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1,3,5-Triazapenta-1,3-dienes: Useful Building Blocks for the Synthesis of 1,2-Dihydro-1,3,5-triazines and Oligonitriles[‡]

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Dedicated to Professor Jochen Mattay on the occasion of his 60th birthday

Keywords: 1,3,5-Triazapenta-1,3-dienes / Tautomerism / Triazines / Oligonitriles / DFT calculations

1,3,5-Triazapentadienes **1**, prepared from amidines and imidoyl chlorides **2**, have been used as nucleophilic building blocks for the reactions with various electrophilic reagents. With aldehydes **4** 1,2-dihydrotriazines **3** were obtained, whereas ketones **5** gave **3** or 1,3,5-triazahexa-1,3,5-trienes **6**, depending on the substitution pattern of **1**. Acyl chlorides **7** reacted with **1** to give 1-oxa-3,5,7-triazahepta-1,3,5-trienes **8**; in a similar manner imidoyl chlorides **2** gave rise to the formation of the new 1,3,5,7-tetraazahepta-1,3,5-trienes **9**. Treatment of *N*-benzoylbenzimidoyl chloride **10** with **1** afforded the 1-oxa-3,5,7,9-tetraazanona-1,3,5,7-tetraenes **11**, or, depending on the substitution pattern, their ring-tautomeric compounds **12** with 1,2-dihydrotriazine structures. 1-Oxa-3,5-diazinium salt **13** as cyclic electrophile produced, when treated with **1g**, 1-oxa-3,5,7,9,11-pentaazaundeca-1,3,5,7,9-pentaene (**14**), a long oligonitrile with push-pull substitution pattern. All new compounds were completely characterized including X-ray diffraction for each type, indicating rather twisted three-dimensional structures for the open-chain compounds. The relative energies of 1,3,5-triazapentadiene isomers were studied by DFT calculations [level: B3LYP/6-31+G(d,p)], as well as the ring-chain tautomerism of selected examples.

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Introduction

1,3,5-Triazapenta-1,3-dienes are polyfunctional, nitrogen-rich analogs of pentadienes with two amidine subunits forming an unsaturated N–C–N–C–N chain. On the other hand, they may also be understood as formal products of a nitrile dimerization, induced by an amine nucleophile. As nitrogen analogs of β-diketones they possess great potential as chelating ligands for various metal ions providing access to six-membered metal complexes.[1] They are accessible by reaction of benzamidines with imidoyl halides as first described by Ley und Müller.[2] Depending on the number of protons at the nitrogen atoms we differentiate primary (three protons at the nitrogen atoms), secondary (two protons at the nitrogen atoms) and tertiary (one NH group) triazapentadienes.

In this report, we describe our experiments with 1,3,5-triazapenta-1,3-dienes as nucleophiles in reactions with various electrophiles in order to extend the length of the unsaturated chain giving rise to a number of new heterocyclic and acyclic products with alternating carbon and nitrogen atoms. The open-chain compounds, namely oligonitriles, are interesting with regard to their electronic properties, which are characterized by competing π–π* and n–π* interactions of the adjacent C=N moieties.[3,4] This often results in unusual three-dimensional structures with low rotational barriers about the C–N single bonds. Besides the synthesis, the full structural characterization of the new open-chain compounds including X-ray diffraction analyses constitutes a second focus of this work.

Results and Discussion

Seven secondary 1,3,5-triazapenta-1,3-dienes **1a**–**g** (**1b**–**1g** were unknown before) were prepared form benzamidine and imidoyl halides **2a**–**g** in 20–78% yield by applying a modification[1] of a procedure given by Ley and Müller[2] (Scheme 1).

In a similar manner, the tertiary 1,3,5-triazapenta-1,3-diene **1h** was prepared from the corresponding *N*-cyclopentylpivalimidoyl chloride (**2h**) and *N*-phenylbenzamidine in 91% yield (Scheme 2).

Two of the 1,3,5-triazapenta-1,3-dienes (**1b**,**e**) could be characterized by X-ray diffraction (Figure 1 for **1b**). In both cases a twisted U-shape structure is adopted in the solid state, which is subject of a weak intramolecular interaction between one of the two amino protons $N5H_2$ and nitrogen

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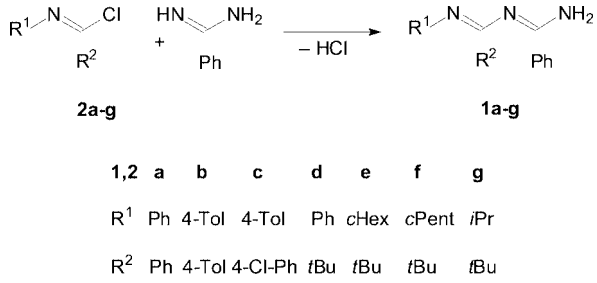
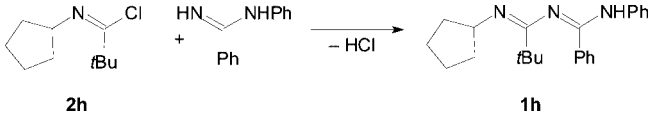


Scheme 1.



Scheme 2.

atom N1 (**1b**: 2.627 Å) and a strong interaction of the other amino protons with N3 of the neighboring molecule in the crystal lattice (**1b**: 2.013 Å). In this way, a continuous linear polymeric structure is realized in the crystal, consisting of ···H–N(1A)H–CR=N(3)R···H–N(1A)H–CR=N(3)R···H motifs with H–N···H angles of 165.15°. Quantum chemical model calculations [B3LYP/6-31+G(d)][5] predict for the (monomeric) parent compound the planar U form with the intramolecular H bond as the structure with the lowest energy (Figure 2). With calculated barriers of rotation of only 2.7–7.4 kcal/mol the interconversion of the various structures is easily achieved under standard conditions.

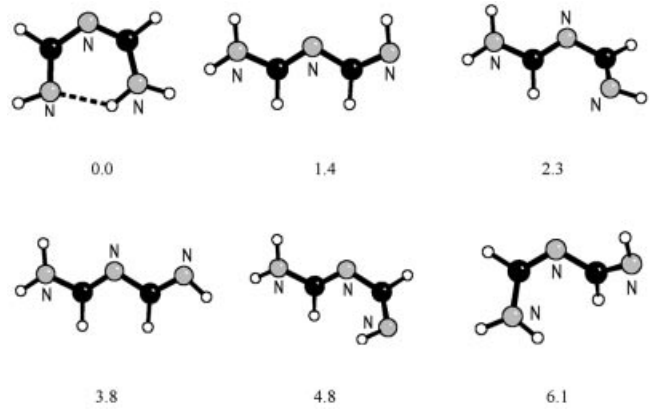


Figure 2. DFT-optimized structures for 1,3,5-triazapenta-1,3-diene isomers with relative energies [kcal/mol], B3LYP/6-31+G(d,p) (incl. ZPE).

Secondary 1,3,5-triazapenta-1,3-dienes (having a terminal NH_2 group or a tautomeric structure) are expected to give condensation reactions with carbonyl compounds like aldehydes and ketones, as it is known for simple amines and amidines, leading to 1,2-dihydro-1,3,5-triazines or their open-chain tautomers 1,3,5-triazahexa-1,3,5-trienes. To the best of our knowledge, such reactions have not yet been reported for 1,3,5-triazapenta-1,3-dienes.

Due to their amidine substructure, the 1,3,5-triazapenta-1,3-dienes do not react easily with benzaldehyde or pivalaldehyde in the presence of base or activated molecular sieves. However, catalysis and water removal by titanium tetrachloride as first reported by White and Weingarten[6] for the synthesis of aldimines and ketimines offers a successful method for condensation reaction using aldehydes and ketones as electrophiles.[7,8] According to this method, three different 1,2-dihydro-1,3,5-triazine derivatives **3a**–**c** were

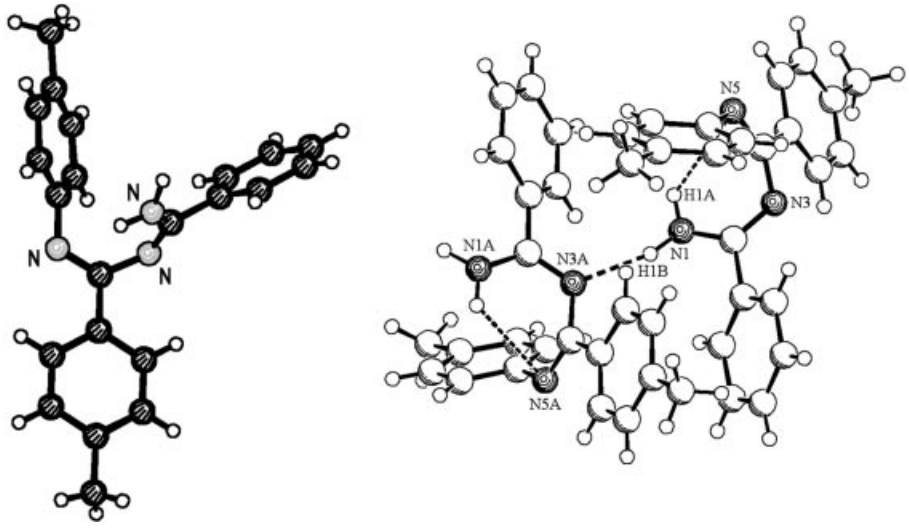


Figure 1. Molecular structure of **1b** in the solid state (left: single molecule; right: two molecules with hydrogen bonding shown). Selected structural parameters: bond lengths [Å]: N1–C2 1.288(2), C2–N3 1.411(2), N3–C4 1.294(2), C4–N5 1.350(2); bond angles [°]: N1–C2–C3 124.32(13), C2–N3–C4 118.26(11), N3–C4–N5 125.30(13); torsional angles [°]: N1–C2–N3–C4–N5 72.04, C2–N3–C4–N5 6.99.

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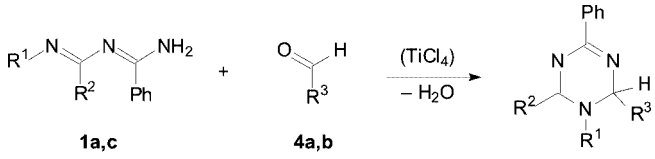
obtained using aldehydes **4** (Scheme 3), whereas the ketones 2-adamantanone (**5a**) und 9*H*-fluoren-9-one (**5b**) gave **3d**–**f** (Scheme 4). The structure of **3a** in the solid state was determined by X-ray diffraction (Figure 3).



	R^1	R^2	R^3	
3a	Ph	Ph	Ph	(26%)
3b	Ph	Ph	*t*Bu	(35%)
3c	*c*Pent	*t*Bu	*t*Bu	(23%)

Scheme 3.

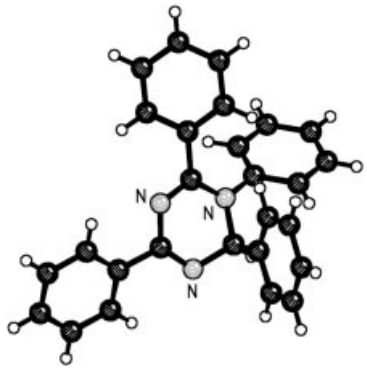
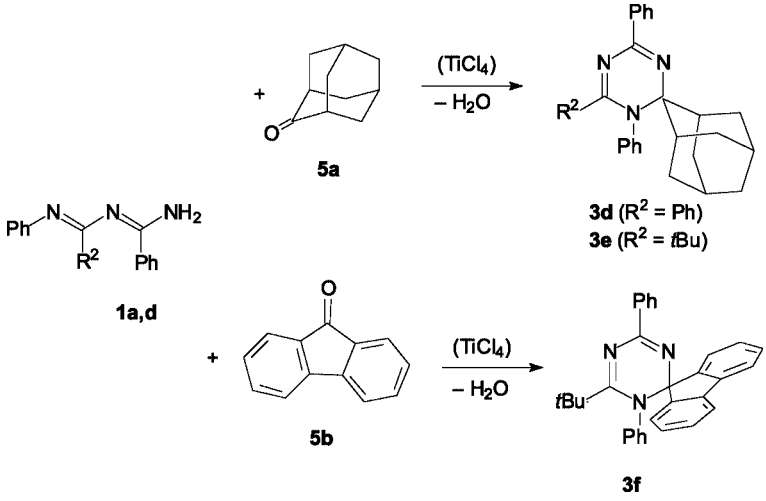


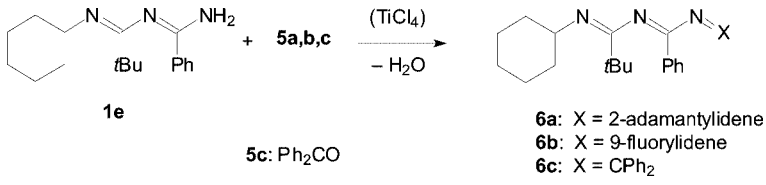
Figure 3. Molecular structure of **3a** in the solid state. Selected structural parameters: bond lengths [Å]: N1–C2 1.463(1), C2–N3 1.480(1), N3–C4 1.363(1), C4–N5 1.306(1); bond angles [°]: N1–C2–C3 110.63(8), C2–N3–C4 115.58(8), N3–C4–N5 121.79(9), C4–N5–C6 115.42(8), N5–C6–N1 126.65(9); torsional angles [°]: N1–C2–N3–C4 42.75, C2–N3–C4–N5 –19.83, N3–C4–N5–C6 –11.42, C4–N5–C6–N1 20.36, N5–C6–N1–C2 4.97.

Surprisingly, the 1,3,5-triazapenta-1,3-diene **1e**, bearing a cyclohexyl group at the nitrogen atom N1 instead of a phenyl group as in **1a**,**c**,**d** behaves quite differently in condensation reactions with **5a**,**b** and benzophenone (**5c**) yielding the 1,3,5-triazahexa-1,3,5-trienes **6a**–**c** (Scheme 5), as determined by X-ray diffraction for **6a**,**b** (Figure 4 for **6b**). There is only very little known in the literature about 1,3,5-triazahexa-1,3,5-trienes;[9] to the best of our knowledge **6a**,**b** are the first examples of this class of compounds studied by X-ray diffraction, which may be considered to consist of nitrile trimers. Both structures exhibit rather nonplanar N=C–N=C–N=C substructures as it is seen from the dihedral angles along the chain: **6a**: –94.25°, –7.60°, 121.36°; **6b**: –100.38°, –0.18°, 104.63°. Besides steric factors, electronic interactions between nitrogen lone-pairs and the adjacent C=N π-systems, which are in competition to the polyene-type π–π* conjugation, are responsible for the observed conformations and configurations.

The structural ambiguity of **3** and **6** is best explained by ring-chain tautomerism, which is typical for unsaturated hetero chains of the oligonitrile type (Scheme 6).[10,11] Obviously, the equilibrium is very sensitive with respect to small changes of the substitution pattern of the compounds involved,[12] as can be seen by comparing **3d** with **6a**, which differ only in the substituent at N1 (phenyl vs. cyclohexyl).



Scheme 4.



Scheme 5.

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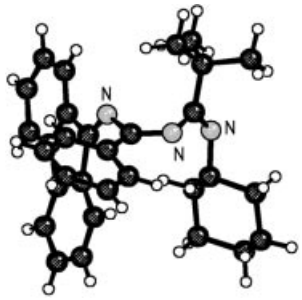
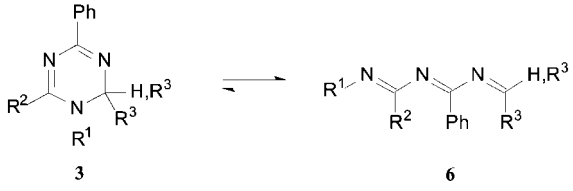


Figure 4. Molecular structure of **6b** in the solid state. Selected structural parameters: bond lengths [Å]: N1–C2 1.265(2), C2–N3 1.420(2), N3–C4 1.279(2), C4–N5 1.404(2), N5–C6 1.276(2); bond angles [°]: N1–C2–C3 125.3(2), C2–N3–C4 119.1(1), N3–C4–N5 120.8(1), C4–N5–C6 124.0(1); torsional angles [°]: N1–C2–N3–C4 –100.4, C2–N3–C4–N5 –0.2, N3–C4–N5–C6 104.6.

