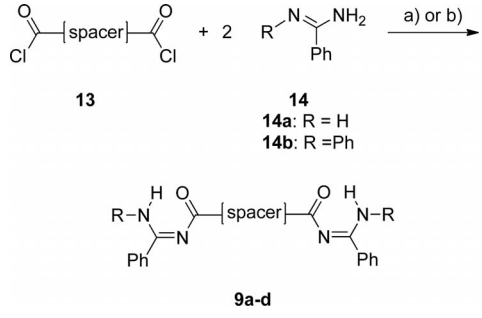
Scheme 6. Synthesis of tris(*N*-acylamidines) **8** linked through the amino moiety.

Table 2. Tris(*N*-acylamidines) **8a**–**c**.

N-Acylimidate	Product	R	Yield [%]
3a	**8a**	*t*Bu	8
3b	**8b**	Ph	30
3c	**8c**	4-CF_3Ph	18

Bis(*N*-acylamidines) 9 Linked Through the Carbonyl Groups

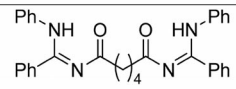
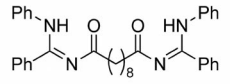
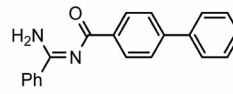
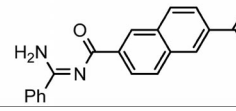
Bis(*N*-acylamidines) **9**, linked through the carbonyl moiety, were synthesized from dicarboxylic acid dichlorides and amidines in good yields in analogy to the work of Katritzky and co-workers on mono(*N*-acylamidines) (Scheme 7 and Table 3)[24] using two different reaction conditions depending on the nature of the spacer. The amidines **14** were deprotonated with potassium *tert*-butoxide and then treated with the diacid dichlorides in tetrahydrofuran to give low yields of products **9a** and **9b**. The synthesis of the primary bis(*N*-acylamidines) linked by inflexible spacers (**9c** and **9d**) using triethylamine as the deprotonating agent in dichloromethane or chloroform solution was more successful. The products were obtained in good yields. They are crystalline solids and their structures were confirmed by X-ray diffraction.



Scheme 7. Synthesis of bis(*N*-acylamidines) **9a**–**d** linked through the carbonyl moiety. Reaction conditions: a) for **9a**,**b**: KO*t*Bu, THF, 10 °C to r.t., 24 h; b) for **9c**,**d**: Et_3N, CH_2Cl_2 or $CHCl_3$, –10 °C to r.t., overnight.

The crystal structures of the bis(*N*-acylamidines) **9c** and **9d** are both characterized by inter- and intramolecular hydrogen bonding leading to supramolecular networks. Exemplarily, the structure of **9c** is shown in Figures 2 and 3. All the hydrogen bonds in the supramolecular network are formed between amino protons and oxygen atoms (tautomer A, Scheme 1). In the framework, two different conformers, the U- and Z-shaped isomers, form as a result of rotation of the central bond of the biphenyl system (Figures 2 and 3). The intramolecular hydrogen bonds have O–N distances of 2.53 and 2.63 Å in the case of the U-shape isomer and 2.65 Å in the case of the Z-shape, whereas we find for the intermolecular hydrogen bonds distances of 2.88 and 2.91 Å.

Table 3. Bis(*N*-acylamidines) **9** linked through the carbonyl moiety.

Product	Structure	Yield
9a	 * 0.25 EtOH	2 % [a]
9b	 * 0.25 EtOH	18 % [a]
9c		75 % [b]
9d		76 % [b]

[a] KO*t*Bu, THF 10 °C to r.t., 24 h. [b] Et_3N, DCM, 0 °C to r.t., 16 h.

Bis(1,3,5-triazapentadienes) 10 Linked Through the Carbon Atoms

To synthesize bis(1,3,5-triazapentadienes), we adapted the procedure of Häger et al. using *N*-imidoylimidates and deprotonated amines as precursors.[9] Thus, bis(*N*-imidoylimidate) **17** was synthesized starting from diamide **15** via the bis(imidoyl chloride) **16** (Scheme 8). The structure of compound **17** was proven by X-ray diffraction. The reaction of bis(*N*-imidoylimidate) **17** with 5 equiv. of deprotonated primary amines gave the novel tertiary bis(1,3,5-triazapenta-1,3-dienes) **10a**–**c** in moderate-to-good yields (Scheme 8 and Table 4).

All compounds are crystalline solids and stable at room temperature. The structure of compound **10a** was characterized by single-crystal X-ray diffraction (Figure 4 and Figure 5).

Compound **10a** assembles to form a supramolecular chain (Figure 5). One side of the bis(triazapentadiene) is connected to another bis(triazapentadiene) through intermolecular hydrogen bonding and the other side forms a hydrogen bond to a tetrahydrofuran solvent molecule. The interaction takes place between two terminal nitrogen atoms within the N–C–N–C–N chain (open-chain tautomer A, Scheme 1). In the resulting structure, N–N distances of the intermolecular hydrogen bonds measure 3.03 Å. This means that the interaction is weak considering the sum of the van der Waals radii N + N of 3.10 Å.[23]

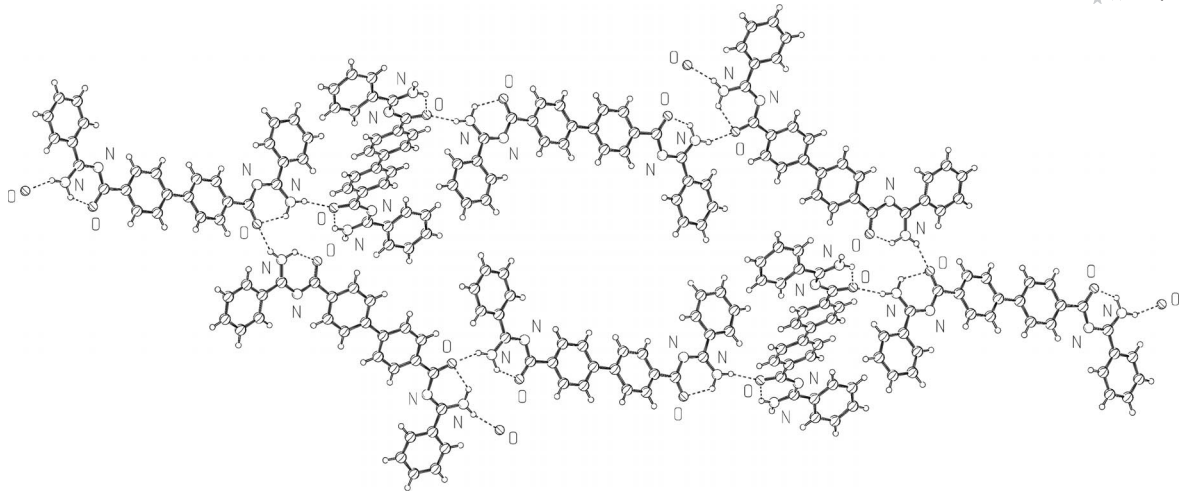
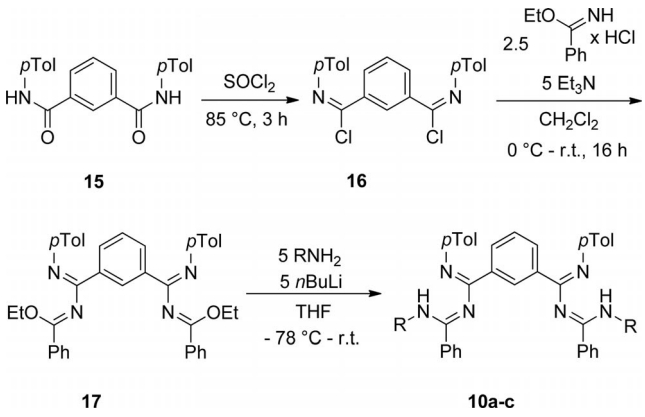


Figure 3. Supramolecular structure of **9c** as obtained by X-ray diffraction.



Scheme 8. Synthesis of bis(triazapentadienes) **10** via bis(*N*-imidoylimidate) **17**.

Table 4. Bis(triazapentadienes) **10a**–**c** prepared from bis(*N*-imidoylimidate) **17**.

Product	R	Yield [%]
10a	Ph	59
10b	*p*Tol	75
10c	4-ClPh	52

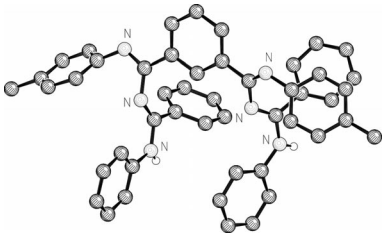


Figure 4. Molecular structure of **10a** as obtained by X-ray diffraction (hydrogen atoms have been omitted for clarity).

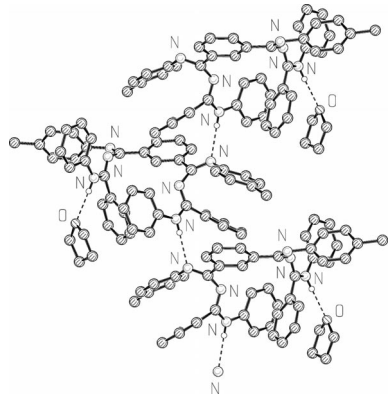


Figure 5. Supramolecular structure of **10a** as obtained by X-ray diffraction (hydrogen atoms have been omitted for clarity).

Conclusions

We have reported the synthesis of 19 different bis(*N*-acylamidines) **7** and **9** linked either through the amino or the carbonyl moieties. The compounds have quite different spacer groups, which affects the geometry: more and less flexible aliphatic chains or inflexible aromatic groups. Furthermore, three tris(*N*-acylamidines) **8** and three bis(triazapentadienes) **10** have been reported. The compounds show interesting aggregation behaviour in the solid state, giving supramolecular arrangements as a result of intra- and intermolecular hydrogen bonding, leading to the formation of polymeric linear chains or large cyclic superstructures. Reports on the coordination chemistry of the bis(*N*-acylamidines) and their catalytic properties in cross-coupling reactions are in preparation.[12,22]

Experimental Section

Materials and Methods: IR: Nicolet 5DXC spectrometer (KBr pellets), Varian 3100 FT-IR spectrometer using a Specac Golden Gate Single Reflection ATR sampling system. ^{1}H NMR: Bruker WM

300 (300.13 MHz) and Bruker AMX 400 (400.13 MHz) spectrometers; internal reference: tetramethylsilane or solvent. ^{13}C NMR: Bruker WM 300 (75.47 MHz) and Bruker AMX 400 (100.61 MHz) spectrometers; internal reference: solvent; Sp = spacer. CHN elemental analysis: Elementar Vario El III Instrument. All solvents were rigorously dried by the 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 amidines were prepared either from lithiated amines (using *n*-butyllithium as base) and nitriles[25] or by reaction of amines and nitriles in the presence of aluminium chloride.[26]

General Procedure for the Synthesis of *N*-Acylimidates 6: Imidates **6** were prepared partially in analogy to a literature procedure.[27] Crude imidate hydrochlorides were dissolved in anhydrous dichloromethane and stirred at room temperature. Then triethylamine (2.2 equiv.) was added dropwise to the solution. The reaction mixture was stirred for 1 h and cooled to –15 °C. Acid chloride (2.2 equiv.), dissolved in dichloromethane, was added dropwise. The reaction mixture was warmed to room temperature and stirred for 20 h. The solvent was then removed under reduced pressure and the residue washed twice with warm pentane or warm tetrahydrofuran. The filtrate was evaporated and the crude products were purified as stated below.

Ethyl *N*-(4-Chlorobenzoyl)benzimidate (3d): Imidate 3d was prepared from ethyl benzimidate hydrochloride (9.30 g, 50.0 mmol),[27] triethylamine (11.10 g, 110.0 mmol) and *p*-chlorobenzoyl chloride (6.5 mL, 8.80 g, 50.0 mmol). The product was purified by recrystallization from a toluene/cyclohexane mixture (1:1) to give 11.40 g, (40.0 mmol, 80%) of a colourless solid; m.p. 68.4 °C. IR (ATR): $\tilde{\nu}$ = 3086 (w), 3076 (w), 3042 (w), 2984 (w), 2938 (w), 2905 (w), 1666 (m), 1647 (vs), 1601 (m), 1585 (m), 1572 (m), 1489 (w), 1472 (w), 1447 (w), 1395 (w), 1366 (w), 1325 (m), 1269 (s), 1256 (s), 1161 (m), 1150 (m), 1107 (m), 1092 (m), 1065 (s), 1028 (m), 1013 (m), 1001 (m), 866 (s), 854 (m), 789 (m), 772 (s), 746 (m), 710 (m), 696 (s), 683 (m), 675 (m), 644 (w), 523 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.48 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3) 4.45 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 7.28–7.36 (m, 2 H, CH_{arom}) 7.37–7.45 (m, 3 H, CH_{arom}), 7.53–7.59 (m, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (OCH_2CH_3), 64.1 (OCH_2CH_3), 128.5, 128.6, 128.9 (*o*/*m*-CH_{arom}), 130.4 (*i*-C_{arom}), 130.8 (CH_{arom}), 131.8 (*p*-CH_{arom}), 133.2, 139.2 (*i*-C_{arom}), 159.4 (C=N), 175.0 (C=O) ppm. HRMS (ESI): calcd. for $C_{16}H_{14}ClNO_2$ + Na 310.0605; found 310.0600. $C_{16}H_{14}ClNO_2$ (287.7): calcd. C 66.79, H 4.90, N 4.87; found C 66.58, H 4.79, N 4.96.

