Synthesis of Bis(*N*-acylamidines) from Amidines and *N*-Acylbenzotriazoles

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Abstract: Bis(*N*-acylamidines) **7**, linked by a spacer connected to the carboxyl groups, were synthesized in moderate to good yields from bis(*N*-acylbenzotriazoles) **6** and amidines **2**. In contrast, the corresponding bis(carboxylic acid) chlorides were not well suited for the synthesis of the compounds **7**. 2-Aminothiazole gave the bis-amide **8**, where the amidine moieties are part of heterocyclic ring systems. Furthermore, the reaction of a bis-amidine **9** with two equivalents of *N*-benzoylbenzotriazole (**10**) gave the bifunctional *N*-acylamidine **11**, linked to the spacer at the amidine carbon atoms. All substances were thoroughly characterized including nine X-ray diffraction studies.

Key words: acylation, amidines, ligands, *N*-acylbenztriazoles, supramolecular chemistry

N-Acylamidines **1** are useful nitrogen and oxygen containing monodentate or bidentate ligands for metal complexation.[1,2] Their coordination sphere resembles that of the well-known β-iminoketones (β-ketoiminates).[3] However, the nitrogen atom in 3-position strongly alters the electronic structure and allows conjugation over all five atoms even in the neutral form of the ligand. Furthermore, these ligands have been shown to amplify the catalytic effects of transition metals in cross-coupling reactions.[1b,1c,4]

Primary (R^1 = H) and secondary *N*-acylamidines **1** are subject to tautomerism, where the proton can be located at one of the nitrogen atoms or – less favored – at the oxygen atom (Figure 1) offering possibilities for various conformers and inter- and intramolecular hydrogen bonding.

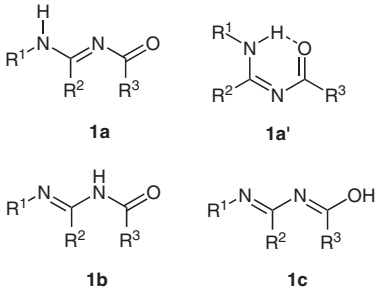
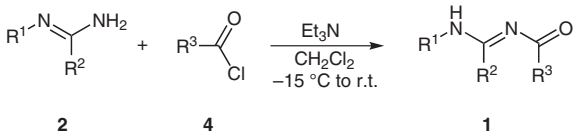


Figure 1 Tautomeric forms of *N*-acylamidines **1**

A look at the tautomers **1a** and **1b** reveals that *N*-acylamidines may be regarded as amide derivatives, which may be synthesized by acylation of amidines **2** using an appropriate acylating agent **3** (e.g., carboxylic acids, structure not shown). The preparation of some *N*-acylamidines has been described by Pinner already in 1889, for example, from benzamidine hydrochloride and benzoic acid anhydride.[5] In the past, several synthetic routes for the synthesis of primary, secondary, and tertiary *N*-acylamidines have been studied in our group.[1,6] One general pathway includes the reaction of carboxylic acid chlorides **4** with amidines[7] **2** according to Katritzky and co-workers[8] (Scheme 1), where R^1 is a proton in the case of the primary *N*-acylamidines.



Scheme 1 Synthesis of *N*-acylamidines according to Katritzky and co-workers[8]

In our work focusing on the synthesis of bi- and polydentate ligands for supramolecular architectures, we investigated the synthesis of bis(*N*-acylamidines) linked via the carboxyl moieties of sterically constrained spacers like adamantyl-, cyclohexyl- or biphenyl dicarboxylic acid derivatives. Unfortunately, experiments starting from bifunctional carboxylic acid chlorides and amidines only led to low yields of crude products difficult to purify.[9]

Due to the failure of the acid chloride experiments we envisaged to utilize other well-studied synthetic pathways for the preparation of our ligands starting from amidines **2** and other carboxylic acid derivatives. However, acylation experiments of amidines with carboxylic acids **3**, using carbodiimides as coupling reagents and hydroxybenzotriazoles as additives, as known from peptide coupling, did not lead to satisfactory results.[10]

Further studies using *N*-acylbenzotriazoles as active esters for our syntheses seemed to be more promising. *N*-Acylbenzotriazoles are useful neutral acylation agents for N-, C-, S-, and O-acylation in cases where the corresponding acid chlorides are unstable or difficult to prepare.[11] Since they are easily accessible in one step from the corresponding carboxylic acids, we decided to investigate these compounds as precursors for the desired ligands.

For the preparation of the new bis(*N*-acylbenzotriazole) derivatives **6** we used a procedure developed by Katritzky et al.,[12] according to which one equivalent of a dicarboxylic acid **5**, eight equivalents of 1*H*-1,2,3-benzotriazole,

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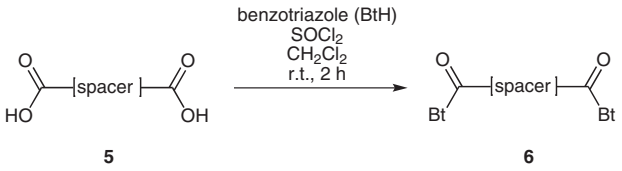
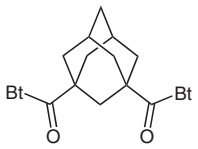
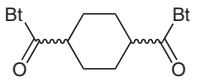
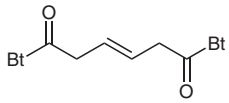
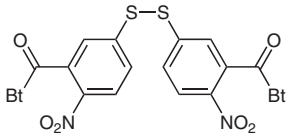
and two equivalents of thionyl chloride in dichloromethane at room temperature were reacted to give the hitherto unknown bis(*N*-acylbenzotriazoles) **6** with aliphatic, aromatic, and olefinic spacers in moderate to good yields (Scheme 2, Table 1).



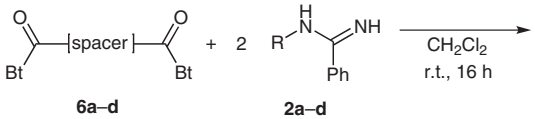
Scheme 2 Synthesis of bifunctional *N*-acylbenzotriazoles **6** in analogy to the work of Katritzky et al.[12]

Table 1 Bis(*N*-acylbenzotriazole) Derivatives Prepared

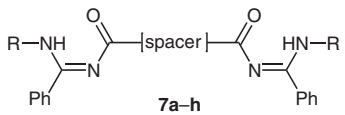
Product	Structure	Yield (%)
6a		70
6b		64 (*cis*/*trans* mixture)
6c		47
6d		74

All compounds **6** are stable at room temperature; they are crystalline and could be characterized by single crystal X-ray diffraction. While the *trans* isomer of **6b** is already known[12b] we obtained *cis*/*trans*-**6b** from a commercially available mixture of the corresponding dicarboxylic acids. *cis*-**6b** could be characterized by X-ray crystal structure analysis, which crystallized preferentially from the mixture of diastereomers.