Thus, aromatic substituents at N1 seem to favor the cyclic tautomer, whereas the alkyl group shifts the equilibrium towards the open-chain form. Quantum chemical calculations (B3LYP/6-31G*) for the gas phase indicate for both systems (**3d** and **6a**) a preferred open-chain structure, which should be favored for cyclohexyl at N1 by 8 kcal/mol, but for phenyl only by 2.5 kcal/mol. It should be mentioned that the parent compound, 1,3,5-triazahexa-1,3,5-triene is calculated to be higher in energy by 16–19 kcal/mol compared to the corresponding cyclic tautomer. The calculated barrier for ring opening amounts to 25–30 kcal/mol. Hence, both electronic as well as packing forces may be the reason for the observed structural preferences. In the case of **6c** the ring-chain tautomerism could be monitored by ^{1}H NMR spectroscopy. At low temperature ([D$_8$]THF, –233 K) a 60:40 ratio in favor for the chain structure was detected; at higher temperature (328 K) an 80:20 ratio is present. More polar solvents (e.g. [D$_6$]acetone) favor slightly the cyclic structure (50:50 at 298 K).



Scheme 6.

Treatment of 1,3,5-triazapenta-1,3-dienes **1a**,**f** with the acid chlorides **7a**,**b** lead – by regioselective acylation at atom N5 – in 46–67% yield to the 1-oxa-3,5,7-triazahepta-1,3,5-trienes **8a**–**c** (Scheme 7). Interestingly, the acylation reaction is accompanied by a 1,5-proton shift resulting in a continuous unsaturated C=N–C=N–C=O chain. Such compounds (with tertiary amino function) have been synthesized previously in our group by nucleophilic displacement of 6-alkoxy-1-oxa-3,5-diazahexa-1,3,5-trienes using secondary amines as nucleophiles.[13] The present method has the advantage to allow the introduction of secondary amine functionalities at C6, and is more versatile with regard to the acylating agent (R^3 at C2).

The X-ray diffraction analysis of **8a** (Figure 5) resulted in a rather irregular, twisted oligonitrile backbone with dihedral angles of –69.2°, –13.8°, 120.6°, 172.9°, 7.2° and –161.2° along the O1=C2–N3=C4–N5=C6–N7 chain, probably due to crystal packing forces, which may influence the rather flexible N–C single bonds quite strongly.

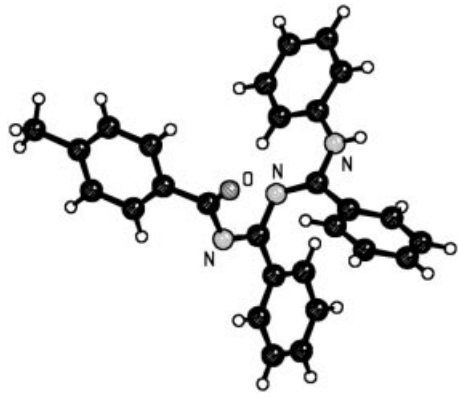
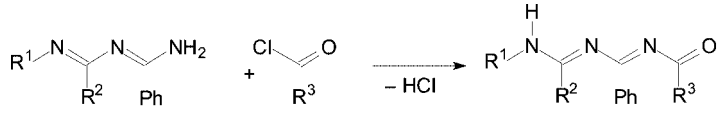


Figure 5. Molecular structure of **8a** in the solid state. Selected structural parameters: bond lengths [Å]: O1–C2 1.221(4), C2–N3 1.391(4), N3–C4 1.294(4), C4–N5 1.388(4), N5–C6 1.291(4), C6–N7 1.363(4); bond angles [°]: O1–C2–C3 121.6(3), C2–N3–C4 121.1(3), N3–C4–N5 121.2(3), C4–N5–C6 123.4(3), N5–C6–N7 121.3(3); torsional angles [°]: O1–C2–N3–C4 –69.21, C2–N3–C4–N5 –13.76, N3–C4–N5–C6 120.56, C4–N5–C6–N7 172.91.

The 1-oxa-3,5,7-triazahepta-1,4,6-triene **8d** was prepared from **1h** and 4-toluoyl chloride (**7a**) in 46% yield after deprotonation of the triazapentadiene using butyllithium (Scheme 8). According to the mass spectra we found regioselective attack at N5 producing the amide derivative **8d** without a mobile proton, which differs from **8a**–**c**.

In a similar manner as with the acyl halides **7**, the triazapentadienes **1** also reacted with the imidoyl chlorides **2e**,**f**,**g** at the terminal primary amino group to give the 1,3,5,7-tetraazahepta-1,3,5-trienes **9a**–**c** in 37–59% yield



a: R^3 = 4-Tol
b: R^3 = *t*Bu

a: R^1 = Ph, R^2 = Ph, R^3 = 4-Tol
b: R^1 = *c*Pent, R^2 = *t*Bu, R^3 = 4-Tol
c: R^1 = *c*Pent, R^2 = *t*Bu, R^3 = *t*Bu

Scheme 7.

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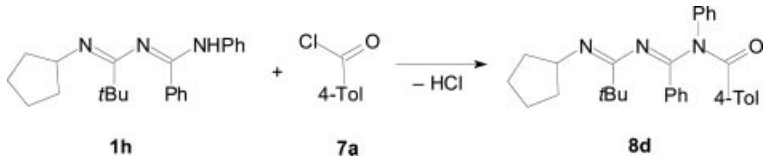
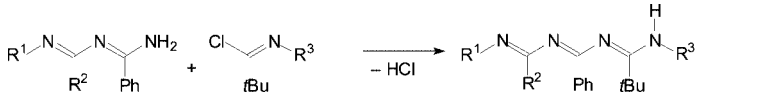


1h **7a** **8d**

Scheme 8.



1a,e,g **2e,f,g**

9a: $R^1 = R^2$ = Ph, R^3 = *c*Pentyl
9b: R^1 = *c*Hexyl, R^2 = *t*Bu, R^3 = *c*Hexyl
9c: $R^1 = R^3$ = *i*Pr, R^2 = *t*Bu

Scheme 9.

(Scheme 9). To the best of our knowledge, this class of compounds has also never been described before. As a formal nitrile trimer they present the next longer homologue in the oligonitrile family after the "dimers" 1,3,5-triazapenta-1,3-dienes **1**. From the X-ray diffraction of **9a** (Figure 6), a three-dimensional structure was obtained, showing three (*Z*)-configured C=N bonds and three C–N bonds with *gauche* conformation resulting in a helix-type arrangement of the oligonitrile main chain (torsional angles along the N=C–N=C–N=C–N=C–NH_2 chain: –1.23°, 77.56°, –7.15° 76.06°, 6.23° and 26.59°), as it is often found in oligonitrile chemistry.[4,10,11,13] We interpret these structural properties by substantial electronic interactions of the lone pair of the imino nitrogen atoms with the adjacent C=N double bonds (n–π* interaction), which seem to be more important compared to polyene-type π–π* conjugation, which would induce a planar structure. The X-ray structure of **9b** shows a more irregular structure than **9a**.

A further electrophile, which was treated successfully with 1,3,5-triazapenta-1,3-dienes **1f**,**g**, was *N*-benzoylbenzimidoyl chloride (**10**) (Scheme 10). It is easily available from dibenzoylamine by chlorination using phosphorus pentachloride.[14] As in the previous cases, we found clean and regioselective electrophilic attack at the amino groups of **1f**,**g** giving rise to 1-oxa-3,5,7,9-tetraazanona-1,3,5,7-tetraenes **11a**,**b** in 35 and 42% yield.

The X-ray diffraction structure of **11b** (Figure 7) presents a 3_1-helix (torsional angles along the chain: 40.73°, 8.93°, 65.58°, 0.67°, 63.81°, 15.00°), whereas **11a** shows a more irregular structure (torsional angles along the chain: –87.73°, 7.92°, –119.96°, 1.58°, 128.94°, –14.61°). Obviously, small differences in the steric requirement of the peripheral groups lead to different structures in the solid state,

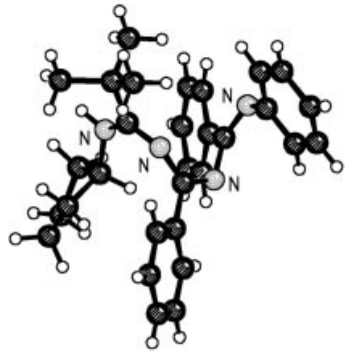
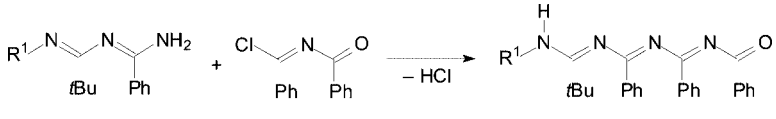


Figure 6. Molecular structure of **9a** in the solid state. Selected structural parameters: bond lengths [Å]: N1–C2 1.278(2), C2–N3 1.399(2), N3–C4 1.288(2), C4–N5 1.376(2), N5–C6 1.279(2), C6–N7 1.357(2); bond angles [°]: N1–C2–C3 126.5(1), C2–N3–C4 121.7(1), N3–C4–N5 126.0(1), C4–N5–C6 129.9(1), N5–C6–N7 126.1(1); torsional angles [°]: N1–C2–N3–C4 77.56, C2–N3–C4–N5 –7.15, N3–C4–N5–C6 76.06, C4–N5–C6–N7 6.23.

where easy conformational changes about the C–N bonds may be caused by the crystal packing forces during the crystallization.[10]

However, 1,3,5-triazapenta-1,3-dienes **1a**,**d** behave differently in reactions with **10** (Scheme 11). Here, all spectroscopic and crystallographic evidence is in favor for 1,2-dihydrotriazine structures **12a**,**b**, which are formed in 44% and 18% yield, respectively (**12b** could not be purified completely). Here again we observe the tendency of oligonitriles to form cyclic tautomers, and again the terminal group at N1 in both 1,3,5-triazapenta-1,3-dienes is a phenyl ring (vide supra), which seem once more to favor cyclic over open-chain isomers. Among the three possibilities to form a



1f,g **10**

11a: R^1 = *c*Pent
11b: R^1 = *i*Pr

Scheme 10.

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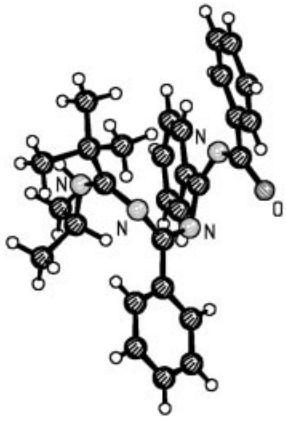


Figure 7. Molecular structure of **11b** in the solid state. Selected structural parameters: bond lengths [Å]: O1–C2 1.236(4), C2–N3 1.377(4), N3–C4 1.294(4), C4–N5 1.372(4), N5–C6 1.291(4), C6–N7 1.369(4), N7–C8 1.287(3), C8–N9 1.349; bond angles [°]: O1–C2–C3 123.5(3), C2–N3–C4 124.9(3), N3–C4–N5 126.9(3), C4–N5–C6 126.5(3), N5–C6–N7 125.8(3), C6–N7–C8 130.8(3), N7–C8–N9 125.8(3); torsional angles [°]: O1–C2–N3–C4 40.73, C2–N3–C4–N5 8.93, N3–C4–N5–C6 65.58, C4–N5–C6–N7 0.67, N5–C6–N7–C8 63.81, C6–N7–C8–N9 15.00.

cyclic six-membered system selectively, the one with a low-energy extracyclic amide function is obtained as it is shown by a X-ray structural analysis of **12a**.

1-Oxa-3,5-diazinium salts **13** present powerful electrophiles that provide access to *N*-acyloligonitriles by nucleophilic ring-opening reactions.[4,15] The 1,3,5-triazapenta-1,3-diene **1g** reacts with **13** to yield the 1-oxa-3,5,7,9,11-pentaazaundeca-1,3,5,7,9-pentaene (**14**) in 17% yield (after recrystallization from triethylamine/ethyl acetate). With its secondary terminal amino group, it is a new type of oligonitrile derivative, not accessible before by other routes (Scheme 12). There is mass-spectrometric evidence that other triazapentadienes also react with **13** by a similar condensation reaction; however, the isolation and purification of these products failed. Unambiguous structural evidence for the open-chain structure in the solid state was again obtained from X-ray analysis, although the analysis was of poor quality due to the crystal properties (Figure 8). In contrast to other oligonitriles which incorporate five double bonds, the present substitution pattern does not give rise to a helix-type structure in the solid state. A more irregular orientation of the chain is realized for **14** (torsional angles starting from C=O: 53°, 4°, 56°, 0°, 108°, –8°, 122°, –160°). Small changes in the substitution pattern again have great influence on the crystal structure obtained.

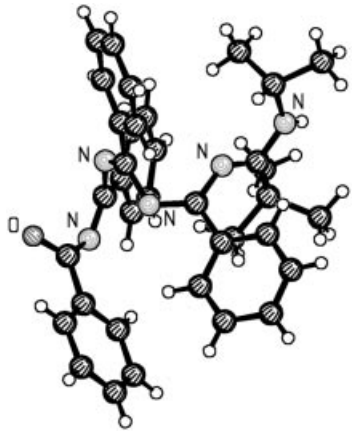
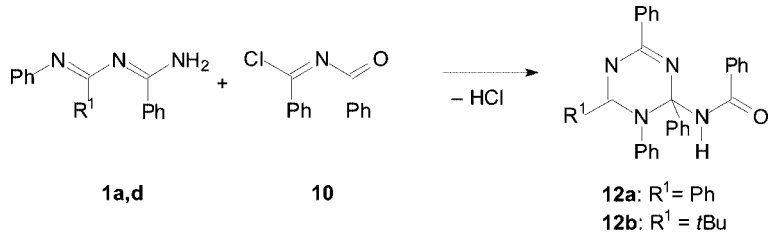


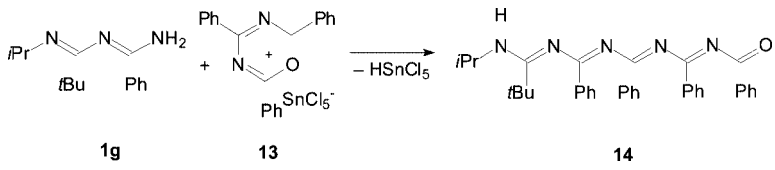
Figure 8. Molecular structure of **14** in the solid state. Bond parameters are not given because of low crystal quality.

Conclusions

1,3,5-Triazapenta-1,3-dienes **1** are valuable nucleophilic building blocks for the synthesis of various open-chain and heterocyclic compounds of the oligonitrile and 1,2-dihydrotriazine type. Simple carbonyl compounds like aldehydes **4** and ketones **5** lead to 1,2-dihydrotriazines **3** or 1,3,5-triazahexa-1,3,5-trienes **6** in dependence of the substitution pattern of **1**. Effective chain elongation was achieved by the use of the acyl chlorides **7** to give 1-oxa-3,5,7-triazahepta-1,3,5-trienes **8** or imidoyl chlorides **2** to prepare the new 1,3,5,7-tetraazahepta-1,3,5-trienes **9**. The azavinylogous electrophile *N*-benzoylbenzimidoyl chloride (**10**) made 1-oxa-3,5,7,9-tetraazanona-1,3,5,7-tetraenes **11** accessible, or, depending on the substitution pattern, their ring-tauto-



Scheme 11.



Scheme 12.

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meric compounds **12** with 1,2-dihydrotriazine structures. 1-Oxa-3,5-diazinium salt **13** is a valuable cyclic electrophile, which gave 1-oxa-3,5,7,9,11-pentaazaundeca-1,3,5,7,9-pentaene **14**, an extended oligonitrile with push-pull substitution pattern. All new compounds were completely characterized including X-ray diffraction for each type. The highly twisted three-dimensional structures are interpreted as results of competing n–π* and π–π* interactions, as indicated by DFT calculations [level: B3LYP/6-31+G(d,p)]. The ring-chain tautomerism was also studied theoretically, showing the influence of *N*-terminal substituents on the ring-chain equilibrium.

Experimental Section

Materials and Methods: IR: Nicolet 5DXC. ^{1}H NMR: Bruker WM 300 (300.13 MHz), Bruker AM 360 (360.13 MHz), Bruker AMX 400 (400.13 MHz) and Varian Unity plus (599.86 MHz), internal reference tetramethylsilane. ^{13}C NMR: Bruker WM 300 (75.47 MHz), Bruker AMX 400 (100.61 MHz) and Varian Unity 600 plus (150.85 MHz), internal reference tetramethylsilane or solvent. MS: MAT C 312, Finnigan (70 eV). ESI-MS: Quattro LC-Z, Micromass. MALDI (16–19 kV), nitrogen (337 nm, 3 ns); matrix: DTBC {2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]-malononitrile}. UV/Vis: Cary 1 Bio, Varian. CHN: Elementar Vario El III. Melting points are uncorrected. DC: SIL G/UV$_{254}$, Macherey–Nagel and silica gel F$_{254}$, Merck. Column chromatography: Silica gel 60, Merck, or Alumina N, ICN Biomedicals, Activity 1. All solvents were rigorously dried by standard methods. When necessary, the experiments were carried out with complete exclusion of moisture (argon, septum-syringe technique) in glassware, which was thoroughly dried by repeated heating under argon and subsequent evacuation.