Ethyl *N*-Benzoylisobutyrimidate (3f): From isobutyrimidate hydrochloride (7.58 g, 50.0 mmol),[27] triethylamine (11.13 g, 110.0 mmol) and benzoyl chloride (7.03 g, 50.0 mmol). Distillation (0.14 mbar; 94 °C) gave 6.30 g (28.7 mmol, 58%) of a colourless oil. IR (NaCl): $\tilde{\nu}$ = 3084 (m), 3065 (m), 3045 (w), 3020 (w), 2980 (vs), 2937 (s), 2914 (m), 2876 (m), 1720 (s), 1664 (vs), 1607 (s), 1582 (s), 1472 (s), 1448 (s), 1396 (m), 1366 (s), 1344 (s), 1302 (vs), 1252 (vs), 1223 (s), 1169 (s), 1088 (vs), 1069 (s), 1024 (s), 918 (s), 866 (vs), 714 (vs), 689 (s), 665 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.13 [d, ^3J = 6.9 Hz, 6 H, 1 H, $CH(CH_3)_2$], 1.37 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.73 [sept., ^3J = 6.9 Hz, 2 H, $CH(CH_3)_2$], 4.27 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 7.36–7.62 (m, 3 H, *m*/*p*-CH_{arom}), 7.96–8.20 (m, 2 H, *o*-CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 [$CH(CH_3)_2$], 19.8 (OCH_2CH_3), 32.9 [$CH(CH_3)_2$], 62.8 (OCH_2CH_3), 128.3 (*p*-CH_{arom}), 129.5, 132.7 (*o*/*m*-CH_{arom}), 134.5 (*i*-C_{arom}), 168.5 (C=N), 177.2 (C=O) ppm. HRMS (ESI): calcd. for $C_{13}H_{17}NO_2$ + Na 242.1151; found 242.1158. $C_{13}H_{17}NO_2$ (219.28): calcd. C 71.21, H 7.81, N 6.39; found C 71.02, H 7.89, N 6.35.

Ethyl *N*-(2,2-Dimethylpropionyl)benzylacetimidate (3g): From ethyl phenylacetimidate hydrochloride (9.98 g, 50.0 mmol),[27] triethylamine (11.13 g, 110.0 mmol) and pivaloyl chloride (6.03 g, 50.0 mmol). Kugelrohr distillation (0.04 mbar; 80 °C) gave 9.14 g (36.9 mmol, 74%) of a colourless oil. IR (NaCl): $\tilde{\nu}$ = 3088 (m), 3065 (m), 3032 (s, CH_{arom}), 2976 (vs), 2932 (s), 2905 (s), 2870 (s, CH_{aliph}), 1686 (vs, C=O), 1645 (vs, C=N), 1603 (vs), 1585 (s), 1497 (s), 1477 (vs), 1456 (vs), 1427 (s), 1393 (s), 1367 (vs), 1317 (s), 1267 (vs), 1167 (vs), 1140 (vs), 1107 (s), 1032 (vs), 941 (vs), 928 (vs), 878 (s), 812 (m), 791 (m), 733 (s), 702 (vs), 619 (w), 609 (m), 579 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.09 [s, 9 H, $C(CH_3)_3$], 1.27 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 3.64 (s, 2 H, $PhCH_2$), 4.13 (q, ^3J = 7.1 Hz, 2 H, OCH_2), 7.26–7.30 (m, 5 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (OCH_2CH_3), 27.1 [$C(CH_3)_3$], 38.1 ($PhCH_2$), 41.2 [$C(CH_3)_3$], 62.8 (OCH_2), 126.9 (*p*-C_{arom}), 128.4, 129.3 (*o*/*m*-C_{arom}), 134.8 (*i*-C_{arom}), 162.5 (C=N), 191.4 (C=O) ppm. HRMS (ESI): calcd. for $C_{15}H_{21}NO_2$ + Na 270.1465; found 270.1464. $C_{15}H_{21}NO_2$ (247.33): calcd. C 72.84, H 8.56, N 5.66; found C 72.65, H 8.55, N 5.62.

General Procedure for the Synthesis of the Bis(*N*-Acylamidines) 7a–j Linked Through the Amino Moiety: Amidines **7a**–**j** were prepared partially in analogy to a literature procedure.[28] The *N*-acylimidate (16.0 mmol) was stirred at 80–90 °C in a dry Schlenk flask under an inert atmosphere. The diamine (8.0 mmol) was added portionwise and the reaction mixture stirred for an additional 5 h at 80–90 °C. After cooling to room temperature the crude products were purified as stated below.

***N*-[(2-{[(Benzoylimino)phenylmethyl]amino}ethylamino)phenylmethylidene]benzamide (7a):** From 1,2-diaminoethane (0.48 g, 8.0 mmol) and ethyl *N*-benzoylbenzimidate (4.05 g, 16.0 mmol).[27] Crystallization from chloroform gave 2.33 g (4.9 mmol, 61%) of colourless crystals; m.p. 202 °C. IR (KBr): $\tilde{\nu}$ = 3435 (s, NH), 3292 (s, NH), 3101 (w), 3061 (w, ν-CH_{arom}), 2937 (vw, ν-CH_{arom}), 1616 (sh), 1589 (s, C=O/C=N), 1560 (vs), 1528 (vs), 1489 (s, ν-C=C_{arom}), 1447 (m), 1429 (m, δ-CH_2), 1371 (s), 1312 (s), 1294 (s), 1163 (m), 1069 (w), 1022 (w), 874 (w), 847 (w), 791 (m), 716 (m), 696 (s, δ-CH_{arom}) cm^{-1}. ^1H NMR (300.13 MHz, DMSO): δ = 3.80 (br., 4 H, NCH_2), 7.35–7.51 (m, 16 H, CH_{arom}), 7.80 (d, ^3J = 7.3 Hz, 4 H, CH_{arom}), 8.58 (br., 2 H, NH) ppm. ^{13}C NMR (75.47 MHz, DMSO): δ = 40.7 (NCH_2), 127.6, 128.0, 128.2, 128.9 (*o*,*m*-CH_{arom}), 130.2, 131.4 (*p*-CH_{arom}), 134.4 (*i*-$C_{arom}R^2$), 136.9 (*i*-$C_{arom}R^3$), 163.2 (C=N), 175.1 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 474 (1) $[M]^+$, 353 (2), 250 (24) $[OC(Ph)NC(Ph)NHCHCH_2]^+$, 225 (28), 209 (2), 145 (10), 105 (100) $[PhCO]^+$, 77 (31) $[Ph]^+$. $C_{30}H_{26}N_4O_2$ (474.56): calcd. C 75.53, H 5.52, N 11.81; found C 75.50, H 5.38, N 11.72.

X-ray Crystal Structure Analysis for 7a:[29] Formula $C_{30}H_{26}N_4O_2$, M = 474.55, colourless crystal, 0.70 × 0.10 × 0.05 mm, a = 9.678(1), b = 10.558(1), c = 13.155(1) Å, α = 104.04(1), β = 108.77(1), γ = 91.99(1)°, V = 1225.3(2) Å^3, $\rho_{calcd.}$ = 1.286 g cm^{-3}, μ = 0.655 cm^{-1}, empirical absorption correction ($0.657 \leq T \leq 0.968$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 15706 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 4316 independent (R_{int} = 0.045) and 3826 observed reflections [$I \geq 2\sigma(I)$], 332 refined parameters, R = 0.108, wR^2 = 0.330, max. (min.) residual electron density 0.78 (–0.32) e Å^{-3}, hydrogen atoms at N from difference Fourier calculations, others calculated and refined as riding atoms, quality of the analysis was very poor, probably due to twinning.

***N*-[(2-{[(2,2-Dimethylpropionylimino)phenylmethyl]amino}ethylamino)phenylmethylidene]-2,2-dimethylpropionamide (7b):** From

1,2-diaminoethane (0.48 g, 8.0 mmol and ethyl *N*-pivaloylbenzimidate (3.73 g, 16.0 mmol).[27] Diethyl ether (10.0 mL) was added to the residue. Ultrasonication led to a yellow solid. The solid was filtered off and washed with diethyl ether to give 1.94 g (4.5 mmol, 56%) of a colourless solid. The compound consists of different tautomers and conformers; m.p. 180–181 °C. IR (KBr): $\tilde{\nu}$ = 3433 (s, NH), 3327 (s), 3271 (s, NH), 3107 (m), 3067 (m, ν-CH_{arom}), 2953 (m), 2926 (m), 2864 (w, ν-$CH_{aliph.}$), 1607 (s), 1582 (s, C=O/C=N), 1531 (vs), 1475 (s, ν-C=C_{arom}), 1393 (s, *t*Bu), 1364 (s, *t*Bu), 1296 (s), 1246 (s), 1136 (s), 920 (m), 862 (m), 770 (s), 698 (m, δ-CH_{arom}) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.09 [br. s, 9 H, $C(CH_3)_3$], 1.16 [s, 8 H, $C(CH_3)_3$], 1.32 [s, 1 H, $C(CH_3)_3$], 3.54–3.80 [br. m, 4 H, NCH_2], 5.55–5.66 (br., NH), 7.27–7.55 [br. m, 10 H, CH_{arom}], 11.22 (br., NH) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 27.5, 27.8 [$C(CH_3)_3$], 38.5, 41.1 [$C(CH_3)_3$], 42.4 (NCH_2), 127.5, 128.4 (br., *o*,*m*-$CH_{arom}R^2$), 130.4 (*p*-$CH_{arom}R^2$), 134.7, 134.8 (*i*-$C_{arom}R^2$), 153.3, 169.1 (C=N), 181.2, 190.6 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 434 (1) $[M]^+$, 419 (1), 377 (100) $[M - C_4H_9]^+$, 334 (7) [M – OC(*t*Bu)NH]$^+$, 276 (13) [OCNHC(Ph)N$(CH_2)_2$NC(Ph)]$^+$, 251 (3), 231 (15) [OC(*t*Bu)NC(Ph)NHCH$_2$CH$_2$]$^+$, 205 (13), 173 (22) [OCNC(Ph)NHCHCH$_2$]$^+$, 147 (13), 128 (14), 104 (10), 57 (35) $[C_4H_9]^+$. $C_{26}H_{34}N_4O_2$ (434.58): calcd. C 71.86, H 7.89, N 12.89; found C 71.79, H 7.71, N 13.03.

***N*-[({3-[(Benzoylimino)phenylmethyl]amino}propylamino)phenylmethylidene]benzamide (7c):** From 1,3-diaminopropane (0.59 g, 8.0 mmol) and ethyl *N*-benzoylbenzimidate (4.05 g, 16.0 mmol).[27] Crystallization from ethanol gave 1.13 g (2.2 mmol, 28%) of a colourless solid (ethanol complex). The compound consists of different tautomers and conformers; m.p. 144–146 °C. IR (KBr): $\tilde{\nu}$ = 3406 (s, NH), 3267 (m, NH), 3061 (m), 3032 (w, ν–CH_{arom}), 2926 (w), 2887 (w, ν-CH_{arom}), 1624 (vs), 1618 (vs), 1597 (vs, C=O/C=N), 1570 (vs), 1560 (vs), 1543 (vs), 1526 (vs), 1489 (s, ν-C=C_{arom}), 1447 (s, δ-CH_2), 1381 (s), 1352 (s), 1310 (s), 1288 (s), 1163 (m), 1067 (m), 1053 (w), 1024 (m), 881 (w), 843 (w), 787 (m), 714 (m), 698 (s, δ-CH_{arom}) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 1.94 (br., 2 H, NCH_2CH_2), 3.55 (br., 4 H, NCH_2), 5.99 (br., NH), 6.99–7.51 (m, 16 H, CH_{arom}), 7.86–8.26 (m, 4 H, CH_{arom}), 11.68 (br., NH) ppm; ethanol: δ = 1.18 (t, ^3J = 7.0 Hz, 1.5 H, CH_3CH_2OH), 3.64 (q, ^3J = 7.1 Hz, 1 H, CH_3CH_2OH) ppm. ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 28.3 (NCH_2CH_2), 39.5, 43.3, 50.8 (NCH_2), 127.2, 128.0, 128.5, 129.3 (*o*,*m*-CH_{arom}), 130.7, 131.7 (*p*-CH_{arom}), 133.8, 136.5 (*i*-C_{arom}), 153.7, 164.0, (C=N), 176.9, 179.9 (C=O) ppm; ethanol: δ = 12.1 (br., CH_3CH_2OH), 45.7 (br., CH_3CH_2OH) ppm. MS (70 eV): *m*/*z* (%) = 488 (3) $[M]^+$, 367 (8) [M – OC(Ph)NH_2]$^+$, 341 (2), 265 (12) [M – OC(Ph)NC(Ph)NH]$^+$, 251 (16) [OC(Ph)NC(Ph)NHCH$_2$CH$_2$]$^+$, 237 (9) [OC(Ph)NC(Ph)NHCH$_2$]$^+$, 225 (11), 159 (20), 105 (100) $[PhCO]^+$, 77 (39) $[Ph]^+$. $C_{31}H_{28}N_4O_2$·0.5C_2H_5OH (511.62): calcd. C 75.12, H 6.11, N 10.95; found C 75.15, H 5.81, N 11.33.