In the second step of the *N*-acylamidine synthesis, one equivalent of the bis(*N*-acylbenzotriazoles) **6** was reacted

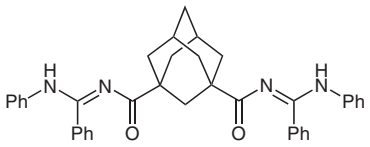
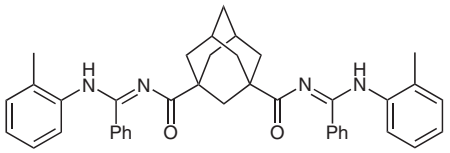
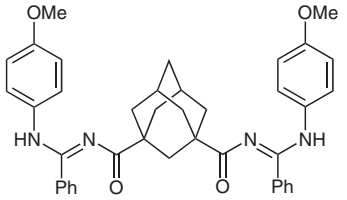
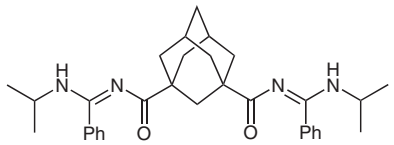
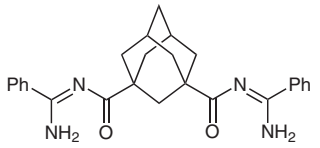
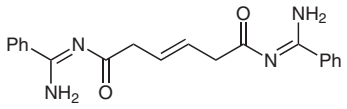
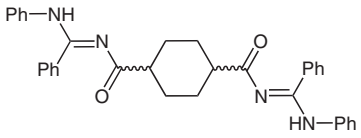
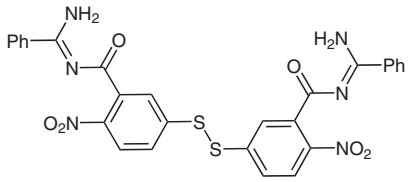


2a: R = Ph; **2b**: R = 4-MeC$_6$H$_4$; **2c**: R = 4-MeOC$_6$H$_4$; **2d**: R = *i*-Pr



Scheme 3 Synthesis of bis(*N*-acylamidines) **7** from bis(*N*-acylbenzotriazoles) **6** and amidines **2**

Table 2 Bis(*N*-acylamidine) Derivatives Prepared

Product	Structure	Yield (%)
7a		71
7b		92
7c		39
7d		46 (86)[a]
7e		62
7f		50
7g		47
7h		62

[a] After 18 h in refluxing CH_2Cl_2.

with two or more equivalents of amidines **2** at room temperature in dichloromethane for 16 hours to give the bis(*N*-acylamidine) derivatives **7a**–**h** in moderate to excellent yields (Scheme 3 and Table 2). These compounds could be easily purified and may be stored at room temperature in the presence of air.

All compounds **7** are crystalline solids; the structures of **7e**, **7f**, and **7g** were confirmed by single crystal X-ray analysis. Thus, this method offers valuable advantages concerning the variability of spacers separating the *N*-

acylamidine functionalities compared to the other methods, especially in comparison to the use of the rather reactive and often unstable acid chlorides.

The crystal structures of the bis(*N*-acylamidines) **7e** and **7f** are both characterized by inter- and intramolecular hydrogen bonding corresponding to tautomer type **1a′**. Figure 2 displays the molecular structure of **7e**·$CHCl_3$. The molecules are interconnected by hydrogen bonding formed by an amino proton of one molecule and the oxygen atom of the next molecule resulting in a molecular chain. The intramolecular hydrogen bonds have O–N distances of 2.64 Å, whereas we find 2.62 and 2.87 Å for the intermolecular hydrogen bonds (the sum of the van der Waals radii of N and O amounts to 3.02 Å).[13]

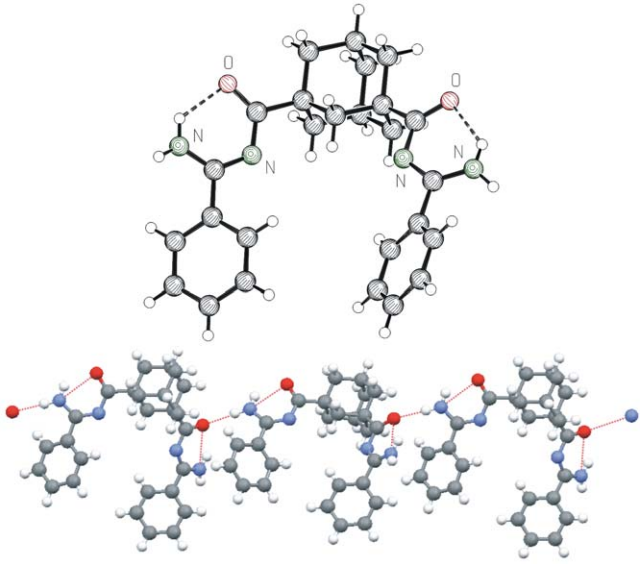


Figure 2 Molecular structure of **7e** in the solid state, single molecule (top), hydrogen-bridged ensemble of three molecules (bottom) [X-ray; solvent molecules ($CHCl_3$) were omitted for clarity]

Figure 3 displays a single molecule of bis(*N*-acylamidine) **7f** in the crystal showing intramolecular hydrogen bonding similar to the structure of **7e**. Additional intermolecular aggregation leads to a non-covalent organic framework. The O–N distances of 2.60 Å for intramolecular hydrogen bonding and 2.93 Å for intermolecular hydrogen bonding were measured.

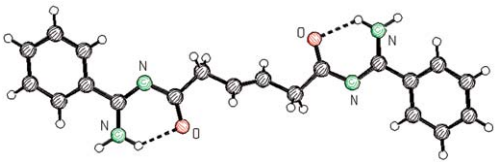
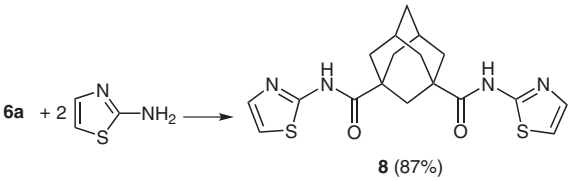


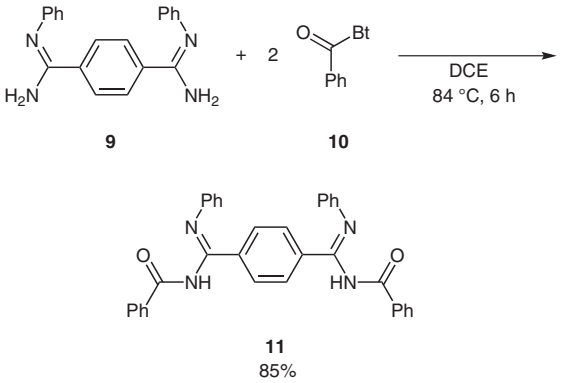
Figure 3 Molecular structure of **7f** in the solid state (X-ray)

For the synthesis of a related derivative, in which the amidine moiety is part of a heterocyclic ring system, we used 2-aminothiazole as a ‘hidden’ amidine. We obtained the bis-amide **8** in 87% yield (Scheme 4).