4-Chloro-*N*-(4-methylphenyl)benzimidoyl Chloride (2c): In analogy to a literature procedure[16] from 4-chloro-*N*-(4-methylphenyl)-benzamide[17] (12.28 g, 50 mmol) and phosphorus pentachloride (10.41 g, 50 mmol) by heating to 110 °C for 1.5 h. Purification by short-path distillation. Yellow solid. Yield: 12.87 g (49 mmol, 97%). B.p. 140 °C/0.042 mbar, m.p. 70 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 6.92–6.95 (m, 2 H, $CH_{arom.}$), 7.18–7.21 (m, 2 H, $CH_{arom.}$), 7.39–7.42 (m, 2 H, *o*-$CH_{arom.}$), 8.05–8.09 (m, 2 H, *o*-$CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.0 (CH_3), 120.6 ($C_{arom.}$), 128.6 ($C_{arom.}$), 129.4 (*o*-$C_{arom.}$), 130.6 (*o*-$C_{arom.}$), 134.2 (*i*-$C_{arom.}$), 135.1 (*i*-$C_{arom.}$), 138.3 (*i*-$C_{arom.}$), 141.2 (*i*-$C_{arom.}$), 144.6 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 230 (34) [M(^{37}Cl)–Cl$^+$], 228 (100) [M(^{35}Cl)–Cl$^+$], 91 (44) [Tol$^+$], 65 (29) [$C_5H_5^+$].

***N*-Cyclopentylpivalimidoyl Chloride (2h):** In analogy to a literature procedure[18] from oxalyl chloride (7.62 g, 60 mmol), dissolved in 10 mL of dry chloroform, and *N*-cyclopentylpivalamide (10.15 g, 60 mmol),[19] dissolved in 40 mL of dry chloroform at 0 °C. After complete addition, the reaction mixture was stirred at 50 °C for 1 h. The solvent was removed in vacuo and the crude product was purified by vacuum distillation using a Vigreux column. Colourless liquid. Yield: 7.17 g (38 mmol, 64%), b.p. 60 °C/10 mbar. IR (KBr): $\tilde{\nu}$ = 2962 (vs, $CH_{aliph.}$), 2870 (s, $CH_{aliph.}$), 1688 (vs, C=N), 1477 (s), 1458 (s), 1392 (m), 1356 (m), 1342 (m), 1365 (s), 1342 (m), 1248 (m), 1205 (m), 1175 (m), 1066 (w), 1034 (m), 955 (s), 914 (s), 852 (m), 789 (s, C–Cl) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (s, 9 H, CH_3), 1.48–1.63 (m, 4 H, CH_2), 1.73–1.90 (m, 4 H, CH_2), 4.08 (quint, ^3J = 5.5 Hz, 1 H, CH) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 24.4 (CH_2), 28.4 (CH_3), 33.4 (CH_2), 43.3 [$C(CH_3)_3$], 63.4 (CH), 150.1 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 187 (1) [M$^+$], 152 (23) [M$^+$–Cl], 84 (100) [$C_5H_{10}N^+$], 57 (38) [*t*Bu$^+$]. $C_{10}H_{18}ClN$ (187.76): calcd. C 63.99 H 9.67 N 7.46; found C 63.84 H 6.69 N 7.42.

General Procedure for the Synthesis of 1,3,5-Triazapenta-1,3-dienes 1:[2] The benzamidine (3.60 g, 30 mmol) was suspended in 20–60 mL of diethyl ether. Then, an equimolar amount of the imidoyl chloride **2** was added dropwise, and the reaction mixture was stirred at room temperature for 2 h and at reflux temperature for 1 h. The precipitate formed was filtered off and treated with hot water under ultrasonication in order to remove benzamidine hydrochloride. The remaining triazapentadiene hydrochloride was collected and treated with 50 mL of 2 N sodium hydroxide solution. The resulting suspension was extracted with several portions of dichloromethane until all solid was removed. The collected dichloromethane extracts were dried with magnesium sulfate. Finally, the solvent was removed in vacuo.

1,2-Bis[4-(methylphenyl)]-4-phenyl-1,3,5-triazapenta-1,3-diene (1b): From benzamidine **10** (4.16 g, 34.6 mmol) in 20 mL of diethyl ether and **2b** (8.44 g, 34.6 mmol),[20] dissolved in 40 mL of diethyl ether. Yield: 3.38 g (10.3 mmol, 30%), yellow solid, m.p. 116–119 °C. IR (KBr): $\tilde{\nu}$ = 3433 (m, NH_2), 3292 (m, NH_2), 3070 (s, $CH_{arom.}$), 3026 (s, $CH_{arom.}$), 2916 (m, $CH_{aliph.}$), 2864 (m, $CH_{aliph.}$), 1643 (vs, C=N), 1610 (vs, C=$C_{arom.}$), 1587 (vs, C=$C_{arom.}$), 1568 (vs, C=$C_{arom.}$), 1564 (vs, C=$C_{arom.}$), 1501, (s), 1447 (s), 1394 (s), 1308 (s), 1283 (s), 1219 (s), 1177 (m), 1105 (m), 1034 (m), 1015 (m), 879 (m), 844 (m), 808 (m), 771 (s), 712 (m), 696 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 4.83 (br., 2 H, NH_2), 6.98 (m, 4 H, $H_{arom.}$), 7.23 (d, 2 H, $CH_{arom.}$), 7.43 (m, 3 H, $CH_{arom.}$), 7.67 (m, 2 H, $CH_{arom.}$), 7.93 (d, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 20.7 (CH_3), 21.3 (CH_3), 121.4, 126.9, 128.1, 128.6, 128.8, 129.2, 129.6, 131.1, 132.5 ($C_{arom.}$), 134.4 (*i*-$C_{arom.}$), 141.1 (*i*-$C_{arom.}$), 147.7 (*i*-$C_{arom.}$), 152.6 (C=N), 161.0 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 327 (72) [M$^+$], 326 (86) [M$^+$–1], 224 (67) [M$^+$–PhCN], 223 (38) [M$^+$–102], 208 (83) [TolCNTol$^+$], 118 (52) [TolCNH$^+$], 107 (100) [TolNH$_2^+$], 106 (57) [TolNH$^+$], 104 (37) [PhCNH$^+$], 103 (75) [PhCN$^+$], 91 (88) [Tol$^+$], 65 (46) [$C_5H_5^+$]. $C_{22}H_{21}N_3$ (327.42): calcd. C 80.71 H 6.46 N 12.83; found C 80.68 H 6.40 N 12.88.

X-ray Crystal Structure Analysis of 1b: [21] Formula $C_{22}H_{21}N_3$, M = 327.42, colorless crystal 0.30 × 0.25 × 0.20 mm, a = 10.229(3), b = 9.738(3), c = 18.831(6) Å, β = 96.11(3)°, V = 1865.1(10) Å^3, $\rho_{calcd.}$ = 1.166 g cm^{-3}, μ = 0.538 mm^{-1}, empirical absorption correction (0.855 ≤ T ≤ 0.900), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 3915 reflections collected (±h, +k, +l), [(sinθ)/λ] = 0.62 Å^{-1}, 3794 independent (R_{int} = 0.034) and 2824 observed reflections [$I \geq 2\sigma(I)$], 235 refined parameters, R = 0.041, wR_2 = 0.124, max. residual electron density 0.22 (–0.15) e·Å^{-3}, hydrogen atoms at N1 from difference Fourier map, other calculated and refined as riding atoms.

2-(4-Chlorophenyl)-1-(4-methylphenyl)-4-phenyl-1,3,5-triazapenta-1,3-diene (1c): From benzamidine (3.54 g, 29.5 mmol), suspended in 20 mL of diethyl ether, and **2c** (7.80 g, 29.5 mmol), dissolved in 40 mL of diethyl ether. Yield: 4.14 g (11.9 mmol, 40%), yellow solid, m.p. 131 °C. IR (KBr): $\tilde{\nu}$ = 3435 (m, NH_2), 3294 (m, NH_2), 3080 (s, $CH_{arom.}$), 3026 (m, $CH_{arom.}$), 2920 (m, $CH_{aliph.}$), 2866 (m, $CH_{aliph.}$), 2773 (m), 1645 (vs, C=N), 1612 (vs, C=$C_{arom.}$), 1585 (vs, C=$C_{arom.}$), 1574 (vs, C=$C_{arom.}$), 1564 (vs, C=$C_{arom.}$), 1502 (vs, C=$C_{arom.}$), 1485 (s), 1447 (s), 1398 (s), 1313 (s), 1302 (s), 1279 (s), 1221 (m), 1169 (m), 1105 (m), 1090 (s), 1032 (m), 1009 (s), 879 (m), 849 (s), 818 (m), 798 (s), 773 (m), 698 (s) cm^{-1}. ^{1}H NMR (300 MHz,

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[D_6]DMSO): δ = 2.25 (s, 3 H, CH_3), 6.85 (br., 2 H, NH_2), 6.98 (m, 2 H, $CH_{arom.}$), 7.05 (m, 2 H, $CH_{arom.}$), 7.42–7.54 (m, 5 H, $CH_{arom.}$), 7.83 (m, 2 H, $CH_{arom.}$), 8.00 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.3 (CH_3), 122.1, 128.0, 128.9, 129.0, 129.5, 130.4, 131.3, 132.2, 135.2 ($C_{arom.}$), 135.6 (*i*-$C_{arom.}$), 136.0 (*i*-$C_{arom.}$), 148.6 (*i*-$C_{arom.}$), 154.9 (C=N), 160.4 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 349 (35) [M(^{37}Cl)$^+$], 347 (100) [M(^{35}Cl)$^+$], 230(28) [$C_{14}H_{11}(^{37}Cl)N^+$], 228 (89) [$C_{14}H_{11}(^{35}Cl)N^+$], 194 (17), 138 (16), 104 (78) [PhCNH$^+$], 91 (74) [Tol$^+$], 77 (29) [Ph$^+$], 65 (36) [$C_5H_5^+$].$C_{21}H_{18}ClN_3$ (349.60): calcd. C 72.51 H 5.22 N 12.08; found C 72.42 H 5.14 N 11.95.

2-*tert*-Butyl-1,4-diphenyl-1,3,5-triazapenta-1,3-diene (1d): From benzamidine (3.72 g, 31.0 mmol), suspended in 60 mL of diethyl ether, and **2d** (6.06 g, 31.0 mmol)[22] as a slowly crystallizing yellow oil. Purity: ca. 95% (NMR). Yield: 1.67 g (6.0 mmol, 20%), m.p. 55–57 °C. IR (KBr): $\tilde{\nu}$ = 3454 (s, NH_2), 3313 (s, NH_2), 3176 (m, $CH_{arom.}$), 3060 (m, $CH_{arom.}$) 2964 (s, $CH_{aliph.}$), 2929 (m, $CH_{aliph.}$), 2866 (m, $CH_{aliph.}$), 1643 (vs, C=N), 1591(vs, C=C), 1583 (vs, C=C), 1560 (vs, C=C), 1477 (s), 1446 (s), 1386 (s), 1315 (m), 1242 (m), 1205 (m), 1174 (m), 1170 (m), 1072 (m), 1055 (m), 1016 (m), 877 (m), 779 (m), 750 (s), 696 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, CH_3), 4.51 (br., 2 H, NH_2), 6.85–6.94 (m, 3 H, $CH_{arom.}$), 7.13–7.18 (m, 2 H, $CH_{arom.}$), 7.27–7.40 (m, 3 H, $CH_{arom.}$), 7.47–7.50 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 28.3 (CH_3), 39.7 [*C*(CH_3)$_3$], 120.9, 122.4, 126.6, 128.4 ($C_{arom.}$), 130.5 (*i*-$C_{arom.}$), 130.5 ($C_{arom.}$), 134.6 (*i*-$C_{arom.}$), 150.3 (C=N), 173.6 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 279 (28) [M$^+$], 278 (12) [M$^+$ – 1], 222 (100) [M$^+$ – *t*Bu], 119 (24) [$C_7H_7N_2^+$], 104 (55) [PhCNH$^+$], 77 (23) [Ph$^+$], 57 (17) [*t*Bu$^+$]. $C_{18}H_{21}N_3$ (279.32). HR MS: calcd. 280.1814; found 280.1849 [$C_{18}H_{21}N_3 + H^+$].

2-*tert*-Butyl-1-cyclohexyl-4-phenyl-1,3,5-triazapenta-1,3-diene (1e): From benzamidine (6.64 g, 55.0 mmol), suspended in 60 mL of diethyl ether, and **2e** (11.10 g, 55.0 mmol).[23] Yield: 12.17 g (42.7 mmol, 78%), colorless solid, m.p 101–104 °C. IR (KBr): $\tilde{\nu}$ = 3462 (s, NH_2), 3452 (m, NH_2), 3308 (br. s, NH_2), 3161 (s, $CH_{arom.}$), 2962 (s, $CH_{aliph.}$), 2924 (s, $CH_{aliph.}$), 2853 (s, $CH_{aliph.}$), 1651 (vs, C=N), 1591 (vs, C=$C_{arom.}$), 1576 (vs, C=$C_{arom.}$), 1499 (w), 1477 (w), 1448 (s), 1377 (vs), 1365 (s), 1275 (m), 1184 (s), 1078 (m), 1042 (m), 1016 (m), 960 (m), 889 (m), 866 (m), 785 (m), 696 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 9 H, CH_3), 1.15–1.43 (m, 6 H, CH_2), 1.54–1.71 (m, 4 H, CH_2), 3.08–3.15 (m, 1 H, CH), 4.79 (br., 2 H, NH_2), 7.37 (m, 3 H, $CH_{arom.}$), 7.78–7.81 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 25.0 (CH_2), 25.8 (CH_2), 28.6 (CH_3), 33.6 (CH_2), 39.1 [*C*(CH_3)$_3$], 56.5 (CH), 126.9, 128.4, 130.4 ($C_{arom.}$), 135.2 (*i*-$C_{arom.}$), 152.6 (C=N), 167.8 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 285 (20) [M$^+$], 228 (41) [M$^+$ – *t*Bu], 146 (100) [228$^+$ – C_6H_{10}], 104 (58) [PhCNH$^+$], 84 (24) [$C_6H_{12}^+$], 57 (24) [$C_4H_9^+$]. $C_{18}H_{27}N_3$ (285.41): calcd. C 75.74 H 9.53 N 14.72; found C 75.56 H 9.16 N 14.76.

X-ray Crystal Structure Analysis of 1e: [21] Formula $C_{18}H_{27}N_3$, *M* = 285.43, colorless crystal 0.30 × 0.25 × 0.20 mm, *a* = 10.678(1), *b* = 11.675(1), *c* = 28.606(1) Å, *V* = 3566.2(5) Å^3, $\rho_{calcd.}$ = 1.063 g cm^{-3}, μ = 0.065 mm^{-1}, empirical absorption correction (0.981 ≤ *T* ≤ 0.987), *Z* = 8, orthorhombic, space group *Pbca* (No. 61), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 7651 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.66 Å^{-1}, 4200 independent (R_{int} = 0.029) and 3061 observed reflections [$I \geq 2\sigma(I)$], 193 refined parameters, *R* = 0.049, wR_2 = 0.130, max. residual electron density 0.21 (–0.18) e·Å^{-3}, hydrogen atoms at N1 from difference Fourier map, other calculated and refined as riding atoms.

