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1,3,5-Triazapentadienes by Nucleophilic Addition to 1,3- and 1,4-Dinitriles—Sterically Constrained Examples by Incorporation into Cyclic Peripheries: Synthesis, Aggregation, and Photophysical Properties

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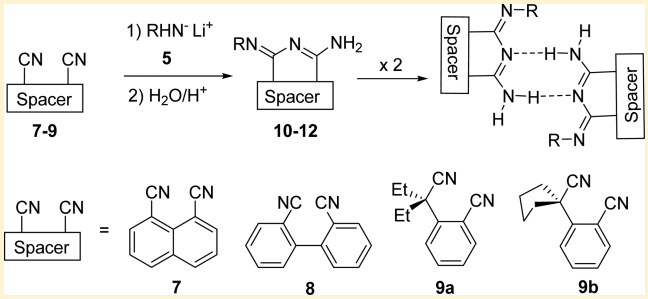
Supporting Information

ABSTRACT: 1,3,5-Triazapentadienes usually show U- or twisted S-shaped conformations along the N−C−N−C−N skeleton due to dominating n/π^* interactions. If, however, the 1,3,5-triazapentadiene unit is part of a ring, its W conformation might be restricted to the plane. Here, we describe the synthesis of 13 new 1,3,5-triazapentadienes **10**−**12**, which are sterically restrained by incorporation into six- or seven-membered ring systems, by addition of a lithiated primary amine or hydrazine **5** to a dinitrile **7**, **8**, or **9** with the two cyano groups in 1,3 or 1,4 distance. These novel compounds show very strong tendency for aggregation due to hydrogen bonding, especially to form homodimers as seen from X-ray data in the solid state. Additional hydrogen bonding generates also linear chains in the crystal. Several of the new compounds show fluorescence in solution. Quantum chemical DFT calculations were used for evaluation of the dimerization energies and for interpretation of the photophysical properties.



INTRODUCTION

The class of 1,3,5-triazapentadienes **3** has been known for more than a century.[1] These interesting nitrogen-containing conjugated ligands with an open chain backbone like **3** tend to prefer U- and twisted S-shaped conformations, the latter due to n/π^* interactions dominating over π /π^* interactions, which would lead to planar structures.[2] They are easily prepared by reaction of imidoyl chlorides **1** and amidines **2** (Scheme 1).[1a] However, in a conformationally restricted W-shaped 1,3,5-triazapentadiene chain, the two n-orbitals at the imino nitrogen atoms point into the same direction, giving rise to new possibilities for hydrogen bonding and coordination chemistry. In this context, 1,3,5-triazapentadienes **6**,**6**′, where the three central C−N−C atoms are part of a five-membered dihydropyrrole ring, have been studied previously in our group (Scheme 2).[3,4] These derivatives **6**,**6**′ were synthesized by reaction of lithiated amines **5** with tetramethylsuccinonitrile **4**.[5,6] The deprotonated amine attacks one of the two electrophilic nitrile carbon atoms forming an amidinate center that itself reacts with the second nitrile group. Thus, a 1,3,5-triazapentadiene anion is formed which is protonated during aqueous workup. If a primary amine is used, in some cases an additional proton shift leads to the tautomer **6**′ shown in Scheme 2. A 3-fold application of this cyclization procedure to give fused tricyclic heterosystems was recently published by Gorman et al.[7]

The aim of the present work is the synthesis of 1,3,5-triazapentadienes with novel cyclic and aromatic backbones by integrating the N−C−N− motive of the triazapentadiene into a six- or seven-membered ring (Scheme 2). These hitherto unknown compounds are new types of heterocycles, which promise to be efficient donors and acceptors for hydrogen bonding, e.g., to form very stable homodimers as well as to function as excellent ligands for the coordination of metal ions,[8] which in the case of Zn(II) complexes are useful catalysts for lactide polymerization and in the case of Pd(II) complexes for cross-coupling reactions.

In this study we show that this goal can be achieved by reaction of deprotonated amines **5** with dinitriles having the two nitrile groups in a 1,3- or 1,4-distance of an alicyclic or aromatic backbone. Thus, novel functionalized bi- and tricyclic heterocycles incorporating 1,3,5-triazapentadiene moieties became accessible. As alicyclic and aromatic dinitriles, three different starting materials have been studied: 1,8-dicyanonaphthalene **7**, 2,2′-dicyanobiphenyl **8**, and substituted *o*-cyanomethylbenzonitriles **9a**,**b** as dinitriles with a mixed aliphatic−aromatic (benzylic) spacer. An additional aspect of this study is the first use of lithiated hydrazines **5** as nucleophiles in the reaction with dicyano compounds. This method allows

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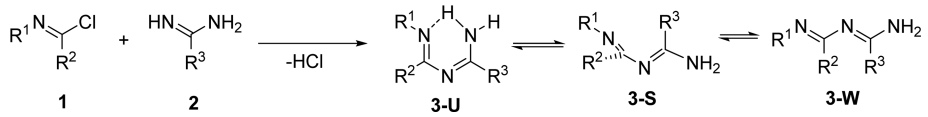
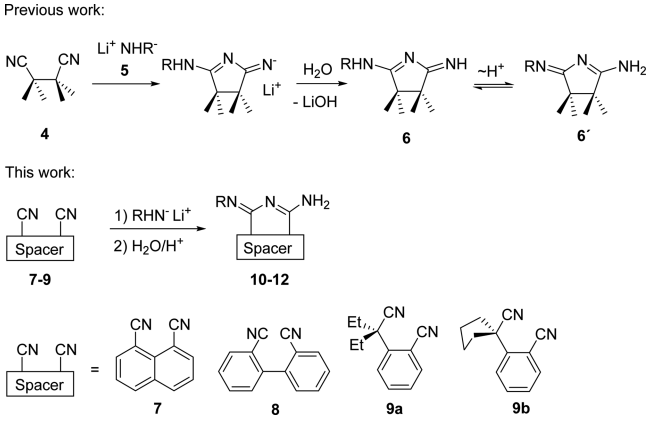
Scheme 1. 1,3,5-Triazapentadienes from Imidoylchlorides and Amidines[1a]



Scheme 2. 1,3,5-Triazapentadienes, Incorporated into Five-,[3,4] **Six-, and Seven-Membered Rings**[a]



[a]Spacer = 1,3- or 1,4-aromatic (**7**,**8**) and 1,3-benzylic-aromatic (**9**) backbones.

introduction of a further nitrogen atom into the unsaturated chain.

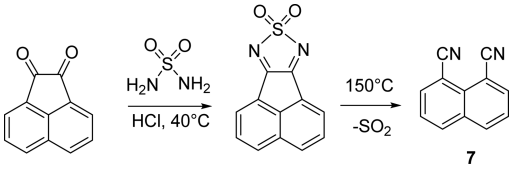
Depending on the chemical distance of the two cyano groups either six-membered heterocycles (from **7** and **9**) or seven-membered systems (from **8**) were expected.[9] The tricyclic triazapentadienes obtained from **7** and **8** consist only of sp^2-hybridized carbon and nitrogen atoms and contain formally 12 π electrons, indicating anti-Hückel-aromatic behavior. In contrast, the ring-forming reactions starting from **9b** lead to the generation of novel bicyclic spiro systems.

In addition to the synthesis, the structural properties in the solid state with special regard to hydrogen bonding as well as the UV−vis spectroscopic properties of these conjugated heterosystems were the subject of this investigation. Quantum chemical DFT calculations were used for evaluation of dimerization energies and for interpretation of the UV−vis spectra.

RESULTS AND DISCUSSION

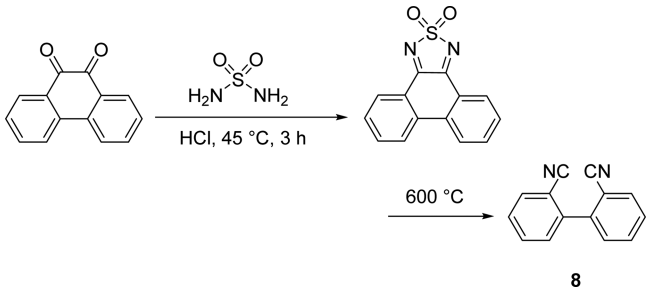
Starting Materials. 1,8-Dicyanonaphthalene **7** was prepared from acenaphthenequinone and sulfamide ($H_2N-SO_2-NH_2$) to form acenaphtho[1,2-*c*-]-1,2,5-thiadiazol-1,2-dioxide and subsequent thermolysis at 150 °C according to literature procedures (Scheme 3).[10−12]

Scheme 3. Synthesis of Dinitrile 7 from Acenaphthenequinone



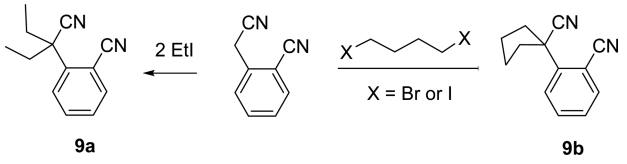
2,2′-Dicyanobiphenyl **8** was prepared in a partially optimized way from 9,10-phenanthrenequinone and sulfamide and subsequent pyrolysis at 600 °C (Scheme 4).[10] In the solid state the two aryl moieties of **8** are twisted by 135.5° with respect to the central single bond (for X-ray details see SI).

Scheme 4. Synthesis of Dinitrile 8 from 9,10-Phenanthrenequinone



Compounds **9a,b** were prepared in 69% and 83% yield by double alkylation at the benzylic position of 2-cyanomethylbenzonitrile using either ethyl iodide or 1,4-dibromobutane in the presence of aqueous sodium hydroxide solution following a literature phase transfer procedure (see Scheme 5).[13] It should

Scheme 5. Synthesis of the Dinitriles 9a,b from 2-Cyanomethylbenzonitrile



be mentioned that 2-cyanomethylbenzonitrile itself does not yield 1,3,5-triazapentadienes upon treatment with lithiated amines but is, as expected, deprotonated at the benzylic position.

Cyclization Reaction of Dinitriles 7−9. Treatment of lithiated primary amines or hydrazines **5** with dinitriles **7**, **8**, and **9** first at −78 °C and then at room temperature or 45 °C in dry THF allowed the synthesis of various 1,3,5-triazapentadienes and 1,2,4,6-tetrazahexatrienes (1-amino-1,3,5-triazapentadienes) with a naphthalene backbone **10a−e** (Type A), a biphenyl backbone (**11a−c** Type B), or an isoquinoline backbone (**12a−e** Type C or D) after aqueous workup. Scheme 6 and Table 1 summarize the products **10−12** obtained from the dinitriles **7−9** and various nucleophiles **5**.

Thus, from dinitrile **7** (1,8-dicyanonaphthalene) and lithiated primary aromatic amines three triazapentadienes **10a−c** of the benz[*de*]isoquinoline (or 2-azaphenylene) type A were synthesized in satisfactory yield; nonaromatic amines only reacted in traces with this dinitrile. Lithiated *N*,*N*-dimethyl hydrazine and *N*-methyl-*N*-phenyl hydrazine reacted with 1,8-

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Scheme 6. Overview over the Synthetic Routes Leading to 1,3,5-Triazapentadienes 10−12 with Aromatic or Benzylic Backbones by Reaction of Lithiated Primary Amines and Hydrazines 5 with Dinitriles 7−9 (see Table 1)

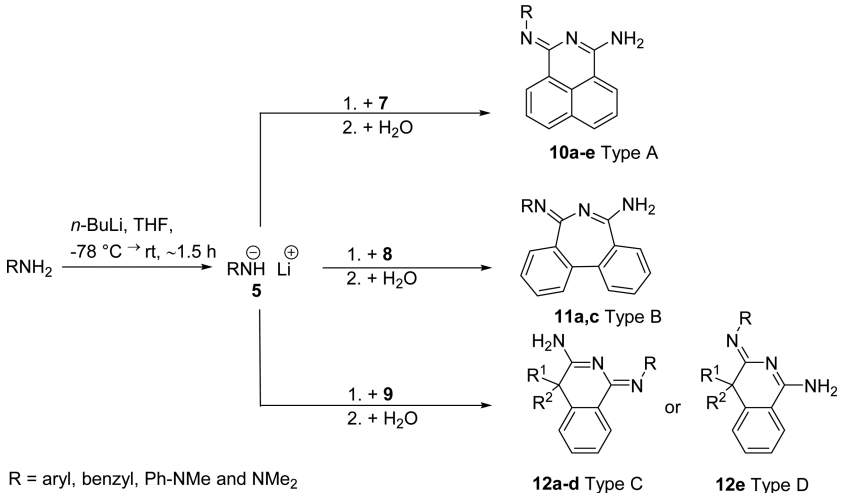


Table 1. Substitution Pattern, Structural Type, and Yields for 1,3,5-Triazapentadienes 10−12

product	type	R	R^1, R^2	yield [%]
10a	A	ph		64
10b	A	*p*tol		48
10c	A	2-pyridyl		50
10d	A	$-N(Me)_2$		94
10e	A	−N(Me)Ph		97
11a	B	*p*tol		26
11b	B	2-pyridyl		14
11c	B	$-N(Me)_2$		47
12a	C	*p*tol	Et	45
12b	C	$-N(Me)_2$	Et	97
12c	C	*p*tol	$-(CH_2)_4-$	46
12d	C	NMePh	$-(CH_2)_4-$	42
12e	D	2-pyridyl	$-(CH_2)_4-$	45

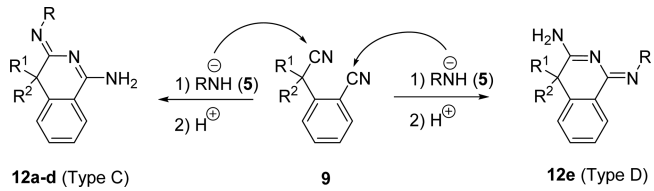
dicyanonaphthalene **7** to give 1,2,4,6-tetraazahexatetraenes **10d,e** in excellent yields (Scheme 6, Table 1).

2,2′-Dicyanobiphenyl **8** reacts in a similar manner with deprotonated primary amines or hydrazines **5** to give the seven-membered heterocyclic compounds **11a−c** of the dibenz[*c,e*]-azepine type B, although mostly in modest yield (Scheme 6, Table 1).