***N*-[(3-{[(2,2-Dimethylpropionylimino)phenylmethyl]amino}propylamino)phenylmethylidene]-2,2-dimethylpropionamide (7d):** From 1,3-diaminopropane (0.59 g, 8.0 mmol) and ethyl *N*-pivaloylbenzimidate (3.73 g, 16.0 mmol).[27] Diethyl ether (10.0 mL) was added to the residue. Ultrasonication led to a colourless solid. The solid was filtered off and washed with diethyl ether to give 2.87 g (6.4 mmol, 80%) of a colourless solid. The compound consists of different tautomers and conformers; m.p. 159 °C. IR (KBr): $\tilde{\nu}$ = 3433 (s, NH), 3275 (s, NH), 3109 (m), 3065 (m, ν-CH_{arom}), 2953 (s), 3926 (m), 2868 (m, ν-$CH_{aliph.}$), 1620 (s), 1580 (vs, C=O/C=N), 1560 (vs), 1543 (vs), 1477 (s, ν-C=C_{arom}), 1393 (s, *t*Bu), 1362 (m, *t*Bu), 1300 (s), 1217 (m), 1132 (m), 926 (w), 772 (m), 696 (m, δ-CH_{arom}) cm^{-1}. ^1H NMR (300.13 MHz, DMSO): δ = 1.13 [br. s, 16.0 H, $C(CH_3)_3$], 1.26 [br. s, 2.0 H, $C(CH_3)_3$], 1.94 (br., 2 H, NCH_2CH_2), 3.41 (br., 4 H, NCH_2), 7.17–7.54 (m, 10 H, CH_{arom}), 11.46 (br., NH) ppm. ^{13}C NMR (75.48 MHz, DMSO): δ = 27.1, 27.4 [$C(CH_3)_3$], 27.6 (NCH_2CH_2), 27.9 [$C(CH_3)_3$], 40.2 [br., NCH_2, $C(CH_3)_3$], 127.3, 128.0 (*o*,*m*-CH_{arom}), 129.8 (*p*-CH_{arom}), 135.1 (*i*-C_{arom}), 161.4 (C=N), 188.2 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 448 (5) $[M]^+$, 391 (100) $[M - C_4H_9]^+$, 348 (5), 290 (2), 245 (51) [M – OC(*t*Bu)NC(Ph)NH]$^+$, 231 (6) [OC(*t*Bu)NC(Ph)NHCH$_2$CH$_2$]$^+$, 187 (19) [OCNC(Ph)NHCH$_2$CHCH$_2$]$^+$, 162 (19), 113 (8), 57 (30) $[C_4H_9]^+$. $C_{27}H_{36}N_4O_2$ (448.60): calcd. C 72.29, H 8.09, N 12.49; found C 72.26, H 8.05, N 12.49.

***N*-[(3-{[(2,2-Dimethylpropionylimino)phenylmethyl]amino}butylamino)phenylmethylidene]-2,2-dimethylpropionamide (7e):** From 1,4-diaminobutane (0.53 g, 6.0 mmol) and ethyl *N*-pivaloylbenzimidate (2.80 g, 12.0 mmol).[27] Diethyl ether (10.0 mL) was added to the residue. Ultrasonication led to a colourless solid. The solid was filtered off and washed with diethyl ether to give 1.98 g (4.3 mmol, 71%) of a colourless solid; m.p. 210 °C. IR (KBr): $\tilde{\nu}$ = 3449 (m, NH), 3312 (s, NH), 3105 (vw), 3055 (vw, ν-CH_{arom}), 2949 (m), 2924 (w), 2903 (vw), 2864 (vw, ν-$CH_{aliph.}$), 1614 (s), 1584 (s, C=O/C=N), 1543 (vs), 1477 (m, ν-C=C_{arom}), 1429 (m, δ-CH_2), 1393 (s, *t*Bu), 1367 (s, *t*Bu), 1296 (m), 1128 (m), 1020 (vw), 897 (w), 777 (m), 752 (m), 690 (m, δ-CH_{arom}) cm^{-1}. ^1H NMR (300.14 MHz, $CDCl_3$): δ = 1.22 [br. s, 18 H, $C(CH_3)_3$], 1.62 (br., 4 H, NCH_2CH_2), 3.33 (br., 4 H, NCH_2), 5.17 (br., NH), 7.44 (br., 10 H, CH_{arom}), 11.29 (br., NH) ppm. ^{13}C NMR (300 MHz, TFA, $CDCl_3$): δ = 28.5 [$C(CH_3)_3$], 31.7 (CH_2), 28.9 [$C(CH_3)_3$], 44.5 (CH_2), 49.7 (C_q), 127.5 (*i*-C_{arom}), 130.3, 132.3, 133.2, 138.0 (CH_{arom}), 169.7, 170.5 (C=O), 187.6 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 461 (1) [M – 1]$^+$, 447 (2), 405 (100) $[M - C_4H_9]^+$, 347 (2) [M – 2C_4H_9 – 1]$^+$, 279 (2), 259 (27) [M – OC(*t*Bu)NC(Ph)NH]$^+$, 201 (21), 176 (24), 174 (25), 159 (6) [OCNC(Ph)NCH_2]$^+$, 147 (7) [OCNC(Ph)NH_2]$^+$, 104 (22)-[PhCNH]$^+$, 70 (11), 57 (50) $[C_4H_9]^+$. $C_{28}H_{38}N_4O_2$ (462.63): calcd. C 72.69, H 8.28, N 12.11; found C 72.46, H 8.11, N 12.07.

***N*-[(5-{[(2,2-Dimethylpropionylimino)phenylmethyl]amino}pentylamino)phenylmethylidene]-2,2-dimethylpropionamide (7f):** From 1,5-diaminopentane (0.61 g, 6.0 mmol) and ethyl *N*-pivaloylbenzimidate (2.80 g, 12.0 mmol).[27] Diethyl ether (10.0 mL) was added to the residue. Ultrasonication led to a solid. The solid was filtered off and washed with diethyl ether to give 1.31 g (2.7 mmol, 46%) of a colourless solid; m.p. 142 °C. IR (KBr): $\tilde{\nu}$ = 3441 (m, NH), 3294 (s NH), 3101 (w), 3057 (w, ν-CH_{arom}), 2953 (s), 2934 (s), 2912 (m), 2864 (m, ν-$CH_{aliph.}$), 1612 (vs), 1582 (vs, C=O/C=N), 1541 (vs), 1477 (s, ν-C=C_{arom}), 1429 (s, δ-CH_2), 1393 (s, *t*Bu), 1364 (vs, *t*Bu), 1298 (s), 1219 (m), 1115 (m), 1026 (vw), 918 (m), 773 (s), 743 (m), 694 (s, δ-CH_{arom}) cm^{-1}. ^1H NMR (300.14 MHz, $CDCl_3$): δ = 1.21 [br. s, 18 H, $C(CH_3)_3$], 1.33–1.91 [br. m, 6 H, $NCH_2(CH_2)_3$], 3.31 (br., 4 H, NCH_2), 5.37 (br., NH), 7.30–7.66 [br. m, 10 H, CH_{arom}], 11.31 (br., NH) ppm. ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 23.9 ($NCH_2CH_2CH_2$), 27.8 [$C(CH_3)_3$], 30.0 (NCH_2CH_2), 41.8 [$C(CH_3)_3$], 45.2 (NCH_2), 128.3 (*o*,*m*-CH_{arom}), 130.2 (*p*-CH_{arom}), 134.6 (*i*-C_{arom}), 169.5 (C=N), 195.6 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 461 (2), 419 (100) $[M - C_4H_9]^+$, 405 (2), 361 (1) [M – 2*t*Bu – 1]$^+$, 273 (35) [M – OC(*t*Bu)NC(Ph)NH]$^+$, 215 (16), 190 (24), 181 (33), 159 (11) [OCNC(Ph)NCH_2]$^+$, 147 (6) [OCNC(Ph)NH_2]$^+$, 104 (33) [PhCNH]$^+$, 57 $[C_4H_9]^+$. $C_{29}H_{40}N_4O_2$ (476.66): calcd. C 73.07, H 8.46, N 11.75; found C 72.95, H 8.38, N 11.72.

***N*-{[(1*R*,2*S*)-2-{[(Benzoylimino)phenylmethyl]amino}cyclohexylamino]phenylmethylidene}benzamide (7g):** From *rac*-*trans*-1,2-diaminocyclohexane (0.80 g, 7.0 mmol) and ethyl *N*-benzoylbenzimidate (3.54 g, 14.0 mmol).[27] Addition of ethanol led to an ethanol complex of the product which was filtered off to give 1.96 g (3.7 mmol, 53%) of colourless crystals; m.p. 174 °C. IR (KBr): $\tilde{\nu}$ =

3437 (m, NH), 3260 (s, NH), 3061 (m, ν-CH_{arom}), 2937 (m), 2858 (m, ν-CH_{arom}), 1616 (vs), 1595 (vs, C=O/C=N), 1572 (vs), 1526 (vs), 1489 (s, ν-C=C_{arom}), 1447 (s, δ-CH_2), 1377 (s), 1315 (vs), 1286 (s), 1265 (s), 1161 (m), 1117 (m), 1070 (m), 1051 (m), 1022 (m), 891 (m), 781 (m), 719 (s), 694 (s, δ-CH_{arom}) cm^{-1}. ^1H NMR (400.14 MHz, $CDCl_3$): δ = 1.21–2.52 (m, 8 H, 3,4,5,6-CH_2R^1-Sp), 4.16 (br., 2 H, 1,2-CHR^1-Sp), 7.22–7.53 (m, 16 H, CH_{arom}), 7.80–8.29 (m, 4 H, CH_{arom}) ppm; ethanol: δ = 1.16 (t, ^3J = 7.0 Hz, 3 H, CH_3CH_2OH), 3.62 (q, ^3J = 7.0 Hz, 2 H, CH_3CH_2OH) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 24.6 (4,5-CH_2R^1-Sp), 32.1 (3,6-CH_2R^1-Sp), 56.6 (1,2-CH_2R^1-Sp), 127.4, 128.0, 128.7, 129.2 (*o*,*m*-CH_{arom}), 130.9, 131.6 (*p*-CH_{arom}), 134.3 (*i*-$C_{arom}R^2$), 136.5 (*i*-$C_{arom}R^3$), 164.1 (C=N), 176.8 (C=O) ppm; ethanol: δ = 18.3 (CH_3CH_2OH), 58.2 (CH_3CH_2OH) ppm. MS (70 eV): *m*/*z* (%) = 528 (5) $[M]^+$, 407 (1), 304 (100) $[M - OC(Ph)NC(Ph)NH_2]^+$, 251 (3), 225 (52), 199 (56) $[M - OC(Ph)NC(Ph)NH_2 - COPh]^+$, 183 (48), 105 (91) $[PhCO]^+$, 96 (15) $[C_6H_9NH]^+$. $C_{34}H_{32}N_4O_2 \cdot C_2H_5OH$ (574.72): calcd. C 75.24, H 6.66, N 9.75; found C 74.72, H 6.65, N 9.64.

X-ray Crystal Structure Analysis for 7g:[29] Formula $C_{34}H_{32}N_4O_2 \cdot C_2H_5OH$, M = 574.70, colourless crystal, 0.25 × 0.15 × 0.15 mm, a = 12.674(1), b = 12.202(3), c = 21.020(2) Å, β = 103.64(1)°, V = 3159.0(9) Å^3, $\rho_{calcd.}$ = 1.208 g cm^{-3}, μ = 0.616 cm^{-1}, empirical absorption correction ($0.861 \leq T \leq 0.913$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 6610 reflections collected ($\pm h$, $-k$, $-l$), $[(\sin\theta)/\lambda]$ = 0.62 Å^{-1}, 6432 independent (R_{int} = 0.038) and 3435 observed reflections [$I \geq 2\sigma(I)$], 406 refined parameters, R = 0.053, wR^2 = 0.170, max. (min.) residual electron density 0.28 (–0.28) e Å^{-3}, hydrogen atoms at N from difference fourier calculations, others calculated and refined as riding atoms.