2-*tert*-Butyl-1-cyclopentyl-4-phenyl-1,3,5-triazapenta-1,3-diene (1f): From benzamidine (7.25 g, 60.0 mmol), suspended in 60 mL of diethyl ether, and the imidoyl chloride **2f** (11.07 g, 60.0 mmol). Yield: 10.53 g (38.8 mmol, 65%), colorless solid, m.p. 94–97 °C. IR (KBr): $\tilde{\nu}$ = 3479 (s, NH_2), 3445 (m, NH_2), 3327 (br. s, NH_2), 3182 (s, $CH_{arom.}$), 3065 (w, $CH_{arom.}$), 2959 (vs, $CH_{aliph.}$), 2907 (s, $CH_{aliph.}$), 2866 (s, $CH_{aliph.}$), 1649 (vs, C=N), 1578 (vs, C=$C_{arom.}$), 1475 (m), 1450 (m), 1371 (s), 1273 (w), 1186 (s), 1078 (m), 1014 (m), 860 (m), 781 (s), 710 (m), 696 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 9 H, CH_3), 1.43–1.48 (m, 4 H, CH_2), 1.52–1.75 (m, 4 H, CH_2), 3.67 (m, 1 H, CH), 4.83 (br., 2 H, NH_2), 7.40–7.45 (m, 3 H, $CH_{arom.}$), 7.79–7.82 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 24.6, (CH_2), 28.5 (CH_3), 34.1 (CH_2), 39.2 [*C*(CH_3)$_3$], 58.6 (CH), 126.8 ($C_{arom.}$), 128.4 (*o*-$C_{arom.}$), 130.4 ($C_{arom.}$), 135.0 (*i*-$C_{arom.}$), 151.7 (C=N), 168.4 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 271 (28) [M$^+$], 214 (50) [M$^+$ – *t*Bu], 146 (100) [214$^+$ – C_5H_8], 104 (59) [PhCNH$^+$], 57 (28) [*t*Bu$^+$]. $C_{17}H_{25}N_3$ (271.38): calcd. C 75.23 H 9.28 N 15.48; found C 75.25 H 9.34 N 15.21.

2-*tert*-Butyl-1-isopropyl-4-phenyl-1,3,5-triazapenta-1,3-diene (1g): From benzamidine (8.29 g, 69.0 mmol), suspended in 60 mL of diethyl ether, and **2g** (11.05 g, 69 mmol).[24] Yield: 4.87 g (19.9 mmol, 29%), colorless solid, m.p. 107–109 °C. IR (KBr): $\tilde{\nu}$ = 3449 (s, NH_2), 3302 (s, NH_2), 3269 (s, NH_2), 3150 (s), 3032 (s, $CH_{arom.}$), 2961 (vs, $CH_{aliph.}$), 2926 (s, $CH_{aliph.}$), 2868 (s, $CH_{aliph.}$), 1645 (vs, C=N), 1591 (vs, C=$C_{arom.}$), 1574 (vs, C=$C_{arom.}$), 1499 (m, C=$C_{arom.}$), 1477 (m), 1454 (s), 1379 (vs), 1362 (s), 1271 (m), 1184 (s), 1134 (m), 1047 (m), 1026 (m), 945 (m), 868 (m), 785 (m), 698 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 [d, ^3J = 6.2 Hz, 6 H, CH(CH_3)$_2$], 1.22 [s, 9 H, C(CH_3)$_3$], 3.46 (sept, ^3J = 6.2 Hz, 1 H, CH), 4.66 (br., 2 H, NH_2), 7.37–7.46 (m, 3 H, $CH_{arom.}$), 7.78–7.82 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 23.6 [CH(*C*H_3)$_2$], 28.6 [C(*C*H_3)$_3$], 39.1 [*C*(CH_3)$_3$], 48.1 (CH), 126.8 ($C_{arom.}$), 128.4 (*o*-$C_{arom.}$), 130.5 ($C_{arom.}$), 135.0 (*i*-$C_{arom.}$), 151.7 (C=N), 168.1 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 245 (20) [M$^+$], 188 (66) [M$^+$ – *t*Bu], 146 (100) [$C_8H_8N_3^+$], 104 (54) [PhCNH$^+$], 84 (27), 77 (13) [Ph$^+$], 57 (27) [*t*Bu$^+$]. $C_{15}H_{23}N_3$ (245.35): calcd. C 73.43 H 9.45 N 17.13; found C 73.37 H 9.26 N 17.14.

2-*tert*-Butyl-1-cyclopentyl-4,5-diphenyl-1,3,5-triazapenta-1,3-diene (1h): From *N*-phenylbenzamidine (3.94 g, 20.0 mmol),[7] suspended in 60 mL of diethyl ether, and **2f** (3.57 g, 20.0 mmol). Yield: 6.30 g (18.1 mmol, 91%), light yellow solid, m.p 84–85 °C. IR (KBr): $\tilde{\nu}$ = 3391 (m, NH), 3061 (m, $CH_{arom.}$), 3026 (m, $CH_{arom.}$), 2957 (s, $CH_{aliph.}$), 2908 (m, $CH_{aliph.}$), 2868 (m, $CH_{aliph.}$), 1655 (vs, C=N), 1587 (s, C=$C_{arom.}$), 1553 (vs, C=$C_{arom.}$), 1502 (vs, C=$C_{arom.}$), 1483 (s), 1464 (m), 1447 (m), 1400 (m), 1340 (s), 1256 (s), 1219 (m), 1200 (m), 916 (m), 787 (m), 766 (m), 698 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02–1.08 (m, 12 H, CH_2/CH_3), 1.49 (br., 5 H, CH_2), 4.02 (br., 1 H, CH), 4.35 (br., 1 H, NH), 6.90–7.01 (m, 1 H, $CH_{arom.}$), 7.03 (m, 2 H, $CH_{arom.}$), 7.20–7.25 (m, 2 H, $CH_{arom.}$), 7.37–7.39 (m, 3 H, $CH_{arom.}$), 8.00–8.01 (m, 2 H, $CH_{arom.}$) ppm.^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 23.7 (CH_2), 28.4 (CH_3), 34.2 (CH_2), 38.3 [*C*(CH_3)$_3$], 52.8 (CH), 122.0, 122.2, 127.9, 127.9, 128.1 ($C_{arom.}$), 129.8 ($C_{arom.}$), 137.7 (*i*-$C_{arom.}$), 151.1 (*i*-$C_{arom.}$), 158.4 (C=N), 160.2 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 347 (15) [M$^+$], 290 (10) [M$^+$ – *t*Bu], 255 (66) [M$^+$ – PhNH], 222 (22) [$C_{14}H_{12}N_3^+$], 180 (100) [PhCNPh$^+$], 127 (15), 84 (15) [$C_5H_{10}N^+$], 77 (47) [Ph$^+$], 57 (20) [*t*Bu$^+$]. $C_{23}H_{29}N_3$ (347.48): calcd. C 79.50 H 8.41 N 12.09; found C 79.44 H 8.34 N 12.07.

General Procedure for the Reaction of 1,3,5-Triazapentadienes with Carbonyl Compounds:[7,25] Under argon, triazapentadiene **1** (2.50 mmol), the carbonyl compound (2.5 mmol) and triethylamine (5 mmol) were dissolved in 15 mL of dry toluene. At 0 °C, a solution of titanium tetrachloride (1.25 mmol), dissolved in 5 mL dry

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toluene, was added slowly. After stirring at room temperature for 1 d, the orange reaction mixture was filtered using a glass frit, which was half filled with Celite. Vacuum was applied after complete precipitation of the suspension. The clear, colorless filtrate was freed from the solvent in vacuo. The crude product was purified by column chromatography.

1,2,4,6-Tetraphenyl-1,2-dihydro-1,3,5-triazine (3a): From triphenyltriazapentadiene **1a** (0.60 g, 2.00 mmol)[1,2] and benzaldehyde (0.21 g, 2.00 mmol). Column chromatography (pentane/TBME, 10:1 + 2% triethylamine). Yield 0.20 g (0.52 mmol, 26%), yellow solid. R_f(DC) = 0.13 (silica gel, pentane/TBME, 10:1 + 2% triethylamine), m.p. 154–155 °C. IR (KBr): $\tilde{\nu}$ = 3088 (m, $CH_{arom.}$), 3058 (s, $CH_{arom.}$), 3026 (s, $CH_{arom.}$), 2924 (s, $CH_{arom.}$), 1605 (vs, C=N), 1597 (s, C=$C_{arom.}$), 1589 (vs, C=$C_{arom.}$), 1579 (s, C=$C_{arom.}$), 1514 (vs, C=$C_{arom.}$), 1489 (vs), 1458 (s), 1445 (s), 1410 (vs), 1337 (vs), 1327 (vs), 1282 (s), 1256 (vs), 1182 (s), 1151 (s), 1107 (s), 1069 (s), 1020 (s), 928 (s), 899 (s), 851 (s), 798 (s), 779 (s), 756 (s), 744 (vs), 710 (vs), 692 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.41 (s, 1 H, CH), 6.97–7.00 (m, 2 H, $CH_{arom.}$), 7.06–7.08 (m, 3 H, $CH_{arom.}$), 7.18–7.44 (m, 9 H, $CH_{arom.}$), 7.69–7.72 (m, 2 H, $CH_{arom.}$), 7.76–7.78 (m, 2 H, $CH_{arom.}$), 8.36–8.40 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 78.7 ($C_{quart.}$), 124.9, 125.9, 126.1, 128.1, 128.3, 128.4, 128.86, 128.92, 130.1, 130.4, 131.2 ($C_{arom.}$), 134.8 (*i*-$C_{arom.}$), 136.5 (*i*-$C_{arom.}$), 141.7 (*i*-$C_{arom.}$), 144.2 (*i*-$C_{arom.}$), 158.4 (C=N), 160.7 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 387 (84) [M^+], 310 (42) [M^+–Ph], 283 [M^+–PhCNH], 180 (100) [$PhCNPh^+$], 104 (26) [$PhCNH^+$], 77 (54) [Ph^+]. $C_{27}H_{21}N_3$ (387.47): calcd. C 83.69 H 5.46 N 10.84; found C 83.26 H 5.37 N 10.76.

X-ray Crystal Structure Analysis of 3a:[21] Formula $C_{27}H_{21}N_3$, M = 387.47, colorless crystal 0.60 × 0.60 × 0.50 mm, a = 13.237(2), b = 10.746(1), c = 14.905(2) Å, β = 110.63(1)°, V = 1984.2(4) Å^3, $\rho_{calcd.}$ = 1.297 g cm^{-3}, μ = 0.597 mm^{-1}, empirical absorption correction (0.716 ≤ T ≤ 0.755), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 8088 reflections collected (±h, –k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 4048 independent (R_{int} = 0.042) and 3819 observed reflections [$I \geq 2\sigma(I)$], 272 refined parameters, R = 0.034, wR_2 = 0.091, max. residual electron density 0.22 (–0.16) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

2-*tert*-Butyl-1,4,6-triphenyl-1,2-dihydro-1,3,5-triazine (3b): From triphenyltriazapentadiene **1a** (1.00 g, 3.00 mmol)[1,2] and pivalaldehyde (0.26 g, 3.00 mmol). Column chromatography (pentane/TBME, 10:1 + 2% triethylamine as eluent). Yield 0.39 g (1.06 mmol, 35%), yellow solid. R_f(DC) = 0.33 (silca gel, pentane/TBME, 10:1 + 2% triethylamine), m.p. 142–143 °C. IR (KBr): $\tilde{\nu}$ = 3066 (m, $CH_{arom.}$), 3028 (m, $CH_{arom.}$), 2961 (s, $CH_{aliph.}$), 2926 (m, $CH_{aliph.}$), 2868 (m, $CH_{aliph.}$), 1610 (s, C=N), 1570 (s, C=$C_{arom.}$), 1533 (vs, C=$C_{arom.}$), 1483 (s), 1477 (s), 1447 (s), 1398 (s), 1393 (s), 1325 (s), 1290 (s), 1256 (s), 1171 (m), 1105 (s), 1067 (m), 1042 (m), 1034 (s), 1018 (s), 1001 (m), 924 (m), 901 (m), 881 (m), 812 (s), 781(s), 760 (s), 733 (m), 712 (vs), 692 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (s, 9 H, CH_3), 5.10 (s, 1 H, CH), 6.98–7.46 (m, 11 H, $CH_{arom.}$), 7.90–7.92 (m, 2 H, $CH_{arom.}$), 8.38 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 26.4, (CH_3), 40.0 [$C(CH_3)_3$], 85.5 ($C_{quart.}$), 125.0, 128.0, 128.1, 128.4, 128.9, 129.8, 130.3, 131.3 ($C_{arom.}$), 135.5 (*i*-$C_{arom.}$), 136.5 (*i*-$C_{arom.}$), 146.4 (*i*-$C_{arom.}$), 158.0 (C=N), 163.1 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 310 (79) [M^+–*t*Bu], 180 (11) [$PhCNPh^+$], 104 (100) [$PhCNH^+$], 77 (53) [Ph^+]. $C_{25}H_{25}N_3$ (367.47): calcd. C 81.71 H 6.86 N 11.43; found C 81.71 H 6.78 N 11.40.

2,6-Di-*tert*-butyl-1-cyclopentyl-4-phenyl-1,2-dihydro-1,3,5-triazine (3c): From **1f** (0.98 g, 3.60 mmol) and pivalaldehyde (0.31 g, 3.60 mmol). Column chromatography (pentane/TBME, 10:1 + 2% triethylamine as eluent). Yield 0.28 g (0.82 mmol, 23%), colorless solid. R_f(DC) = 0.24 (silica gel, pentane/TBME, 10:1 + 2% triethylamine), m.p. 102–104 °C. IR (KBr): $\tilde{\nu}$ = 3057 (m, $CH_{arom.}$), 3026 (m, $CH_{arom.}$), 2999 (m, $CH_{arom.}$), 2970 (s, $CH_{aliph.}$), 2955 (s, $CH_{aliph.}$), 2872 (s, $CH_{aliph.}$), 1612 (s, C=N), 1576 (s, C=$C_{arom.}$), 1522 (vs, C=$C_{arom.}$), 1487 (m), 1458 (m), 1448 (s), 1408 (s), 1389 (m), 1367 (s), 1358 (s), 1321 (s), 1317 (s), 1298 (s), 1283 (m), 1217 (m), 1194 (m), 1159 (s), 1136 (s), 1115 (m), 1063 (m), 1024 (m), 957 (m), 910 (m), 868 (m), 802 (m), 764 (m), 696 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (s, 9 H, CH_3), 1.42–1.57 (m, 12 H, CH_3/CH_2), 1.57–1.67 (m, 2 H, CH_2), 1.69–1.75 (m, 2 H, CH_2), 1.88–1.94 (m, 1 H, CH_2), 4.14 (quint, 1 H, CH), 4.60 (s, 1 H, $CH_{quart.}$), 7.34–7.39 (m, 3 H, $CH_{arom.}$), 8.14–8.17 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.8 (CH_2), 23.3 (CH_2), 26.1 (CH_3), 30.0 (CH_3), 30.1 (CH_2), 32.3 (CH_2), 38.7 [$C(CH_3)_3$], 39.0 [$C(CH_3)_3$], 61.7 (CH), 75.1 ($C_{quart.}$), 127.8, 127.9, 129.7 ($C_{arom.}$), 137.2 (*i*-$C_{arom.}$), 160.0 (C=N), 175.5 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 282 (100) [M^+–*t*Bu], 214 (75) [282^+–C_5H_8], 104 (42) [$PhCNH^+$], 69 (27) [$C_5H_9^+$]. $C_{22}H_{33}N_3$ (339.49): calcd. C 77.83 H 9.80 N 12.38; found C 77.78 H 9.69 N 12.33.

1′,4′,6′-Triphenyl-1′,2′-dihydrospiro[adamantane-2,2′-[1,3,5]triazine] (3d): From **1a** (1.00 g, 3.00 mmol)[1,2] and 2-adamantanone (0.45 g, 3.00 mmol). Column chromatography (pentane/TBME, 20:1). Yield 0.32 g (0.70 mmol, 25%), colorless solid, R_f(DC) = 0.24 (silica gel, pentane/TBME, 20:1), m.p 190 °C. IR (KBr): $\tilde{\nu}$ = 3082 (m, $CH_{arom.}$), 3055 (m, $CH_{arom.}$), 3024 (m, $CH_{arom.}$), 2951 (s, $CH_{aliph.}$), 2935 (s, $CH_{aliph.}$), 2920 (vs, $CH_{aliph.}$), 2912 (vs, $CH_{aliph.}$), 2854 (s, $CH_{aliph.}$), 1605 (s, C=N), 1570 (s, C=$C_{arom.}$), 1514 (vs, C=$C_{arom.}$), 1485 (vs, C=$C_{arom.}$), 1445 (s), 1379 (m), 1331 (vs), 1325 (s), 1312 (s), 1296 (s), 1259 (m), 1246 (s), 1213 (m), 1171 (m), 1119 (s), 1059 (m), 1026 (m), 999 (m), 951 (m), 768 (m), 756 (m), 719 (s), 702 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (d, 4 H, CH/CH_2), 1.76 (s, 2 H, CH/CH_2), 1.94 (br., 2 H, CH/CH_2), 2.11 (s, 2 H, CH/CH_2), 2.33 (d, 2 H, CH/CH_2), 2.66 (d, 2 H, CH/CH_2), 7.03–7.09 (m, 3 H, $CH_{arom.}$), 7.19–7.22 (m, 2 H, $CH_{arom.}$), 7.27–7.34 (m, 3 H, $CH_{arom.}$), 7.44–7.46 (m, 3 H, $CH_{arom.}$), 7.82–7.85 (m, 2 H, *o*-$CH_{arom.}$), 8.41–8.44 (m, 2 H, *o*-$CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 27.1 (CH), 27.2 (CH), 33.7 (CH_2), 33.9 (CH_2), 34.0 (CH_2), 38.0 (CH_2), 77.9 ($C_{quart.}$), 127.6, 127.9, 128.0, 128.1, 130.2, 130.5, 131.0, 132.3 ($C_{arom.}$), 136.2 (*i*-$C_{arom.}$), 137.0 (*i*-$C_{arom.}$), 139.9 (*i*-$C_{arom.}$), 158.6 (C=N), 166.1 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 431 (100) [M^+], 354 (23) [M^+–Ph], 180 (95) [$PhCNPh^+$], 104 (14) [$PhCNH^+$], 77 (29) [Ph^+]. $C_{30}H_{29}N_3$ (431.55): calcd. C 83.49 H 6.77 N 9.74; found C 83.35 H 6.84 N 9.56.