In contrast to the symmetrical dinitriles **7** and **8**, compound **9** contains two chemically different cyano groups: one of them is attached to an aromatic moiety and the other to a benzylic quarternary carbon atom; thus, the formation of two regioisomeric 3,4-dihydroisoquinolin-1-amines (type C) and 1,4-dihydroisoquinolin-3-amines (type D) may be expected (Scheme 7).

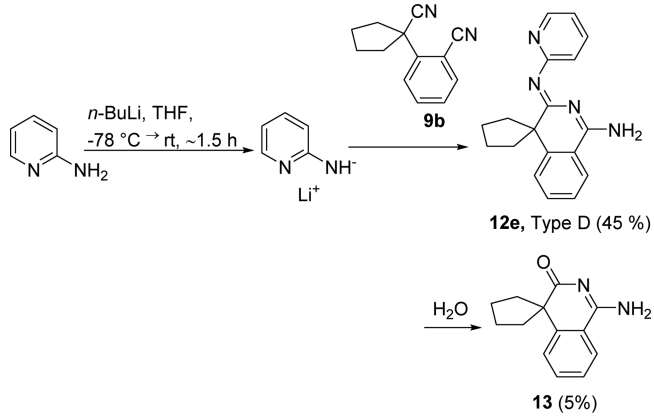
Lithiated primary amines attack in the first step preferentially the cyano group at the aromatic moiety of **9a** or **9b** before the intramolecular ring closure reaction by nucleophilic addition to the benzylic cyano group takes place as seen in the isoquinoline derivatives **12a−d**, which all show structural type C (Scheme 6, Table 1). In contrast, use of the lithiated 2-aminopyridine as nucleophile leads in a 45% yield to product **12e** of structural type D with an intramolecular hydrogen bond, resulting from initial attack at the benzylic cyano group (for X-ray see below). Possibly, the two coordination sites for the lithium counterion of the attacking nucleophile may have an influence on the

Scheme 7. Site of the Nucleophilic Attack at Substituted 2-Cyanomethyl Benzonitriles and Resulting Products of Type C and D



reaction pathway. In addition to **12e**, an impure hydrolysis product **13** could be isolated in 5% yield and characterized by X-ray diffraction (Scheme 8).

Scheme 8. Synthesis of the 1,3,5-Triazapentadienes 12e by Reaction of Lithiated Primary Amines with the Benzylic Dinitrile 9b and Hydrolysis To Give Product 13



The carbon atom of a cyano group bound to a sp^3 carbon atom is supposed to be more electrophilic compared to the corresponding carbon atom bound to a sp^2-hybridized carbon atom of an aromatic ring, as the latter interacts electronically by conjugation with the π-system of the aromatic ring. This is well in line with NBO charges[14] of **9b** based on a geometry optimization at the DFT level M062x/6-311++G(d,p)//M062x/6-311++G(d,p).[15,16] According to these calculations

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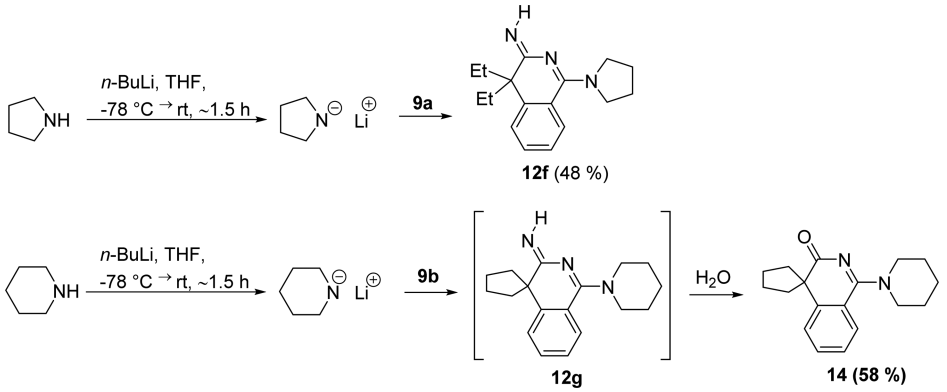
Scheme 9. Synthesis of the 1,3,5-Triazapentadienes 12f,g by Reaction of Lithiated Secondary Amines with the Benzylic Dinitriles 9a,b and Hydrolysis to *N*-Acylamidine 14



the nitrile carbon atom attached to the aromatic moiety has a positive natural charge of +0.279 e and the one bound to the spiro cycle a slightly higher charge of +0.295e. In comparison, the calculated NBO charges at the nitrogen atoms of typical nitrogen nucleophiles like *N*-deprotonated aniline (−0.892 e) and 2-aminopyridine (amine anion −0.870 e, pyridyl −0.625 e, calculated without counterions) indicate similar nucleophilicities for both reagents at the deprotonated amine groups.

Furthermore, two secondary lithiated amines were examined in reactions with dinitrile **9**. Whereas product **12f** (from lithiated pyrrolidine) could be obtained in 48% yield after aqueous workup, the corresponding product **12g** (from lithiated piperidine) could not be isolated but was obtained as hydrolysis product (*N*-acylamidine) **14** after aqueous workup in 58% yield. Both examples confirm again the preferred attack of the nucleophile at the cyano group bound to the aromatic ring (Scheme 9). In general, *N*-acylamidines have found manifold applications in metal coordination.[17]

Structural Properties. Due to their conjugated multiple π-bonds all 1,3,5-triazapentadienes reported here are highly potent hydrogen bond donor and acceptor molecules, thus being typical examples for the concept of resonance-assisted hydrogen bonding.[18] This is convincingly seen in the solid state X-ray diffraction structures we were able to obtain from several of these novel compounds. In most cases, homodimers with strong 2-fold hydrogen bridges were found; in some cases, cocrystallizing solvent (water or acetone) led to chain structures. 2-Pyridyl substituents as in **10c** favor strong intramolecular hydrogen bonding; here, a monomer with additional intermolecular contacts was obtained. Of special interest is also compound **11c**, where a chain structure of enantiomers of conformer **11c-B** with additional peripheral enantiomeric conformers **11c-A** is observed.

Derivatives with a Naphthyl Backbone 10a−e. X-ray analyses of **10a** and **10b** show the formation of homodimers in the form of eight-membered rings involving two N−C−N subunits in the solid state with N−N distances in **10a** of 3.02 Å and in **10b** of 3.12 Å; for comparison, the sum of the van der Waals radii of two N atoms amounts to 3.10 Å[19] (Figure 1 for the X-ray structure of **10b**), thus indicating quite strong hydrogen bonding. The gas-phase dimerization energy of **10b** calculated by the DFT functional M062x using the 6-311++G(d,p) basis set and the Grimme GD3 dispersion correction[20] amounts to −29.13 kcal/mol (complete geometry optimization including zero-point energy; Gaussian 09[15]). This value is significantly larger compared, for example, to the aggregation

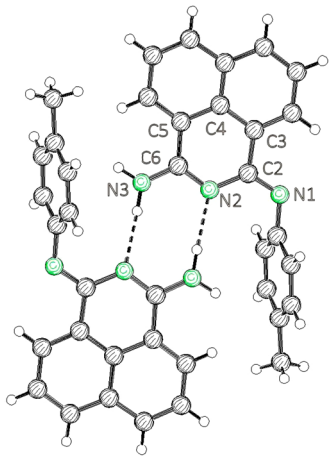


Figure 1. Homodimeric structure of **10b** in the solid state (Schakal plot).

energy of the adenine−thymine nucleobase pair (−14.14 kcal/mol) at the same level of theory and is in a similar range as the guanine−cytosine base pair (−27.57 kcal/mol) which shows three hydrogen bridges.[21]

Triazapentadiene **10c** shows another tautomeric form in the solid phase compared to triazapentadienes **10a** and **10b** (see Figure 2) due to strong intramolecular hydrogen bonding caused by the proton attached to N2 and the nitrogen atom of the pyridine substituent. The respective intramolecular N−N bond distance amounts to 2.62 Å. In addition to the intramolecular hydrogen bond, also intermolecular hydrogen bonding is observed, leading to a network of molecules as shown in Figure 2. The intermolecular N−N distances amount to 3.09 Å. As anticipated, triazapentadienes **10a−c** show almost planar triazapentadiene chains with dihedral angles along the backbone close to 180°, in contrast to noncyclic examples[2] (**10a**: N1−C2−N2−C6 −175.21°, C2−N2−C6−N3 −178.64°; **10b**: N1−C2−N2−C6 −174.53°, C2−N2−C6−N3 179.85°; **10c**: N1−C2−N2−C6 179.31°, C2−N2−C6−N3 179.22°).

Formally, the 1*H*-benz[*de*]isoquinoline or 2-aza-phenalenyl compounds **10a−c** accommodate each of the 12 π-electrons in the tricyclic system, which, according to the Hückel definition, means that these molecules have to be considered to be antiaromatic in character. Indeed, X-ray analyses show quite long bond lengths for the C2−C3 and C5−C6 bonds of 1.48 (**10b**) and 1.47 Å (**10c**) (see Figure 2). These values are very

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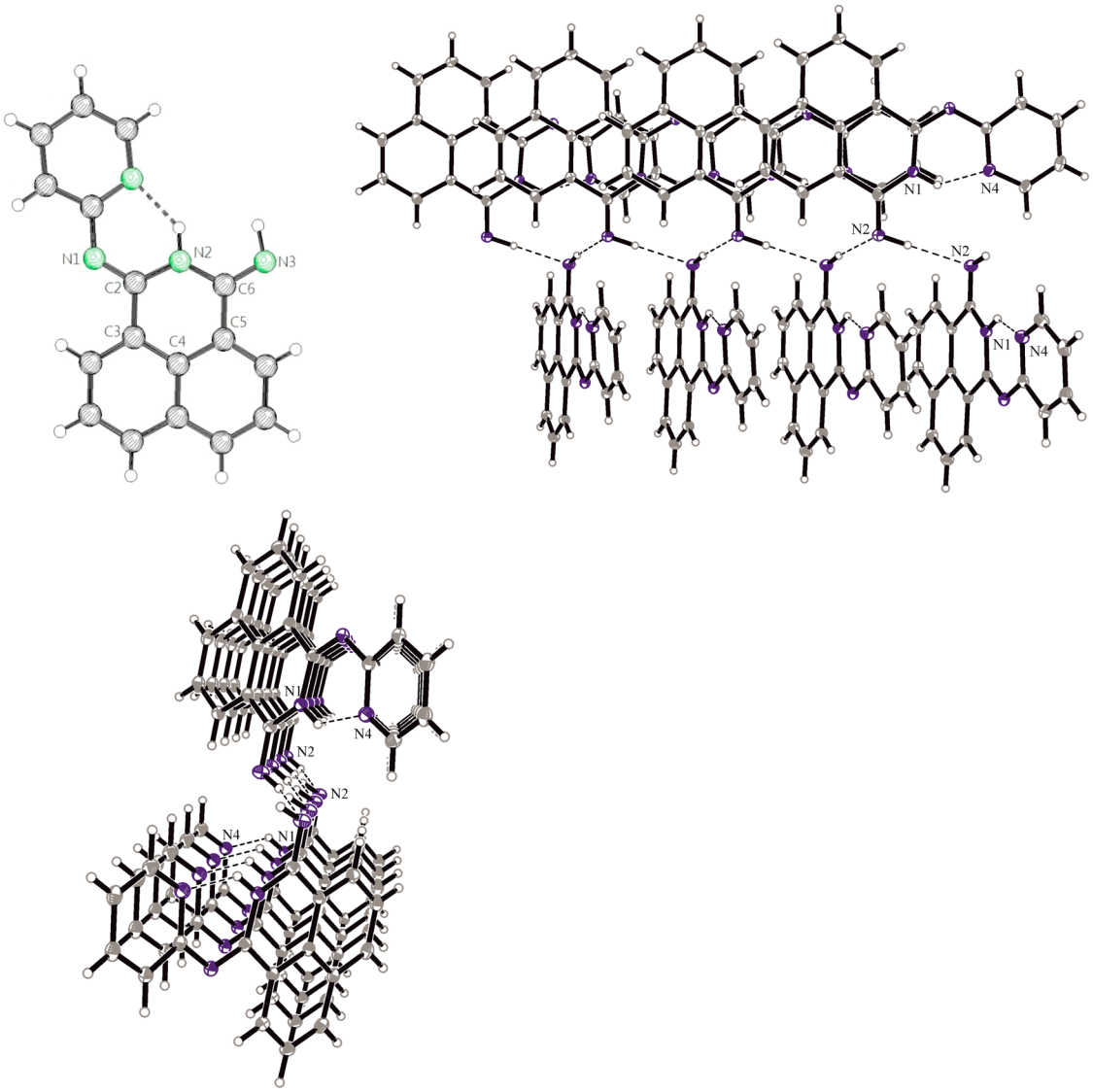

Figure 2. Intra- and intermolecular hydrogen bonding in the solid state structure of **10c** shown from two perspectives (Schakal and XP plots).

close to those of nonconjugated $C_{sp2}-C_{sp2}$ single bonds (1.48 Å) and much longer than aromatic $C_{sp2}-C_{sp2}$ bonds (1.39 Å in benzene).[22] Hence, electronic interaction of the 1,3,5-triazapentadiene chain with the naphthalene backbone is substantially reduced by pushing the triazapentadiene subunit away in order to avoid the unfavorable antiaromatic character, thus achieving two electronically better separated π-systems.[23]

Derivatives with a Biphenyl Backbone 11. The X-ray structure of 2-pyridyl derivative **11b** also shows the formation of homodimers from two monomeric enantiomers and one molecule of water. The molecules are connected via two NH–N hydrogen bonds (N1–N2′ and N2–N1′ 3.03 Å) involving two of the three 1,3,5-triazapentadiene nitrogen atoms and bind additionally to two molecules of water (N1–O1 and N1′–O2 2.90 Å, N4–O2 and N4′–O1 2.88 Å; see Figure 3) with the pyridyl nitrogen atoms as hydrogen bond acceptors. In **11b** and in the tetrazahexatetraene **11c** the phenyl moieties of the biphenyl system are twisted by about 40° relative to each other. Consequently, the triazapentadiene chain is also bent out of plain (**11b**: $N(H_2)-C-N-C$ 166.7°, $C-N-C-N(py)$ −141.1°). Similarly, as in compounds **10**, here also the 1,3,5-triazpentadiene subunit is quite distant from the biphenyl moiety (C–C bond lengths: C4–C5 1.487 Å and C1–C6 1.493 Å), indicating the absence of strong aromatic interactions between both subunits.