Scheme 4 Synthesis of bis-amide **8**

One bis(*N*-acylamidine) **11**, linked via the amidine moiety, was synthesized under similar reaction conditions using bis-amidine **9** and *N*-benzoylbenzotriazole (**10**) as precursors (Scheme 5). Because of the low solubility of amidine **9** 1,2-dichloroethane was used as solvent and the reaction mixture was heated to 84 °C for six hours.



Scheme 5 Synthesis of a bis(*N*-acylamidine) **11** linked via the carbon atoms of the amidine groups

In summary, we have shown that the reaction of *N*-acylbenzotriazoles with amidines is a facile method to synthesize bis(*N*-acylamidines) linked by different spacers between the two functionalities. The new ligands are studied now to build up supramolecular architectures, for example, networks or cavities interconnected by hydrogen bonding and metal coordination.

Melting Points: Büchi Melting Point B-540; melting points are uncorrected. ^1H, ^{13}C, GCOSY, GHSQC and GHMBC spectroscopy: Varian INOVA, AMX 400, Bruker WM 300 spectrometer. TMS (^1H) (0.00 ppm), DMSO-d_6 (^1H) 2.50 ppm (^{13}C) 39.5 ppm, pyridine-d_5 (^1H) 8.74 ppm (^{13}C) 150.5 ppm (^{13}C), DMSO-d_6, $CDCl_3$ (^{13}C) (77.0 ppm), were used as internal references; IR: Varian 3100 FT-IR (Excalibur Series). MS: mass spectra were recorded on a Finnigan MAT 4200S, or Bruker Daltonics micrOTOF, or Waters-Micromass Quatro LCZ (ESI) spectrometer. Elemental analysis: automated Elementar Vario EL III CHNS analyzer. All solvents (TBME: *tert*-butyl methyl ether; TFA: trifluoroacetic acid) and reagents were rigorously dried and purified by standard methods or were used as received from Aldrich, Acros or Fluka. Column chromatography: silica gel Merck 60 (0.040–0.063 mm). TLC: Merck silica gel plates (silica gel 60 F254), detection with UV light.

***N*-2-Methylphenylbenzamidine (2b)**

Prepared partially in analogy to a literature procedure.[7] Benzonitrile (6.20 g, 60 mmol) and $AlCl_3$ (8.00 g, 60 mmol) were mixed together in a dry flask and cooled to 0 °C. *o*-Toluidene (6.43 g, 60 mmol) was added dropwise. The mixture was heated to 160 °C until homo-

geneity was achieved. The melt was poured into an ice-cold solution of concd HCl (2.5 mL) and H_2O (200 mL) and stirred for 20 min. The aqueous mixture was filtered and added to a cold solution of NaOH (20 g) in H_2O (150 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried ($MgSO_4$) and evaporated; yield: 10.25 g (82%); light yellow solid; mp 108.4 °C.

IR (KBr): 3439 (m), 3150 (m), 3059 (m), 2967 (m), 2914 (m), 1630 (s), 1595 (s), 1564 (s), 1499 (m), 1479 (s), 1447 (m), 1385 cm^{-1} (s).

^1H NMR (400 MHz, $CDCl_3$): δ = 2.17 (s, 3 H, CH_3), 6.84–6.86 (m, 1 H_{arom}), 6.95–6.99 (m, 1 H_{arom}), 7.14–7.23 (m, 2 H_{arom}), 7.39–7.48 (m, 3 H_{arom}), 7.85–7.87 (m, 2 H_{arom}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.6 (CH_3), 121.0, 123.0, 126.7, 126.8, 128.4 (CH_{arom}), 129.4 (C_{ipso}), 130.4, 130.7 (CH_{arom}), 135.6, 148.0 (C_{ipso}), 153.8 (C=N).

HRMS (ESI): *m/z* calcd for $C_{14}H_{14}N_2$: 211.1230; found: 211.1232.

Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.67; H, 6.67; N, 13.18.

N-Isopropylbenzamidine (2d)

Prepared from benzonitrile (6.20 g, 60 mmol), $AlCl_3$ (8.00 g, 60 mmol) and *i*-$PrNH_2$ (3.55 g, 60 mmol) as described for **2b**. Vacuum distillation gave 4.21 g (43%) of a colorless oil, which solidified slowly to a colorless solid; bp 90 °C/0.83 mbar; mp 63.0 °C (Lit.[7] mp 63–64 °C).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.25 [d, ^3J = 6.5 Hz, 6 H, $CH(CH_3)_2$], 4.05 [sept, ^3J = 6.4 Hz, 1 H, $CH(CH_3)_2$], 7.30–7.50 (m, 5 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.5 [$CH(CH_3)_3$], 42.7 [$CH(CH_3)_3$], 125.8 (*p*-CH_{arom}), 128.4, 131.9 (*o*/*m*-CH_{arom}), 138.3 (C_{ipso}), 163.3 (C=N).

Bis(*N*-acylbenzotriazoles) 6a–d; General Procedure

These compounds were synthesized according to a general procedure by Katritzky et al.[12a]

To a solution of benzotriazole (8 equiv) dissolved in CH_2Cl_2 (100 mL) were added $SOCl_2$ (2 equiv) at 25 °C with stirring. After 30 min, the appropriate dicarboxylic acid (1 equiv) was added in one portion and the stirring was continued overnight. The white precipitate was filtered off and dissolved in CH_2Cl_2 (2 × 50 mL). The combined organic layers were washed with aq 2 N NaOH (3 × 60 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude products were purified as stated below.

[3-(Benzotriazol-1-carbonyl)tricyclo[4.3.1.1^{3,8}]undec-1-yl]benzotriazol-1-ylmethanone (6a)

Prepared from 1,3-adamantanedicarboxylic acid (5.33 g, 25.3 mmol), benzotriazole (24.02 g 202.4 mmol), and $SOCl_2$ (5.98 g, 50.6 mmol). Crystallization from THF gave 7.70 g (70%) of **6a** as colorless needles; mp 193 °C.

IR (KBr): 3103 (vw), 2976 (m), 2887 (s), 1717 (vs), 1595 (s), 1485 (s), 1448 (s), 1360 (vs), 1325 (s), 1310 (s), 1283 (vs), 1240 cm^{-1} (s).