6′-*tert*-Butyl-1′,4′-diphenyl-1′,2′-dihydrospiro[adamantane-2,2′-[1,3,5]triazine] (3e): From **1d** (0.84 g, 3.00 mmol) and 2-adamantanone (0.45 g, 3.00 mmol). Column chromatography (pentane/TBME, 20:1). Yield 0.36 g (0.90 mmol, 29%), colorless solid. R_f(DC) = 0.38 (silica gel, pentane/TBME, 20:1), m.p. 155 °C. IR (KBr): $\tilde{\nu}$ = 3080 (m, $CH_{arom.}$), 3065 (m, $CH_{arom.}$), 3026 (m, $CH_{arom.}$), 2980 (s, $CH_{aliph.}$), 2959 (m, $CH_{aliph.}$), 2934 (s, $CH_{aliph.}$), 2924 (vs, $CH_{aliph.}$), 2903 (vs, $CH_{aliph.}$), 2853 (s, CH_{aliph}), 1609 (vs, C=N), 1574 (s, C=$C_{arom.}$), 1529 (vs, C=$C_{arom.}$), 1487 (s), 1447 (s), 1362 (s), 1325 (s), 1296 (s), 1290 (s), 1273 (m), 1244 (m), 1173 (s), 1161 (m), 1121 (m), 1072 (m), 1026 (m), 783 (m), 759 (m), 729 (m), 704 (vs), 698 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (s, 9 H, CH_3), 1.54 (br., 6 H, CH_2), 1.72 (br., 4 H, CH_2), 1.90 (br., 2 H, CH), 2.34 (br., 2 H, CH), 6.78 (br., 1 H, $CH_{arom.}$), 7.15–7.25 (m, 3 H, $CH_{arom.}$), 7.41–7.43 (m, 4 H, $CH_{arom.}$), 8.28–8.32 (m, 2 H, *o*-$CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 27.1 (CH_2), 27.2 (CH), 29.8 (CH_3), 34.1 (CH_2), 38.0 (CH_2), 40.0 [$C(CH_3)_3$], 78.0 ($C_{quart.}$), 128.0, 130.0, 132.3 ($C_{arom.}$), 137.2

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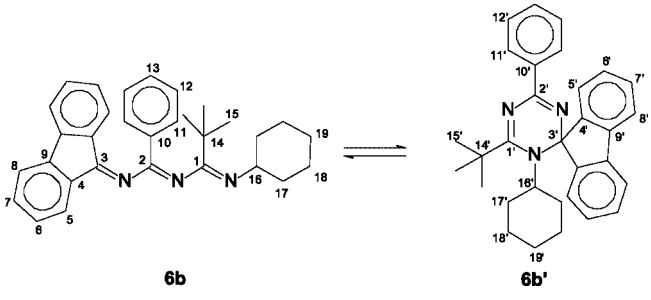
(i-$C_{arom.}$), 140.0 (i-$C_{arom.}$), 158.4 (C=N), 176.1 (C=N) ppm. MS (70 eV): m/z (%) = 411 (67) [M^+], 354 (100) [$M^+ - t$Bu], 334 (14) [$M^+ - $Ph], 263 (90) [$M^+ - $AdN], 251 (25) [$M^+ - 160$], 160 (16) [$t$BuCNPh$^+$], 104 (41) [PhCNH$^+$], 57 (14) [$tBu^+$]. $C_{28}H_{33}N_3$ (411.56): calcd. C 81.71 H 8.08 N 10.21; found C 81.71 H 7.95 N 10.16.

6′-*tert*-Butyl-1′,4′-diphenyl-1′,2′-dihydrospiro[9*H*-fluorene-9,2′-[1,3,5]triazine] (3f): From **1d** (0.84 g, 3.00 mmol), 9*H*-fluoren-9-one (0.54 g, 3.00 mmol), triethylamine (0.61 g, 6.00 mmol) and $TiCl_4$ (0.29 g, 1.50 mmol). Column chromatography (pentane/TBME, 20:1). High purity according to the NMR spectra, but small deficiencies in the C, H, N analyses. Yield 0.08 g (0.20 mmol, 6%), yellow solid. R_f(DC) = 0.13 (silica gel, pentane/TBME, 20:1), m.p. 202 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3065 (s, $CH_{arom.}$), 3055 (s, $CH_{arom.}$), 3042 (s, $CH_{arom.}$), 3024 (s, $CH_{arom.}$), 2999 (s, $CH_{aliph.}$), 2962 (s, $CH_{aliph.}$), 2926 (s, $CH_{aliph.}$), 2854 (s, $CH_{aliph.}$), 1603 (vs, C=N), 1568 (s, C=$C_{arom.}$), 1504 (vs, C=$C_{arom.}$), 1489 (vs), 1474 (vs), 1452 (s), 1394 (s), 1369 (s), 1358 (s), 1315 (vs), 1290 (s), 1250 (m), 1209 (s), 1196 (s), 1173 (m), 1119 (m), 1099 (m), 1067 (m), 1024 (m), 1005 (m), 937 (m), 914 (w), 872 (w), 845 (w), 783 (s), 770 (s), 733 (s), 712 (m), 700 (s), 696 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (s, 9 H, CH_3), 6.65 (m, 2 H, $CH_{arom.}$), 6.88–7.01 (m, 3 H, $CH_{arom.}$), 7.09–7.14 (m, 2 H, $CH_{arom.}$), 7.22–7.27 (m, 2 H, $CH_{arom.}$), 7.35–7.41 (m, 3 H, $CH_{arom.}$), 7.41–7.47 (m, 2 H, $CH_{arom.}$), 7.51–7.53 (m, 2 H, $CH_{arom.}$), 8.30–8.33 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 30.4 (CH_3), 40.8 [$C(CH_3)_3$], 86.0 ($C_{quart.}$), 119.6, 125.9, 127.5, 127.7, 127.9, 128.0, 128.2, 129.3, 130.1, 130.5 ($C_{arom.}$), 137.6 (i-$C_{arom.}$), 139.3 (i-$C_{arom.}$), 140.7 (i-$C_{arom.}$), 148.3 (i-$C_{arom.}$), 161.4 (C=N), 171.5 (C=N) ppm. MS (70 eV): m/z (%) = 441 (80) [M^+], 384 (100) [$M^+ - t$Bu], 281 (24) [$M^+ -$ PhNCtBu], 267 (40) [$C_{13}H_8$NCPh$^+$], 164 (54) [$C_{13}H_8^+$], 104 (25) [PhCNH$^+$], 57 (10) [tBu$^+$]. $C_{31}H_{27}N_3$ (441.55) HR MS: calcd. 442.2283; found 442.2303 [$C_{31}H_{27}N_3 + H^+$].

6-(Adamantan-2-ylidene)-2-*tert*-butyl-1-cyclohexyl-4-phenyl-1,3,5-triazahexa-1,3,5-triene (6a): From **1e** (0.87 g, 3.00 mmol) and 2-adamantanone (0.45 g, 3.00 mmol). Column chromatography (acetone). Yield 0.47 g (1.10 mmol, 38%), colorless solid. R_f(DC) = 0.09 (silica gel, acetone), m.p. 151–152 °C. IR (KBr): $\tilde{\nu}$ = 3080 (m, $CH_{arom.}$), 3053 (m, $CH_{arom.}$), 3026 (m, $CH_{arom.}$), 2984 (s, $CH_{aliph.}$), 2924 (vs, $CH_{aliph.}$), 2854 (vs, $CH_{aliph.}$), 1704 (m), 1666 (vs, C=N), 1609 (vs, C=$C_{arom.}$), 1576 (s, C=$C_{arom.}$), 1526 (m, C=$C_{arom.}$), 1479 (m), 1450 (s), 1385 (m), 1364 (s), 1350 (s), 1311 (m), 1288 (m), 1267 (m), 1252 (s), 1232 (m), 1153 (s), 1134 (s), 1069 (s), 1026 (m), 1018 (m), 997 (m), 951 (m), 890 (s), 864 (m), 845 (m), 829 (m), 795 (m), 777 (s), 719 (s), 698 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17–1.23 (m, 13 H, CH_3/CH_2), 1.74–1.96 (m, 18 H, $CH_{2,Ad.}$/CH_2/$CH_{Ad.}$), 2.58 (br., 2 H, $CH_{Ad.}$), 3.06 (br., 1 H, CH), 7.35 (m, 3 H, $CH_{arom.}$), 7.76–7.80 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 25.1 (CH_2), 26.1 (CH_2), 27.3 ($CH_{Ad.}$), 29.5 [$C(CH_3)_3$], 36.2 (CH_2), 38.9 ($CH_{2Ad.}$), 41.1 [$C(CH_3)_3$/$CH_{Ad.}$] 57.1 (CH), 127.7, 128.3, 130.4 ($C_{arom.}$), 135.7 (i-$C_{arom.}$), 155.7 (C=N), 168.8 (C=N), 181.5 (C=N) ppm. MS (70 eV): m/z (%) = 417 (2) [M^+], 360 (15) [$M^+ - t$Bu], 334 (11) [$M^+ - C_6H_{11}$], 278 (29) [$334 - t$Bu$^+ + 1$], 269 (100) [$M^+ - NC_{10}H_{14}$], 237 (77) [PhCN$C_{10}H_{14}^+$], 165 (18) [C_6H_{11}NCtBu$^+ - 1$], 84 (44) [$C_6H_{12}^+$]. $C_{28}H_{39}N_3$ (417.60): calcd. C 80.53 H 9.41 N 10.03; found C 80.38 H 9.35 N 9.94.

X-ray Crystal Structure Analysis of 6a:[21] Formula $C_{28}H_{39}N_3$, M = 417.62, colorless crystal 0.25 × 0.20 × 0.15 mm, a = 10.937(1), b = 11.182(2), c = 20.010(5) Å, β = 90.91(1)°, V = 2446.9(8) Å^3, $\rho_{calcd.}$ = 1.134 g cm^{-3}, μ = 0.501 mm^{-1}, empirical absorption correction (0.885 ≤ T ≤ 0.929), Z = 4, monoclinic, space group $P2_1$ (No. 4), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 5519 reflections collected ($+h$, $-k$, $\pm l$), [(sinθ)/λ] = 0.62 Å^{-1}, 5244 independent (R_{int} = 0.028) and 3360 observed reflections [$I \geq 2\sigma(I)$], 565 refined parameters, R = 0.063, wR_2 = 0.194, max. residual electron density 0.34 (–0.25) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

2-*tert*-Butyl-1-cyclohexyl-4-phenyl-6-(9*H*-fluorene-9-ylidene)-1,3,5-triazahexa-1,3,5-triene (6b) and 6′-*tert*-Butyl-1′-cyclohexyl-4′-phenyl-1′,2′-dihydrospiro[9*H*-fluorene-9,2′-[1,3,5]triazine] (6b′): From **1e** (0.86 g, 3.00 mmol) and 9*H*-fluoren-9-one (0.54 g, 3.00 mmol). Column chromatography (acetone). In solution, the compound exists in equilibrium with its cyclic tautomer (dihydrotriazine) (Scheme 13). Yield 0.31 g (0.70 mmol, 23%), yellow solid. R_f(DC) = 0.25 (silica gel, acetone), m.p. 149–151 °C. IR (KBr): $\tilde{\nu}$ = 3084 (m, $CH_{arom.}$), 3069 (m, $CH_{arom.}$), 3045 (m, $CH_{arom.}$), 2964 (s, $CH_{aliph.}$), 2927 (vs, $CH_{aliph.}$), 2854 (s, $CH_{aliph.}$), 1659 (vs, C=N), 1643 (s, C=N), 1607 (vs, C=$C_{arom.}$), 1574 (s, C=$C_{arom.}$), 1490 (m), 1477 (m), 1448 (s), 1387 (w), 1355 (w), 1315 (m), 1305 (m), 1275 (m), 1163 (m), 1155 (m), 1123 (s), 1101 (m), 1043 (m), 1018 (m), 935 (w), 924 (w), 889 (w), 852 (w), 792 (m), 773 (w), 723 (vs), 694 (s) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.35 (br., 0.7 H, CH_2), 0.97–1.07 (m, 4.2 H, CH_2), 1.16 (br., 2.8 H, CH_2); 1.26 [s, 9 H, H(15)], 1.31–1.36 (m, 2.6 H, CH_2), 1.46–1.47 (m, 0.9 H, CH_2), 1.51 [s, 2.7 H, H(15′)], 1.62 (br., 1.8 H, CH_2), 3.08 [br., 1 H, H(16)], 3.98–4.03 [m, 0.3 H, H(16′)], 7.16 (br., 2 H, $CH_{arom.}$), 7.23–7.25 (m, 1 H, $CH_{arom.}$), 7.28–7.34 (m, 1.2 H, $CH_{arom.}$), 7.34–7.40 (m, 6.1 H, $CH_{arom.}$), 7.42–7.44 (m, 1.1 H, $CH_{arom.}$), 7.47–7.52 (m, 1 H, $CH_{arom.}$), 7.54–7.56 [m, 2 H, H(5)], 7.61–7.62 [m, 0.6 H, H(5′)], 7.65–7.66 [m, 0.6 H, H(8′)], 7.88–7.90 [m, 2 H, H(11)], 8.17–8.19 [m, 0.6 H, H(11′)] ppm. ^{13}C NMR (150.84 MHz, $CDCl_3$): δ = 25.1, (CH_2), 25.7 (CH_2), 27.1 (CH_2), 29.3 [C(15)], 29.9 [C(15′)], 32.8 (CH_2), 39.4 [C(14)], 40.1 [C(14′)], 56.6 [C(16)], 59.4 [C(16′)], 83.3 [C(3′)], 119.9 [C(5′)], 120.2 [C(5)], 126.7 (C8′)) , 127.6, 127.7, 127.8, 127.9, 128.3, 128.6, 129.2 ($C_{arom.}$), 129.8 [$C_{arom.}$, C(10′)], 131.0 [$C_{arom.}$, C(10)], 132.2 [C(9)], 132.6 ($C_{arom.}$), 137.7 [C(4)], 138.8 [C(9′)], 150.8 [C(4′)], 156.3 [C(2)], 159.9 [C(2′)], 161.9 [C(3)], 168.3 [C(1)], 171.9 [C(1′)] ppm. MS (70 eV): m/z (%) = 447 (66) [M^+], 390 (36) [$M^+ - t$Bu], 308 (58) [$M^+ - t$Bu$ - C_6H_{10}$], 267 (100) [$C_{13}H_8$NCPh$^+$], 205 (35) [$C_{13}H_8$NCNH$^+$], 164 (43) [$C_{13}H_8^+$], 84 (41) [$C_6H_{12}^+$]. $C_{31}H_{33}N_3$ (447.53): calcd. C 83.18 H 7.43 N 9.39; found C 83.08 H 7.35 N 9.31.



Scheme 13. Numbering of **6b**/**6b′** for NMR assignment.