***N*-{[(1*R*,2*S*)-2-{[(2,2-Dimethylpropionylimino)phenylmethyl]amino}-cyclohexylamino]phenylmethylidene}-2,2-dimethylpropionamide (7h):** From *rac*-*trans*-1,2-diaminocyclohexane (0.91 g, 8.0 mmol) and ethyl *N*-pivaloylbenzimidate (3.73 g, 16.0 mmol).[27] Addition of ethanol led to an ethanol complex of the product which was filtered off to give 1.07 g (2.2 mmol, 27%) of colourless crystals. The compound consists of different tautomers and conformers; m.p. 175 °C. IR (KBr): $\tilde{\nu}$ = 3433 (s, NH), 3262 (s, NH), 3090 (m, ν-CH_{arom}), 2934 (s), 2862 (m, ν-CH_{arom}), 1722 (m), 1665 (s), 1626 (s), 1609 (s), 1584 (s, C=O/C=N), 1535 (vs, ν-C=C_{arom}), 1447 (s, δ-CH_2), 1393 (m, *t*Bu), 1366 (m, *t*Bu), 1277 (s), 1188 (m), 1117 (m), 934 (w), 773 (m), 692 (m, δ-CH_{arom}) cm^{-1}. ^1H NMR (300.14 MHz, $CDCl_3$): δ = 0.95 [br. s, 5.9 H, $C(CH_3)_3$], 1.03 [br. s, 12.1 H, $C(CH_3)_3$], 1.20–2.45 (m, 8 H, 3,4,5,6-CH_2R^1-Sp), 3.55 (br., 1 H, 1,2-CH_2R^1-Sp), 3.91 (br., 1 H, 1,2-CHR^1-Sp), 7.29–7.52 [br. m, 10 H, CH_{arom}] ppm; ethanol: δ = 1.15 (t, ^3J = 7.0 Hz, 3 H, CH_3CH_2OH), 3.59 (q, ^3J = 7.0 Hz, 2 H, CH_3CH_2OH) ppm. ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 24.3, 24.6 (4,5-CH_2R^1-Sp), 26.8, 27.7 [$C(CH_3)_3$], 32.1, 32.8 (3,6-CH_2R^1-Sp), 39.3, 41.0 [$C(CH_3)_3$], 56.3, 64.7 (1,2-CH_2R^1-Sp), 127.6, 128.5 (*o*,*m*-CH_{arom}), 130.4 (*p*-CH_{arom}), 135.1, 135.7 (*i*-C_{arom}), 154.1, 162.2 (C=N), 177.0, 190.4 (C=O) ppm; ethanol: δ = 18.3 (CH_3CH_2OH), 58.1 (CH_3CH_2OH) ppm. MS (70 eV): *m*/*z* (%) = 488 (1) $[M]^+$, 431 (100) $[M - C_4H_9]^+$, 388 (1) $[M - OC(tBu)NH]^+$, 348 (2), 305 (4), 285 (21) $[M - OC(tBu)NC(Ph)NH]^+$, 227 (24) $[M - OC(tBu)NC(Ph)NH - tBu]^+$, 184 (19), 147 (8), 104 (11) $[PhCNH]^+$, 81 (12), 57 (41) $[C_4H_9]^+$. $C_{30}H_{40}N_4O_2$ (488.67): calcd. C 73.74, H 8.25, N 11.47; found C 73.39, H 8.16, N 11.40.

***N*-{[3-({[(2,2-Dimethylpropionylimino)phenylmethyl]amino}methyl)-benzylamino]phenylmethylidene}-2,2-dimethylpropionamide (7i):** From α,α′-diamino-*m*-xylene (1.09 g, 8.0 mmol) and ethyl *N*-pivaloylbenzimidate (3.73 g, 16.0 mmol).[27] Diethyl ether (10.0 mL) was added to the residue. Ultrasonication led to a colourless solid. The solid was filtered off and washed with diethyl ether to give 2.54 g (5.0 mmol, 62%) of a colourless solid. The compound consists as different tautomers and conformers; m.p. 168 °C. IR (KBr): $\tilde{\nu}$ = 3424 (m, NH), 3298 (s, NH), 3061 (w), 3030 (w, ν-CH_{arom}), 2953 (s), 2926 (m), 2866 (m, ν-$CH_{aliph.}$), 1618 (vs), 1584 (vs, C=O/C=N), 1533 (vs), 1477 (s, ν-C=C_{arom}), 1421 (s, δ-CH_2), 1391 (s, *t*Bu), 1364 (s, *t*Bu), 1306 (s), 1215 (m), 1119 (m), 1016 (w), 907 (m), 773 (s), 696 (s, δ-CH_{arom}) cm^{-1}. ^1H NMR (400.14 MHz, $CDCl_3$): δ = 1.17 [s, 16.7 H, $C(CH_3)_3$], 1.32 [s, 1.3 H, $C(CH_3)_3$], 4.50 (s, 3.7 H, CH_2), 4.62 (s, 0.3 H, CH_2), 5.65 (br., 1 H, NH), 7.06–7.56 (m, 13 H, CH_{arom}), 7.68–7.80 (m, 1 H, 4-$CH_{arom}R^1$-Sp), 11.50 (br., 1 H, NH) ppm. ^{13}C NMR (100.61 MHz, DMSO): δ = 27.1, 27.7 [$C(CH_3)_3$], 40.3 [$C(CH_3)_3$], 44.8, 53.8 (CH_2), 125.9 (3,5-$CH_{arom}R^1$-Sp), 126.7 (1-$CH_{arom}R^1$-Sp), 127.3 (*o*,*m*-$CH_{arom}R^2$), 127.5 (4-$CH_{arom}R^1$-Sp), 128.1 (*o*,*m*-$CH_{arom}R^2$), 129.9 (*p*-$CH_{arom}R^2$), 134.8, 136.5 (*i*-$C_{arom}R^2$), 138.9, 140 (2,6-$C_{arom}R^1$-Sp), 150.6, 160.6 (C=N), 176.3, 188.3 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 510 (9) $[M]^+$, 495 (3), 453 (100) $[M - C_4H_9]^+$, 410 (1) $[M - OC(tBu)NH]^+$, 350 (1), 307 (68) $[M - OC(tBu)NC(Ph)NH]^+$, 278 (5), 250 (13) $[M - OC(tBu)NC(Ph)NH - tBu]^+$, 204 (30) $[OC(tBu)NC(Ph)NH_2]^+$, 146 (11) $[OCNC(Ph)NH]^+$, 104 (17), 85 (5) $[tBuCO]^+$, 57 (29) $[C_4H_9]^+$. $C_{32}H_{38}N_4O_2$ (510.67): calcd. C 75.26, H 7.50, N 10.97; found C 75.24, H 7.31, N 10.96.

***N*-[(6-{[(2,2-Dimethylpropionylimino)phenylmethyl]amino}pyridin-2-ylamino)phenylmethylidene]-2,2-dimethylpropionamide (7j):** From 2,6-diaminopyridine (0.49 g, 4.5 mmol) and ethyl *N*-pivaloylbenzimidate (2.10 g, 9.0 mmol).[27] After column chromatography using acetone/*n*-pentane (1:3) + 10% of triethylamine as eluent, 0.83 g (1.7 mmol, 38%) of colourless crystals were obtained. The compound consists of different tautomers and conformers; m.p. 151 °C. IR (KBr): $\tilde{\nu}$ = 3443 (s, NH), 3248 (m, NH), 3059 (vw, ν-CH_{arom}), 2970 (w), 2930 (w), 2868 (vw, ν-$CH_{aliph.}$), 1719 (s), 1711 (s, C=O/C=N), 1620 (vs, C=O/C=N), 1580 (s), 1543 (s), 1475 (m, ν-C=C_{arom}), 1414 (m), 1396 (m, *t*Bu), 1366 (m, *t*Bu), 1321 (s), 1312 (m), 1140 (s), 937 (w), 829 (w), 696 (m, δ-CH_{arom}) cm^{-1}. ^1H NMR (400.14 MHz, $CDCl_3$): δ = 1.18 [s, 13.2 H, $C(CH_3)_3$], 1.32 [s, 4.8 H, $C(CH_3)_3$], 7.10 (d, ^3J = 7.8 Hz, 2 H, *m*-$CH_{arom}R^1$-Sp), 7.43–7.52 (m, 6 H, *m*,*p*-$CH_{arom}R^2$), 7.71 (d, ^3J = 7.1 Hz, 4 H, *o*-$CH_{arom}R^2$), 7.87 (t, ^3J = 7.8 Hz, 1 H, *p*-$CH_{arom}R^1$-Sp), 11.26 (s, NH) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.0 [$C(CH_3)_3$], 40.0 [$C(CH_3)_3$], 117.3 (*m*-$CH_{arom}R^1$-Sp), 128.1 (*o*,*m*-$CH_{arom}R^2$), 130.9 (*p*-$CH_{arom}R^2$), 135.9 (*i*-$C_{arom}R^2$), 141.1 (*p*-$CH_{arom}R^1$-Sp), 155.0 (C=N), 157.7 (*o*-$C_{arom}R^1$-Sp), 176.6 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 483 (6) $[M]^+$, 426 (100) $[M - C_4H_9]^+$, 383 (2) $[M - OC(tBu)NH]^+$, 342 (5), 325 (39), 280 (7) $[M - OC(tBu)-NC(Ph)NHPy]^+$, 222 (10), 196 (9) $[HNC(Ph)NHPy]^+$, 179 (9), 154 (1), 105 (23), 85 (5) $[tBuCO]^+$, 57 (39) $[C_4H_9]^+$. $C_{29}H_{33}N_5O_2$ (483.61): calcd. C 72.02, H 6.88, N 14.48; found C 71.73, H 6.79, N 14.11.

X-ray Crystal Structure Analysis for 7j:[29] Formula $C_{29}H_{33}N_5O_2$, M = 483.60, colourless crystal, 0.30 × 0.10 × 0.05 mm, a = 10.191(1), b = 17.369(1), c = 29.866(1) Å, V = 5286.5(6) Å^3, $\rho_{calcd.}$ = 1.215 g cm^{-3}, μ = 0.621 cm^{-1}, empirical absorption correction ($0.836 \leq T \leq 0.970$), Z = 8, orthorhombic, space group *Pbca* (No. 61), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 37692 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.60 Å^{-1}, 4748 independent (R_{int} = 0.081) and 3539 observed reflections [$I \geq 2\sigma(I)$], 339 refined parameters, R = 0.052, wR^2 = 0.114, max. (min.) residual electron density 0.15 (–0.19) e Å^{-3}, hydrogen atoms at N from difference fourier calculations, others calculated and refined as riding atoms.

General Procedure for the Synthesis of Bis(*N*-acylamidines) 7k–o Linked Through the Amino Moiety: *N*-Acylimidate (2 equiv.) was dissolved in a small amount of dioxane and heated at 80 °C until the *N*-acylimidate had completely dissolved. Then the diamine (1 equiv.) was added portionwise, the mixture was heated at reflux for 16 h and the solvents evaporated. The crude products were purified as stated below.

***N*-[(4-{4-[(Benzoylimino)-*p*-tolylmethylamino]benzyl}phenylamino)-*p*-tolylmethylidene]benzamide (7k):** From ethyl *N*-benzoylpivalimidate (0.54 g, 2.00 mmol)[27] and 4-[(4-aminophenyl)methyl]aniline (0.20 g, 1.00 mmol). Crystallization from acetonitrile gave 0.34 g (0.53 mmol, 53%) of colourless needles; m.p. 157.6 °C. IR (ATR): $\tilde{\nu}$ = 3264 (m), 3194 (m), 3067 (m), 3030 (m), 2994 (m), 2920 (m), 1609 (m), 1584 (m), 1564 (m), 1506 (s), 1491 (m), 1449 (m), 1406 (m), 1383 (m), 1319 (s), 1302 (m), 1267 (m), 1229 (m), 1184 (m), 1175 (m), 1155 (m), 1119 (m), 1059 (m), 1022 (m), 945 (m), 912 (m), 895 (m), 868 (m), 818 (m), 795 (m), 777 (m), 758 (m), 710 (s), 689 (m), 662 (m), 638 (m), 623 (m), 577 (m), 557 (m), 532 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 6 H, CH_3), 3.88 (s, 2 H, CH_2), 7.01 (br., 8 H, CH_{arom}), 7.13 (d, ^3J = 7.8 Hz, 4 H, CH_{arom}), 7.43–7.56 (m, 10 H, CH_{arom}), 8.33 (d, ^3J = 7.0 Hz, 4 H, CH_{arom}), 12.01 (s, 2 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_3), 40.6 (CH_2), 123.6, 128.2, 129.1, 129.5, 129.6 (CH_{arom}), 131.5 (*i*-C_{arom}), 132.2 (CH_{arom}), 136.9, 138.1, 141.6 (*i*-C_{arom}), 164.8 (C=N), 179.0 (C=O) ppm. HRMS (ESI): calcd. for $C_{43}H_{36}N_4O_2$ + H 641.2911; found 641.2913. $C_{43}H_{36}N_4O_2$ (640.8): calcd. C 80.60, H 5.66, N 8.74; found C 80.33, H 5.73, N 8.60.