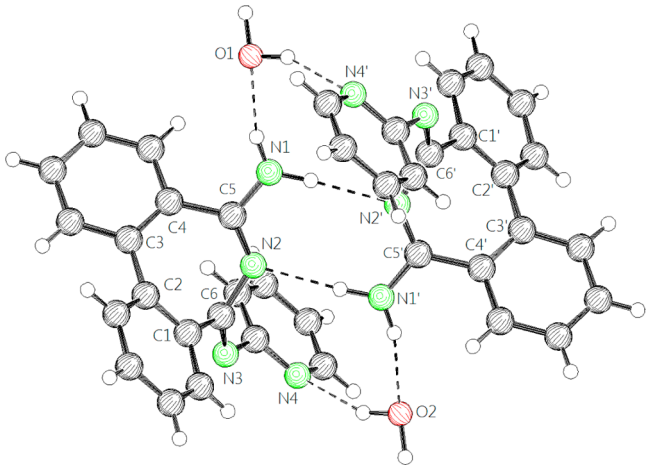

Figure 3. Homodimeric structure of **11b** in the solid state (Schakal plot).

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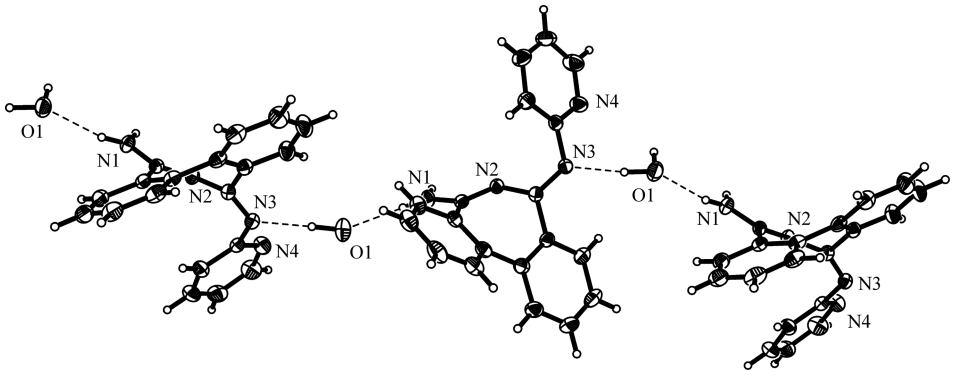

Figure 4. Linear arrangement of **11b** (XP plot).

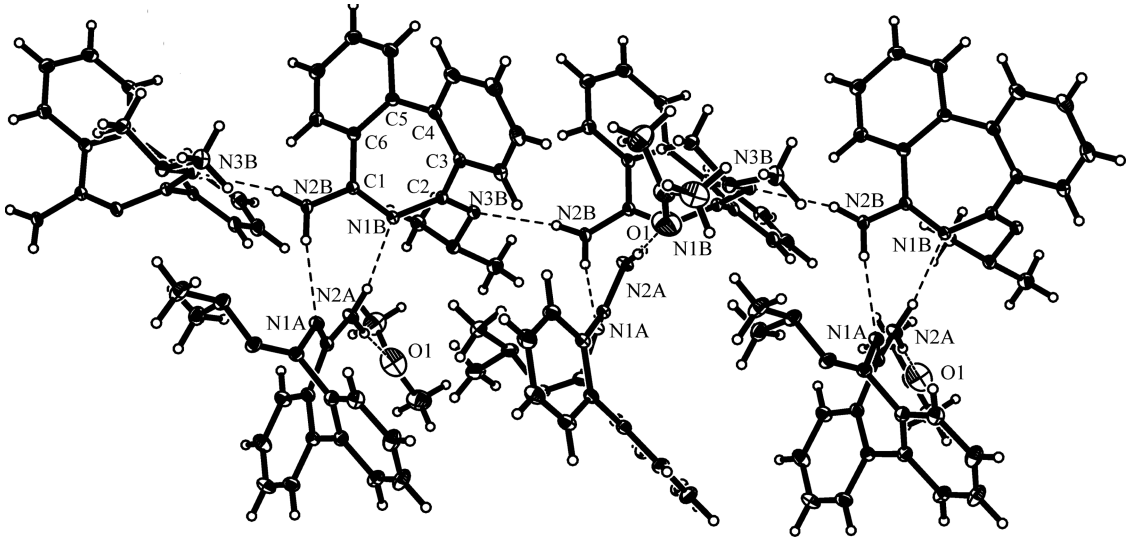

Figure 5. Linear arrangement of enantiomeric molecules **11c-B** with neighboring molecules of type **11c-A** bonded by 2-fold hydrogen bonds in the solid state. Furthermore, acetone molecules are hold by hydrogen bonding to **11c-A** (XP plot).

Furthermore, for **11b** chain-like structures are observed. These are formed by intermolecular hydrogen bonds from N1−H to an oxygen atom of water followed by a hydrogen bond from OH to N1 as acceptor (N−O 2.90 Å). Each molecule has a parallel adjustment to its next but one neighbor (see Figure 4).

Characteristic for the solid state structure of **11c** is the presence of crystallographically independent molecules **11c-A** and **11c-B**. Thus, enantiomeric molecules of structural type **11c-B** form by alternating arrangement of linear chains based on intermolecular hydrogen bonding (N2B−N3B 3.083 Å) (Figures 5 and 6). Each of the chain molecules **11c-B** is also part of a homodimer formed by 2-fold hydrogen bonding (N1B−N2A 3.072 Å, N1A−N2B 3.075 Å) to the respective enantiomer of conformer **11c-A** with slightly different structural properties compared to **11c-B** as best seen from the torsional angles. Furthermore, one molecule of acetone (from the recrystallization) cocrystallizes per dimer via hydrogen bonding using the second NH of N2A. Thus, all available NH moieties are subject to hydrogen bonding.

The calculated gas-phase dimerization energy for the formation of a homodimer of **11c** amounts to −15.34 kcal/mol. This is about 14 kcal/mol less in comparison to the dimerization energy of the six-membered system **10b**, probably due to conformational ring strain exerted by the seven-membered ring with regard to the hydrogen bonding ability.

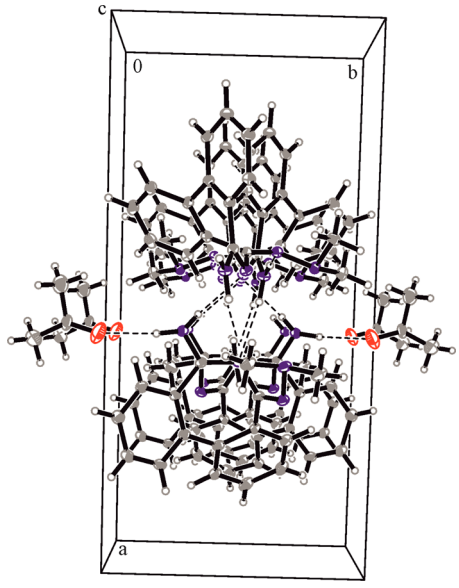

Figure 6. Packing of **11c** as determined by X-ray analysis involving also hydrogen bonding to acetone molecules. View along the *c* axis (XP plot).

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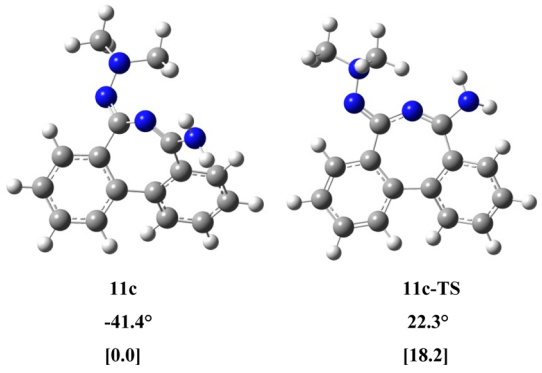

Figure 7. Calculated structures, biphenyl torsional angles of atoms C3−C4−C5−C6 (for atom numbering see Figure 5), and relative energies of **11c** and transition structure **11c-TS** (M062x/6-311++G(d,p)//M062x/6-311++G(d,p)+GD3+ZPE) (Gaussview plot).

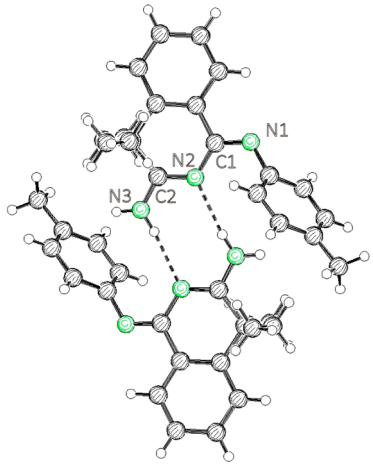

Figure 8. Homodimeric structure of **12a** in the solid state (Schakal plot).

This observation is supported by the relatively long measured N−N distances.

By rotation about the central biphenyl C−C single bond, conformer **11c** can be converted into its enantiomer by passing a significantly less twisted (about 22°) transition state **11c-TS** with a relative energy of 18.2 kcal/mol according to quantum chemical calculations at the M062x//6-311++G(d,p)//M062*x*/6-311++G(d,p)+GD3+ZPE level.[15,24] Transition state structure **11c-TS** was localized by scanning the rotation about the biphenyl axis as well as using the QST2 approach[25] and verified by IRC calculations.[26] It is characterized by a relatively planar triazapentadienyl subunit and a substantially twisted biphenyl torsional angle (Figure 7). Thus, at room temperature in solution an equilibrium between both enantiomers is expected.

Derivatives with an Isoquinoline Backbone 12. The compounds with isoquinoline substructures **12a−d** and **12f** form also homodimers in the solid state (see Supporting Information). As a structural example the X-ray structure of **12a** (type C, Scheme 6) is shown in Figure 8. The triazapentadiene chain is almost planar (N1−C1−N2−C2 171.10°, C1−N2−C2−N3 173.02°). The formation of the homodimeric structure is based on 2-fold intermolecular hydrogen bonding (NH−N 3.01 Å).

In derivative **12e** (structural type D, Scheme 6) a linear arrangement of molecules is formed due to intermolecular hydrogen bonding (N−N distance amounts to 2.98 Å, see Figure 9). To each molecule of **12e** one molecule of acetone, which was used for crystallization, is attached by N−O hydrogen bonding with a N−O distance of 2.99 Å. The triazapentadiene chain is twisted, which is visualized by dihedral angles of −172.54° for the N1−C1−N2−C2 chain and −160.10° for the C1−N2−C2−N3 chain (see Figure 9).

N-Acylamidine **13** is a hydrolysis product of **12e**. **13** forms stable dimers with its tautomer bonded by 3-fold hydrogen bonding in the solid state (see Figure 10). The calculated gas-phase dimerization energy (M062x/6-311++G(d,p)+gd3+zpe) amounts to −20.04 kcal/mol (with respect to the sum of both tautomers).

For the homodimeric tetraazatetraenes **12b,d** the structure of **12b** is shown here as an example (Figure 11). Besides the "normal" hydrogen bonding as seen in the other examples (N1−N2′; N−N distance 3.01 Å), here also bifurcated hydrogen bonding involving the tertiary hydrazine nitrogen atom is found, with the NH_2 group (N1) acting as hydrogen bond donor and the nitrogen atoms N2 and N4 acting as hydrogen bond acceptors (N1−N4′; N−N distance 3.06 Å). For **12d**, the corresponding hydrogen bond parameters amount to 2.94 and 2.933 Å, indicating a stronger interaction compared to **12b**. The triazapentadiene chains are slightly twisted as shown by the dihedral angles (**12b**: N1−C1−N2−C2 178.49°, C1−N2−C2−N3: 172.51°, N2−C3−N3−N4 −3.27°; **12d**:

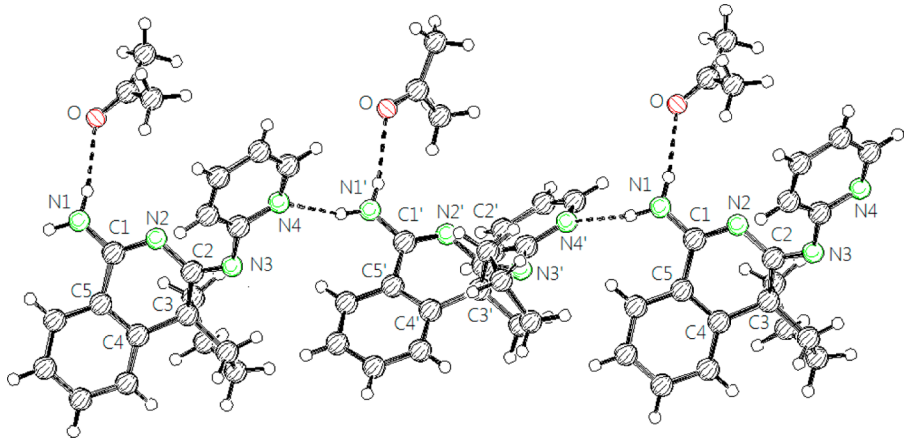

Figure 9. X-ray structure of **12e** with intermolecular hydrogen bonds (Schakal plot).

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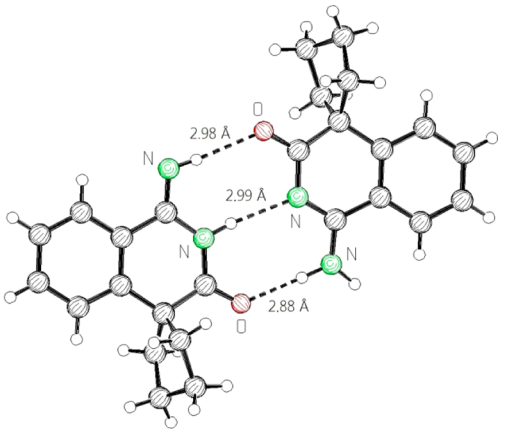

Figure 10. X-ray structure of **13** with N−O and N−N hydrogen bond distances (Schakal plot).