X-ray Crystal Structure Analysis of 6b:[21] Formula $C_{31}H_{33}N_3$, M = 447.60, yellow crystal 0.50 × 0.35 × 0.25 mm, a = 9.765(2), b = 10.640(2), c = 14.606(4) Å, α = 94.58(3), β = 108.17(2), γ = 113.45(1)°, V = 1286.1(5) Å^3, $\rho_{calcd.}$ = 1.156 g cm^{-3}, μ = 0.517 mm^{-1}, empirical absorption correction (0.782 ≤ T ≤ 0.882), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 5543 reflections collected ($\pm h$, $-k$, $\pm l$), [(sinθ)/λ] = 0.62 Å^{-1}, 5247 independent (R_{int} = 0.037) and 4145 observed reflections [$I \geq 2\sigma(I)$], 310 refined parameters, R = 0.057, wR_2 = 0.164,

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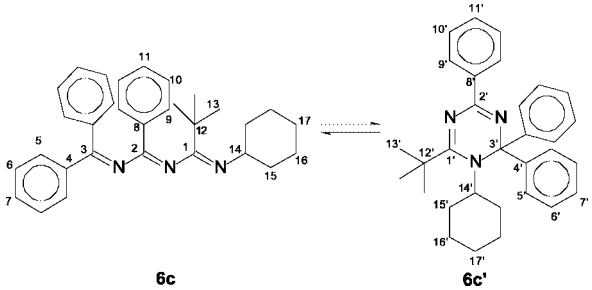
max. residual electron density 0.29 (–0.35) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

2-*tert*-Butyl-1-cyclohexyl-4,6,6-triphenyl-1,3,5-triazahexa-1,3,5-triene (6c) and 6-*tert*-Butyl-1-cyclohexyl-2,2,4-triphenyl-1,2-dihydro-1,3,5-triazine (6c′): From **1e** (0.86 g, 3.00 mmol) and benzophenone (0.55 g, 3.00 mmol). Column chromatography (acetone). Yield 0.21 g (0.50 mmol, 15%), yellow oil, slowly crystallizing to give a colorless solid. R_f(DC) = 0.13 (silica gel, acetone), m.p 77–83 °C. It was difficult to differentiate the open-chain structure from a possible cyclic form by spectroscopic means. Comparisons with the other compounds **6** indicate equilibrium of the tautomers in solution (Scheme 14). IR (KBr): ṽ = 3082 (m, $CH_{arom.}$), 3057 (m, $CH_{arom.}$), 3028 (m, $CH_{arom.}$), 2962 (s, $CH_{aliph.}$), 2930 (s, $CH_{aliph.}$), 2854 (m, $CH_{aliph.}$), 1637 (m, C=N), 1603 (s, C=$C_{arom.}$), 1570 (s, C=$C_{arom.}$), 1516 (s, C=$C_{arom.}$), 1489 (s), 1448 (s), 1400 (m), 1367 (m), 1325 (s), 1296 (m), 1263 (m), 1223 (m), 1184 (m), 1167 (m), 1115 (m), 1076 (m), 1028 (m), 995 (m), 933 (w), 895 (w), 870 (m), 779 (m), 754 (m), 746 (m), 704 (vs) cm^{-1}. ^{1}H NMR (600 MHz, [D$_8$]THF): δ = 0.84–0.91 (m, 0.8 H, CH_2), 1.01 [s, 9 H, H(13)], 1.13–1.20 (m, 5.8 H, CH_2), 1.22–1.34 (m, 3.2 H, CH_2), 1.46 [s, 3.6 H, H(13′)], 1.46 (br., 1.8 H, CH_2), 1.64 (br., 2.4 H, CH_2), 2.77 [br., 1 H, H(14)], 3.44–3.49 [m, 0.4 H, H(14′)], 7.14 (br., 1.4 H, $CH_{arom.}$) 7.34–7.38 (m, 7.6 H, $CH_{arom.}$), 7.40–7.41 (m, 1.2 H, $CH_{arom.}$), 7.43–7.44 (m, 8 H, $CH_{arom.}$), 7.77–7.78 [m, 2 H, H(9)], 8.35–8.37 [m, 0.8 H, H(9′)] ppm. ^{13}C NMR (150.84 MHz, [D$_8$]THF): δ = 27.0 (CH_2), 28.0 (CH_2), 29.2 (CH_2), 30.4 [C(13)], 31.6 [C(13′)], 35.1 (CH_2), 40.6 [C(12)], 41.1 [C(12′)], 57.5 [C(14)], 63.1 [C(14′)], 80.3 [C(3′)], 129.3, 129.4, 129.6, 129.9, 130.1, 131.0, 131.6, 132.1, 132.4 ($C_{arom.}$),138.5 [C(4′)], 138.7 [C(4)], 138.9 [C(4′)], 156.8 [C(2)], 162.3 [C(2′)], 167.8 [C(3)], 167.9 [C(1)], 179.6 [C(1′)] ppm. MS [70 eV]: *m*/*z* (%) = 449 (26) [M$^+$], 392 (19) [M$^+$ – *t*Bu], 310 (33) [392$^+$ – C_6H_{11} + 1], 269 (100) [M$^+$ – Ph_2CN], 165 (35) [$C_6H_{11}NC$*t*Bu$^+$ – 1], 104 (15) [PhCNH$^+$], 84 (34) [$C_6H_{12}^+$]. $C_{31}H_{35}N_3$ (449.61): calcd. C 82.81 H 7.85 N 9.35; found C 82.46 H 8.03 N 8.88.



Scheme 14. Numbering of **6c**/**6c′** for NMR assignment.

General Procedure for the Acylation of 1,3,5-Triazapenta-1,3-dienes: Triazapentadiene **1** (3.50 mmol), triethylamine (3.85 mmol) and a small amount of 4-(dimethylamino)pyridine (DMAP) were dissolved in 20 mL of dichloromethane. At 0 °C acid chloride **7** (3.50 mmol) was added dropwise. After stirring at room temperature for 2 h, the reaction mixture was treated with 20 mL of water. The aqueous layer was extracted twice with dichloromethane. The combined organic layers were dried with magnesium sulfate. After evaporation of the solvent, the crude product is purified by recrystallization.

2-(4-Methylphenyl)-4,6,8-triphenyl-1-oxa-3,5,7-triazahepta-1,3,5-triene (8a): From **1a**[1,2] (1.05 g, 3.50 mmol) and 4-methylbenzoyl chloride (**7a**) (0.54 g, 3.50 mmol). Byproducts were removed by extraction with 20 mL of boiling ethanol. The residue was filtered off und dried in vacuo. Yield 0.67 g (1.60 mmol, 46%), colorless solid, m.p. 198 °C. IR (KBr): ṽ = 3315 (s, NH), 3134 (w, $CH_{arom.}$), 3063 (m, $CH_{arom.}$), 3028 (w, $CH_{arom.}$), 2922 (w, $CH_{aliph.}$), 1649 (vs, C=O/C=N), 1607 (C=$C_{arom.}$), 1572 (vs, C=$C_{arom.}$), 1497 (C=$C_{arom.}$), 1441 (vs), 1354 (m), 1329 (s), 1315 (s), 1265 (s), 1177 (m), 1161 (m), 1094 (m), 1045 (m), 1016 (m), 914 (m), 899 (m), 847 (m), 758 (s), 690 (s) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.37 (s, 3 H, CH_3), 7.08–7.12 (m, 1 H, $CH_{arom.}$), 7.17–7.30 (m, 6 H, $CH_{arom.}$), 7.40–7.69 (m, 6 H, $CH_{arom.}$), 7.60–7.69 (m, 4 H, $CH_{arom.}$), 7.95 (m, 2 H, $CH_{arom.}$), 9.98 (s, 1 H, NH) ppm. ^{13}C NMR (75.47 MHz, [D$_6$]DMSO): δ = 22.0 (CH_3), 121.7, 124.6, 128.7, 128.8, 129.1, 129.3, 129.5, 131.5, 132.1, 133.0 ($C_{arom.}$), 134.5 (*i*-$C_{arom.}$), 136.8 (*i*-$C_{arom.}$), 140.5 (*i*-$C_{arom.}$), 142.8 (*i*-$C_{arom.}$), 157.1 (C=N), 162.3 (C=N), 179.4 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 417 (44) [M$^+$], 194 (38) [$(Ph)_2CN_2^+$], 180 (85) [PhCNPh$^+$], 119 (100) [TolCO$^+$], 105 (77) [PhCNH_2^+], 91 (25) [Tol$^+$], 77 (43) [Ph$^+$]. $C_{28}H_{23}N_3O$ (417.49): calcd. C 80.55 H 5.55 N 10.06; found C 80.03 H 5.58 N 10.01.

X-ray Crystal Structure Analysis of 8a:[21] Formula $C_{28}H_{23}N_3O$, *M* = 417.49, colorless crystal 0.40 × 0.03 × 0.03 mm, *a* = 24.460(1), *b* = 19.060(1), *c* = 9.791(1) Å, *V* = 4564.6(6) Å^3, $\rho_{calcd.}$ = 1.215 g cm^{-3}, μ = 0.075 mm^{-1}, empirical absorption correction (0.971 ≤ *T* ≤ 0.998), *Z* = 8, orthorhombic, space group *Aba*2 (No. 41), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 12490 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.59 Å^{-1}, 3923 independent (R_{int} = 0.113) and 2568 observed reflections [$I \geq 2\sigma(I)$], 295 refined parameters, *R* = 0.062, wR_2 = 0.135, max. residual electron density 0.14 (–0.19) e·Å^{-3}, hydrogen atom at N6 from difference Fourier map, other calculated and refined as riding atoms.

6-*tert*-Butyl-7-cyclopentyl-2-(4-methylphenyl)-4-phenyl-1-oxa-3,5,7-triazahepta-1,3,5-triene (8b): From **1f** (950 mg, 3.5 mmol) and 4-methylbenzoyl chloride (**7a**) (541 mg, 3.5 mmol). Purification by dissolving the crude product in a small amount of hot ethyl acetate and precipitation using *n*-heptane. Yield 0.92 g (2.40 mmol, 67%), colorless solid, m.p 116 °C. IR (KBr): ṽ = 3348 (s, NH), 3329 (s, NH), 3082 (m, $CH_{arom.}$), 3053 (m, $CH_{arom.}$), 3028 (m, $CH_{arom.}$), 2959 (s, $CH_{aliph.}$), 2914 (m, $CH_{aliph.}$), 2870 (m, $CH_{aliph.}$), 1664 (vs, C=N/C=O), 1624 (vs, C=$C_{arom.}$), 1603 (vs, C=$C_{arom.}$), 1572 (s), 1558 (s), 1522 (vs), 1447 (s), 1400 (s), 1381 (s), 1360 (m), 1313 (s), 1271 (s), 1222 (s), 1211 (s), 1177 (s), 1096 (m), 1067 (m), 1049 (m), 1018 (m), 912 (m), 847 (m), 770 (s), 698 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12–1.18 [m, 11 H, $C(CH_3)_3/CH_2$], 1.40–1.64 (m, 6 H, CH_2), 2.37 (s, 3 H, CH_3), 3.90 (m, 1 H, CH), 7.15–7.18 (m, 2 H, $CH_{arom.}$), 7.41–7.46 (m, 3 H, $CH_{arom.}$), 7.94–7.96 (m, 2 H, $CH_{arom.}$), 8.05–8.07 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.5 (CH_3), 23.8 (CH_2), 28.5 [$C(CH_3)_3$], 33.4 (CH_2), 38.9 [$C(CH)_3$]$_3$, 53.5 (CH), 128.0, 128.5, 128.6, 129.4, 130.8, 133.1 ($C_{arom.}$), 136.5 (*i*-$C_{arom.}$), 141.9 (*i*-$C_{arom.}$), 158.4 (C=N), 162.3 (C=N), 179.7 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 389 (9) [M$^+$], 306 (18) [M$^+$ – C_5H_9N], 270 (22) [M$^+$ – TolCO], 223 (11) [PhCNCTolOH$^+$], 187 (13), 167 (24) [C_5H_9NHC*t*BuN$^+$], 151 (33) [C_5H_8NC*t*Bu$^+$], 119 (100) [TolCO$^+$], 104 (51) [PhCNH$^+$], 91 (25) [Tol$^+$], 84 (49) [$C_5H_9NH^+$], 57 (21) [*t*Bu$^+$]. $C_{25}H_{31}N_3O$ (389.51): calcd. C 77.08 H 8.02 N 10.79; found C 76.93 H 7.79 N 10.68.

2,6-Di-*tert*-butyl-7-cyclopentyl-4-phenyl-1-oxa-3,5,7-triazahepta-1,3,5-triene (8c): From **1f** (0.95 g, 3.50 mmol) and pivaloyl chloride (**7b**) (0.42 g, 3.50 mmol). Recrystallization from ethyl acetate/*n*-heptane. Yield 0.70 g (1.97 mmol, 56%), colorless solid, m.p 144 °C. IR (KBr): ṽ = 3369 (s, NH), 3065 (m, $CH_{arom.}$), 3028 (m, $CH_{arom.}$), 2961 (s, $CH_{aliph.}$), 2914 (m, $CH_{aliph.}$), 2868 (m, $CH_{aliph.}$), 1668 (vs, C=N/C=O), 1639 (s, C=$C_{arom.}$), 1591 (vs, C=$C_{arom.}$), 1566 (vs, C=$C_{arom.}$), 1535 (s), 1477 (s), 1448 (m), 1389 (m), 1362 (m), 1335 (s), 1275 (m), 1220 (m), 1146 (s), 1084 (m), 1072 (m), 1028 (m), 906 (m), 860 (m), 827 (m), 775 (m), 740 (m), 692 (m) cm^{-1}. ^{1}H NMR

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(360 MHz, [D$_6$]DMSO, 373 K): δ = 1.23 (s, 9 H, CH_3), 1.26 (s, 9 H, CH_3), 1.40 (br., 4 H, CH_2), 1.64 (br., 4 H, CH_2), 3.99 (m, 1 H, CH), 6.32 (br., 1 H, NH), 7.42–7.47 (m, 3 H, $CH_{arom.}$), 7.86–7.88 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (90.56 MHz, [D$_6$]DMSO, 373 K): δ = 23.9 (CH_2), 27.7 (CH_3), 28.6 (CH_3), 32.7 (CH_2), 39.3 [$C(CH_3)_3$], 41.2 [$C(CH_3)_3$], 53.6 (CH), 128.1 ($C_{arom.}$), 128.3 (o-$C_{arom.}$), 130.6 ($C_{arom.}$), 137.4 (i-$C_{arom.}$), 156.7 (C=N), 162.5 (C=N), 192.0 (C=O) ppm. MS (70 eV): m/z (%) = 355 (1) [M$^+$], 298 (100) [M$^+$ – tBu], 127 (13), 84 (15), [$C_5H_9NH^+$], 57 (25) [tBu$^+$]. $C_{22}H_{33}N_3O$ (355.49): calcd. C 74.32 H 9.36 N 11.82; found C 74.13 H 9.25 N 11.85.

6-*tert*-Butyl-7-cyclopentyl-2-(4-methylphenyl)-3,4-diphenyl-1-oxa-3,5,7-triazahepta-1,4,6-triene (8d): Compound **1h** (0.52 g, 1.50 mmol) was dissolved in 20 mL of dry THF. At –78 °C nBuLi (1.9 mL, 3.00 mmol; 1.6 M solution in n-hexane) was added dropwise. After stirring at 0 °C for 15 min, the yellow reaction mixture was cooled to –78 °C and treated with 4-methylbenzoyl chloride (**7a**) (0.46 g, 3.00 mmol). Then, the reaction mixture was warmed in an ice bath and stirred at room temperature overnight. The solution was washed with 20 mL of water. The aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried with magnesium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography [silica gel, petroleum ether/TMBE, 2:1). Yield 322 mg (0.70 mmol, 46%), light yellow solid. R_f(DC) = 0.15 (silica gel, petroleum ether/TBME, 2:2), m.p. 99–108 °C. IR (KBr): $\tilde{\nu}$ = 3074 (w, $CH_{arom.}$), 2939 (vs, $CH_{aliph.}$), 2852 (m, $CH_{aliph.}$), 1657 (vs, C=O), 1635 (vs, C=N), 1483 (s, C=$C_{arom.}$), 1439 (m), 1400 (w), 1330 (vs), 1296 (m), 1261 (s), 1174 (m), 1104 (m), 1043 (w), 1009 (w), 835 (m), 748 (s) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.87 [s, 9 H, C(CH_3)$_3$], 1.91–1.24 [m, 1 H, CH_2], 1.35–1.41 (m, 1 H, CH_2), 1.44–1.52 (m, 3 H, CH_2), 1.59–1.62 (m, 1 H, CH_2), 1.69–1.73 (m, 2 H, CH_2), 2.28 (s, 3 H, CH_3), 3.60 (quint, ^3J = 6.0 Hz, 1 H, CH), 7.01–7.02 (m, 2 H, $CH_{arom.}$), 7.19–7.22 (m, 3 H, $CH_{arom.}$), 7.28–7.33 (m, 5 H, $CH_{arom.}$), 7.46–7.47 (m, 2 H, $CH_{arom.}$), 7.62–7.63 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (150.84 MHz, $CDCl_3$): δ = 21.4 (CH_3), 24.4 (CH_2), 24.7 (CH_2), 28.6 [C(CH_3)$_3$], 33.3 (CH_2), 33.5 (CH_2), 38.9 [$C(CH_3)_3$], 59.4 (CH), 127.1, 127.9, 128.3, 128.5, 128.7, 129.1, 129.3, 130.5, 132.8 ($C_{arom.}$), 135.4, 141.6, 142.0 (i-$C_{arom.}$), 152.5 (C=N), 164.6 (C=N), 172.0 (C=O) ppm. MS (70 eV): m/z (%) = 465 (4) [M$^+$], 255 (54) [$C_5H_9NC$$t$BuNCPh$^+$], 211 (12) [PhNCTolH$^+$], 180 (83) [PhCNPh$^+$], 152 (34) [$C_5H_9NC$$tBu^+$], 119 (100) [TolCO$^+$], 84 (60) [$C_5H_9NH^+$], 57 (48) [$tBu^+$]. $C_{31}H_{35}N_3O$ (465.61): calcd. C 79.96 H 7.58 N 9.02; found C 80.02 H 7.44 N 9.04.