***N*-[(4-{4-[(4-Chlorobenzoylimino)-*p*-tolylmethylamino]benzyl}-phenylamino)-*p*-tolylmethylidene]-4-chlorobenzamide (7l):** From ethyl *N*-(4-chlorobenzoyl)benzimidate (**3d**; 3.16 g, 11.0 mmol) and 4-[(4-aminophenyl)methyl]aniline (0.99 g, 5.0 mmol). The crude product was dissolved in chloroform (3 mL), *tert*-butyl methyl ether (5 mL) was added and the mixture was sonicated for 30 min. The precipitate was filtered off and dried at 120 °C under vacuum to give 1.92 g (2.8 mmol, 56%) of a yellow solid; m.p. 109.9–114.4 °C. IR (ATR): $\tilde{\nu}$ = 3287 (w), 3204 (w), 3061 (w), 3034 (w), 1587 (m), 1551 (m), 1510 (s), 1485 (m), 1445 (w), 1410 (m), 1317 (m), 1263 (m), 1231 (m), 1167 (w), 1152 (w), 1088 (m), 1061 (w), 1024 (w), 1013 (m), 920 (w), 897 (w), 847 (w), 762 (m), 692 (m), 621 (w), 588 (w), 565 (w), 523 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 2 H, CH_2), 6.93–7.01 (m, 8 H, CH_{arom}), 7.29–7.45 (m, 10 H, CH_{arom}), 7.57 (d, ^3J = 7.3 Hz, 4 H, CH_{arom}), 8.25 (d, ^3J = 8.4 Hz, 4 H, CH_{arom}), 12.28 (br., 2 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.8 (CH_2), 124.0, 128.6, 128.6, 129.7, 129.7, 131.3, 131.4 (CH_{arom}), 134.4, 135.7, 136.7, 138.4, 138.6 (*i*-C_{arom}), 165.7 (C=N), 178.4 (C=O) ppm. HRMS (ESI): calcd. for $C_{41}H_{30}Cl_2N_4O_2$ + H 681.1819; found 681.1811. $C_{41}H_{30}Cl_2N_4O_2$ (681.6): calcd. C 72.25, H 4.44, N 8.22; found C 72.04, H 4.35, N 8.12.

***N*-{1-[4′-(1-Benzoylimino-2,2-dimethylpropylamino)-3,3′-dimethylbiphenyl-4-ylamino]-2,2-dimethylpropylidene}benzamide (7m):** From ethyl *N*-benzoylpivalimidate (2.00 g, 8.6 mmol)[27] and *o*-tolidine (0.91 g, 4.3 mmol; *caution*: tolidine is toxic and possibly carcinogenic). Crystallization from ethanol gave 1.96 g (3.4 mmol, 79%) of a colourless solid. The compound consists of different tautomers; m.p. 205.6 °C. IR (ATR): $\tilde{\nu}$ = 3225 (w), 3067 (w), 2968 (w), 2870 (w), 1665 (m), 1609 (s), 1576 (m), 1514 (s), 1491 (m), 1449 (m), 1400 (w), 1369 (m), 1331 (s), 1281 (m), 1250 (m), 1196 (w), 1169 (m), 1121 (w), 1096 (w), 1069 (w), 1026 (w), 908 (m), 893 (m), 839 (w), 787 (m), 725 (m), 696 (s), 658 (s), 592 (w), 567 (m) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.30, 1.32, 1.38, 1.40 [s, 18 H, $C(CH_3)_3$], 2.10, 2.13, 2.17, 2.20 (s, 6 H, CH_3), 6.69–6.82 (m, 2 H, CH_{arom}), 6.98–7.04 (m, 14 H, CH_{arom}), 7.17–7.61 (m, 11 H, CH_{arom}), 7.56–7.61 (m, 14 H, CH_{arom}), 8.62, 8.66, 9.60, 9.64 (s, 2 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.6, 17.7 (CH_3), 27.7, 28.3 [$C(CH_3)_3$], 39.8 (C_q), 118.3, 122.9, 123.2, 123.4, 123.6, 127.2, 127.5, 127.8, 128.0, 128.1, 128.6, 128.7 (CH_{arom}), 128.9, 129.0 (*i*-C_{arom}), 130.9, 131.0, 131.4, 131.5 (CH_{arom}), 133.8, 134.5, 135.6, 135.7, 135.8, 136.1, 136.2, 137.7, 138.0, 146.4, 147.0 (*i*-C_{arom}), 160.2, 163.2, 165.4 (C=N), 173.3, 173.3 (C=O) ppm. HRMS (ESI): calcd. for $C_{38}H_{42}N_4O_2$ + Na 609.3200; found 609.3210. $C_{38}H_{42}N_4O_2$ (586.8): calcd. C 77.78, H 7.21, N 9.55; found C 77.70, H 7.12, N 9.43.

***N*-{1-[5-(1-Benzoylimino-2-methylpropylamino)-1-naphthylamino]-2-methylpropylidene}benzamide (7n):** From ethyl *N*-benzoylisobutyrimidate (0.82 g, 3.71 mmol)[27] and 1,5-diaminonaphthalene (0.29 g, 1.81 mmol). The solid was filtered off and washed with dioxane to give 0.57 g (0.88 mmol, 47%) of a colourless solid; m.p. 230 °C. IR (KBr): $\tilde{\nu}$ = 3375 (m, NH), 3087 (w), 3064 (w), 3051 (vw), 3030 (w), 2974 (m, CH_{aliph}), 2935 (w), 2869 (w), 1689 (s, C=N/C=O), 1644 (vs, C=N/C=O), 1602 (m), 1585 (w), 1488 (s, C=C), 1467 (m), 1419 (m), 1397 (m), 1368 (w), 1340 (m), 1324 (m), 1301 (m), 1282 (s), 1249 (s), 1224 (w), 1205 (m), 1185 (s), 1143 (m), 1075 (w), 1064 (w), 1029 (w), 981 (m), 929 (w), 890 (vw), 850 (vw), 807 (vw), 774 (m), 757 (w), 740 (m), 718 (w), 699 (m), 676 (w), 641 (m), 618 (w), 610 (w), 510 (w), 500 (w), 471 (w) cm^{-1}. ^{1}H NMR (300 MHz, TFA, $CDCl_3$): δ = 1.46 [d, ^3J = 6.8 Hz, 12 H, $CH(CH_3)_2$], 3.13 [m, 2 H, $CH(CH_3)_2$], 7.61–7.68 (m, 4 H, CH_{arom}), 7.80–8.03 (m, 10 H, CH_{arom}), 8.15–8.24 (m, 2 H, CH_{arom}), 10.24, 13.92 (s, NH) ppm. ^{13}C NMR (300 MHz, TFA, $CDCl_3$): δ = 18.2 [$CH(CH_3)_2$], 31.7 [$CH(CH_3)_2$], 124.7, 126.8, 128.8, 129.0 (CH_{arom}), 129.1, 129.7 (*i*-C_{arom}), 129.8, 136.8 (CH_{arom}), 171.9 (C=O), 178.4 (C=N) ppm. HRMS (ESI): calcd. for $C_{32}H_{32}N_4O_2$ + Na 527.2417; found 527.2421. $C_{32}H_{32}N_4O_2$ (504.60): calcd. C 76.16, H 6.39, N 11.10; found C 75.76, H 6.38, N 10.99.

***N*-(1-{5-[1–(2,2-Dimethylpropionylimino)-2-phenylethylamino]-1-naphthylamino}-2-phenylethylidene)-2,2-dimethylpropionamide (7o):** From ethyl *N*-(2,2-dimethylpropionyl)benzylacetimidate (**3g**; 1.11 g, 4.5 mmol) and 1,5-diaminonaphthalene (0.35 g, 2.2 mmol). After column chromatography using *tert*-butyl methyl ether/*n*-pentane (1:8) + 5% of triethylamine as eluent, 0.65 g (1.2 mmol, 86%, R_f = 0.93) of a light-yellow solid was obtained. The compound consists of different tautomers and conformers; m.p. 143 °C. IR (KBr): $\tilde{\nu}$ = 3375 (m, NH), 3088 (w, CH_{ar}), 3063 (w, CH_{ar}), 3051 (vw, CH_{ar}), 3028 (w, CH_{ar}), 2972 (m, CH_{aliph}), 2934 (w, CH_{aliph}), 2870 (w, CH_{aliph}), 1690 (s, C=O/C=N), 1645 (vs, C=O/C=N), 1603 (m), 1585 (w), 1487 (s, C=C), 1466 (m), 1418 (m), 1396 (m), 1367 (w), 1339 (m), 1325 (m), 1300 (m), 1281 (s), 1250 (s), 1223 (w), 1205 (m), 1184 (s), 1144 (m), 1074 (w), 1063 (w), 1030 (w), 980 (m), 928 (w), 889 (vw), 785 (w), 775 (m), 758 (w), 739 (m), 717 (w), 698 (m), 675 (w), 640 (m), 617 (w), 611 (w), 509 (w), 501 (w), 473 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.72, 0.76, 1.20 [s, 18 H, $C(CH_3)_3$], 4.05 (br. s, NH), 4.17, 4.48 (s, 2 H, CH_2Ph), 6.90–7.20 (m, 8 H, *m*/*p*-CH_{spacer}, *m*/*p*-CH_{arom}), 7.20–7.70 (m, *o*-CH_{spacer}, *o*-CH_{arom}), 8.14 (br. s, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.6, 26.7, 26.9, 27.1 [$C(CH_3)_3$], 39.9, 40.0 [$C(CH_3)_3$], 41.4, 41.4 (CH_2Ph), 116.0, 116.2 (*o*-CH_{arom}), 126.1 (*p*-CH_{arom}), 126.5 (*i*-C_{arom}), 126.6, 126.6, 126.7, 126.8 (*m*-C_{arom}), 128.2, 128.3, 128.3, 128.4 (*m*-C_{arom}), 129.4 (*o*-C_{arom}), 136.5, 136.6 (*i*-C_{arom}), 143.6 (*i*-C_{arom}), 154.5, 154.5 (C=N), 175.4, 175.4 (C=O) ppm. HRMS (ESI): calcd. for $C_{36}H_{40}N_4O_2$ + H 561.3224; found 561.3213. $C_{36}H_{40}N_4O_2$ (560.73): calcd. C 77.11, H 7.19, N 9.99; found C 76.81, H 7.34, N 10.00.

General Procedure for the Synthesis of Tris(*N*-acylamidines) 8a–c: *N*-Acylimidate (15.0 mmol) was dissolved in dioxane (10.0 mL).

Tris(2-aminoethyl)amine (5.0 mmol) was added dropwise at 70–90 °C. The reaction mixture was stirred overnight at 70–90 °C and the solvent was evaporated. The crude products were purified as stated below.

***N*-(1-{2-[Bis(2-{[(2,2-dimethylpropionylimino)phenylmethyl]amino}-ethyl)amino]ethylamino}-2,2-dimethylpropylidene)benzamide (8a):** From tris(2-aminoethyl)amine (0.73 g, 5.0 mmol) and ethyl *N*-pivaloylbenzimidate (3.50 g, 15.0 mmol).[27] After column chromatography using acetone/*n*-pentane (1:3) + 10% of triethylamine as eluent, 0.30 g (0.4 mmol, 8%) of a colourless solid were obtained. The compound consists of different tautomers and conformers; m.p. 127 °C. IR (KBr): $\tilde{\nu}$ = 3424 (m, NH), 3262 (m, NH), 3107 (w), 3063 (w, ν-CH_{arom}), 2955 (s), 2928 (m), 2903 (w), 2866 (w), 2801 (w, ν-$CH_{aliph.}$), 1589 (vs, C=O/C=N), 1560 (vs, C=O/C=N), 1493 (s, C=C_{arom}), 1477 (s), 1456 (s), 1433 (s, δ-CH_2), 1396 (s, *t*Bu), 1362 (s, *t*Bu), 1308 (m), 1223 (m), 1171 (vw), 1119 (w), 1072 (w), 1026 (w), 920 (w), 772 (m), 735 (w), 689 (m, δ-CH_{arom}) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 0.91 [br. s, 6.9 H, $C(CH_3)_3$], 1.19 [br. s, 16.8 H, $C(CH_3)_3$], 1.28 [br. s, 3.3 H, $C(CH_3)_3$], 2.58 [br., 2 H, $N(CH_2CH_2)_3$], 2.83 [br., 4 H, $N(CH_2CH_2)_3$], 3.46 [br., 6 H, $N(CH_2CH_2)_3$], 6.84–7.60 (m, 15 H, CH_{arom}), 8.62 (br., NH), 11.62 (br., NH) ppm. ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 27.8, 28.0, 28.4 [$C(CH_3)_3$], 39.6, 40.7 [$N(CH_2CH_2)_3$], 41.1, 41.6 [$C(CH_3)_3$], 43.3 [$N(CH_2CH_2)_3$], 50.6, 52.7, 54.3 [$N(CH_2CH_2)_3$], 127.0, 128.1, 128.3, 128.7 (*o*,*m*-CH_{arom}), 130.2, 130.9 (*p*-$CH_{arom}R^2$), 134.7 (*i*-$C_{arom}R^2$), 160.6, 164.1, 168.7 (C=N), 190.6, 193.7, 195.3 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 650 (8) [M – C_4H_9]$^+$, 547 (2) [M – 2*t*Bu – Ph]$^+$, 503 (5) [M – OC(*t*Bu)NC(Ph)NH_2]$^+$, 490 (8) [M – 2*t*Bu – PhCN]$^+$, 387 (5) [M – 2*t*Bu – 2PhCN]$^+$, 362 (2), 299 (9), 231 (5), 205 (10), 147 (14), 104 (16), 95 (23), 57 (100) [C_4H_9]$^+$, 56 (7). $C_{42}H_{57}N_7O_3$ (707.95): calcd. C 71.26, H 8.12, N 13.85; found C 71.02, H 7.95, N 13.76.