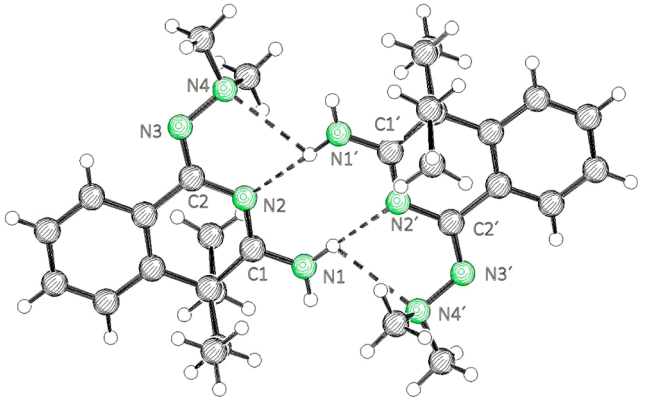

Figure 11. Derivative **12b** as homodimer in the solid state (Schakal plot).

N1−C1−N2−C2 −175.88°, C1−N2−C2−N3: −170.53°, N2−C3−N3−N4 5.10°).

For **12b** the calculated gas-phase dimerization energy (M062x/6-311++G(d,p)+GD3+ZPE) amounts to −24.09 kcal/mol and that for **12d** −31.26 kcal/mol, which is well in line with shorter measured and calculated hydrogen bond distances of **12d**.

Photophysical Properties of 1,3,5-Triazapentadienes. In general, compounds **10**−**12** are mostly yellow (**12**) or red (**10**) solids, indicating their dyestuff nature as donor−acceptor-substituted imines (aza-vinylogous amidines) as seen by their UV−vis absorption properties. Furthermore, the three 1,3,5-triazapentadienes **10a**−**c** and the tetraazahexadienes **10e** show fluorescence (at relatively high concentrations of about 10^{-4} mol/L) in dichloromethane solution. The tetraazahexadiene **12d** shows a more intense fluorescence in solution (at 10^{-5} mol/L). In contrast, **10d** does not show any fluorescence, and **10e** exhibits only very weak emission. Table 2 summarizes characteristic values of the absorption and emission spectra (including the irradiation wavelength for the fluorescence) as well as the TD-DFT results for the calculated absorption properties. The Stokes shifts amount to approximately 90−150 nm (5000−8600 cm^{-1}).

In order to interpret the spectroscopic absorption data TD-DFT (CAM-B3LYP/6-311+G(d,p)//CAM-B3LYP/6-311+G-(d,p) including dichloromethane as solvent (IEF-PCM)) calculations were performed for the monomeric compound **10c** as well as for the monomer and homodimers of compounds **10a,b** and **12d**. In general, the calculated shapes of the spectra match reasonably well with the experimental curves. The deviations between experimental and calculated longest wavelength maxima amount to 0.09−0.49 eV. The calculated maxima and the assignment for the respective transitions are shown in Table 2.

As expected, compounds **10a** and **10b** exhibit similar UV−vis properties (**10b**: Figure 12, for spectra of **10a** see SI) with the typical two-band pattern. The emission at about 500 nm leads to a Stokes shift of 149 nm (8570 cm^{-1}) with the almost perpendiculary placed *N*-substituent not taking extensively part in conjugation to the triazapentadienyl moiety. We assume the presence of dimeric structures of **10a,b** also in solution as found in the solid state. The quantum-chemical calculations for **10b** indicate a blue shift of about 19 nm due to dimerization. The calculated longest absorption maximum for **10b** deviates from the experimental value by 9 nm (0.09 eV) for the dimer and 19 nm (0.27 eV) for the monomer. The main transitions are assigned to HOMO → LUMO, HOMO−1 → LUMO, and HOMO → LUMO+1 transitions (Figure 13). Interestingly, the occupied orbitals HOMO and HOMO−1 show large coefficients both at the central moiety and also at the *N*-substituent, whereas LUMO and LUMO−1 only have large coefficients at the main part of the molecule, indicating the possibility of intramolecular charge transfer (ICT).

The UV−vis absorption and emission spectra of the monomeric derivative **10c**, which is expected to be planar in

Table 2. Characteristic Experimental Absorption and Emissions Data (measured in dichloromethane, $c = 1.0 \times 10^{-4}$ mol/L) and Calculated Absorption Spectra (dichloromethane, TD-CAM-B3LYP/6-311+G(d,p)/6-311+G(d,p)) of the Derivatives 10b, 10c, and 12d (see SI for details)

compound	absorption maxima [nm] (ε [$L \cdot M^{-1} \cdot cm^{-1}$])	calculated longest wavelength absorption maxima [nm], oscillator strength *f*, assignment	emission maxima [nm] (irradiation wavelength)
10b	349 nm (16 085)	monomer: 377.6, f = 0.470, HOMO → LUMO	498 (350)
	243 nm (35 238)	monomer: 320.8, f = 0.129, HOMO−1 → LUMO	
		dimer: 358.0, f = 0.797, HOMO−1 → LUMO, HOMO → LUMO+1	
		dimer: 315.5, f = 0.241, HOMO−3 → LUMO+1, HOMO−2 → LUMO	
10c	365 nm (31 554)	342.3, f = 0.767, HOMO → LUMO)	506 (350)
	249 nm (44 820)	301.7, f = 0.089, HOMO−1 → LUMO	
12d	378 (7902)[a]	monomer: 334.8, f = 0.269, HOMO → LUMO	471 (415)
	256 (38 757)[a]	monomer: 268.6, f = 0.104, HOMO → LUMO+3	
		dimer: 330.8, f = 0.594, HOMO → LUMO+1, HOMO−1 → LUMO	

[a] $c = 1.0 \times 10^{-5}$ mol/L

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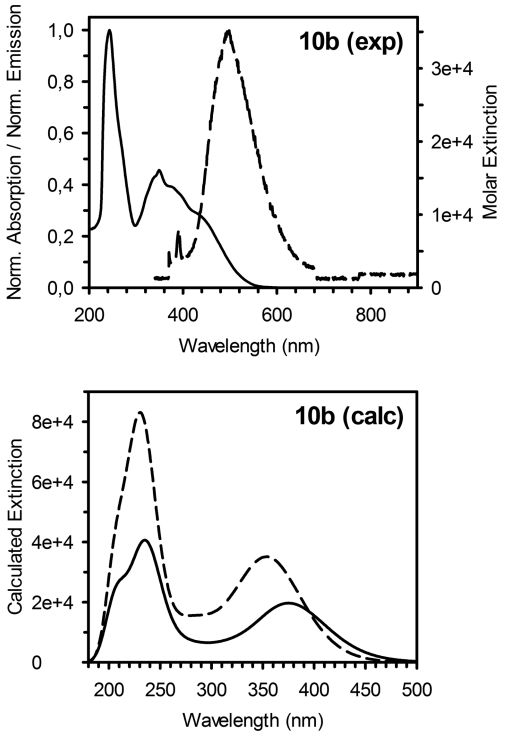

Figure 12. Absorption spectrum (normalized and molar extinction, solid line) and emission spectrum (normalized emission, dashed line, irradiation at 350 nm) measured in dichloromethane (top) and calculated absorption spectra for the monomeric form (solid line) and the dimer (dashed line) (bottom, CAM-B3LYP/6-311+G(d,p)//CAM-B3LYP/6-311+G(d,p) including dichloromethane as solvent (IEF-PCM)) of **10b**.

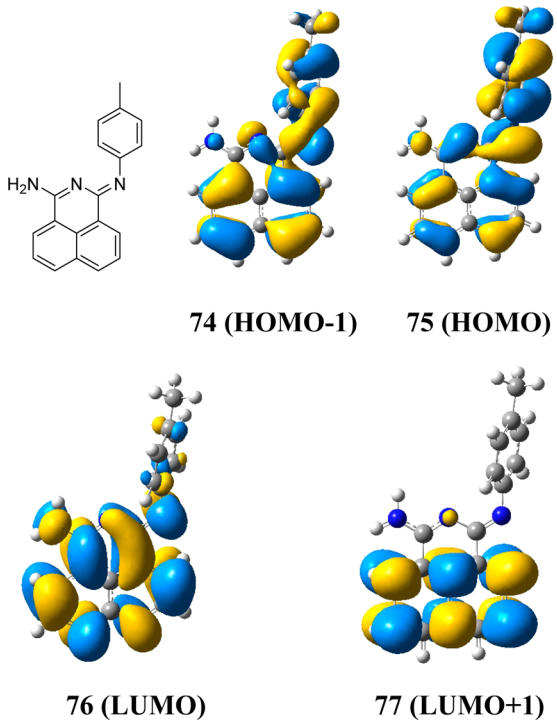

Figure 13. Four frontier orbitals from HOMO−1 to LUMO+1 (orbital numbers 74−77) (CAM-B3LYP/6-311+G(d,p)//CAM-B3LYP/6-311+G(d,p) calculated including dichloromethane as solvent (IEF-PCM)) and Lewis formula (top left) of **10b** (Gaussview plot).

solution due to the intramolecular hydrogen bridge, are shown in Figure 14. The UV−vis spectrum is characterized by a broad longest wavelength absorption at 365 nm and a typical aromatic band at about 250 nm. The red shift of the longest wavelength absorption in comparison to **10a,b** may be taken as a hint for their nonplanar structures (see Figure 1). The emission spectrum shows a single, broad band at about 500 nm, resulting in a Stokes shift of about 140 nm (7630 cm^{-1}). According to TD-DFT calculations we assign the longest wavelength absorption maximum of **10c** (calculated at 342 nm, deviation 23 nm = 0.22 eV) to a HOMO → LUMO transition (see Figure 15). Both the HOMO and the LUMO show coefficients all over the molecule with characteristic nodal patterns along the 1,3,5-triazapentadienyl subunit.

For **12d** absorption maxima are detected in the UV spectrum at 256 and 378 nm, thus red-shifted compared to **10b,c** (Figure 16). In contrast to compounds **10** and **11** the triazapentadienyl moiety of compound **12** is not involved in thorough cyclic conjugation. Relatively strong emission is observed at 471 nm, resulting in a small Stokes shift of 5224 cm^{-1}. TD-DFT calculations give two maxima (238 and 334 nm, see SI) in less satisfactory agreement with the measured values (deviation of 0.42 and 0.46 eV). On the basis of the calculations excitation of an electron from the HOMO to the LUMO is assigned to the maximum at 335 nm, while the transition from HOMO−1 to LUMO contributes to the maximum at 238 nm (Figure 17). HOMO−1 and the HOMO have large coefficients at the triazapentadienyl subunit and at the *N*-substituent. The LUMO has large coefficients at the backbone but not at the *N*-

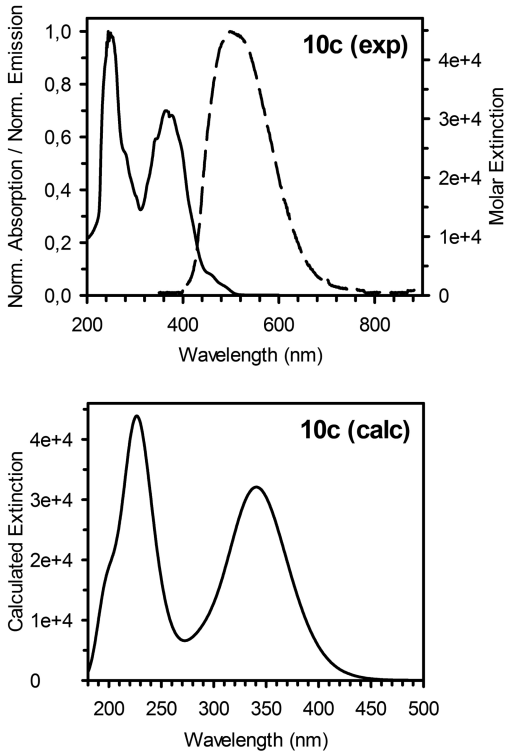

Figure 14. Absorption spectrum (normalized and molar extinction, solid line) and emission spectrum (normalized emission, dashed line, irradiation at 350 nm) measured in dichloromethane (top) and calculated absorption spectrum (bottom, CAM-B3LYP/6-311+G-(d,p)//CAM-B3LYP/6-311+G(d,p) calculated including dichloromethane as solvent (IEF-PCM)) of **10c**.

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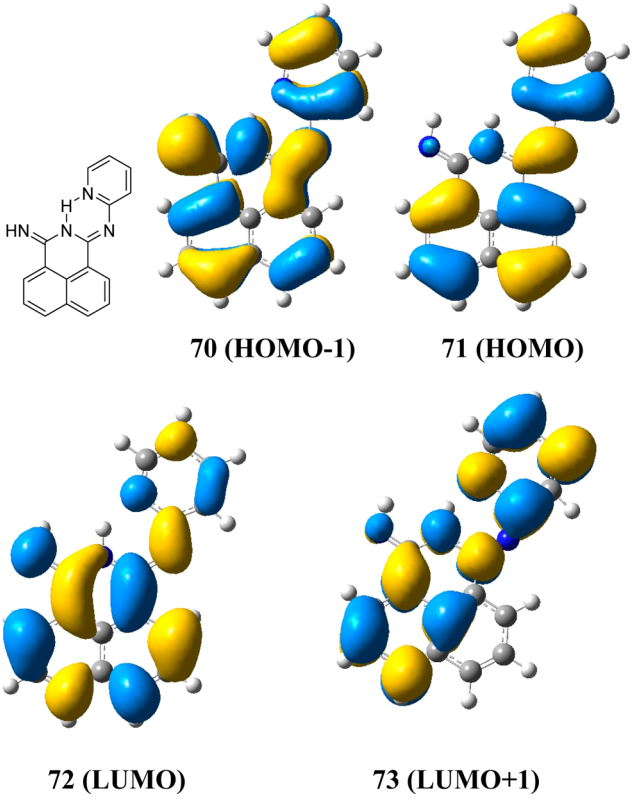

Figure 15. Four frontier orbitals from HOMO−1 to LUMO+1 (orbital numbers 70−73) (CAM-B3LYP/6-311+G(d,p)//CAM-B3LYP/6-311+G(d,p) calculated including dichloromethane as solvent (IEF-PCM)) and Lewis formula (top left) of **10c** (Gaussview plot).