6-*tert*-Butyl-7-cyclopentyl-1,3,5-triphenyl-1,3,5,7-tetraazahepta-1,3,5-triene (9a): Under argon at 0 °C, **1a** (1090 mg, 3.60 mmol),[1,2] dissolved in 15 mL of dry THF, was added dropwise to a solution of KOtBu (0.41 g, 3.60 mmol) in 5 mL of dry THF. After stirring for 5 min with ice cooling, the reaction mixture was stirred at room temperature for 15 min. After cooling to 0 °C, the reaction mixture was treated with a solution of **2f** (676 mg, 3.6 mmol) in THF (10 mL) and then stirred at room temperature overnight. The reaction mixture was diluted by adding 30 mL of dichloromethane and then washed with water. The layers were separated, and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were dried with magnesium sulfate, and the solvent was evaporated. The residue was purified by column chromatography (silica gel, pentane/TBME, 10:1 + 2% triethylamine). Yield 0.93 g (2.10 mmol, 57%), yellow solid. R_f(DC) = 0.13 (silica gel, pentane/TBME, 10:1 + 2% triethylamine), m.p. 153 °C. IR (KBr): $\tilde{\nu}$ = 3389 (s, NH), 3074 (m, $CH_{arom.}$), 3061 (m, $CH_{arom.}$), 3026 (m, $CH_{arom.}$), 2964 (s, $CH_{aliph.}$), 2931 (s, CH_{aliph}), 2866 (s, $CH_{aliph.}$), 1657 (vs, C=N), 1597 (vs, C=$C_{arom.}$), 1585 (vs, C=$C_{arom.}$), 1568 (vs, C=$C_{arom.}$), 1518 (s), 1489 (s), 1481 (s), 1448 (s), 1396 (m), 1364 (m), 1327 (s), 1313 (s), 1286 (s), 1269 (s), 1227 (m), 1207 (s), 1167 (m), 1045 (m), 1026 (m), 926 (m), 905 (m), 895 (m), 831 (m), 819 (m), 770 (m), 746 (m), 696 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.63–0.71 (m, 2 H, CH_2), 0.84 (s, 9 H, CH_3), 0.94–1.15 (m, 4 H, CH_2), 1.21–1.30 (m, 2 H, CH_2), 3.11 (br., 1 H, CH), 4.33 (br., 1 H, NH), 6.83–6.88 (m, 1 H, $CH_{arom.}$), 7.12–7.17 (m, 2 H, $CH_{arom.}$), 7.23–7.34 (m, 8 H, $CH_{arom.}$), 7.72–7.74 (m, 2 H, CH_{arom}), 7.87 (br., 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 23.3 (CH_2), 28.4 (CH_3), 33.3 (CH_2), 38.5 (CCH_3), 53.3 (CH), 122.7, 123.1, 127.7, 127.9, 128.0, 128.2, 129.3, 130.2 ($C_{arom.}$), 136.6 (i-$C_{arom.}$), 137.6 (i-$C_{arom.}$), 149.7 (C=N), 158.1 (C=N), 159.4 (C=N) ppm. MS (70 eV): m/z (%) = 450 (64) [M$^+$], 283 (17) [$Ph_3C_2N_2^+$], 255 (10) [PhCNCtBuNC$_5$H$_9^+$], 180 (100) [PhCNPh$^+$], 151 (10) [tBuCNC$_5$H$_8^+$], 104 (139) [PhCNH$^+$], 77 (39) [Ph$^+$]. $C_{30}H_{34}N_4$ (450.60): calcd. C 79.96 H 7.60 N 12.43; found C 79.73 H 7.20 N 12.39.

X-ray Crystal Structure Analysis of 9a:[21] Formula $C_{30}H_{34}N_4$, M = 450.61, light yellow crystal 0.45 × 0.30 × 0.20 mm, a = 10.460(1), b = 17.769(1), c = 14.653(1) Å, β = 109.91(1)°, V = 2560.7(3) Å^3, $\rho_{calcd.}$ = 1.169 g cm^{-3}, μ = 0.069 mm^{-1}, empirical absorption correction (0.969 ≤ T ≤ 0.993), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 16420 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 6113 independent (R_{int} = 0.045) and 4389 observed reflections [$I \geq 2\sigma(I)$], 313 refined parameters, R = 0.052, wR_2 = 0.133, max. residual electron density 0.23 (–0.18) e·Å^{-3}, hydrogen atom at N1 from difference Fourier map, other calculated and refined as riding atoms.

General Procedure for the Synthesis of 1,3,5,7-Tetraazahepta-1,3,5,7-trienes 9b,c: Under argon a solution of **1** (2.00 mmol) in 8 mL of anhydrous diethyl ether was treated with imidoyl chloride **2** (1.1 equiv.). After stirring at room temperature for 1 h, the reaction mixture was heated to reflux for 2 h. The resulting colorless precipitate was filtered off and added to 20 mL of a 2 N sodium hydroxide solution. The suspension was extracted with three portions of 30 mL of dichloromethane. After drying of the combined organic extracts, the solvent was removed in vacuo. Purification was achieved by column chromatography (neutral alumina, Alox N, activity 1, pentane/TBME, 2:1 + 4% triethylamine).

2,6-Di-*tert*-butyl-1,7-dicyclohexyl-4-phenyl-1,3,5,7-tetraazahepta-1,3,5-triene (9b): From **1e** (0.71 g, 2.50 mmol) and **2e** (0.56 g).[23] Colorless oil, slowly crystallizing. Yield 0.67 g (1.50 mmol, 59%). R_f(DC) = 0.24 (silica gel, pentane/TBME, 2:1 + 4% triethylamine), m.p. 83–85 °C. IR (KBr): $\tilde{\nu}$ = 3431 (s, NH), 3283 (s, NH), 3063 (m, $CH_{arom.}$) 3026 (m, $CH_{arom.}$), 2966 (s, $CH_{aliph.}$), 2930 (vs, $CH_{aliph.}$), 2854 (s, $CH_{aliph.}$), 1647 (vs, C=N), 1614 (vs, C=$C_{arom.}$), 1589 (vs, C=$C_{arom.}$), 1574 (vs), 1516 (vs), 1479 (s), 1448 (s), 1398 (m), 1389 (m), 1367 (s), 1329 (s), 1315 (s), 1275 (s), 1258 (m), 1227 (m), 1161 (s), 1136 (s), 1090 (m), 1063 (m), 1026 (m), 966 (m), 941 (m), 889 (m), 864 (m), 802 (m), 770 (m), 723 (m), 694 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (br., 7 H, CH_2), 1.22 (m, 20 H, CH_3/CH_2), 1.48–1.57 (m, 11 H, CH_2), 3.23 (br., 2 H, CH), 7.32–7.36 (m, 3 H, $CH_{arom.}$), 7.65–7.69 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 25.0 (CH_2), 25.5 (CH_2), 27.5 (CH_2), 29.0 (CH_3), 33.1 (CH_2), 33.9 (CH_2), 38.8 [C(CH_3)$_3$], 48.0 (CH), 127.5 ($C_{arom.}$), 128.1 (o-$C_{arom.}$), 129.4 ($C_{arom.}$), 137.6 (i-$C_{arom.}$), 155.9 (C=N), 177.4 (C=N) ppm. MS (70 eV): m/z (%) = 450 (14) [M$^+$], 393 (97) [M$^+$ – tBu], 311 (32) [M$^+$ – tBu – C_6H_{10}], 269 (89) [M$^+$ – (HNCtBuNC$_6$H$_{11}$)], 173 (31) [PhCNCtBuH$^+$], 163 (22), 129 (18), 110 (51), 104 (28) [PhCNH$^+$], 84 (100) [$C_6H_{12}^+$], 57 (68) [tBu$^+$]. HR MS: calcd. 451.3801; found 451.3019 [$C_{29}H_{46}N_4$ + H$^+$]. $C_{29}H_{46}N_4$ (450.67): calcd. C 77.28, H 10.29, N 12.43; found C 76.51, H 10.34, N 11.71.

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X-ray Crystal Structure Analysis of 9b:[21] Formula $C_{29}H_{46}N_4 \cdot 1/3H_3OCl$, M = 486.86, colorless crystal 0.40×0.30×0.03 mm, a = 17.157(1), c = 52.859(2) Å, V = 13475.1(12) Å^3, $\rho_{calcd.}$ = 1.040 g cm^{-3}, μ = 0.736 mm^{-1}, empirical absorption correction (0.757 ≤ T ≤ 0.978), Z = 18, trigonal, space group $R\bar{3}$ (No. 148), λ = 1.54178 Å, T = 223 K, ω and φ scans, 8577 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 5044 independent (R_{int} = 0.038) and 2785 observed reflections [$I \geq 2\sigma(I)$], 317 refined parameters, R = 0.055, wR_2 = 0.148, max. residual electron density 0.23 (–0.226) e·Å^{-3}, hydrogen atom at N7 from difference Fourier map, other calculated and refined as riding atoms.

2,6-Di-*tert*-butyl-1,7-diisopropyl-4-phenyl-1,3,5,7-tetraazahepta-1,3,5-triene (9c): From **1g** (0.42 g, 1.72 mmol) and **2g** (0.31 g, 1.72 mmol).[24] Yield 0.24 mg (0.60 mmol, 37%), colorless solid. R_f(DC) = 0.14 (silica gel, pentane/TBME, 2:1 + 4% triethylamine), m.p. 75–81 °C. IR (KBr): $\tilde{\nu}$ = 3425 (s, NH), 3339 (s, NH), 3062 (m, $CH_{arom.}$), 2962 (vs, $CH_{aliph.}$), 2924 (vs, $CH_{aliph.}$), 2866 (s, $CH_{aliph.}$), 2856 (s, $CH_{aliph.}$), 1632 (vs, C=N), 1616 (s, C=$C_{arom.}$), 1589 (vs, C=$C_{arom.}$), 1566 (vs), 1526 (s), 1479 (m), 1456 (s), 1389 (m), 1356 (m), 1321 (s), 1263 (m), 1227 (m), 1213 (m), 1166 (m), 1157 (m), 1109 (m), 1057 (m), 1026 (m), 960 (m), 925 (m), 802 (m), 773 (m), 696 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79 [d, ^3J = 6.2 Hz, 12 H, CH(CH_3)$_2$], 1.15 [s, 18 H, C(CH_3)$_3$], 3.51 (sept, ^3J = 6.2 Hz, 2 H, CH), 4.07 (br., 1 H, NH), 7.26–7.30 (m, 3 H, $CH_{arom.}$), 7.60–7.63 (m, 2 H, *o*-$CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 23.6 [CH(CH_3)$_2$], 29.0 [C(CH_3)$_3$], 38.8 [C(CH_3)$_3$], 46.2 [CH(CH_3)$_2$], 127.8, 128.1, 129.5 ($C_{arom.}$), 137.3 (*i*-$C_{arom.}$), 155.9 (C=N), 164.7 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 370 (14) [M$^+$], 313 (100) [MH$^+$ – *t*Bu – *iPr*], 271 (16) [*iPr*NC*t*BuNCPhNH$_2^+$], 229 (52) [M$^+$ – *iPr*NC*t*BuNH], 173 (12), 127 (61) [*iPr*NHC*t*Bu$^+$], 84 (64) [*iPr*NCNH$^+$], 57 (50) [*t*Bu$^+$]. HR MS: calcd. 371.3175; found 371.3151 [$C_{23}H_{38}N_4$ + H$^+$]. $C_{23}H_{38}N_4$ (370.55): calcd. C 74.55 H 10.34 N 15.12; found C 72.47 H 10.49 N 14.67.

General Procedure for the Reaction of 1 with *N*-Benzoylbenzimidoyl Chloride (10): Potassium *tert*-butoxide (0.18 g, 1.60 mmol), dissolved in 7 mL of dry THF, was treated dropwise at 0 °C with **1** (1.60 mmol), dissolved in 15 mL of dry THF. After 5 min, the mixture was warmed to room temperature and stirred for another 10 min. After cooling to 0 °C, the reaction mixture was treated dropwise with *N*-benzoylbenzimidoyl chloride (**10**) (0.39 g, 1.60 mmol),[14] dissolved in 5 mL of dry THF. After stirring at room temperature for 1 d, the light yellow, slightly turbid reaction mixture was diluted with 30 mL of dichloromethane and washed with 30 mL of water. After separation of the layers, the aqueous layer was extracted twice with dichloromethane. The combined organic layers were dried with magnesium sulfate, and the solvent was removed in vacuo. The crude material was purified by column chromatography (silica gel) or recrystallized.

8-*tert*-Butyl-9-cyclopentyl-2,4,6-triphenyl-1-oxa-3,5,7,9-tetraazanonatetra-1,3,5,7-ene (11a): From 0.43 g (3.80 mmol) of KO*t*Bu, 1.03 g (3.80 mmol) of **1f** and 0.93 g (3.80 mmol) **10**.[14] Column chromatography (silica gel, eluent pentane/TBME, 2:1 + 4% triethylamine). Yield 0.62 g (1.60 mmol, 42%), colorless solid. R_f(DC) = 0.24 (silica gel, pentane/TBME, 2:1 + 4% triethylamine), m.p. 141 – 143 °C IR (KBr): $\tilde{\nu}$ = 3335 (s, NH), 3082 (m, $CH_{arom.}$), 3061 (m, $CH_{arom.}$), 3026 (m, $CH_{arom.}$), 2966 (m, $CH_{aliph.}$), 2953 (m, $CH_{aliph.}$), 2872 (m, $CH_{aliph.}$), 1655 (C=O), 1643 (C=N), 1614 (vs, C=$C_{arom.}$), 1585 (vs, C=$C_{arom.}$), 1549 (vs, C=$C_{arom.}$), 1537 (vs, C=$C_{arom.}$), 1489 (m), 1448 (s), 1400 (m), 1348 (s), 1313 (s), 1258 (s), 1175 (8m), 1069 (m), 1040 (m), 1026 (m), 1016 (m), 914 (m), 852 (m), 804 (m), 795 (m), 779 (m), 744 (m), 712 (m), 694 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92–1.05 (m, 11 H, CH_3/CH_2), 1.29–1.52 (m, 6 H, CH_2), 3.45 (br., 1 H, CH), 7.26–7.51 (m, 9 H, $CH_{arom.}$), 7.69–7.72 (m, 2 H, $CH_{arom.}$), 7.92 (m, 2 H, $CH_{arom.}$), 8.10 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 23.6 (CH_2), 28.4 (CH_3), 33.4 (CH_2), 38.7 (CCH_3), 53.6 (CH), 127.9, 128.0, 128.3, 128.8, 129.4, 130.5, 130.7 ($C_{arom.}$), 131.8 (*i*-$C_{arom.}$), 134.8 (*i*-$C_{arom.}$), 134.9 (*i*-$C_{arom.}$), 136.2 (*i*-$C_{arom.}$), 159.8 (C=N), 160.7 (C=N), 163.4 (C=N), 179.9 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 478 (22) [M$^+$], 312 (22) [$Ph_3C_3N_2O^+$], 289 (14), 255 (12) [C_5H_9NC*t*BuNCPh$^+$], 180 (26) [PhCNPh$^+$], 146 (32), 105 (100) [PhCO$^+$], 84 (56) [$C_5H_9NH^+$]. $C_{31}H_{34}N_4O$ (478.61): calcd. C 77.79 H 7.16 N 11.71, found C 77.64 H 7.02 N 11.73.