^1H NMR (400 MHz, $CDCl_3$): δ = 1.90 (s, 2 H, CH_2), 2.33–2.56 (m, 10 H, CH_2, CH), 2.97 (s, 2 H, CH_2), 7.38–7.44 (m, 2 H_{arom}), 7.53–7.60 (m, 2 H_{arom}), 8.01–8.05 (m, 2 H_{arom}), 8.20–8.24 (m, 2 H_{arom}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.2 (CH), 35.3(CH_2), 37.8 (CH_2), 39.4 (CH_2), 45.5 (C_q), 115.1 (*m*-CH_{arom}), 119.9 (*p*-CH_{arom}), 126.0 (*m*-CH_{arom}), 130.4 (*o*-CH_{arom}), 132.2 (C_{ipso}), 144.7 (C_{ipso}), 175.4 (C=O).

HRMS (ESI): *m/z* calcd for $C_{24}H_{22}N_6O_2$ + Na: 449.1687; found: 449.1696.

Anal. Calcd for $C_{24}H_{22}N_6O_2$; C, 67.62; H, 5.22; N, 19.68. Found: C, 67.59; H, 5.20; N, 19.71.

X-ray Crystal Structure Analysis for 6a[14–20]

$C_{24}H_{22}N_6O_2$, *M* = 426.48, colorless crystal 0.60 × 0.10 × 0.07 mm, *a* = 21.0320(1), *b* = 14.2679(1), *c* = 6.9020(1) Å, β = 99.840(1)°, *V* = 2040.70(3) Å^3, ρ_{calc} = 1.388 g cm^{-3}, μ = 0.748 mm^{-1}, empirical absorption correction (0.662 ≤ *T* ≤ 0.950), *Z* = 4, monoclinic, space group *C*2/c (No. 15), λ = 1.54178 Å, *T* = 223(2) K, ω and φ scans, 7575 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å^{-1}, 1766 independent (R_{int} = 0.065) and 1405 observed reflections [$I \geq 2\sigma(I)$], 146 refined parameters, *R* = 0.050, wR^2 = 0.132, max. (min.) residual electron density 0.17 (–0.22) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

[4-(Benzotriazol-1-carbonyl)cyclohexyl]benzotriazol-1-ylmethanone (6b)

Prepared from a *cis/trans* mixture of 1,4-cyclohexanedicarboxylic acid (1.72 g, 10.0 mmol). Crystallization from THF gave 2.41 g (64%) of *cis/trans* mixture of **6b** as colorless needles; mp 193 °C.

IR (KBr): 3045 (vw), 3024 (vw), 2955 (m), 2868 (w), 1728 (vs), 1595 (m), 1485 (s), 1450 (s), 1391 (s), 1350 (s), 1286 cm^{-1} (s).

^1H NMR (400 MHz, $CDCl_3$): δ = 1.90–2.20 (m, 4 H, CH_2), 2.30–2.45 (m, 4 H, CH_2), 4.04 (m, 0.6 H), 4.18 (1.4 H, CH), 7.47–7.53 (m, 2 H_{arom}), 7.61–7.69 (m, 2 H_{arom}), 8.09–8.13 (m, 2 H_{arom}), 8.29–8.31 (m, 2 H_{arom}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.0, 28.0 (CH_2), 40.2, 42.5 (CH), 114.5, 114.5, 120.1, 120.1, 126.1, 126.2, 130.4, 130.4 (CH_{arom}), 131.1, 131.2, 146.0, 146.1 (C_{ipso}), 174.5, 174.6 (C=O).

HRMS (ESI): *m/z* calcd for $C_{20}H_{18}N_6O_2$ + Na: 397.1383; found: 397.1382.

Anal. Calcd for $C_{20}H_{18}N_6O_2$: C, 64.16; H, 4.85; N, 22.45. Found: C, 63.81; H, 4.82; N, 22.15.

X-ray Crystal Structure Analysis for 6b[14–20]

$C_{20}H_{18}N_6O_2$, *M* = 374.40, colorless crystal 0.15 × 0.10 × 0.05 mm, *a* = 6.7907(1), *b* = 34.0197(6), *c* = 7.6258(2) Å, β = 90.883(1)°, *V* = 1761.48(6) Å^3, ρ_{calc} = 1.412 g cm^{-3}, μ = 0.785 mm^{-1}, empirical absorption correction (0.891 ≤ *T* ≤ 0.962), *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, *T* = 223(2) K, ω and φ scans, 9846 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å^{-1}, 2770 independent (R_{int} = 0.069) and 2050 observed reflections [$I \geq 2\sigma(I)$], 253 refined parameters, *R* = 0.060, wR^2 = 0.168, max. (min.) residual electron density 0.20 (–0.18) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

(*E*)-1,6-Di(benzotriazol-1-yl)hex-3-ene-1,6-dione (6c)

Prepared from *trans*-hex-3-enedicarboxylic acid (1.44 g, 10 mmol), benzotriazole (9.53 g 80 mmol), and $SOCl_2$ (2.36 g, 20.0 mmol). Crystallization from THF gave 1.64 g (47%) of **6c** as light yellow needles; mp 189.6 °C.

IR (ATR): 3088 (m), 3030 (m), 2949 (m), 2897 (m), 1736 (s), 1605 (m), 1597 (m), 1485 (m), 1452 (m), 1387 (vs), 1348 (s), 1288 cm^{-1} (s).

^1H NMR (300 MHz, $CDCl_3$): δ = 4.27–4.30 (m, 4 H, CH_2), 6.10–6.20 (m, 2 H, CH=CH), 7.50–7.55 (m, 2 H_{arom}), 7.64–7.70 (m, 2 H_{arom}), 8.11–8.14 (m, 2 H_{arom}), 8.26–8.30 (m, 2 H_{arom}).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 39.0 (CH_2), 114.3 (*m*-CH_{arom}), 120.2 (*p*-CH_{arom}), 126.3 (*m*-CH_{arom}), 126.3 (CH=CH), 130.5 (*o*-CH_{arom}), 131.0 (C_{ipso}), 146.2 (C_{ipso}), 170.0 (C=O).

HRMS (ESI): *m/z* calcd for $C_{18}H_{14}N_6O_2$ + Na: 369.1055; found: 369.1070.

Anal. Calcd for $C_{18}H_{14}N_6O_2$: C, 62.42; H, 4.07; N, 24.27. Found: C, 62.24; H, 3.85; N, 23.92.