***N*-(1-{2-[Bis(2-{[(benzoylimino)phenylmethyl]amino}ethyl)amino]-ethylamino}phenylidene)benzamide (8b):** From tris(2-aminoethyl)-amine (0.73 g, 5.0 mmol) and ethyl *N*-benzoylbenzimidate (3.80 g, 15.0 mmol).[27] Addition of ethanol led to an ethanol complex of the product which was filtered off to give 1.22 g (1.5 mmol, 30%) of a colourless solid. The compound consists of different tautomers and conformers; m.p. 127 °C. IR (KBr): $\tilde{\nu}$ = 3431 (s, NH), 3061 (w), 3030 (vw, ν-CH_{arom}), 2953 (vw), 2841 (vw, ν-$CH_{aliph.}$), 1593 (vs, C=O/C=N), 1558 (vs, C=O/C=N), 1489 (m, C=C_{arom}), 1445 (s, δ-CH_2), 1367 (s), 1323 (s), 1296 (s), 1161 (w), 1065 (w), 1051 (w), 1024 (w), 930 (vw), 876 (vw), 849 (vw), 785 (w), 716 (m), 694 (m, δ-CH_{arom}) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.72 [br., 2.5 H, $N(CH_2CH_2)_3$], 2.87 [br., 0.9 H, $N(CH_2CH_2)_3$], 2.99 [br., 2.6 H, $N(CH_2CH_2)_3$], 3.57 [br., 2.0 H, $N(CH_2CH_2)_3$], 3.66 [br., 1.2 H, $N(CH_2CH_2)_3$], 3.73 [br., 2.8 H, $N(CH_2CH_2)_3$], 6.84–7.51 (m, 22 H, CH_{arom}), 7.60–7.65 (m, 4 H, *o*-$CH_{arom}R^2$, *o*-$CH_{arom}R^3$), 8.10–8.22 (m, 4 H, *o*-$CH_{arom}R^3$), 8.42 (br., 0.5 H, NH), 9.26 (br., 0.5 H, NH), 11.95 (br., NH), 12.21 (br., NH) ppm; ethanol: δ = 1.14–1.19 (m, 2.3 H, CH_3CH_2OH), 3.60–3.65 (m, 1.5 H, CH_3CH_2OH) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 39.7, 41.0, 43.1 [$N(CH_2CH_2)_3$], 50.7, 53.0, 53.9 [$N(CH_2CH_2)_3$], 127.2, 127.6, 128.0, 128.4, 128.5, 128.7, 129.4 (*o*,*m*-CH_{arom}), 130.4, 131.1, 131.6 (*p*-CH_{arom}), 134.0, 134.1 (*i*-$C_{arom}R^2$), 136.8, 137.2 (*i*-$C_{arom}R^3$), 163.3, 165.7, 169.5 (C=N), 174.2, 176.9, 179.8 (C=O) ppm; ethanol: δ = 18.3 (CH_3CH_2OH), 58.2 (CH_3CH_2OH) ppm. HRMS (ESI): calcd for $C_{48}H_{45}N_7O_3$ + Na 790.3482; found 790.3463. $C_{48}H_{45}N_7O_3 \cdot 0.75C_2H_5OH$ (802.48): calcd. C 74.09, H 6.22, N 12.22; found C 73.86, H 5.93, N 12.42.

***N*-(1-{2-[Bis(2-{[(4-trifluoromethylbenzoylimino)phenylmethyl]-amino}ethyl)amino]ethylamino}phenylidene)-4-trifluoromethylbenz-amide (8c):** From tris(2-aminoethyl)amine (0.58 g, 4.0 mmol) and ethyl *N*-(4-trifluormethylphenyl)benzimidate (3.86 g, 12.0 mmol).[27] After column chromatography using acetone/*n*-pentane (1:3) + 10% of triethylamine as eluent, 0.71 g (0.7 mmol, 18%) of a colourless solid was obtained. The compound consists of different tautomers and conformers; m.p. 172–173 °C. IR (KBr): $\tilde{\nu}$ = 3429 (m, NH), 3254 (m, NH), 3071 (w, ν-CH_{arom}), 2964 (w), 2930 (vw), 2851 (vw, ν-$CH_{aliph.}$), 1595 (vs, C=O/C=N), 1560 (vs, C=O/C=N), 1510 (s, C=$C_{arom.}$), 1445 (m), 1437 (m, δ-CH_2), 1410 (s), 1385 (s), 1323 (vs), 1163 (vs), 1126 (vs, CF_3), 1101 (s), 1065 (vs), 1016 (s), 862 (m), 802 (w), 775 (m), 746 (w), 706 (m), 694 (m, δ-CH_{arom}) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.75 [br., 2.2 H, $N(CH_2CH_2)_3$], 2.87 [br., 1.0 H, $N(CH_2CH_2)_3$], 2.96 [br., 0.7 H, $N(CH_2CH_2)_3$], 3.02 [br., 2.1 H, $N(CH_2CH_2)_3$], 3.66 [br., 3.3 H, $N(CH_2CH_2)_3$], 3.77 [br., 2.7 H, $N(CH_2CH_2)_3$], 6.87 (t, ^3J = 7.9 Hz, 1 H, CH_{arom}), 7.11 (t, ^3J = 7.2 Hz, 2 H, CH_{arom}), 7.21 (t, ^3J = 6.8 Hz, 1 H, CH_{arom}), 7.32 (d, ^3J = 7.3 Hz, 2 H, CH_{arom}), 7.40–7.78 (m, 16 H, CH_{arom}), 8.11 (d, ^3J = 7.8 Hz, 1 H, *o*-$CH_{arom}R^3$), 8.22 (d, ^3J = 8.0 Hz, 2 H, *o*-$CH_{arom}R^3$), 8.32 (d, ^3J = 8.0 Hz, 2 H, *o*-$CH_{arom}R^3$), 8.74 (br., 0.4 H, NH), 9.52 (t, ^3J = 4.8 Hz, 0.6 H, NH), 12.01 (br., NH), 12.27 (br., NH) ppm. ^{13}C NMR (100.13 MHz, $CDCl_3$): δ = 39.8, 41.2, 43.2, 43.9 [$N(CH_2CH_2)_3$], 50.6, 53.1, 53.7, 54.7 [$N(CH_2CH_2)_3$], 123.9 (q, ^3J = 271.9 Hz, CF_3), 124.6, 125.1 (br. m, *m*-$CH_{arom}R^3$), 127.2, 127.6, 128.5, 128.6, 128.7, 129.0, 129.7, 129.8 (*o*,*m*-CH_{arom}), 130.8, 131.5, 131.6 (*p*-$CH_{arom}R^2$), 132.2–133.8 (*m*, *p*-$C_{arom}R^3$), 134.3 (*i*-$C_{arom}R^2$), 140.0, 140.2, 140.6 (*i*-$C_{arom}R^3$), 164.8, 167.3, 170.0, 170.3 (C=N), 172.1, 175.1, 177.9, 178.3 (C=O) ppm. MS (ESI): *m*/*z* (%) = 997–995 (43) [M + Na]$^+$, 973 (22) [M + H]$^+$, 381 (13), 102 (66), 58 (100); daughters of 973: 972 (27) [M]$^+$, 680 (21), 465 (49), 388 (5), 362 (46), 319 (100), 242 (5), 216 (15), 173 (45), 147 (18), 70 (14). $C_{51}H_{42}F_9N_7O_3$ (971.92): calcd. C 63.03, H 4.36, N 10.09; found C 63.27, H 4.42, N 10.11.

General Procedure for the Synthesis of Bis(*N*-Acylamidines) 9a,b Linked Through the Carbonyl Moiety: A dry Schlenk flask was equipped with amidine (20.0 mmol) and potassium *tert*-butoxide (20.0 mmol) under an inert atmosphere. The mixture was cooled with an ice bath. Dry tetrahydrofuran (70.0 mL) was added and stirred for 10 min at 10 °C. A solution of dicarboxylic acid (9.8 mmol) dissolved in dry tetrahydrofuran (40.0 mL) was added dropwise to the mixture. The reaction mixture was warmed to room temperature and stirred for 24 h. The organic layer was washed three times with water (30.0 mL). The aqueous layer was extracted dichloromethane (3 × 20.0 mL). All organic layers were dried with magnesium sulfate and the solvents evaporated. The crude products were purified as stated below.

Hexanedioic Acid Bis[phenyl(phenylamino)methylideneamide] (9a): From *N*-phenylbenzamidine[26] (3.93 g, 20.0 mmol) and adipoyl chloride (1.79 g, 9.8 mmol). After column chromatography using ethanol/*n*-pentane (1:7) + 5% of triethylamine as eluent, 0.095 g (0.2 mmol, 2%) of colourless crystals of an ethanol complex were obtained. The compound consists of different conformers and tautomers; m.p. 144–153 °C. IR (KBr): $\tilde{\nu}$ = 3387 (m, NH), 3236 (s, NH), 3059 (m), 3030 (m, ν-CH_{arom}), 2951 (m), 2868 (m, ν-$CH_{aliph.}$), 1661 (s, C=O/C=N), 1628 (vs, C=O/C=N), 1591 (vs), 1491 (vs, C=C_{arom}), 1447 (s, δ-CH_2), 1292 (s), 1213 (s), 1173 (m), 1144 (m), 1072 (m), 1026 (m), 912 (vw), 754 (s), 694 (vs, δ-CH_{arom}) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.44–1.77 (m, 4 H, $COCH_2CH_2$), 2.07–2.18 (m, 1.7 H, $COCH_2CH_2$), 2.54–2.62 (m, 2.3 H, $COCH_2CH_2$), 6.84–7.46 (m, 18 H, CH_{arom}), 7.71–7.75 (m, 2 H, CH_{arom}), 11.89 (br., NH) ppm; ethanol: δ = 1.21 (t, ^3J = 7.0 Hz, 0.75 H, CH_3CH_2OH), 3.67 (q, ^3J = 7.0 Hz, 0.5 H, CH_3CH_2OH) ppm. ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 23.9, 24.3, 24.5, 24.8 ($COCH_2CH_2$), 35.8, 36.3, 39.9 (br., $COCH_2CH_2$), 120.3

(o-$CH_{arom}R^1$), 122.8 (p-$CH_{arom}R^1$), 124.4, 128.2, 128.3, 128.3, 129.5 (CH_{arom}), 130.8 (p-$CH_{arom}R^2$), 135.3 (i-$C_{arom}R^2$), 148.0 (i-$C_{arom}R^1$), 151.5 (C=N), 166.0 (br., C=N), 171.2 (C=O), 187.8 (br., C=O) ppm; ethanol: δ = 16.0 (CH_3CH_2OH), 50.2 (CH_3CH_2OH) ppm. MS (70 eV): m/z (%) = 502 (8) $[C_{32}H_{30}N_4O_2$ (M)]$^+$, 399 (8), 341 (3), 306 (17) [M – PhNC(Ph)NH]$^+$, 265 (6) [PhNHC(Ph)NCO$(CH_2)_3$]$^+$, 251 (14) [PhNHC(Ph)NCO$(CH_2)_2$]$^+$, 237 (8) [PhNHC(Ph)NCOCH_2]$^+$, 223 (17) [PhNHC(Ph)NCO]$^+$, 196 (85) [PhNHC(Ph)NH]$^+$, 180 (90) [PhNCPh]$^+$, 103 (100) [PhCN]$^+$, 93 (77) [$PhNH_2$]$^+$, 77 (90) [Ph]$^+$. $C_{32}H_{30}N_4O_2$·$0.25C_2H_5OH$ (514.13): calcd. C 75.93, H 6.18, N 10.90; found C 75.67, H 5.87, N 11.11.