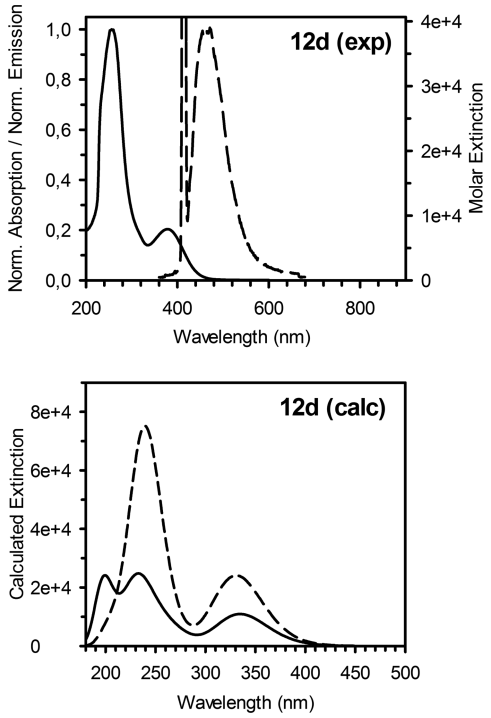

Figure 16. Absorption spectrum (normalized and molar extinction, solid line) and emission spectrum (normalized emission, dashed line, irradiation at 415 nm) measured in dichloromethane (top) and calculated absorption spectra for the monomeric form (solid line) and the dimer (dashed line) (bottom, CAM-B3LYP/6-311+G (d,p)//CAM-B3LYP/6-311+G(d,p) including dichloromethane as solvent (IEF-PCM)) of **12d**.

substituent, indicating internal charge transfer (ICT) (Figure 17).

CONCLUSION

Starting from three different types of dinitriles **7**−**9** (featuring 1,3- or 1,4-nitrile distances) three novel types of sterically constrained 1,3,5-triazapenta-1,3-dienes (and 1,2,4,6-tetraaza-hexa-2,4-dienes) **10**−**12** were synthesized by nucleophilic addition of lithiated amines or hydrazines **5** and subsequent protonation by aqueous workup. According to X-ray diffraction studies the resulting polycyclic heterocyclic compounds show strong tendencies to aggregation, either by homodimerization due to 2-fold hydrogen bridging or by formation of infinite chains or a combination of both in the solid state. This aggregation behavior suggests the use of these novel ligands also for metal coordination. The yellow to red 1,3,5-triazapentadienyl compounds **10**−**12** have the chromophore of an aza-vinylogous amidine, which is well recognized from the UV−vis spectra. High-level TD-DFT calculations including the dichloromethane solvent sphere were used to evaluate the dimerization energies and to assign the electronic transitions. Some of the new compounds show fluorescence upon irradiation with UV light.

EXPERIMENTAL SELECTION

General. All solvents were dried by standard methods. When necessary, the experiments were carried out with complete exclusion of moisture using argon, septum and syringe technique, and glassware, which was thoroughly dried by heating under vacuum and subsequent venting with argon. NMR spectra were recorded at 298 K: ^{1}H 300.13

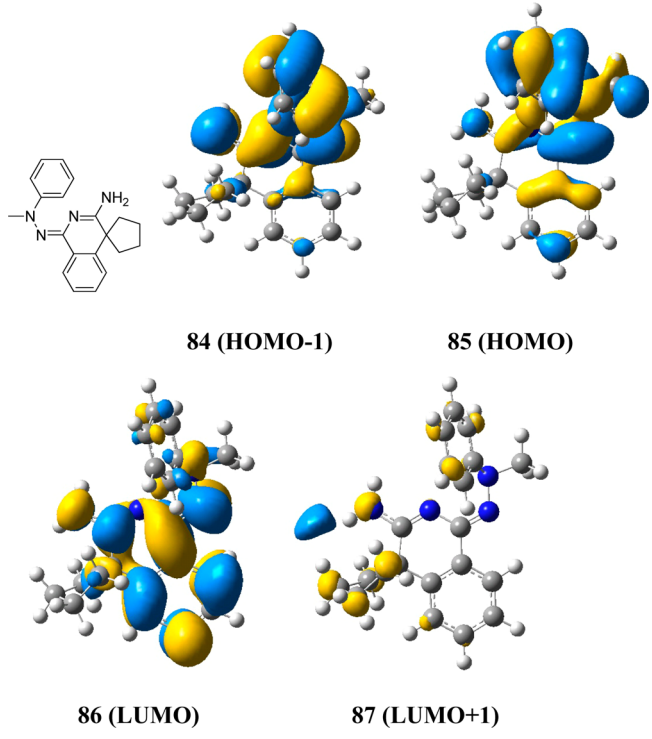

Figure 17. Four frontier orbitals from HOMO−1 to LUMO+1 (orbital numbers 84−87) (CAM-B3LYP/6-311+G(d,p)//CAM-B3LYP/6-311+G(d,p) calculated including dichloromethane as solvent (IEF-PCM)) and Lewis formula (top left) of **12d** (Gaussview plot).

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MHz and ^{13}C 75.48 MHz; ^{1}H 400.03 and ^{13}C 100.59 MHz; ^{1}H 499.85 MHz and ^{13}C 125.67 MHz; ^{1}H 599.79 MHz and ^{13}C 150.83 MHz. Assignments of the resonances were supported by 2D experiments and referenced internally to residual solvent resonances (chemical shift data in δ). ^{13}C NMR spectra were all proton decoupled. IR spectra were recorded as Nujol mull between CsI plates or with an ATR sampling system. Electron impact (EI) mass and electrospray ionization (ESI) spectra were recorded. Elemental analyses were determined by the microanalytic laboratory in our institute. Melting points are uncorrected.

1,8-Dicyanonaphthaline **7** was prepared according to literature procedures.[10−12]

*2,2′-Dicyanobiphenyl (**8**).* In our work, an optimized pathway for the synthesis of compound **8** was adapted from a literature procedure[10] as follows: 10.2 g (38 mmol) of phenanthro[9,10-*c*][1,2, 5]thiadiazole, 2,2-dioxide[10,27] was divided into 5 portions of about 2 g. Each of them was dissolved in little dry acetone and put into a 100 mL Schlenk flask. This solution was freed from the solvent using a rotatory evaporator, resulting in a thin film at the flask. This flask was then equipped with a foam brake and a reflux condenser filled with glass wool. Under a weak argon stream the flask was heated to about 630 °C using a heat gun. The resulting product **8** precipitated in the foam brake, reflux condenser, and at the glass wool, from which it was washed off using dichloromethane. This procedure was repeated for each of the portions. The resulting solutions of the raw products were brought together, freed from the solvent in vacuo, and dissolved in a minimal amount of boiling dry chloroform. After cooling to room temperature and filtering off the insoluble residue, the yellow solution was freed from the solvent in vacuo. Product **8** was obtained as yellow solid (mp 173 °C, 173 °C[10]) in a yield of 3.5 g (17 mmol, 45%, lit.:[10] 80%). $C_{14}H_8N_2$ (204.23): HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{14}H_8N_2Na$ 227.0577. Found 227.0580. The other analytical data are in coincidence with literature data.[28] For X-ray crystal structure data see the Supporting Information.

*2-(1-Cyano-1-ethyl-propyl)-benzonitrile (**9a**).* This compound was prepared in analogy to a procedure by Snow et al.[13] To a solution of sodium hydroxide (7.5 g, 0.19 mol) in 70 mL of water 2-cyanomethyl benzonitrile (1.4 g, 10 mmol), tetrabutylammonium bromide (0.2 g, 0.6 mmol) and ethyl iodide (4.7 g, 30 mmol) were added. The reaction mixture was stirred for 2 days and poured onto ice. The aqueous layer was extracted with ethyl acetate three times. The combined organic layers were dried with magnesium sulfate. Subsequent purification by flash chromatography (pentane/ethyl acetate =10:1) gave 1.4 g (6.9 mmol, 69%) of **3a** as colorless oil. R_f = 0.32 (pentane/ethyl acetate = 10:1). IR: $\tilde{\nu}$ = 617 (m), 667 (w), 741 (w), 750 (w), 768 (vs), 791 (s), 895 (m), 934 (w), 962 (vw), 997 (vw), 1026 (m), 1038 (w), 1084 (m), 1124 (vw), 1167 (w), 1194 (vw), 1207 (vw), 1260 (vw), 1285 (vw), 1325 (m), 1348 (m), 1383 (m), 1414 (vw), 1441 (vs), 1460 (s), 1470 (vs), 1481 (vs), 1503 (vw), 1514 (vw), 1530 (w), 1551 (w), 1574 (w), 1597 (s), 1612 (w), 1620 (w), 1632 (w), 1641 (w), 1649 (w), 1659 (w), 1666 (w), 1680 (vw), 1692 (vw), 1836 (vw), 1958 (vw), 1992 (vw), 2222 (vs), 2237 (w), 2326 (vw), 2342 (vw), 2357 (vw), 2880 (w), 2938 (w), 2959 (m), 2968 (s), 2978 (s), 3071 (vw), 3605 (vw), 3624 (vw), 3638 (vw), 3665 (vw), 3684 (vw), 3705 (vw), 3717 (vw), 3740 (vw), 3748 (vw), 3790 (w), 3811 (w), 3829 (vw), 3848 (w), 3860 (w), 3877 (vw), 3896 (vw), 3912 (vw) cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.93 (t, ^{3}J = 7.4 Hz, 6 H, CH_3), 2.19 (dq, ^{2}J = 17.7 Hz, ^{3}J = 7.4 Hz, 2 H, CH_2), 2.54 (dq, ^{2}J = 17.7 Hz, ^{3}J = 7.4 Hz, 2 H, CH_2), 7.46 (dt, ^{3}J = 7.6 Hz, ^{4}J = 1.1 Hz, 1 H, $NCC_{ipso}CH_{ar}CH_{ar}$), 7.65 (dt, ^{3}J = 7.8 Hz, ^{4}J = 1.5 Hz, 1 H, $C_qC_{ipso}CH_{ar}CH_{ar}$), 7.77 (dd, ^{3}J = 7.6 Hz, ^{4}J = 1.1 Hz, 1 H, $NCC_{ipso}CH_{ar}$), 7.85 (dd, ^{3}J = 8.0 Hz, ^{4}J = 0.7 Hz, 1 H, $C_qC_{ipso}CH_{ar}$) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 10.2 (CH_3), 31.7 (CH_2), 51.9 (C_q), 108.9 ($C_{ipso}CN$), 118.5 ($C_{ipso}CN$), 121.4 (C_qCN), 128.5 ($CNC_{ipso}CH_{ar}CH_{ar}$), 130.7 ($C_qC_{ipso}CH_{ar}$), 133.4 ($C_qC_{ipso}CCH_{ar}CH_{ar}$), 136.3 ($CNC_{ipso}CH_{ar}$), 140.6 ($CH_{ar}C_{ipso}$) ppm. HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{13}H_{14}N_2Na$ 221.1049. Found 221.1041.

Anal. Calcd for $C_{13}H_{14}N_2$ (198.27): C, 78.75; H, 7.12; N, 14.13. Found: C, 78.53; H, 7.24; N, 14.05.

*2-(1-Cyano-cyclopentyl)-benzonitrile (**9b**).* In analogy to the literature procedure by Snow et al.[13] sodium hydroxide (19.78 g, 0.5 mol) was dissolved in water (150 mL). 2-Cyanophenyl cyanomethane (3.58 g, 25.2 mmol), tetrabutylammonium bromide (0.48 g, 1.5 mmol), and 1,4-dibromobutane (6.52 g, 30.0 mmol) were added. The reaction mixture was stirred for 3 days, poured onto ice, and extracted three times with ethyl acetate. The combined organic layers were dried with sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (pentane/ethyl acetate, 15:1 → 10:1); 4.14 g (21.1 mmol, 83%) of **9b** was obtained as colorless oil. R_f = 0.32 (pentane/ethyl acetate = 15:1). IR: $\tilde{\nu}$ = 610 (s), 633 (vs), 654 (s), 667 (s), 677 (s), 764 (s), 827 (w), 957 (vw), 1169 (vw), 1194 (vw), 1233 (vw), 1287 (vw), 1323 (vw), 1445 (s), 1483 (s), 1597 (m), 2226 (vs), 2322 (w), 2342 (w), 2361 (m), 2878 (m), 2918 (w), 2961 (s), 3076 (vw) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.00−2.18 (m, 4 H, CH_2), 2.27−2.42 (m, 2 H, CH_2), 2.63−2.76 (m, 2 H, CH_2), 7.46 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.4 Hz, 1 H, CH_{ar}), 7.46 (td, ^{3}J = 7.7 Hz, ^{3}J = 8.1 Hz, ^{4}J = 1.5 Hz, 1 H, CH_{ar}), 7.77 (ddd, ^{3}J = 7.6 Hz, ^{4}J = 0.5 Hz, ^{4}J = 1.5 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 24.6 (CH_2), 39.4 (CH_2), 47.8 (C_q), 111.2, 118.0, 122.8 (2 CN, *i*-C_{ar}), 127.8 (CH_{ar}), 128.6 (CH_{ar}), 133.3 (CH_{ar}), 135.7 (CH_{ar}), 142.3 (*i*-C_{ar}) ppm. HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{13}H_{12}N_2Na$ 219.0893. Found 219.0888. Anal. Calcd for $C_{13}H_{12}N_2$ (196.27): C, 79.56; H, 6.16; N, 14.27. Found: C, 79.28; H, 6.06; N, 14.26.

General Procedure for the Synthesis of 1,3,5-Triazapenta-1,3-dienes and 1,2,4,6-Tetraazahexa-2,4-dienes. In analogy to the literature procedure by Würthwein et al.[3] a secondary or primary amine or a hydrazine was dissolved in dry tetrahydrofuran and cooled to −78 °C. One equivalent of *n*-butyllithium (1.6 M solution in *n*-hexane) was added dropwise. The reaction mixture was stirred at −78 °C for 30 min or the specified time and at room temperature for 1 h or the time stated, before it was cooled to −78 °C again. A solution of the respective dinitrile **7**−**9** in tetrahydrofuran was added, and the solution was slowly warmed to room temperature and stirred at room temperature or 45 °C overnight. The reaction was quenched by addition of water, and the aqueous layer was extracted with diethyl ether three times. The combined organic layers were dried with magnesium sulfate, and the solvent was removed under reduced pressure.