X-ray Crystal Structure Analysis for 6c[14–20]

$C_{18}H_{14}N_6O_2$, M = 346.35, light yellow crystal 0.40 × 0.25 × 0.10 mm, a = 7.5662(2), b = 10.0801(3), c = 10.6640(3) Å, β = 102.475(2)°, V = 794.12(4) Å^3, ρ_{calc} = 1.448 g cm^{-3}, = 0.824 mm^{-1}, empirical absorption correction (0.734 ≤ T ≤ 0.922), Z = 2, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 4834 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 1394 independent (R_{int} = 0.037) and 1266 observed reflections [I ≥ 2 σ(I)], 118 refined parameters, R = 0.038, wR^2 = 0.102, max. (min.) residual electron density 0.15 (–0.11) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

{5-[3-(Benzotriazole-1-carbonyl)-4-nitrophenyldisulfanyl]-2-nitrophenyl}benzotriazol-1-ylmethanone (6d)

Prepared from 5,5′-dithiobis(2-nitrobenzoic acid) (1.00 g, 2.5 mmol), benzotriazole (2.38 g, 20 mmol), $SOCl_2$ (60 g, 5.0 mmol). Crystallization from THF gave 1.11 g (74%) of **6d** as colorless needles; mp 235.5 °C.

IR (ATR): 3107 (m), 3026 (m), 1726 (s), 1599 (m), 1566 (s), 1518 (vs), 1485 (s), 1450 (s), 1395 (vs), 1371 (s), 1337 (vs), 1219 cm^{-1} (s).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (ddd, 2 H, ^4J = 1.0 Hz, ^3J = 7.2, 8.2 Hz, CH_{bt}), 7.75 (ddd, 2 H, ^4J = 1.0, ^3J = 7.2, 8.2 Hz, CH_{bt}), 7.79–7.88 (m, 4 H_{arom}), 8.10 (m, 2 H, CH_{bt}), 8.28–8.28 (m, 2 H_{arom}), 8.38–8.42 (m, 2 H, CH_{bt}).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 114.2, 120.5 (CH_{bt}), 125.6, 126.4, 126.9, 128.6 (CH_{arom}, CH_{bt}), 130.8, 131.0 (C_{ipso}, $C_{ipso,bt}$), 131.0 (CH_{bt}), 144.1, 145.2, 146.2 (C_{ipso}, $C_{ipso,bt}$), 164.0 (C=O).

HRMS (ESI): m/z calcd for $C_{26}H_{14}N_8O_6S_2$ + Na: 621.0369; found: 621.0370.

Anal. Calcd for $C_{26}H_{14}N_8O_6S_2$: C, 52.17; H, 2.36; N, 18.72. Found: C, 52.40; H, 2.22; N, 18.73.

X-ray Crystal Structure Analysis for 6d[14–20]

$C_{26}H_{14}N_8O_6S_2$, M = 598.57, colorless crystal 0.30 × 0.20 × 0.10 mm, a = 14.8146(2), b = 11.2958(2), c = 15.6873(2) Å, β = 104.184(1)°, V = 2545.12(7) Å^3, ρ_{calc} = 1.562 g cm^{-3}, μ = 2.435 mm^{-1}, empirical absorption correction (0.529 ≤ T ≤ 0.793), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 18775 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 4485 independent (R_{int} = 0.044) and 4152 observed reflections [I ≥ 2 σ(I)], 379 refined parameters, R = 0.041, wR^2 = 0.110, max. (min.) residual electron density 0.29 (–0.20) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Bis(*N*-acylamidines) 7a–i; General Procedure

Bis(*N*-acylbenzotriazole) (1 equiv) was added in small portions to a solution of a primary or secondary amidine (at least 2 equiv) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 16 h at r. t. and then concentrated in vacuo. The crude product was purified as stated below.

Adamantane-1,3-dicarboxylic Acid Bis(1-phenyl-1-phenylaminomethylideneamide) (7a)

Prepared from *N*-phenylbenzamidine (**2a**;[7] 0.88 g, 4.5 mmol) and bis(*N*-acylbenzotriazole) **6a** (0.85 g, 2.0 mmol) according to the general procedure at r.t. The precipitate was collected by filtration and washed with CH_2Cl_2 (5 mL) and Et_2O (5 mL) to give 0.83 g (71%) of **7a** as a white solid; mp 244.9 °C.

IR (ATR): 3254 (vw), 3059 (vw), 2928 (vw), 2853 (vw), 1657 (vs), 1622 (m), 1593 (m), 1580 (vw), 1479 (vs), 1449 (m), 1250 (m), 1213 cm^{-1} (s).

^{1}H NMR (400 MHz, $CDCl_3$–TFA, 1:1): δ = 1.85 (br s, 2 H, CH_{2ad}), 2.09–2.20 (m, 8 H, CH_{2ad}), 2.41, 2.46 (br s, 4 H, CH_{ad}, CH_{2ad}), 7.09 (d, ^3J = 6.9 Hz, 4 H_{arom}), 7.30–7.56 (m, 14 H_{arom}), 7.67–7.70 (m, 2 H_{arom}), 10.07, 13.48 (br s, 4 H, NH).

^{13}C NMR (100 MHz, $CDCl_3$–TFA, 1:1): δ = 29.7 (CH_{ad}), 36.2, 38.7, 39.5 (CH_{2ad}), 46.5 (C_q), 127.2 (*o*/*m*-CH_{arom}), 127.3 (C_{ipso}), 131.3, 132.3, 132.7 (*o*/*m*-CH_{arom}), 132.8 (*p*-CH_{arom}), 135.7 (C_{ipso}), 137.7 (*p*-CH_{arom}), 168.8 (C=O), 184.2 (C=N).

HRMS (ESI): m/z calcd for $C_{38}H_{36}N_4O_2$ + H: 581.2911; found: 581.2914.

Anal. Calcd for $C_{38}H_{36}N_4O_2$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.20; H, 6.26; N, 9.42.

Adamantane-1,3-dicarboxylic Acid Bis(1-phenyl-1-*o*-tolylaminomethylideneamide) (7b)

Prepared from *N*-2-methylphenylbenzamidine (**2b**; 1.05 g, 5.0 mmol) and bis(*N*-acylbenzotriazole) **6a** (0.85 g, 2.0 mmol) according to the general procedure at r.t. The residue was purified by flash chromatography (pentane–acetone; 5:1, 5% Et_3N, R_f = 0.44) to give 1.13 g (92%) of **7b** as a colorless solid; mp 159 °C.

IR (ATR): 3071 (vw), 3030 (vw), 2980 (vw), 2936 (vw), 2899 (vw), 1655 (s), 1587 (m), 1562 (w), 1510 (vw), 1449 (vw), 1404 (vw), 1393 (vw), 1325 cm^{-1} (vw).

^{1}H NMR (400 MHz, pyridine-d_5): δ = 1.40–2.54 (m, 20 H, CH_3, CH_2, CH), 7.03–7.56, 8.21–8.33 (m, 18 H_{arom}).

^{13}C NMR (100 MHz, pyridine-d_5): δ = 18.6 (CH_3), 29.0 (CH), 35.9, 38.7, 40.6 (CH_2), 42.8 (C_q), 119.8, 125.1, 126.9, 129.2, 129.2 (CH_{arom}), 131.1 (C_{ipso}), 131.2, 131.7 (CH_{arom}), 137.7, 148.8 (C_{ipso}), 152.9 (C=N), 177.1 (C=O).