Octanedioic Acid Bis[phenyl(phenylamino)methylideneamide] (9b): From *N*-phenylbenzamidine[26] (3.93 g, 20.0 mmol) and sebacoyl chloride (2.34 g, 9.8 mmol). Addition of ethanol led to an ethanol complex of the product which was filtered off and recrystallized from ethanol to give 1.03 g (1.8 mmol, 18%) of a colourless solid. The compound consists of different conformers and tautomers; m.p. 127 and 145 °C. IR (KBr): $\tilde{\nu}$ = 3443 (vs, NH), 3267 (s, NH), 3082 (w), 3059 (w), 3030 (vw, ν-CH_{arom}), 2928 (m), 2855 (m, ν-$CH_{aliph.}$), 1665 (vs, C=O/C=N), 1628 (vs, C=O/C=N), 1593 (s), 1491 (vs, C=C_{arom}), 1447 (m, δ-CH_2), 1313 (m), 1277 (m), 1250 (m), 1217 (m), 1175 (m), 1072 (w), 1026 (w), 908 (vw), 779 (m), 758 (m, δ-CH_{arom}) cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.17 (br., 2 H, CH_2), 1.23 (br., 2 H, CH_2), 1.33 (br., 4 H, CH_2), 1.48 (br., 2 H, CH_2), 1.67 (br., 2 H, CH_2), 2.11 (t, ^3J = 7.3 Hz, 2 H, $COCH_2$), 2.55 (t, ^3J = 7.4 Hz, 2 H, $COCH_2$), 6.82–7.48 (m, 18 H, CH_{arom}), 7.72–7.75 (m, 2 H, CH_{arom}) ppm; ethanol: δ = 1.21 (t, ^3J = 7.0 Hz, 0.75 H, CH_3CH_2OH), 3.67 (q, ^3J = 7.0 Hz, 0.5 H, CH_3CH_2OH) ppm. ^{13}C NMR (100.13 MHz, $CDCl_3$): δ = 24.9, 25.1, 28.9, 29.0, 29.1, 29.2, 36.6, 39.5 (CH_2), 120.3 (o-$CH_{arom}R^1$), 122.7 (p-$CH_{arom}R^1$), 124.4, 128.2, 128.8, 129.5 (CH_{arom}), 130.8 (p-$CH_{arom}R^2$), 133.5, 135.3 (i-$C_{arom}R^2$), 148.0 (i-$C_{arom}R^1$), 151.5 (C=N), 166.9 (br., C=N), 171.5 (C=O), 188.3 (br., C=O) ppm; ethanol: δ = 17.1 (CH_3CH_2OH), 51.2 (CH_3CH_2OH) ppm. MS (70 eV): m/z (%) = 558 (1) $[C_{36}H_{38}N_4O_2$ (M)]$^+$, 455 (4), 352 (4), 321 (5), 251 (9) [PhNHC(Ph)NCO$(CH_2)_2$]$^+$, 237 (6) [PhNHC(Ph)NCO(CH_2)]$^+$, 223 (8) [PhNHC(Ph)NCO]$^+$, 196 (35) [PhNHC(Ph)NH]$^+$, 180 (26) [PhNCPh]$^+$, 103 (100) [PhCN]$^+$, 93 (58) [$PhNH_2$]$^+$, 77 (55) [Ph]$^+$, 41 (16) [CH_2=$CHCH_2$]$^+$. $C_{36}H_{38}N_4O_2$·$0.25C_2H_5OH$ (570.24): calcd. C 76.88, H 6.98, N 9.83; found C 76.97, H 6.89, N 9.81.

General Procedure for the Synthesis of Bis(*N*-Acylamidines) 9c,d Linked Through the Carbonyl Moiety: Prepared partially in analogy to a literature procedure.[30] A primary amidine (2 equiv.) was dissolved in anhydrous chloroform or dichloromethane and stirred at room temperature in a dry round-bottomed flask. Triethylamine (4 equiv.) was added slowly to the solution; which was stirred for 30 min and cooled to –10 °C. An aromatic diacid dichloride (1 equiv.) dissolved in anhydrous dichloromethane or chloroform was added dropwise to the solution to precipitate the product. The reaction mixture was warmed to room temperature and stirred overnight. The solid was filtered off, washed with dichloromethane and purified as stated below.

Biphenyl-4,4′-Dicarboxylic Acid Bis[amino(phenyl)methylideneamide] (9c): From biphenyl-4,4′-dicarbonyl dichloride (1.67 g, 6.0 mmol),[31] triethylamine (3.3 mL, 2.43 g, 24.0 mmol) and benzamidine (1.40 g, 12.0 mmol). The crude product was recrystallized from chloroform/diethyl ether (3:1) to give 1.80 g, (4.0 mmol, 75%) of a colourless solid; m.p. 225–229 °C. IR (ATR): $\tilde{\nu}$ = 3389 (m), 3300 (m), 3271 (m), 3179 (m), 3067 (m), 1597 (s), 1574 (s), 1557 (s), 1547 (s), 1462 (s), 1439 (s), 1312 (s), 1292 (s), 1190 (m), 1177 (s), 1159 (m), 1123 (s), 1034 (m), 1001 (m), 930 (m), 893 (m), 854 (m), 808 (m), 766 (s), 691 (s), 646 (s), 619 (s), 613 (s), 598 (s), 579 (s), 571 (s), 546 (s), 536 (s), 528 (s), 523 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 7.53–7.68 (m, 6 H, m/p-CH_{arom}), 7.85–7.89 (m, 4 H, CH_{spacer}), 8.21–8.25 (m, 4 H, CH_{spacer}), 8.37–8.40 (m, 4 H, o-CH_{arom}), 9.43 (s, 2 H, NH_2), 10.51 (s, 2 H, NH_2) ppm. ^{13}C NMR (300 MHz, [D_6]DMSO): δ = 126.7 (CH_{spacer}), 130.0 (CH_{arom}), 128.5 (CH_{arom}), 129.8 (CH_{spacer}), 132.2 (CH_{arom}), 134.5 (i-C_{arom}), 137.3 (i-C_{spacer}), 142.5 (i-C_{spacer}), 166.1 (C=N), 177.9 (C=O) ppm. HRMS (ESI): calcd. for $C_{28}H_{22}N_4O_2$ + H 447.1812; found 447.1816. $C_{28}H_{22}N_4O_2$ (446.5): calcd. C 75.32, H 4.97, N 12.55; found C 74.96, H 4.74, N 12.39.

X-ray Crystal Structure Analysis for 9c:[29] Formula $C_{28}H_{22}N_4O_2$, M = 446.50, colourless crystal, 0.50 × 0.10 × 0.10 mm, a = 14.2876(6), b = 29.4336(11), c = 8.2604(3) Å, β = 105.564(2)°, V = 3346.4(2) Å^3, $\rho_{calcd.}$ = 1.329 g cm^{-3}, μ = 0.687 cm^{-1}, empirical absorption correction (0.725 ≤ T ≤ 0.935), Z = 6, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 24644 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 5833 independent (R_{int} = 0.051) and 4454 observed reflections [$I \geq 2\sigma(I)$], 478 refined parameters, R = 0.057, wR^2 = 0.150, max. (min.) residual electron density 0.21 (–0.20) e Å^{-3}, asymmetric unit contains 1.5 molecules, hydrogen atoms at N from difference fourier calculations, others calculated and refined as riding atoms.

Naphthalene-2,6-Dicarboxylic Acid Bis[amino(phenyl)methylideneamide] (9d): From naphthalene-2,6-dicarbonyl dichloride (0.76 g, 3.0 mmol),[31] triethylamine (1.7 mL, 1.21 g, 12.0 mmol) and benzamidine (0.70 g, 6.0 mmol). The crude product was recrystallized from ethanol/chloroform (1:1) to give 0.96 g, (2.3 mmol, 76%) of a colourless solid; m.p. 229.3 °C. IR (ATR): $\tilde{\nu}$ = 3358 (m), 3208 (m), 3073 (m), 3053 (m), 1599 (m), 1555 (s), 1501 (m), 1466 (s), 1439 (s), 1385 (m), 1331 (m), 1314 (s), 1290 (s), 1198 (m), 1190 (m), 1148 (m), 1126 (s), 1101 (m), 1030 (m), 999 (m), 908 (m), 847 (m), 802 (m), 779 (s), 748 (s), 692 (s), 681 (s), 654 (m), 621 (s), 613 (s), 583 (s), 548 (s), 525 (m), 511 (m) cm^{-1}. ^{1}H NMR (300 MHz, [D_6]-DMSO): δ = 7.56–7.89 (m, 6 H, o/m-CH_{arom}), 8.21–8.32 (m, 6 H, CH_{spacer}), 8.38–8.41 (m, 2 H, p-CH_{arom}), 8.96 (s, 2 H, CH_{spacer}), 9.49 (s, 2 H, NH_2), 10.57 (s, 2 H, NH_2) ppm. ^{13}C NMR (300 MHz, [D_6]DMSO): δ = 126.0 (CH_{spacer}), 128.1, 128.5 (o/m-CH_{arom}), 129.2, 129.4 (CH_{spacer}), 132.2 (p-CH_{arom}), 134.0 (i-C_{spacer}), 134.5 (i-C_{arom}), 136.8 (i-C_{spacer}), 166.3 (C=N), 178.1 (C=O) ppm. HRMS (ESI): calcd. for $C_{26}H_{20}N_4O_2$ + H 421.1652; found 421.1659. $C_{26}H_{20}N_4O_2$ (420.5): calcd. C 74.27, H 4.79, N 13.33; found C 74.04, H 4.60, N 13.14.

X-ray Crystal Structure Analysis for 9d:[29] Formula $C_{26}H_{20}N_4O_2$·$2CHCl_3$, M = 659.20, colourless crystal, 0.25 × 0.25 × 0.20 mm, a = 7.7156(4), b = 20.5542(10), c = 9.8880(5) Å, β = 107.627(3)°, V = 1494.49(13) Å^3, $\rho_{calcd.}$ = 1.465 g cm^{-3}, μ = 5.523 cm^{-1}, empirical absorption correction (0.339 ≤ T ≤ 0.405), Z = 2, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 15208 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 2663 independent (R_{int} = 0.049) and 2429 observed reflections [$I \geq 2\sigma(I)$], 189 refined parameters, R = 0.055, wR^2 = 0.152, max. (min.) residual electron density 0.68 (–0.54) e Å^{-3}, hydrogen atoms at N from difference fourier calculations, others calculated and refined as riding atoms.

Synthesis of the Bis(triazapentadiene) Precursors

***N*^{1},*N*^{3}-Di-*p*-tolylisophthalodiimidoyl Dichloride (16):** *N*,*N*′-Di-*p*-tolylisophthalamide (**15**; 7.69 g, 22.3 mmol)[32] was dissolved in thionyl chloride (14.5 mL, 23.80 g, 200 mmol) and heated at 85 °C for 3 h. All volatile compounds were removed under reduced pressure. The crude product was recrystallized from dry diethyl ether/dichloromethane (1:1) to give 7.00 g (18.5 mmol, 82%) of yellow needles;

m.p. 113.3–116.5 °C. IR (ATR): $\tilde{\nu}$ = 3277 (w), 3084 (w), 3032 (w), 2918 (w), 2858 (w), 1647 (s), 1609 (m), 1578 (m), 1503 (s), 1423 (m), 1134 (s), 1107 (m), 1020 (m), 1007 (m), 934 (m), 922 (m), 887 (m), 839 (m), 802 (s), 762 (m), 710 (m), 648 (vs), 598 (vs), 503 (vs) cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.30 (s, 6 H, CH_3), 6.90 (d, ^3J = 8.3 Hz, 4 H, CH_{arom}), 7.14 (d, ^3J = 7.7 Hz, 4 H, CH_{arom}), 7.48 (t, ^3J = 7.9 Hz, 1 H, CH_{arom}), 8.23 (dd, ^4J = 1.9, ^3J = 7.9 Hz, 1 H, CH_{arom}), 8.84 (t, ^4J = 1.7 Hz, 1 H, CH_{arom}) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.0 (CH_3), 120.6, 128.6, 129.5, 130.3, 132.5, 135.1 (CH_{arom}), 136.2 (*i*-C_{arom}), 141.6 (*i*-C_{arom}-N), 144.6 (C=N) ppm. $C_{22}H_{18}Cl_2N_2$ (381.3): calcd. C 69.30, H 4.76, N 7.35; found C 69.00, H 4.53, N 7.25.