X-ray Crystal Structure Analysis of 11a:[21] Formula $C_{31}H_{34}N_4O$, M = 478.62, colorless crystal 0.35×0.35×0.30 mm, a = 11.591(2), b = 19.038(2), c = 12.397(2) Å, β = 100.71(1)°, V = 2688.0(7) Å^3, $\rho_{calcd.}$ = 1.183 g cm^{-3}, μ = 0.566 mm^{-1}, empirical absorption correction (0.826 ≤ T ≤ 0.849), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 5796 reflections collected (±h, –k, –l), [(sinθ)/λ] = 0.62 Å^{-1}, 5477 independent (R_{int} = 0.020) and 4208 observed reflections [$I \geq 2\sigma(I)$], 332 refined parameters, R = 0.058, wR_2 = 0.188, max. residual electron density 0.49 (–0.45) e·Å^{-3}, hydrogen atom at N1 from difference Fourier map, other calculated and refined as riding atoms.

8-*tert*-Butyl-9-isopropyl-2,4,6-triphenyl-1-oxa-3,5,7,9-tetraazanonatetra-1,3,5,7-tetraene (11b): From 0.45 g (4.00 mmol) of KO*t*Bu, 0.98 g (4.00 mmol) of **1g** and 1.10 g (4.00 mmol) of **10**.[14] Recrystallization from triethylamine/ethyl acetate. Yield 0.63 g (1.38 mmol, 35%), yellow crystals, m.p. 171–172 °C. IR (KBr): $\tilde{\nu}$ = 3312 cm^{-1} (s, NH), 3082 (m, $CH_{arom.}$), 3065 (m, $CH_{arom.}$), 3026 (m, $CH_{arom.}$), 2978 (m, $CH_{aliph.}$), 2970 (m, $CH_{aliph.}$), 2932 (m, $CH_{aliph.}$), 2870 (m, $CH_{aliph.}$), 1647 (vs, C=O), 1626 (vs, C=N), 1601 (vs, C=$C_{arom.}$), 1572 (vs, C=$C_{arom.}$), 1549 (vs, C=$C_{arom.}$), 1528 (vs), 1489 (s), 1450 (s), 1398 (s), 1369 (s), 1339 (s), 1315 (s), 1269 (s), 1211 (s), 1173 (s), 1134 (m), 1065 (m), 1042 (m), 1024 (m), 1018 (m), 893 (m), 806 (s), 777 (m), 704 (s), 694 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.76 (d, ^3J = 6.4 Hz, 6 H, CH(CH_3)$_2$), 1.00 [s, 9 H, C(CH_3)$_3$], 3.31 (br., 1 H, CH), 4.56 (br., 1 H, NH), 7.25–7.50 (m, 9 H, $CH_{arom.}$), 7.70–7.73 (m, 2 H, *o*-$CH_{arom.}$), 7.91–7.94 (m, 2 H, *o*-$CH_{arom.}$), 8.50–8.10 (m, 2 H, *o*-$CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.8 [CH(CH_3)$_2$], 28.4 [C(CH_3)$_3$], 38.8 [C(CH_3)$_3$], 43.7 [CH(CH_3)$_2$], 127.9, 128.0, 128.3, 128.8, 129.4, 130.5, 130.6, 131.8 ($C_{arom.}$), 134.9 (*i*-$C_{arom.}$), 135.0 (*i*-$C_{arom.}$), 136.3 (*i*-$C_{arom.}$), 159.6 (C=N), 160.2 (C=N), 163.4 (C=N), 180.0 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 452 (26) [M$^+$], 312 (20) [$Ph_3C_3N_2OH^+$], 229 (13) [*iPr*NC*t*BuNCPh$^+$], 180 (32) [PhCNPh$^+$], 125 (21) [*iPr*NC*t*Bu$^+$ – 1], 105 (100) [PhCO$^+$], 84 (36) [*iPr*NHCN$^+$], 77 (24) [Ph$^+$], 57 (39) [*t*Bu$^+$]. $C_{29}H_{32}N_4O$ (452.57): calcd. C 76.96 H 7.13 N 12.38; found C 76.86 H 7.24 N 12.33.

X-ray Crystal Structure Analysis of 11b:[21] Formula $C_{29}H_{32}N_4O$, M = 452.59, yellow crystal 0.45×0.15×0.10 mm, a = 11.548(1), b = 15.869(1), c = 28.183(1) Å, V = 5164.7(6) Å^3, $\rho_{calcd.}$ = 1.164 g cm^{-3}, μ = 0.561 mm^{-1}, empirical absorption correction (0.786 ≤ T ≤ 0.946), Z = 8, orthorhombic, space group *Pbca* (No. 61), λ = 1.54178 Å, T = 198 K, ω and φ scans, 7076 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 4142 independent (R_{int} = 0.033) and 2290 observed reflections [$I \geq 2\sigma(I)$], 317 refined parameters, R = 0.059, wR_2 = 0.187, max. residual electron density 0.29 (–0.21) e·Å^{-3}, hydrogen atom at N9 from difference Fourier map, other calculated and refined as riding atoms.

***N*-(1,2,4,6-Tetraphenyl-1,2-dihydro-1,3,5-triazin-2-yl)benzamide (12a):** From **1a**[1,2] (0.48 g, 1.6 mmol) and **10** (0.39 g, 1.6 mmol).[14] Column chromatography (silica gel, pentane/TBME, 2:1 + 5% triethylamine). Yield 0.36 g (0.71 mmol, 44%), colorless solid. R_f(DC)

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= 0.20 (silica gel, pentane/TBME, 2:1 + 5% triethylamine), m.p. 173–177 °C. IR (KBr): $\tilde{\nu}$ = 3449 (m, NH), 3061 (m, $CH_{arom.}$), 3028 (m, $CH_{arom.}$), 1684 (s, C=O), 1670 (m, C=N), 1614 (s), 1605 (m, $C{=}C_{arom.}$), 1574 (s, $C{=}C_{arom.}$), 1560 (m), 1522 (vs, $C{=}C_{arom.}$), 1489 (vs), 1466 (vs), 1445 (s), 1394 (m), 1371 (m), 1337 (vs), 1269 (s), 1258 (s), 1175 (m), 1136 (m), 1065 (m), 1030 (m), 768 (m), 737 (m) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 6.66 (br., 1 H, NH), 6.96 (br., 3 H, $CH_{arom.}$), 7.13–7.24 (m, 4 H, $CH_{arom.}$), 7.30–7.36 (m, 6 H, $CH_{arom.}$), 7.40–7.44 (m, 4 H, $CH_{arom.}$), 7.58–7.59 (m, 2 H, $CH_{arom.}$), 7.63–7.65 (m, 4 H, $CH_{arom.}$), 8.39–8.42 (m, 2 H, $CH_{arom.}$) ppm. ^{13}C NMR (150.84 MHz, $CDCl_3$): δ = 86.9 ($C_{quart.}$), 126.8, 126.8, 127.3, 127.7, 127.9, 128.2, 128.4, 128.5, 128.6, 129.8, 130.5, 131.6 ($C_{arom.}$), 135.2 (*i*-$C_{arom.}$), 135.8 (*i*-$C_{arom.}$), 137.0 (*i*-$C_{arom.}$), 140.2 (*i*-$C_{arom.}$), 142.3 (*i*-$C_{arom.}$), 159.4 (C=N), 162.4 (C=N), 167.2 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 506 (4) [M^+], 309 (56) [$Ph_3C_3N_3^+$], 180 (32) [$PhCNPh^+$], 121 (35) [$PhCN_2H_4^+$], 105 (100) [$PhCO^+$], 77 (69) [Ph^+]. $C_{34}H_{26}N_4O$ (506.58): calcd. C 80.61, H 5.17, N 11.06; found C 80.41, H 4.88, N 11.04.

X-ray Crystal Structure Analysis of 12a:[21] Formula $C_{34}H_{26}N_4O$, M = 506.59, colorless crystal 0.50 × 0.30 × 0.30 mm, a = 21.918(3), b = 11.400(4), c = 24.069(5) Å, β = 115.75(1)°, V = 5417(2) $Å^3$, $\rho_{calcd.}$ = 1.242 $g cm^{-3}$, μ = 0.601 mm^{-1}, empirical absorption correction (0.753 ≤ T ≤ 0.840), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 5677 reflections collected (±h, +k, +l), [(sinθ)/λ] = 0.62 $Å^{-1}$, 5535 independent (R_{int} = 0.023) and 4808 observed reflections [$I \geq 2\sigma(I)$], 356 refined parameters, R = 0.041, wR_2 = 0.120, max. residual electron density 0.21 (–0.17) e·$Å^{-3}$, hydrogen atom at N7 from difference Fourier map, other calculated and refined as riding atoms.

***N*-(6-*tert*-Butyl-1,2,4-triphenyl-1,2-dihydro-1,3,5-triazin-2-yl)benzamide (12b):** From **1d** (0.84 g, 3.00 mmol), KO*t*Bu (0.34 g, 3.00 mmol) and **10**[14] (0.73 g, 3.00 mmol) following the procedure for **12a**. Column chromatography (silica gel, pentane/TBME, 2:1 + 5% triethylamine) did not lead to completely pure product. Yield 0.27 mg (0.60 mmol, 18%), colorless solid. R_f(DC) = 0.21 (silica gel, pentane/TBME, 5:1 + 1% triethylamine), m.p. 96–101 °C. IR (KBr): $\tilde{\nu}$ = 3312 (m, NH), 3061 (m, $CH_{arom.}$), 3034 (m, $CH_{arom.}$), 2966 (m, $CH_{aliph.}$), 2870 (m, $CH_{aliph.}$), 1734 (m, C=O), 1661 (vs, C=N), 1597 (s, $C{=}C_{arom.}$), 1518 (vs, $C{=}C_{arom.}$), 1491 (s), 1439 (s), 1394 (m), 1366 (s), 1319 (s), 1273 (m), 1242 (m), 1171 (m), 1074 (w), 1030 (m), 929 (w), 905 (w), 754 (m), 717 (m), 698 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.31 (s, 9 H, CH_3), 7.08–7.66 (m, $CH_{arom.}$), 8.35–8.36 (m, *o*-$CH_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 27.6 (CH_3), 39.5 [$C(CH_3)_3$], 87.7 ($C_{quart.}$), 126.8–131.7 ($C_{arom.}$), 135.1 (*i*-$C_{arom.}$), 136.6 (*i*-$C_{arom.}$), 137.7 (*i*-$C_{arom.}$), 160.7 (C=N), 166.6 (C=O), 176.5 (C=N) ppm. MS (70 eV): *m*/*z* (%) = 486 (4) [M^+], 429 (13) [$M^+ - t$Bu], 180 (69) [$PhCNPh^+$], 105 (100) [$PhCO^+$], 77 (46) [Ph^+].

10-*tert*-Butyl-11-isopropyl-2,4,6,8-tetraphenyl-1-oxa-3,5,7,9,11-pentaazaundeca-1,3,5,7,9-pentaene (14): Under argon, KO*t*Bu (0.22 g, 2.00 mmol), dissolved in 10 mL of dry THF, was treated dropwise at 0 °C with **1g** (0.49 g, 2.00 mmol), dissolved in 10 mL of THF. After stirring at 0 °C for 5 min and at room temperature for another 10 min, 2,4,6-triphenyl-1,3,5-oxadiazinium pentachlorostannate (**13**)[26] (1.21 g, 2.00 mmol) was added. Within a few minutes of stirring at 0 °C, the yellow solid dissolved, yielding a yellow, slightly turbid reaction mixture. After stirring at 0 °C for 1 h, stirring was continued at room temperature for another 1 h. Then the reaction mixture was poured into 20 mL of a 2 N sodium hydroxide solution. After three extractions with dichloromethane, the combined organic extracts were dried with magnesium sulfate. The solvent was removed in vacuo and the crude product was recrystallized form triethylamine/ethyl acetate. Yield 0.14 g (0.30 mmol, 12%), light yellow solid, m.p. 166–168 °C. IR (KBr): $\tilde{\nu}$ = 3339 (s, NH), 3084 (m, $CH_{arom.}$), 3065 (m, $CH_{arom.}$), 3028 (m, $CH_{arom.}$), 2970 (s, $CH_{aliph.}$), 2934 (m, $CH_{aliph.}$), 2872 (m, $CH_{aliph.}$),1641 (vs, C=O), 1595 (vs, C=N), 1582 (vs, $C{=}C_{arom.}$), 1568 (vs, $C{=}C_{arom.}$), 1489 (vs, $C{=}C_{arom.}$), 1404 (s), 1377 (s), 1362 (s), 1317 (s), 1267 (vs), 1225 (s), 1173 (s), 1134 (m), 1101 (m), 1067 (m), 1055 (s), 1024 (s), 929 (m), 918 (m), 858 (m), 839 (s), 810 (m), 775 (s), 723 (m), 706 (s), 692 (s) cm^{-1}. ^1H NMR (600 MHz, [D_6]DMSO): δ = 0.40 [d, ^3J = 6.6 Hz, 6 H, $CH(CH_3)_2$], 0.75 [s, 9 H, $C(CH_3)_3$], 2.92 (sept, ^3J = 6.6 Hz, 1 H, CH), 4.37 (br., 1 H, NH), 7.03–7.04 (m, 2 H, $CH_{arom.}$), 7.08–7.10 (m, 2 H, $CH_{arom.}$), 7.23–7.35 (m, 3 H, $CH_{arom.}$), 7.38–7.41 (m, 2 H, $CH_{arom.}$), 7.44–7.50 (m, 4 H, $CH_{arom.}$), 7.54–7.56 (m, 1 H, $CH_{arom.}$), 7.76–7.77 (m, 2 H, *o*-$CH_{arom.}$), 7.97–7.98 (m, 2 H, *o*-$CH_{arom.}$), 8.13–8.15 (m, 2 H, *o*-$CH_{arom.}$) ppm. ^{13}C NMR (150.84 MHz, [D_6]DMSO): δ = 21.5 [$CH(CH_3)_2$], 27.8 [$C(CH_3)_3$], 38.7 [$C(CH_3)_3$], 43.2 [$CH(CH_3)_2$], 127.5, 127.9, 128.1, 128.2, 128.2, 128.4, 128.6, 128.8, 130.4, 130.8, 131.5, 132.0 ($C_{arom.}$), 135.0, 135.2, 135.4 136.2 (*i*-$C_{arom.}$), 158.6 (C=N), 160.8 (C=N), 161.1 (C=N), 163.0 (C=N), 176.8 (C=O) ppm. MS (70 eV): *m*/*z* (%) = 555 (5) [M^+], 450 (9) [M^+–PhCO], 309 (45) [$(PhCN)_3^+$], 274 (31), 284 (22), 230 (12) [$iPrNHCtBuNCPh^+$], 180 (16) [$PhNCPh^+$], 127 (22) [$iPrNHCtBu^+$], 105 (100) [$PhCO^+$], 103 (93) [$PhCN^+$], 84 (43) [$iPrNHCN^+$], 77 (46) [Ph^+], 57 (22) [tBu^+]. $C_{36}H_{37}N_5O$ (555.69): calcd. C 77.81 H 6.71 N 12.60; found C 77.85 H 6.55 N 12.59.

X-ray Crystal Structure Analysis of 14: Formula $C_{36}H_{37}N_5O$, M = 555.71, colorless crystal 0.30 × 0.05 × 0.03 mm, a = 15.432(1), b = 11.652(1), c = 17.553(1) Å, β = 96.77(1)°, V = 3134.3(4) $Å^3$, $\rho_{calcd.}$ = 1.178 $g cm^{-3}$, μ = 0.565 mm^{-1}, empirical absorption correction (0.849 ≤ T ≤ 0.983), Z = 4, monoclinic, space group $P2_1/c$ (No. 45), λ = 1.54178 Å, T = 223 K, ω and φ scans, 18488 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.54 $Å^{-1}$, 3983 independent (R_{int} = 0.127) and 1987 observed reflections [$I \geq 2\sigma(I)$], 385 refined parameters, R = 0.126, wR_2 = 0.412, max. residual electron density 0.29 (–0.27) e·$Å^{-3}$, hydrogen atom at N1 from difference Fourier map, other calculated and refined as riding atoms, due to size and quality of the crystals this analysis is of very poor quality and was only done to confirm the connectivity and conformation of the molecule.

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