HRMS (ESI): m/z calcd for $C_{40}H_{40}N_4O_2$ + H: 609.3224; found: 609.3222.

Anal. Calcd for $C_{40}H_{40}N_4O_2$: C, 78.92; H, 6.62; N, 9.20. Found: C, 78.68; H, 6.57; N, 9.18.

Adamantane-1,3-dicarboxylic Acid Bis[1-(4-methoxyphenylamino)-1-phenylmethylideneamide] (7c)

Prepared from *N*-methoxyphenylbenzamidine (**2c**;[21] 0.45 g, 2.2 mmol) and bis(*N*-acylbenzotriazole) **6a** (0.43 g, 1.0 mmol) according to the general procedure at r.t. The precipitate was collected by filtration and washed with CH_2Cl_2 and Et_2O to give 0.25 g (39%) of a yellow solid; mp 217.9 °C.

IR (ATR): 3237 (m), 3003 (w), 2932 (m), 2837 (w), 1655 (s), 1576 (m), 1501 (s), 1462 (m), 1296 (m), 1246 (s), 1209 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$–TFA, 1:1): δ = 1.84 (s, 2 H, CH_{2ad}), 2.07–2.18 (m, 8 H, CH_{2ad}), 2.39, 2.45 (s, 4 H, CH_{2ad}, CH_{ad}), 3.87 (s, 6 H, OCH_3), 6.93 (d, ^3J = 9.0 Hz, 4 H_{arom}), 7.04 (d, ^3J = 9.0 Hz, 4 H_{arom}), 7.43–7.57 (m, 8 H_{arom}), 7.70 (t, ^3J = 7.2 Hz, 2 H_{arom}), 10.01, 13.41 (s, 4 H, NH).

^{13}C NMR (75 MHz, $CDCl_3$–TFA, 1:1): δ = 27.7 (CH_{ad}), 34.2, 36.7, 37.4 (CH_{2ad}), 44.5 (C_q), 56.1 (OCH_3), 116.0 (CH_{arom}), 125.5 (C_{ipso}), 126.7 (CH_{arom}), 126.9 (C_{ipso}), 129.3, 130.4, 135.7 (CH_{arom}), 160.6 (C_{ipso}), 166.2 (C=O), 182.2 (C=N).

HRMS (ESI): m/z calcd for $C_{40}H_{40}N_4O_4$ + H: 641.3122; found: 641.3126.

Anal. Calcd for $C_{40}H_{40}N_4O_4$: C, 74.98; H, 6.29; N, 8.74. Found: C, 74.86; H, 6.02; N, 8.44.

Adamantane-1,3-dicarboxylic Acid Bis(1-isopropylamino-1-phenylmethylideneamide) (7d)

Prepared from amidine **2d** (0.41 g, 2.0 mmol) and bis(*N*-acylbenzotriazole) **6a** (0.43 g, 1.0 mmol) according to the general procedure

at r.t. Purified by column chromatography (EtOAc + 5% Et_3N) to give 0.18 g (46%) of a white solid; mp 189.4 °C, R_f = 0.47.

IR (ATR): 3250 (s), 3101 (w), 2968 (w), 2930 (m), 1611 (s), 1585 (m), 1522 (vs), 1456 (m), 1447 (m), 1346 (m), 1327 (m), 1279 cm^{-1} (m).

^1H NMR (500 MHz, $CDCl_3$, 348 K): δ = 1.21 [d, ^3J = 6.5 Hz, 12 H, $CH(CH_3)_2$], 1.60 (br s, 2 H, CH_{2ad}), 1.73 (br s, 8 H, CH_{2ad}), 1.88 (br s, 2 H, CH_{2ad}), 2.06 (br s, 2 H, CH_{ad}), 4.04 [br s, 2 H, $CH(CH_3)_2$], 7.33–7.50 (m, 10 H_{arom}).

^{13}C NMR (500 MHz, $CDCl_3$, 348 K): δ = 21.3 [$CH(CH_3)_2$], 27.9 (CH_{ad}), 35.4 (CH_{2ad}), 38.6 (CH_{2ad}), 41.5 (CH_{2ad}), 42.5 [$CH(CH_3)_2$], 43.0 (C_q), 127.0, 127.4, 129.2 (CH_{arom}), 135.1 (C_{ipso}), 160.1 (C=N), 186.8 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{32}H_{40}N_4O_2$ + H: 513.3217; found: 513.3224.

Anal. Calcd for $C_{32}H_{40}N_4O_2$: C, 74.97; H, 7.86; N, 10.93. Found: C, 74.70; H, 7.47; N, 10.92.

Adamantane-1,3-dicarboxylic Acid Bis(1-amino-1-phenylmethylideneamide) (7e)

Prepared from benzamidine (0.36 g, 3.10 mmol) and bis(*N*-acylbenzotriazole) **6a** (0.66 g, 1.55 mmol) according to the general procedure. The solution was washed with aq 2 N NaOH (2 × 20 mL), dried ($MgSO_4$), and evaporated. In order to obtain single crystals, the solid was recrystallized from $CHCl_3$–pentane mixtures; yield: 0.41 g (62%); colorless solid; mp 130–140 °C.

IR (ATR): 3327 (w), 3069 (w), 2934 (vw), 2851 (vw), 1661 (vw), 1597 (s), 1570 (s), 1520 (s), 1506 (s), 1470 (m), 1443 (m), 1304 (m), 1275 cm^{-1} (m).

^1H NMR (400 MHz, DMSO-d_6): δ = 1.65 (s, 2 H, CH_{2ad}), 1.87 (br s, 8 H, CH_{2ad}), 2.06 (s, 2 H, CH_{2ad}), 2.13 (s, 2 H, CH_{ad}), 7.47–7.60 (m, 6 H_{arom}) 8.04–8.08 (m, 4 H_{arom}), 9.02 (br s, 2 H, NH_2), 10.05 (br s, 2 H, NH_2).

^{13}C NMR (400 MHz, DMSO-d_6): δ = 28.1 (CH_{ad}), 35.7 (CH_{2ad}), 38.6 (CH_{2ad}), 41.1 (CH_{2ad}), 43.8 (C_q) 127.7 (*m*-C_{arom}), 128.3 (*o*-C_{arom}), 131.8 (*p*-C_{arom}), 134.8 (C_{ipso}), 164.9 (C=N), 192.3 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{26}H_{28}N_4O_2$ + H: 429.2275; found: 429.2285.

Anal. Calcd for $C_{26}H_{28}N_4O_2$: C, 72.87; H, 6.59; N, 13.07. Found: C, 73.16; H, 6.52; N, 12.77.