*3-Phenylimino-3H-benzo[de]isoquinolin-1-ylamine (**10a**).* **10a** was obtained from a solution of aniline (0.56 g, 6.0 mmol) in 10 mL of tetrahydrofuran, *n*-butyllithium (3.75 mL, 6.0 mmol) and a solution of **7** (0.53 g, 3.0 mmol) in 100 mL of tetrahydrofuran according to the general procedure. Subsequent crystallization from acetone gave 0.52 mg (1.92 mmol, 64%) of **10a** as red solid (mp 120 °C, decomp.). IR: $\tilde{\nu}$ = 669 (m), 683 (s), 702 (vs), 766 (vs), 799 (w), 826 (w), 839 (s), 907 (w), 926 (w), 934 (w), 972 (w), 1024 (w), 1032 (vw), 1057 (w), 1065 (w), 1076 (w), 1117 (m), 1152 (m), 1167 (w), 1194 (w), 1231 (s), 1246 (w), 1306 (s), 1352 (m), 1387 (s), 1441 (s), 1485 (vs), 1497 (vs), 1526 (vs), 1570 (vs), 1585 (m), 1611 (s), 1655 (vs), 1715 (vw), 1749 (vw), 1809 (vw), 1877 (vw), 1944 (vw), 2720 (vw), 2776 (vw), 2889 (vw), 3053 (m, br), 3325 (w), 3456 (s) cm^{-1}. UV−vis (DCM): λ_{Abs} ($\tilde{\nu}$, ε) = 240 nm (41 666 cm^{-1}, 25 683 L M^{-1} cm^{-1}), 349 nm (28 653 cm^{-1}, 9081 L M^{-1} cm^{-1}). Fluorescence (DCM, 10^{-4} mol/L, $\lambda_{Irradiation}$ = 380 nm): λ_{Em} ($\tilde{\nu}$) = 498 nm (20 080 cm^{-1}), 513 nm (19 493 cm^{-1}). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (s, 1 H, CH_3), 7.12−7.04 (m, 2H, CH_{ar}), 7.18 (dd, ^{3}J = 10.4, ^{4}J = 4.3 Hz, 1 H, CH_{ar}), 7.47−7.38 (m, 2 H, CH_{ar}), 7.60 (d, ^{3}J = 5.2 Hz, 2 H, CH_{ar}), 7.68 (dd, ^{3}J = 8.1, 7.5 Hz, 1 H, CH_{ar}), 8.00 (dd, ^{3}J = 8.2, ^{4}J = 0.9 Hz, 1 H, CH_{ar}), 8.10−8.04 (m, 1 H, CH_{ar}), 8.70 (dd, ^{3}J = 7.4, ^{4}J = 1.1 Hz, 1 H, CH_{ar}). ^{13}C NMR (100.62 MHz, $(CD_3)_2SO$): δ = 119.6 ($C_{ipso,naph}$), 121.7 (*p*-CH_{ph}), 122.9 (CH_{ph}), 124.5, 126.1, 126.5, 126.9 (CH_{naph}), 127.2 ($C_{ipso,naph}$), 128.1 (CH_{ph}), 129.0 ($C_{ipso,naph}$), 130.0 (CH_{naph}), 131.8 ($C_{ipso,naph}$), 132.3 (CH_{naph}), 151.6 ($C_{ipso,ph}$), 154.2, 159.9 (C═N) ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{14}N_3$ 272.1182. Found 272.1191. Anal. Calcd for $C_{18}H_{13}N_3$ (271.32): C, 79.68; H, 4.83; N, 15.49. Found: C, 79.43; H, 4.52; N, 15.41. For X-ray crystal structure data see the Supporting Information.

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*[3-Amino-benzo[de]isoquinolin-(1Z)-yliden]-p-tolyl-amine (**10b**).* **10b** was obtained from a solution of *p*-toluidine (0.10 g, 1.0 mmol) in 5 mL of tetrahydrofuran and *n*-butyllithium (0.63 mL, 1.0 mmol) according to the general procedure. **7** (0.12 mg, 1.0 mmol) was however dissolved in 15 mL of bromobenzene and added to the reaction mixture. The solution was stirred for 2 h before it was quenched. Subsequent crystallization from toluene gave 0.13 g (0.5 mmol, 46%) of **10b** as red solid (mp 239−240 °C). IR: $\tilde{\nu}$ = 653 (m), 682 (m), 715 (m), 725 (w), 773 (vs), 785 (w), 810 (m), 840 (m), 856 (m), 881 (vw), 933 (w), 964 (vw), 974 (vw), 1016 (vw), 1029 (w), 1056 (vw), 1074 (vw), 1105 (w), 1116 (w), 1161 (w), 1192 (vw), 1207 (vw), 1230 (w), 1242 (vw), 1307 (m), 1350 (w), 1386 (m), 1435 (m), 1498 (vs), 1527 (vs), 1570 (s), 1585 (w), 1608 (s), 1652 (vs), 1894 (vw), 1951 (vw), 2027 (vw), 2036 (vw), 2085 (vw), 2094 (vw), 2139 (vw), 2162 (vw), 2185 (vw), 2248 (vw), 2360 (vw), 2717 (vw), 2918 (vw), 3018 (w), 3319 (w), 3072 (w), 3055 (w), 3450 (s) cm^{-1}. UV−vis (DCM): λ_{Abs} ($\tilde{\nu}$, ε) = 243 nm (41 152 cm^{-1}, 35 238 L M^{-1} cm^{-1}), 349 nm (28 653 cm^{-1}, 16 085 L M^{-1} cm^{-1}). Fluorescence (DCM, 10^{-4} mol/L, $\lambda_{Irradiation}$ = 350 nm): λ_{Em} ($\tilde{\nu}$) = 498 nm (20 080 cm^{-1}). ^{1}H NMR (300.13 MHz, $(CD_3)_2SO$): δ = 2.28 (s, 3H, CH_3), 6.98−7.09 (m, 4H, CH_{ar}), 7.64−7.73 (m, 2H, CH_{ar}), 7.45−8.05 (br, 2H, NH_2), 8.12 (dd, ^3J = 8.15 Hz, ^4J = 0.8 Hz, 1H), 8.20 (d, ^3J = 8.1 Hz, 1H) 8.28 (d, ^3J = 6.8 Hz, 1H), 8.56 (dd, ^3J = 7.4, ^4J = 1.1 Hz, 1H) ppm. ^{13}C NMR (75.48 MHz, $(CD_3)_2SO$): δ = 20.6 (CH_3), 119.6 (C_{ipso}), 123.0 (CH_{ph}), 124.4, 126.1, 126.3, 126.9 (CH_{naph}), 127.3 (C_{ipso}), 128.6 (CH_{ph}), 129.0 (C_{ipso}), 129.8 (CH_{naph}), 130.5 (C_{ipso}), 131.8 (C_{ipso}), 132.3(CH_{naph}), 154.0, 159.7 (*C*═N) ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{16}N_3$ 286.1339. Found 286.1340. Anal. Calcd for $C_{19}H_{15}N_3$ (*M* = 285.34): C, 79.98; H, 5.30; N, 14.73. Found: C, 79.73; H, 5.07; N, 14.49. For X-ray crystal structure data see the Supporting Information.

*(1Z)-1-(Pyridin-2-ylimino)-1H-benzo[de]isoquinolin-3-amine (**10c**).* **10c** was obtained from a solution of 2-aminopyridine (1.04 g, 11.0 mmol) in 15 mL of tetrahydrofuran, *n*-butyllithium (6.9 mL, 11.0 mmol), and a solution of **7** (1.78 g, 10.0 mmol) in 200 mL of tetrahydrofuran according to the general procedure. The reaction mixture was refluxed for 5 h and quenched afterward. The crude product was crystallized twice from toluene, giving 0.27 g (1.5 mmol, 50%) of **10c** as red solid (mp 166 °C, decomp.). IR: $\tilde{\nu}$ = 617 (w), 679 (vw), 700 (s), 714 (vw), 733 (vs), 770 (vs), 843 (s), 870 (s), 916 (w), 932 (w), 941 (w), 974 (w), 993 (s), 1028 (w), 1049 (w), 1078 (w), 1097 (w), 1128 (m), 1146 (w), 1155 (m), 1165 (w), 1200 (m), 1236 (vs), 1256 (s), 1267 (s), 1279 (m), 1287 (m), 1323 (vs), 1356 (s), 1369 (w), 1387 (m), 1418 (s), 1447 (s), 1464 (vs), 1491 (s), 1522 (vs), 1547 (s), 1566 (s), 1587 (s), 1603 (w), 1626 (m), 1672 (vs), 1711 (vw), 1771 (vw), 3003 (s), 3038 (s), 3225 (w), 3358 (vw) cm^{-1}. UV−vis (DCM): λ_{Abs} ($\tilde{\nu}$, ε) = 249 nm (40 160 cm^{-1}, 44 820 L M^{-1} cm^{-1}), 365 nm (27 397 cm^{-1}, 31 554 L M^{-1} cm^{-1}). Fluorescence (DCM, 10^{-4} mol/L, $\lambda_{irradiation}$ = 350 nm): λ_{Em} ($\tilde{\nu}$) = 506 nm (broad, 19763 cm^{-1}). ^{1}H NMR (400.13 MHz, $(CD_3)_2SO$): δ = 6.95 (t, ^3J = 6.1, 2 H, CH_{ar}), 7.64 (dt, ^3J = 6.8, ^4J = 1.7, 1 H, CH_{ar}), 7.67−7.79 (m, 2 H, CH_{ar}), 8.19 (dd, ^3J = 8.1, ^4J = 0.8, 1 H, CH_{ar}), 8.25 (d, ^3J = 8.1, 1 H, CH_{ar}), 8.35 (t, ^3J = 6.5, 1 H, CH_{ar}), 8.59 (dd, ^3J = 6.6, ^3J = 0.9, 1 H, CH_{ar}) ppm. ^{13}C NMR (100.62 MHz, $(CD_3)_2SO$): δ = 117.4 (CH_{ar}), 117.7 (C_{ipso}), 119.5 (C_{ipso}), 125.1, 126.2 (CH_{ar}), 126.4 (C_{ipso}), 127.0 (126.98), 127.0 (127.01) (CH_{ar}), 128.8 (C_{ipso}), 130.7 (CH_{ar}), 131.8 (CH_{ar}), 132.6 (CH_{ar}), 136.6 (CH_{ar}), 148.0 (CH_{ar}), 155.1, 160.0, 164.2 (*C*═N) ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{13}N_4$ 273.1135. Found 273.1133. Anal. Calcd for $C_{17}H_{12}N_4$ (272.30): C, 74.98; H, 4.44; N, 20.58. Found: C, 74.61; H, 4.43; N, 20.18. For X-ray crystal structure data see the Supporting Information.

*3-(Dimethyl-hydrazono)-3H-benzo[d,e]isoquinolin-1-ylamine (**10d**).* **10d** was obtained from a solution of *N*,*N*-dimethylhydrazine (0.35 mL, 0.27 mg, 4.5 mmol) in 10 mL of tetrahydrofuran, *n*-butyllithium (2.80 mL, 4.5 mmol), and a solution of **7** (0.53 g, 3.0 mmol) in 40 mL of tetrahydrofuran according to the general procedure. The mixture was warmed to 50 °C overnight; 0.39 mg (2.83 mmol, 94%) of **10d** was obtained as red resin. Further purification was not possible due to the sensitivity of the compound. IR: $\tilde{\nu}$ = 613 (vs), 644 (s), 667 (vw), 719 (vw), 770 (vs), 799 (w), 824 (vs), 837 (vs), 926 (m), 989 (vs), 1016 (w), 1038 (vw), 1078 (vw), 1126 (w), 1225 (w), 1317 (m), 1352 (vw), 1364 (vw), 1381 (w), 1418 (w), 1437 (m), 1466 (w), 1501 (m), 1528 (vs), 1585 (vw), 1603 (vw), 1636 (s), 1734 (vw), 1987 (vw), 2021 (vw), 2052 (vw), 2168 (vw), 2191 (vw), 2222 (vw), 2326 (vw), 2361 (vw), 2770 (vw), 2814 (vw), 2853 (w), 2951 (vw), 3057 (vw), 3146 (vw), 3157 (vw), 3167 (vw), 3310 (vw), 3319 (vw), 3329 (vw) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.70 (s, 6 H, CH_3), 7.54−7.60 (m, 2 H, CH_{ar}), 7.92 (dd, ^3J = 8.2 Hz, ^4J = 1.0 Hz, 1 H, CH_{ar}), 7.98−8.06 (m, 2 H, CH_{ar}), 8.49 (dd, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 47.5 (CH_3), 121.8 (C_{ipso}), 124.0 (123.96, CH_{ar}), 124.0 (123.99, CH_{ar}), 124.8 (C_{ipso}), 125.9, 126.8 (CH_{ar}), 128.5 (C_{ipso}), 129.7, 131.9 (CH_{ar}), 132.6 (C_{ipso}), 150.0, 155.8 (*C*═N) ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{14}H_{15}N_4$ 239.1290. Found 239.1291.