Ethyl *N*-[{3-[{[Phenyl(ethoxy)methylidene]amino}(*p*-tolylimino)-methyl]phenyl}(*p*-tolylimino)methyl]benzimidate (17): The synthesis was carried out following a protocol by Häger et al.[9] Ethyl benzimidate hydrochloride[27] (3.29 g, 17.8 mmol) was dissolved in anhydrous dichloromethane (100 mL) and stirred at room temperature. Triethylamine (3.59 g, 35.5 mmol) was added dropwise to the solution whereby triethylamine hydrochloride precipitated. The reaction mixture was stirred for 1 h and cooled down to –15 °C. Imidoyl chloride **16** (2.72 g, 7.1 mmol) dissolved in anhydrous dichloromethane was added dropwise and the reaction mixture was warmed to room temperature and stirred for 20 h. The solvent was removed under reduced pressure and the residue was washed several times with warm pentane. The filtrate was evaporated and the crude product obtained was purified by column chromatography [pentane/ethyl acetate (20:1) + 5% triethylamine] to give 1.28 g (2.1 mmol, 30%) of a yellow solid. R_f = 0.23 (pentane/ethyl acetate, 15:1 + 5% triethylamine); m.p. 129.2 °C. IR (ATR): $\tilde{\nu}$ = 3059 (vw), 3022 (vw), 2984 (vw), 2941 (vw), 2893 (vw), 1655 (m), 1639 (m), 1599 (m), 1580 (s), 1504 (m), 1477 (w), 1449 (w), 1368 (w), 1308 (w), 1298 (w), 1275 (s), 1250 (m), 1223 (w), 1179 (w), 1155 (m), 1126 (w), 1113 (w), 1084 (w), 1070 (w), 1055 (s), 1032 (m), 1016 (w), 1001 (vw), 897 (m), 826 (w), 816 (m), 779 (w), 766 (w), 748 (w), 731 (vw), 719 (m), 692 (vs), 681 (s), 642 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (t, ^3J = 7.1 Hz, 6 H, OCH_2CH_3), 2.18 (s, 6 H, CH_3), 4.23 (q, ^3J = 7.1 Hz, 4 H, OCH_2CH_3), 6.48 (d, ^3J = 8.2 Hz, 4 H, CH_{arom}), 6.84 (d, ^3J = 8.1 Hz, 4 H, CH_{arom}), 7.27–7.05 (m, 10 H, CH_{arom}), 7.41 (t, ^3J = 7.8 Hz, 1 H, CH_{arom}), 8.12 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 2 H, CH_{arom}), 8.45 (t, ^4J = 1.5 Hz, 1 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (OCH_2CH_3), 20.9 (CH_3), 63.2 (OCH_2CH_3), 121.5, 127.6, 127.8, 128.2, 128.5, 128.8, 130.0, 130.9 (CH_{arom}), 131.4, 131.9, 136.7, 146.9 (*i*-C_{arom}), 157.5, 157.6 (C=N) ppm. HRMS (ESI): calcd. for $C_{40}H_{38}N_4O_2$ + H 607.3068; found 607.3058. $C_{40}H_{38}N_4O_2$ (606.8): calcd. C 79.18, H 6.31, N 9.23; found C 78.90, H 6.05, N 9.22.

X-ray Crystal Structure Analysis for 17:[29] $C_{40}H_{38}N_4O_2$, M = 606.74, yellow crystal, 0.30 × 0.20 × 0.10 mm, a = 9.0854(2), b = 11.2202(3), c = 17.4172(5) Å, α = 107.755(1), β = 100.193(1), γ = 93.689(1)°, V = 1650.94(7) Å^3, $\rho_{calcd.}$ = 1.221 g cm^{-3}, μ = 0.596 cm^{-1}, empirical absorption correction (0.841 ≤ T ≤ 0.943), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 19024 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 5747 independent (R_{int} = 0.054) and 4775 observed reflections [$I \geq 2\sigma(I)$], 430 refined parameters, R = 0.047, wR^2 = 0.123, max. (min.) residual electron density 0.17 (–0.21) e Å^{-3}, group C8B–C11B refined with split positions, hydrogen atoms calculated and refined as riding atoms.

General Procedure for the Syntheses of Bis(triazapentadienes) 10a–c: The synthesis was carried out following the protocol of Häger et al.[9] A primary amine (5 equiv.) dissolved in dry tetrahydrofuran was deprotonated with an equimolar amount of *n*-butyllithium at –78 °C and the mixture was stirred for 10 min. Bis(*N*-imidoylimidate) **17** (5 equiv.) dissolved in dry tetrahydrofuran was added dropwise and the reaction mixture was slowly warmed to room temperature and stirred overnight. The organic layer was washed three times with water whereby precipitation of the product occurred. The product was filtered off, washed with tetrahydrofuran (5 mL) and purified as stated below.

***N*-Phenyl-*N*′-[(3-{[(*N*-phenylbenzimidoyl)amino](*p*-tolylimino)-methyl}phenyl)(*p*-tolylimino)methyl]benzamidine (10a):** From bis(*N*-imidoylimidate) **17** (0.43 g, 0.7 mmol), aniline (0.32 mL, 0.32 g, 3.5 mmol) and *n*-butyllithium (2.20 mL, 3.5 mmol, 1.6 m in hexane). Crystallization from chloroform/tetrahydrofuran (1:1) gave 0.29 g of a light-yellow solid (0.4 mmol, 59%); m.p. 210 °C. IR (ATR): $\tilde{\nu}$ = 3063 (w), 3024 (w), 1624 (m), 1591 (m), 1580 (m), 1535 (s), 1499 (s), 1489 (s), 1441 (s), 1362 (m), 1310 (m), 1261 (m), 1227 (s), 1179 (w), 1161 (m), 1126 (m), 1057 (m), 1028 (m), 955 (w), 916 (w), 901 (w), 829 (m), 770 (m), 754 (vs), 729 (m), 694 (vs), 679 (s), 665 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$ + TFA): δ = 2.58 (s, 6 H, CH_3), 7.28 (d, ^3J = 8.2 Hz, 4 H, CH_{arom}), 7.37 (d, ^3J = 8.1 Hz, 4 H, CH_{arom}), 7.44 (d, ^3J = 7.5 Hz, 4 H, CH_{arom}), 7.58–7.67 (m, 15 H, CH_{arom}), 7.80 (t, ^3J = 7.5 Hz, 2 H, CH_{arom}), 8.05 (d, ^3J = 7.6 Hz, 2 H, CH_{arom}), 8.2 (br. s, 1 H, CH_{arom}), 9.25 (br. s, 2 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ + TFA): δ = 20.2 (CH_3), 122.2, 122.9, 126.8, 127.0, 128.4, 129.7, 130.3, 130.8 (CH_{arom}), 131.0, 132.2 (*i*-C_{arom}), 132.4, 134.3 (CH_{arom}), 135.5, 139.6 (*i*-C_{arom}), 162.8, 164.1 (C=N) ppm. HRMS (ESI): calcd. for $C_{48}H_{40}N_6$ + H 701.3387; found 701.3377. $C_{48}H_{40}N_6$ (700.9): calcd. C 82.26, H 5.75, N 11.99; found C 81.84, H 5.85, N 12.25.

X-ray Crystal Structure Analysis for 10a:[29] $C_{52}H_{48}N_6O$ ($C_{48}H_{40}N_6 \cdot C_4H_8O$), M = 772.96, colourless crystal, 0.35 × 0.20 × 0.05 mm, a = 22.7484(9), b = 12.5454(4), c = 18.1993(5) Å, β = 109.251(2)°, V = 4903.4(3) Å^3, $\rho_{calcd.}$ = 1.047 g cm^{-3}, μ = 0.493 cm^{-1}, empirical absorption correction (0.846 ≤ T ≤ 0.976), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223 K, ω and ϕ scans, 41266 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 8223 independent (R_{int} = 0.078) and 5262 observed reflections [$I \geq 2\sigma(I)$], 540 refined parameters, R = 0.077, wR^2 = 0.247, max. (min.) residual electron density 0.33 (–0.3) e Å^{-3}, solvent molecules in the voids could not be described and therefore the SQUEEZE routine was used, hydrogen atoms at N from difference fourier calculations, others calculated and refined as riding atoms.

***N*-(*p*-Tolyl)-*N*′-[(3-{[(*N*-*p*-tolylbenzimidoyl)amino](*p*-tolylimino)-methyl}phenyl)(*p*-tolylimino)methyl]benzamidine (10b):** From bis(*N*-imidoylimidate) **17** (1.82 g, 3.0 mmol), 4-methylaniline (1.61 g, 15.0 mmol) and *n*-butyllithium (9.4 mL, 15.0 mmol, 1.6 м in hexane). Crystallization from tetrahydrofuran/ethyl ether (10:1) gave 1.65 g (2.3 mmol, 75%) of a light-yellow solid; m.p. 223 °C. IR (ATR): $\tilde{\nu}$ = 3279 (vw), 3208 (vw), 3115 (vw), 3063 (vw), 3021 (vw), 2918 (vw), 2864 (vw), 1624 (m), 1593 (s), 1580 (m), 1566 (m), 1531 (vs), 1512 (vs), 1447 (m), 1406 (m), 1360 (m), 1312 (m), 1290 (m), 1273 (m), 1260 (m), 1225 (s), 1159 (m), 1124 (m), 1057 (m), 1028 (m), 955 (w), 916 (w), 851 (m), 816 (s), 781 (m), 773 (m), 752 (m), 727 (m), 696 (s), 679 (s), 658 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$ + TFA): δ = 2.40 (s, 12 H, CH_3), 7.10 (d, ^3J = 8.1 Hz, 4 H, CH_{arom}), 7.20 (d, ^3J = 8.1 Hz, 4 H, CH_{arom}), 7.22–7.29 (m, 8 H, CH_{arom}), 7.38–7.43 (m, 8 H, CH_{arom}), 7.61 (br. t, ^3J = 7.5 Hz, 3 H, CH_{arom}), 7.87 (d, ^3J = 7.7 Hz, 2 H, CH_{arom}), 8.04 (s, 1 H, CH_{arom}), 8.57, 9.03 (br. s, 2 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ + TFA): δ = 20.2, 20.2 (CH_3), 122.0, 122.9, 126.8, 127.0, 129.7, 130.2, 130.3, 130.7, 130.8 (CH_{arom}), 132.3, 132.3, 133.0, 133.3 (*i*-C_{arom}), 134.2 (CH_{arom}), 139.3, 139.5 (*i*-C_{arom}), 162.6, 164.1 (C=N) ppm. HRMS

(ESI): calcd. for $C_{50}H_{44}N_6$ + H 729.3700; found 729.3698. $C_{50}H_{44}N_6$ (728.9): calcd. C 82.39, H 6.08, N 11.53; found C 82.05, H 6.08, N 11.57.

***N*-(4-Chlorophenyl)-*N*′-{[3-({[*N*-(4-chlorophenyl)benzimidoyl]-amino}(*p*-tolylimino)methyl)phenyl](*p*-tolylimino)methyl}benzamidine (10c):** From bis(*N*-imidoylimidate) **17** (1.82 g, 3.00 mmol), 4-chloraniline (1.91 g, 15.00 mmol) and *n*-butyllithium (9.4 mL, 15.00 mmol, 1.6 M in hexane). Crystallization from tetrahydrofuran/ethyl ether (10:1) gave 1.19 g (1.54 mmol, 52%) of a yellow solid; m.p. 136 °C. IR (ATR) $\tilde{\nu}$ = 3402 (vw), 3059 (vw), 3030 (vw), 2922 (vw), 1630 (m), 1591 (m), 1568 (m), 1512 (vs), 1491 (vs), 1481 (s), 1447 (m), 1400 (m), 1342 (m), 1312 (m), 1288 (m), 1248 (m), 1221 (m), 1173 (w), 1130 (w), 1090 (m), 1051 (m), 1026 (m), 1011 (m), 910 (m), 812 (s), 775 (m), 762 (m), 739 (m), 723 (m), 694 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$ + TFA): δ = 2.19 (s, 6 H, CH_3), 6.86 (d, ^3J = 8.2 Hz, 4 H, CH_{arom}), 6.99 (d, ^3J = 8.1 Hz, 8 H, CH_{arom}), 7.15–7.22 (m, 9 H, CH_{arom}), 7.24–7.34 (m, 5 H, CH_{arom}), 7.41 (t, ^3J = 7.7 Hz, 3 H, CH_{arom}), 7.72 (d, ^3J = 7.7 Hz, 2 H, CH_{arom}), 7.91 (s, 1 H, CH_{arom}), 8.94 (br. s, 2 H, NH) ppm. ^{13}C NMR (300 MHz, $CDCl_3$ + TFA): δ = 20.1 (CH_3), 122.9, 123.2, 126.7, 127.3, 129.7, 129.8, 130.4, 130.9 (CH_{arom}), 131.0, 132.1 (*i*-C_{arom}), 132.5 (CH_{arom}), 133.1, 134.2, 134.2 (*i*-C_{arom}), 134.3 (CH_{arom}), 139.9 (*i*-C_{arom}), 163.4, 164.0 (C=N) ppm. HRMS (ESI): calcd. for $C_{48}H_{38}Cl_2N_6$ + H 769.2593; found 769.2608. $C_{48}H_{38}Cl_2N_6$ (769.8): calcd. C 74.90, H 4.98, N 10.92; found C 74.47, H 5.12, N 10.90.

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