X-ray Crystal Structure Analysis for 7e[14–20]

$C_{26}H_{28}N_4O_2 \cdot CHCl_3$, *M* = 547.89, colorless crystal 0.30 × 0.15 × 0.07 mm, *a* = 12.3543(5), *b* = 9.9727(4), *c* = 21.6838(9) Å, *β* = 92.895(2)°, *V* = 2668.16(19) Å^3, ρ_{calc} = 1.364 g cm^{-3}, μ = 3.368 mm^{-1}, empirical absorption correction (0.432 ≤ *T* ≤ 0.798), *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, *T* = 223(2) K, ω and φ scans, 16303 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å^{-1}, 4682 independent (R_{int} = 0.047) and 4081 observed reflections [$I \geq 2\sigma(I)$], 337 refined parameters, *R* = 0.056, wR^2 = 0.161, max. (min.) residual electron density 0.15 (–0.11) e Å^{-3}, hydrogen atoms at N1 and N18 from difference Fourier maps, others calculated and refined as riding atoms.

(*E*)-Hex-3-enedioic Acid Bis(1-amino-1-phenylmethylideneamide) (7f)

Prepared from benzamidine (1.20 g, 10 mmol) and bis(*N*-acylbenzotriazole) **6c** (1.71 g, 5 mmol) according to the general procedure. The precipitate was collected by filtration and washed with CH_2Cl_2 (2 × 5 mL). In order to obtain single crystals, the solid was recrystallized from CH_2Cl_2–DMF mixtures; yield: 0.86 g (50%); light-orange solid; mp 162.4 °C.

IR (KBr): 3312 (m), 3177 (m), 2916 (vw), 2893 (vw), 1599 (vs), 1574 (s), 1506 (s), 1472 (s), 1443 (s), 1325 (m), 1312 (s), 1300 cm^{-1} (s).

^1H NMR (300 MHz, DMSO-d_6): δ = 3.18 (m, 4 H, CH_2), 5.74 (br s, 2 H, CH=CH), 7.44–7.57 (m, 6 H_{arom}), 7.99 (br s, 4 H_{arom}), 9.15, 10.08 (br s, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 44.7 (br, CH_2), 126.8, 127.7 (br), 128.3 (CH=CH, CH_{arom}), 131.9 (C_{ipso}), 134.3, 165.2 (C=N), 186.3 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{20}N_4O_2$ + H: 349.1659; found: 349.1653.

X-ray Crystal Structure Analysis for 7f[14–20]

$C_{20}H_{20}N_4O_2$, *M* = 348.40, colorless crystal 0.40 × 0.20 × 0.07 mm, *a* = 8.2780(2), *b* = 9.7590(2), *c* = 11.6178(3) Å, *β* = 105.713(1)°, *V* = 903.47(4) Å^3, ρ_{calc} = 1.281 g cm^{-3}, μ = 0.689 mm^{-1}, empirical absorption correction (0.770 ≤ *T* ≤ 0.953), *Z* = 2, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, *T* = 223(2) K, ω and φ scans, 6118 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å^{-1}, 1589 independent (R_{int} = 0.039) and 1500 observed reflections [$I \geq 2\sigma(I)$], 124 refined parameters, *R* = 0.041, wR^2 = 0.109, max. (min.) residual electron density 0.15 (–0.16) e Å^{-3}, hydrogen atom at N1 from difference Fourier maps, others calculated and refined as riding atoms.

Cyclohexane-1,4-dicarboxylic Acid Bis(1-phenyl-1-phenylaminomethylideneamide) (7g)

Prepared from amidine **2a** (1.37 g, 7 mmol) and bis(*N*-acylbenzotriazole) **6b** (1.12 g, 3 mmol) according to the general procedure. The solution was washed twice with aq 2 N NaOH (2 × 20 mL), dried ($MgSO_4$), and evaporated. Crystallization from DMF gave 0.75 g (47%) of **7g** as a colorless solid; mp 216.4 °C.

IR (KBr): 3238 (m), 3036 (m), 2951 (m), 2866 (m), 1684 (m), 1659 (s), 1624 (s), 1595 (m), 1483 (s), 1447 (s), 1315 (m), 1294 cm^{-1} (m).

^1H NMR (400 MHz, pyridine-d_5): δ = 1.41–1.81 (m, 4 H, CH_2), 1.97–2.36 (m, 4 H, CH_2), 2.45–2.66 (m, 2 H, CH), 6.84–8.07 (m, 18 H_{arom}), 8.19–8.37 (m, 2 H_{arom}), 10.91 (NH).

^{13}C NMR (100 MHz, pyridine-d_5): δ = 29.4 (CH_2), 44.8 (CH), 121.7 (CH_{arom}), 124.7 (*p*-CH_{arom}), 129.2, 129.4, 129.7 (*o*/*m*-CH_{arom}), 131.7 (*p*-CH_{arom}), 137.6, 150.6 (C_{ipso}), 153.3 (C=N), 175.8 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{34}H_{32}N_4O_2$ + H: 529.2598; found: 529.2627.

Anal. Calcd for $C_{34}H_{32}N_4O_2$: C, 77.25; H, 6.10; N, 10.60. Found: C, 76.92; H, 5.99; N, 10.18.

X-ray Crystal Structure Analysis for 7g[14–20]

$C_{34}H_{32}N_4O_2 \cdot 2\ C_3H_7NO$, *M* = 674.83, colorless crystal 0.20 × 0.20 × 0.07 mm, *a* = 15.2107(6), *b* = 13.3684(6), *c* = 19.7555(9) Å, *β* = 112.288(3)°, *V* = 3717.0(3) Å^3, ρ_{calc} = 1.206 g cm^{-3}, μ = 0.633 mm^{-1}, empirical absorption correction (0.884 ≤ *T* ≤ 0.957), *Z* = 4, monoclinic, space group *C*2/c (No. 15), λ = 1.54178 Å, *T* = 223(2) K, ω and φ scans, 13024 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å^{-1}, 3253 independent (R_{int} = 0.041) and 2733 observed reflections [$I \geq 2\sigma(I)$], 231 refined parameters, *R* = 0.048, wR^2 = 0.129, max. (min.) residual electron density 0.23 (–0.17) e Å^{-3}, hydrogen atom at N3 from difference Fourier maps, others calculated and refined as riding atoms.

5,5′-Dithiobis(2-nitrobenzoic Acid) Bis(1-amino-1-phenylmethylideneamide) (7h)

Prepared from benzamidine (0.18 g, 0.7 mmol) and bis(*N*-acylbenzotriazole) **6d** (0.42 g, 0.7 mmol) according to the general procedure. After removal of the solvents by evaporation, TBME (5 mL) was added to the residue. Ultrasonication led to a yellow solid. The

solid was collected by filtration and washed with TBME (5 mL) to give 0.26 g (62%) of **7h** as a light-yellow solid; mp 101.3 °C (dec.).