*3-(Methyl-phenyl-hydrazono)-3H-benzo[de]isoquinolin-1-ylamine (**10e**).* **10e** was obtained from a solution of *N*-methyl-*N*-phenylhydrazine (0.96 g, 7.9 mmol) in 20 mL of tetrahydrofuran, *n*-butyllithium (4.9 mL, 7.8 mmol), and a solution of **7** (0.90 g, 5.1 mmol) in 130 mL of tetrahydrofuran according to the general procedure. In this case, the solution of the dinitrile was cooled to −78 °C and the solution of the deprotonated hydrazine was added. The crude product was purified with flash chromatography (dichloromethane/triethylamine, 10:1) twice. The product was solved in toluene and filtered over Celite. The Celite was washed thoroughly with toluene; 1.46 g (4.9 mmol, 97%) of **10e** as dark purple solid was obtained (mp 162 °C, decomp.). R_f = 0.51 (dichloromethane/triethylamine = 10:1). IR: $\tilde{\nu}$ = 615 (m), 665 (w), 691 (vs), 708 (m), 721 (vw), 750 (vs), 764 (vs), 773 (s), 785 (vs), 799 (vw), 837 (m), 856 (vw), 872 (w), 901 (m), 957 (w), 964 (w), 991 (m), 1026 (m), 1080 (w), 1097 (s), 1155 (vw), 1184 (w), 1202 (vw), 1233 (w), 1290 (s), 1310 (vs), 1350 (w), 1385 (w), 1416 (w), 1435 (m), 1458 (w), 1487 (vs), 1528 (s), 1591 (s), 1641 (vs), 2874 (vw), 2909 (vw), 3046 (w, br), 3285 (vw), 3482 (w) cm^{-1}. UV−vis (DCM): λ_{Abs} ($\tilde{\nu}$, ε) = 469 nm (21 322 cm^{-1}, 29 742 L M^{-1} cm^{-1}). Fluorescence (DCM, 10^{-4} mol/L, $\lambda_{Irradiation}$ = 480 nm): λ_{Em} ($\tilde{\nu}$) = 595 nm (16805 cm^{-1}). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.36 (s, 3 H, CH_3), 6.89 (t, ^3J = 7.2 Hz, 1 H, CH_{ar}), 7.11−7.20 (m, 2 H, CH_{ar}), 7.22−7.34 (m, 2 H, CH_{ar}), 7.58 (dd, ^3J = 8.2, 7.5 Hz, 1 H, CH_{ar}), 7.60−7.67 (m, 1 H, CH_{ar}), 7.92 (d, ^3J = 7.2 Hz, 1 H, CH_{ar}), 7.96 (dd, ^3J = 8.2, ^4J = 0.8 Hz, 1 H, CH_{ar}), 8.03 (d, ^3J = 7.9 Hz, 1 H, CH_{ar}), 8.71 (dd, ^3J = 7.5, ^4J = 1.1 Hz, 1 H, CH_{ar}). ^{13}C NMR (75.47 MHz, $(CD_3)_2SO$): δ = 41.0 (CH_3), 113.7 (CH_{ph}), 117.8 (CH_{ar}), 119.9 (C_{ipso}), 123.2 (CH_{ar}), 123.5 (CH_{ar}), 126.1 (CH_{ar}), 126.8 (CH_{ar}), 127.1 (C_{ipso}), 127.8 (CH_{ar}), 128.5 (CH_{ph}), 128.9 (C_{ipso}), 131.5 (CH_{ar}), 132.2 (C_{ipso}), 148.7, 151.2, 156.2 (N-C_{ipso}, *C*═N, C═N) ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{17}N_4$ 301.1448. Found 301.1452. Anal. Calcd for $C_{19}H_{16}N_4$ (300.36): C, 75.98; H, 5.37; N, 18.65. Found: C, 76.00; H, 5.35; N, 18.63.

*5-(p-Tolylimino)-5H-dibenzo[c,e]azepin-7-amine (**11a**).* **11a** was obtained from a solution of *p*-toluidine (0.32 g, 3.0 mmol) in 30 mL of tetrahydrofuran, *n*-butyllithium (1.9 mL, 3.0 mmol), and a solution of **8** (0.61 g, 3.0 mmol) in 15 mL of tetrahydrofuran according to the general procedure. The crude product was crystallized from toluene. Some unreacted 2,2′-dicyanobiphenyl (**8**) could be separated from the filtrate. The residue was purified by flash chromatography (*tert*-butylmethyl ether + 5% triethylamine). Subsequent crystallization from acetonitrile/dichloromethane gave 0.24 g (0.8 mmol, 26%) of **11a** as yellow solid (mp 197−199 °C). R_f = 0.43 (*tert*-butylmethyl ether + 5% triethylamine). IR: $\tilde{\nu}$ = 615 (w), 669 (m), 687 (m), 712 (vw), 743 (vs), 764 (w), 775 (s), 808 (vs), 841 (vw), 864 (w), 937 (vw), 953 (vw), 986 (vw), 1018 (w), 1034 (w), 1055 (w), 1065 (vw), 1111 (w), 1136 (vw), 1165 (vw), 1179 (vw), 1227 (m), 1261 (w), 1319 (vs), 1379 (w), 1404 (vs), 1437 (m), 1504 (s), 1570 (vs), 1587 (vs), 1628 (s), 1709 (vw), 2336 (vw), 2359 (vw), 2864 (vw), 2916 (vw), 3022 (vw), 3051 (vw), 3063 (vw), 3136 (w), 3258 (vw), 3296 (vw), 3445 (w) cm^{-1}. ^{1}H NMR (300.13 MHz, $(CD_3)_2SO$): δ = 2.24 (s, 3 H, CH_3), 6.72 (d, ^3J = 8.1 Hz, 2 H, CH_{ar}), 7.03 (d, ^3J = 8.1 Hz, 2 H, CH_{ar}), 7.15 (s, br, 2 H, NH_{ar}), 7.47−7.60 (m, 3 H, CH_{ar}), 7.60−7.71 (m, 2 H, CH_{ar}), 7.71−7.81 (m, 3 H, CH_{ar}) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 20.5 (CH_3), 109.6, 122.6, 127.2, 127.5, 127.9, 128.0, 128.1, 128.6, 129.0, 129.7, 130.7 (CH_{ar}), 131.5, 133.0, 134.9,

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137.5, 142.3, 147.3 (C_{ipso}), 157.6, 158.9 (*C*═N) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{18}N_3$ 312.1495. Found 312.1493. Anal. Calcd for $C_{21}H_{17}N_3$ (311.38): C, 81.00; H, 5.50; N, 13.49. Found: C, 80.94; H, 5.62; N, 13.11.

*[7-Amino-dibenzo[c,e]acepin-(5Z)-yliden]-pyridin-2-ylamine (**11b**).* **11b** was obtained from a solution of 2-aminopyridine (0.28 g, 3.0 mmol) in 10 mL of tetrahydrofuran, *n*-butyllithium (1.9 mL, 3.0 mmol), and a solution of **8** (0.41 g, 2.0 mmol) in 20 mL of tetrahydrofuran according to the general procedure. However, in this case, the solution of the dinitrile was cooled to −78 °C and the solution of the deprotonated amine was added. Subsequent crystallization from toluene and dichloromethane gave 0.14 mg (0.4 mmol, 14%) of **11b** as colorless solid (mp 157−158 °C). IR: $\tilde{\nu}$ = 613 (vs), 642 (s), 689 (m), 735 (vs), 770 (s), 775 (vs), 791 (w), 864 (w), 878 (vw), 959 (w), 995 (m), 1034 (m), 1051 (w), 1061 (w), 1096 (vw), 1123 (w), 1150 (w), 1163 (vw), 1179 (w), 1244 (m), 1265 (s), 1287 (w), 1325 (vs), 1423 (vs), 1437 (vw), 1466 (s), 1485 (vw), 1497 (vw), 1553 (vs), 1570 (m), 1585 (s), 1595 (m), 1655 (m), 1674 (w), 3003 (vw), 3065 (w), 3107 (w), 3335 (vw) cm^{-1}. ^1H NMR (300.13 MHz, $(CD_3)_2SO$): δ = 6.65 (d, ^3J = 7.0 Hz, 1 H, CH_{ar}), 6.95 (dd, ^3J = 6.4, ^3J = 5.0, 1 H, CH_{ar}), 7.32 (s, br, 2 H, NH_2), 7.50−7.71 (m, 5 H, CH_{ar}), 7.71−7.86 (m, 4 H, CH_{ar}), 8.29 (dd, ^3J = 4.8, ^4J = 1.0 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (75.47 MHz, $(CD_3)_2SO$): δ = 116.8 (CH_{ar}), 118.2 (CH_{ar}), 127.5 (CH_{ar}), 127.8 (CH_{ar}), 128.0 (CH_{ar}), 128.2 (CH_{ar}), 128.3 (CH_{ar}), 129.4 (CH_{ar}), 129.7 (CH_{ar}), 130.8 (CH_{ar}), 132.8 (C_{ipso}), 134.9 (C_{ipso}), 136.9 (CH_{ar}), 137.3 (C_{ipso}), 141.6 (C_{ipso}), 148.3 (CH_{ar}), 158. Nine (*C*═N), 160.6 (*C*═N), 162.8 (*C*═N) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{15}N_4$ 299.1291. Found 299.1280. Anal. Calcd for $C_{19}H_{14}N_4$ (298.34), $C_{19}H_{14}N_4{\cdot}H_2O$: C, 72.13; H, 5.10; N, 17.71. Found: C, 72.27; H, 5.19; N, 17.57. For X-ray crystal structure data see the Supporting Information.

*7-(Dimethyl-hydrazono)-7H-dibenzo[c,e]-azepin-5-ylamine (**11c**).* **11c** was obtained from a solution of *N,N*-dimethylhydrazine (0.37 mL, 288 mg, 4.8 mmol) in 10 mL of tetrahydrofuran, *n*-butyllithium (3.0 mL, 4.8 mmol), and a solution of **8** (817 mg, 4.0 mmol) in 20 mL of tetrahydrofuran according to the general procedure. Subsequent crystallization from toluene gave 1.51 g (5.0 mmol, 46%) of **11c** as colorless solid (mp 179−180 °C). IR: $\tilde{\nu}$ = 615 (w), 664 (vs), 679 (s), 737 (vs), 768 (vs), 835 (w), 866 (m), 874 (m), 955 (w), 988 (vs), 1018 (s), 1034 (m), 1055 (w), 1123 (w), 1144 (w), 1169 (vw), 1179 (vw), 1217 (w), 1231 (w), 1261 (w), 1321 (s), 1389 (m), 1398 (w), 1435 (w), 1443 (w), 1468 (w), 1483 (w), 1497 (vw), 1537 (vw), 1557 (m), 1572 (vs), 1589 (vs), 1607 (s), 1649 (vs), 2768 (w), 2810 (m), 2849 (w), 2955 (vw), 3065 (vw), 3165 (w), 3316 (vw), 3372 (vw) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.52 (s, 6 H, CH_3), 7.35−7.47 (m, 3 H, CH_{ar}), 7.50−7.59 (m, 2 H, CH_{ar}), 7.60−7.66 (m, 2 H, CH_{ar}), 7.69 (dd, ^3J = 7.8, ^4J = 1.2 Hz, 1 H, CH_{ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.1 (CH_3), 126.5 (CH_{ar}), 127.8 (CH_{ar}), 128.1 (CH_{ar}), 128.2 (CH_{ar}), 128.6 (CH_{ar}), 129.0 (CH_{ar}), 130.5 (CH_{ar}), 131.0 (CH_{ar}), 132.1 (C_{ipso}), 135.9 (C_{ipso}), 139.3 (C_{ipso}), 140.3 (C_{ipso}), 155.8 (C_{im}), 156.2 (C_{im}). HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{17}N_4$ 265.1448. Found 265.1432. Anal. Calcd for $C_{16}H_{16}N_4$ (264.33): C, 72.70; H, 6.10; N, 21.20. Found: C, 72.90; H, 6.09; N, 21.23. For X-ray crystal structure data see the Supporting Information.

*[3-Amino-4,4-diethyl-4H-isoquinoliline-(1Z)-yliden]-p-tolyl-amin (**12a**).* **12a** was obtained from a solution of *p*-toluidine (0.43 g, 4.0 mmol) in 10 mL of tetrahydrofuran, *n*-butyllithium (2.5 mL, 4.0 mmol), and a solution of **9a** (0.40 g, 2.0 mmol) in 15 mL of tetrahydrofuran according to the general procedure. Column chromatography (pentane/*tert*-butylmethyl ether = 2:1 + 3% triethylamine) and subsequent crystallization from *n*-heptane gave 0.55 g (1.8 mmol, 45%) of **12a** as yellow solid (mp 252−254 °C). R_f = 0.47 (pentane/*tert*-butylmethyl ether = 2:1 + 3% triethylamine). IR: $\tilde{\nu}$ = 665 (vw), 678 (s), 692 (vs), 715 (s), 758 (vs), 775 (m), 806 (s), 831 (w), 852 (s), 877 (w), 906 (w), 929 (w), 947 (vw), 962 (vw), 991 (w), 1014 (vw), 1035 (w), 1055 (vw), 1080 (vw), 1105 (m), 1118 (w), 1155 (m), 1172 (w), 1209 (w), 1246 (s), 1257 (w), 1313 (s), 1330 (vs), 1382 (w), 1409 (w), 1452 (s), 1481 (s), 1498 (vs), 1531 (vs), 1597 (s), 1612 (s), 1649 (vs), 1138 (vw), 1884 (vw), 1950 (vw), 1977 (vw), 2875 (w), 2918 (w), 2933 (w), 2966 (m), 3012 (w), 3057 (w), 3126 (w), 3319 (vw), 3462 (m) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$) δ = 0.53 (t, 6 H, ^3J = 7.3, CH_2CH_3), 1.54−1.63 (m, CH_2), 1.89−1.98 (m, CH_2), 2.39 (s, 3 H, CH_3), 6.84 (d, ^3J = 8.1, 2 H, CH_{ar}), 7.15 (d, ^3J = 8.0, 2 H, CH_{ar}), 7.25 (d, ^3J = 9.2, 1 H, $C_qC_{ipso}CH_{ar}$), 7.30−7.34 (m, 1 H, $C_{im}CH_{ar}CH_{ar}$), 7.45 (dt, ^3J = 8.0, ^4J = 1.4, 1 H, CH_{ar}), 8.38 (dd, ^3J = 7.9, ^4J = 1.2, 1 H, CH_{ar}) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 9.2 (CH_2CH_3), 21.3 ($C_{ar}CH_3$), 35.7 (CH_2), 47.7 (C_q), 122.4 (CH_{ar}), 124.0 ($C_qC_{ipso}CH_{ar}$), 126.7, 126.8 ($C_{im}C_{ipso}CH_{ar}$, $C_{im}C_{ipso}CH_{ar}CH_{ar}$), 128.7 ($C_qC_{ipso}$), 129.3 ($CH_{ar}$), 130.9 ($C_qC_{ipso}CH_{ar}CH_{ar}$), 130.9 ($CH_3C_{ipso}$), 139.3 ($C_{im}C_{ipso}$), 149.8 ($NC_{ipso}$), 153.3 ($C_{ipso}N-C$═N), 170.9 (N═$C-NH_2$) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{24}N_3$ 306.1965. Found 306.1963. Anal. Calcd for $C_{20}H_{23}N_3$ (305.42): C, 78.65; H, 7.59; N, 13.76. Found: C, 78.50; H, 7.76; N, 13.49. For X-ray crystal structure data see the Supporting Information.