IR (ATR): 3333 (m), 3308 (m), 3184 (w), 3088 (m), 1605 (s), 1562 (s), 1530 (s), 1477 (s), 1441 (s), 1369 (s), 1319 (vs), 1290 cm^{-1} (m).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.47 (t, ^3J = 7.6 Hz, 4 H, CH_{arom}), 7.56 (t, ^3J = 7.3 Hz, 2 H, CH_{arom}), 7.85 (dd, ^4J = 2.2, ^3J = 8.5 Hz, 2 H, CH_{arom}), 7.98–7.90 (m, 6 H_{arom}), 8.15 (d, ^4J = 2.2 Hz, 2 H_{arom}), 9.69 (s, 2 H, NH), 10.24 (s, 2 H, NH).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 121.1, 124.7, 126.8, 128.2, 128.5, 132.6 (CH_{arom}), 133.5, 134.4, 140.1, 148.0 (C_{ipso}), 167.0 (C=N), 175.4 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{28}H_{20}N_6O_6S_2$ + H: 601.0959; found: 601.0957.

Anal. Calcd for $C_{28}H_{20}N_6O_6S_2$: C, 55.99; H, 3.36; N, 13.99. Found: C, 55.88; H, 3.73; N, 14.21.

N,*N*′-Di(1,3-thiazol-2-yl)-1,3-adamantanedicarboxamide (8)

Prepared from 2-aminothiazole (0.6 g, 6.0 mmol) and bis(*N*-acylbenzotriazole) **6a** (1.28 g, 3.0 mmol) according to the general procedure at r.t. Crystallization from EtOH gave 1.02 g (87%) of **10** as a light orange solid; mp 275.0–277.6 °C.

IR (ATR): 3186 (w), 3055 (vw), 2911 (m), 2853 (m), 1678 (vs), 1530 (vs), 1487 (s), 1458 (s), 1447 (s), 1435 (s), 1331 (s), 1269 cm^{-1} (vs).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.68 (br s, 2 H, CH_{ad}), 1.82–2.02 (m, 8 H, CH_{ad}), 2.16 (br s, 4 H, CH_{ad}), 7.18–7.19 (d, ^3J = 3.6 Hz, 2 H_{arom}), 7.48–7.49 (d, ^3J = 3.6 Hz, 2 H_{arom}).

^{13}C NMR (300 MHz, DMSO-d_6): δ = 27.6 (CH_{ad}), 34.4, 36.6, 38.2 (CH_{2ad}), 41.0 ($C_{q,ad}$), 113.4 ($SCH_{thiazolyl}$), 137.5 ($NCH_{thiazolyl}$), 158.5 (C=N), 175.3 (C=O).

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{20}N_4O_2S_2$ + H: 398.1106; found: 398.1100.

Anal. Calcd for $C_{18}H_{20}N_4O_2S_2$: C, 55.65; H, 5.19; N, 14.42. Found: C, 55.48; H, 5.03; N, 14.38.

X-ray Crystal Structure Analysis for 8[14–20]

$C_{18}H_{20}N_4O_2S_2$, M = 388.50, colorless crystal 0.30 × 0.20 × 0.10 mm, a = 7.2609(4), b = 12.1746(7), c = 19.6542(10) Å, V = 1737.4(2) Å^3, ρ_{calc} = 1.485 g cm^{-3}, μ = 2.963 mm^{-1}, empirical absorption correction (0.470 ≤ T ≤ 0.756), Z = 4, orthorhombic, space group $Pna2_1$ (No. 33), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 9365 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 2815 independent (R_{int} = 0.035) and 2801 observed reflections [I ≥ 2 σ(I)], 242 refined parameters, R = 0.032, wR^2 = 0.087, max. (min.) residual electron density 0.27 (–0.16) e Å^{-3}, refined as racemic twin, hydrogen atoms at N3 and N21 from difference Fourier maps, others calculated and refined as riding atoms.

N-(1-Phenylamino-1-{4-[phenylamino(benzoylimino)methyl]phenyl}methylidene)benzamide (11)

Diamidine **9**[21,22](0.31 g, 1.0 mmol) and *N*-benzoylbenzotriazole (**10**; 0.47 g, 2.1 mmol) were suspended in CH_2Cl_2 (20 mL) and refluxed for 6 h. The solvent was removed under reduced pressure, TBME (5 mL) was added to the residue and the white precipitate was collected by filtration after sonication. The solid was dissolved in CH_2Cl_2 (50 mL) and the CH_2Cl_2 layer was washed with aq 0.1 N NaOH (20 mL). The organic layer was dried ($MgSO_4$), filtered, and evaporated to give 0.44 g (85%) of a colorless solid; mp 225.7 °C.

IR (ATR): 3267 (w), 3132 (w), 3034 (w), 2984 (w), 1601 (m), 1578 (s), 1522 (s), 1497 (s), 1443 (s), 1406 (m), 1369 (s), 1267 cm^{-1} (s).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94–7.02 (m, 4 H_{arom}), 7.10–7.22 (m, 6 H_{arom}), 7.40–7.47 (m, 4 H_{arom}), 7.52–7.54 (m, 2 H_{arom}), 7.56 (s, 4 $H_{arom,spacer}$), 8.30–8.31 (m, 4 H_{arom}), 12.27 (s, 2 H, NH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.9, 126.1, 128.4, 129.4, 129.7, 129.8, 132.6 (CH_{arom}), 137.0, 138.5, 147.7, 151.2 (C_{ipso}), 164.0 (br, C=N), 165.6 (C=N), 179.5 (br, C=O).

HRMS (ESI): *m*/*z* calcd for $C_{34}H_{26}N_4O_2$ + H: 523.2129; found: 523.2116.

Anal. Calcd for $C_{34}H_{26}N_4O_2$: C, 78.14; H, 5.01; N, 10.72. Found: C, 77.82; H, 5.12; N, 10.55.

X-ray Crystal Structure Analysis for 11[14–20]

$C_{34}H_{26}N_4O_2 \cdot 2\ C_2H_6OS$, M = 678.84, colorless crystal 0.10 × 0.08 × 0.05 mm, a = 5.4554(1), b = 11.5381(2), c = 13.3390(3) Å, α = 98.112(1), β = 92.331(1), γ = 96.284(1)°, V = 824.88(3) Å^3, ρ_{calc} = 1.367 g cm^{-3}, μ = 1.853 mm^{-1}, empirical absorption correction (0.836 ≤ T ≤ 0.913), Z = 1, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 8843 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 2924 independent (R_{int} = 0.050) and 2525 observed reflections [I ≥ 2 σ(I)], 239 refined parameters, R = 0.043, wR^2 = 0.107, max. (min.) residual electron density 0.20 (–0.27) e Å^{-3}, hydrogen atom at N5 from difference Fourier maps, others calculated and refined as riding atoms.

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