*(1Z)-1-(Dimethylhydrazinylidene)-4,4-diethyl-1,4-dihydroisoquinolin-3-amine (**12b**).* **12b** was obtained from a solution of *N,N*-dimethylhydrazine (0.73 mL, 0.57 g, 9.5 mmol) in 20 mL of tetrahydrofuran, *n*-butyllithium (5.96 mL, 9.5 mmol), and a solution of **9a** (1.71 g, 8.6 mmol) in 20 mL tetrahydrofuran according to the general procedure; 2.12 g (8.4 mmol, 97%) of **12b** was obtained as yellow solid without further purification (mp 140 °C). IR: $\tilde{\nu}$ = 664 (w), 687 (vs), 716 (w), 758 (s), 777 (s), 814 (w), 849 (m), 903 (w), 945 (w), 961 (m), 974 (vs), 1011 (m), 1036 (w), 1088 (vw), 1125 (vw), 1155 (s), 1171 (w), 1206 (w), 1223 (w), 1258 (vw), 1308 (m), 1339 (vs), 1377 (w), 1393 (w), 1402 (w), 1425 (w), 1439 (s), 1452 (s), 1470 (w), 1483 (m), 1539 (vs), 1591 (m), 1609 (m), 1636 (m), 2776 (w), 2816 (w), 2860 (w), 2876 (w), 2943 (w), 2968 (m), 3030 (vw), 3073 (w), 3279 (vw), 3505 (s) cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 0.60 (t, ^3J = 7.3 Hz, 6 H, CH_2CH_3), 1.98 (q, ^3J = 7.3 Hz, 4 H, CH_2), 2.62 (s, 6 H, $N(CH_3)_2$), 6.45−7.21 (br, 2 H, NH_2), 7.26−7.32 (m, 2 H, CH_{ar}), 7.40−7.48 (m, 2 H, CH_{ar}), 8.24 (dd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 9.1 (CH_2CH_3), 36.4 (CH_2), 47.4 ($N(CH_3)_2$), 49.0 (C_q), 124.5 (CH_{ar}), 124.7 (CH_{ar}), 126.5 (CH_{ar}), 128.3 (*i*-C_{ar}), 130.7 (CH_{ar}), 138.5 (*i*-C_{ar}), 149.8 (C_{im}), 165.9 (C_{im}) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{23}N_4$ 259.1917. Found 295.1916. Anal. Calcd for $C_{15}H_{22}N_4$ (258.36): C, 69.73; H, 8.58; N, 21.69. Found: C, 69.69; H, 8.18; N, 21.57. For X-ray crystal structure data see the Supporting Information.

*3-Amino-(1Z)-ylidene-p-tolyl-amin-spiro[cyclopentan-1′,4-4H-isoquinoline] (**12c**).* **12c** was obtained from a solution of *p*-toluidine (1.39 g, 12.9 mmol) in 10 mL of tetrahydrofuran, *n*-butyllithium (8.1 mL, 13.0 mmol), and a solution of **9b** (2.11 g, 11.8 mmol) in 10 mL of tetrahydrofuran according to the general procedure. Subsequent crystallization from toluene gave 1.51 g (5.0 mmol, 46%) of **12c** as yellow solid (mp 225 °C). IR: $\tilde{\nu}$ = 673 (w), 686 (s), 698 (s), 721 (m), 750 (vs), 777 (w), 798 (s), 821 (s), 831 (m), 844 (w), 867 (m), 904 (vw), 939 (w), 954 (m),981 (w), 1016 (m), 1035 (m), 1049 (vw), 1101 (w), 1118 (w), 1157 (m), 1170 (w), 1207 (vw), 1238 (m), 1246 (m), 1271 (m), 1288 (m), 1307 (m), 1328 (vs), 1411 (m), 1452 (s), 1479 (s), 1500 (vs), 1533 (vs), 1593 (s), 1610 (s), 1656 (vs), 2870 (w), 2914 (w), 2956 (m), 2972 (w), 3024 (w), 3327 (vw), 3466 (s) cm^{-1}. ^1H NMR (400.13 MHz, $(CD_3)_2SO$): δ = 1.87 − 2.03 (m, 6 H, CH_2), 2.16−2.26 (m, 5 H, CH_3, C_qCH_2), 6.86 (d, ^3J = 8,0 Hz, 2 H, CH_{ph}), 6.97 (br, 1 H, N*H*), 7.03 (d, ^3J = 8.0 Hz, 2 H, CH_{ph}), 7.32 (t, ^3J = 7.4 Hz, 1 H, $C_{im}C_{ipso}CHCH$), 7.38 (d, ^3J = 7.4 Hz, 1 H, $C_qC_{ipso}CH$), 7.42−7.50 (m, 1 H, $C_qC_{ipso}CHCH$), 8.17 (dd, ^3J = 7.8 Hz, ^4J = 1.3 Hz, 1 H, $C_{im}C_{ipso}CH$) ppm. ^{13}C NMR (100.62 MHz, $(CD_3)_2SO$): δ = 20.5 (CH_3), 26.4 (CH_2), 41.5 (CH_2), 47.7 (C_q), 122.7 (CH_{ph}), 128.4 (CH_{ph}), 129.2 ($C_{im}C_{ipso}C_q$), 124.6 (CH_{ar}), 125.6 (CH_{ar}), 125.9 (CH_{ar}), 130.0 (CH_{ar}), 130.1 (*p*-C_{ph}), 144.8 ($C_qC_{ipso}C_q$), 148.9 (N-C_{ph}), 154.0 (C═N), 174.0 ($C_{im}NH_2$) ppm. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{22}N_3$ 304.1808. Found 304.1804. Anal. Calcd for $C_{20}H_{21}N_3$ (303.40): C, 79.17; H, 6.98; N, 13.85. Found: C, 78.96; H, 6.94; N, 13.87. For X-ray crystal structure data see the Supporting Information.

*(1′Z)-1′-(2-Methyl-2-phenylhydrazinylidene)-1′H-spiro-[cyclopentane-1,4′-isoquinolin]-3′-amine (**12d**).* **12d** was obtained from a solution of *N,N*-methylphenylhydrazine (0.61 g, 5.0 mmol) in 10 mL of tetrahydrofuran, *n*-butyllithium (3.1 mL, 5.0 mmol), and a solution of **9b** (1.04 g, 5.3 mmol) in 10 mL of tetrahydrofuran

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according to the general procedure. Subsequent crystallization from toluene gave 0.66 g (2.1 mmol, 42%) of **12d** as orange solid (mp 194 °C). IR: $\tilde{\nu}$ = 650 (w), 689 (vs), 704 (m), 723 (w), 748 (vs), 772 (s), 829 (w), 868 (m), 878 (w), 935 (m), 955 (vw), 991 (m), 1026 (m), 1038 (w), 1105 (s), 1159 (w), 1192 (m), 1269 (w), 1283 (w), 1302 (w), 1325 (s), 1354 (vs), 1412 (w), 1420 (w), 1454 (m), 1476 (m), 1495 (s), 1537 (vs), 1564 (vw), 1589 (s), 1607 (w), 1643 (vs), 2344 (vw), 2361 (vw), 2799 (vw), 2859 (w), 2893 (vw), 2959 (w), 3022 (vw), 3059 (vw), 3296 (vw), 3472 (m) cm^{-1}. UV/vis (DCM): λ_{Abs} ($\tilde{\nu}$, ε) = 256 nm (39 063 cm^{-1}, 38 757 L M^{-1} cm^{-1}), 378 nm (26 455 cm^{-1}, 7902 L M^{-1} cm^{-1}). Fluorescence (DCM, 10^{-5} mol/L, $\lambda_{Irradiation}$ = 415 nm): λ_{Em} ($\tilde{\nu}$) = 471 nm (broad, 21186 cm^{-1}). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.66 − 1.78 (m, 2 H, CH_2), 1.85−2.00 (m, 2 H, CH_2), 2.00−2.18 (m, 4 H, CH_2), 3.14 (s, 3 H, CH_3), 6.83 (t, ^3J = 7.3 Hz, 1 H, CH_{ar}), 6.99 (dd, ^3J = 8.8, ^4J = 1.0 Hz, 2 H, CH_{ar}), 7.23−7.32 (m, 4 H, CH_{ar}), 7.38−7.44 (m, 1H, CH_{ar}), 8.35 (dd, ^3J = 8.2, ^4J = 1.4 Hz, 1 H, CH_2). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.0 (CH_2), 41.1 (CH_3), 42.1 (CH_2), 49.6 (C_q), 114.1 (CH_{ar}), 116.0 (C_{ipso}), 118.8 (CH_{ar}), 124.5 (CH_{ar}), 125.3 (CH_{ar}), 126.6 (CH_{ar}), 129.0 (C_{ipso}), 129.1 (CH_{ar}), 130.6 (CH_{ar}), 143.4 (C_{ipso}), 151.3 (C_{im}), 155.4 (C_{im}). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}N_4$ 319.1917. Found 319.1919. Anal. Calcd for $C_{20}H_{22}N_4$ (318.42): C, 75.44; H, 6.96; N, 17.60. Found: C, 75.64; H, 6.97; N, 17.44. For X-ray crystal structure data see the Supporting Information.

(3′Z)-3′-(Pyridin-2-ylimino)-3′H-spiro[cyclopentane-1,4′-isoquinoline]-1′-amine (**12e**). **12e** was obtained from a solution of 1-aminopyridine (2.40 g, 25.6 mmol) in 20 mL of tetrahydrofuran, *n*-butyllithium (15.6 mL, 25.6 mmol), and a solution of **9b** (4.09 g, 20.8 mmol) in 15 mL of tetrahydrofuran according to the general procedure. Subsequent repeated crystallization from acetone gave 1.30 g (4.5 mmol, 22%) of **12e** as yellow solid (mp 174 °C). As a side product, hydrolysis product **13** could be separated in a small amount from the reaction mixture in impure form (see below). IR: $\tilde{\nu}$ = 619 (vw), 658 (s), 675 (s), 689 (m), 694 (m), 739 (vw), 760 (vw), 781 (s), 806 (vw), 835 (w), 853 (m), 876 (w), 908 (vw), 947 (w), 964 (vw), 989 (m), 1049 (m), 1069 (vw), 1096 (vw), 1115 (vw), 1146 (m), 1177 (w), 1240 (s), 1256 (s), 1277 (s), 1287 (s), 1302 (s), 1333 (m), 1420 (vw), 1435 (s), 1447 (s), 1464 (vw), 1520 (vw), 1558 (w), 1582 (vw), 1616 (w), 1636 (vw), 1665 (vw), 2332 (w), 2342 (w), 2359 (w), 2776 (vw), 2830 (vw), 2870 (w), 2938 (m), 2947 (m), 2978 (w), 3007 (m), 3063 (m), 3171 (vw), 3337 (vw), 3383 (vw), 3426 (w) cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.92−2.15 (m, 6 H, CH_2), 2.51−2.58 (m, 2 H, CH_2), 7.06 (ddd, ^3J = 7.4 Hz, ^3J = 5.0 Hz, ^4J = 1.1 Hz, 1 H, CH_{ar}), 7.35−7.40 (m, 3 H, CH_{ar}), 7.52−7.56 (m, 1 H, CH_{ar}), 7.74 (ddd, ^3J = 8.1 Hz, ^3J = 7.4 Hz, ^4J = 2.0 Hz, 1 H, CH_{ar}), 8.43 (ddd, ^3J = 5.0 Hz, ^4J = 2.0 Hz, ^4J = 0.8 Hz, 1 H, CH_{ar}), 8.50 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 1 H, CH_{ar}), 13.57 (s, 1 H, NH) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 28.0 (CH_2), 43.2 (CH_2), 52.6 (C_q), 119.8 (CH_{ar}), 123.9 (CH_{ar}), 125.8 (CH_{ar}), 126.1 (*i*-C_{ar}), 126.5 (CH_{ar}), 126.8 (CH_{ar}), 132.5 (CH_{ar}), 138.2 (CH_{ar}), 146.4 (*i*-C_{ar}), 146.5 (CH_{ar}), 146.9 (*i*-C_{ar}), 160.6 (*i*-C_{ar}−NH_2), 177.3 (C_qC_{im}) ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}N_4$ 291.1604. Found 291.1594. Anal. Calcd for $C_{18}H_{18}N_4$ (290.36): C, 74.46; H, 6.25; N, 19.30. Found: C, 74.48; H, 6.18; N, 19.62. For X-ray crystal structure data see the Supporting Information.

4,4-Diethyl-1-pyrrolidin-1-yl-4H-isoquinoline-(3Z)-ylidenamine (**12f**). **12f** was obtained from a solution of pyrrolidine (0.3 mL, 0.33 g, 4.0 mmol), 15 mL of tetrahydrofuran, *n*-butyllithium (2.5 mL, 4.0 mmol), and a solution of **9a** (0.79 g, 4.0 mmol) in 5 mL of tetrahydrofuran according to the general procedure. Subsequent crystallization from *n*-heptane gave 0.52 g (1.9 mmol, 48%) of **12f** as yellow solid (mp 101 °C). IR: $\tilde{\nu}$ = 680 (vs), 704 (vs), 734 (m), 758 (vs), 783 (vs), 794 (m), 815 (w), 848 (w), 875 (vs), 891 (s), 906 (w), 923 (m), 945 (w), 979 (w), 1037 (m), 1051 (m), 1074 (m), 1082 (m), 1101 (w), 1120 (w), 1155 (m), 1163 (m), 1182 (m), 1219 (m), 1232 (m), 1257 (m), 1303 (s), 1313 (s), 1332 (vs), 1340 (vs), 1365 (m), 1377 (m), 1436 (vs), 1481 (m), 1516 (vs), 1579 (s), 1620 (m), 1629 (m), 1674 (w), 1842 (vw), 1975 (vw), 2004 (vw), 2015 (vw), 2025 (vw), 2160 (vw), 2341 (w), 2362 (w), 2873 (m), 2935 (m), 2968 (s), 3016 (w), 3176 (vw), 3315 (m) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$) δ = 0.70 (t, 6 H, ^3J = 7.3, CH_3), 1.79−1.92 (m, 2 H, CH_2), 1.92−2.01 (m, 6 H, CH_2CH_3, NCH_2CH_2), 2.13−2.25 (m, 2 H, CH_2CH_3), 3.80 (t, ^3J = 6.6, 4 H, NCH_2), 7.24−7.32 (m, 2 H, CH_{ar}), 7.42−7.52 (m, 2 H, CH_{ar}), 7.71 (d, ^3J = 7.8, 1 H, CH_{ar}) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$) δ = 9.7 (CH_3), 25.9 (CH_2), 34.2 (NCH_2CH_2), 49.2, 50.9 (NCH_2, C_q), 125.2, 126.3, 126.5, 126.6, 130.9, 145.9 (CH_{ar}, C_{ipso}), 159.3, 173.8 (NCN) ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{24}N_3$ 270.1965. Found 270.1957. Anal. Calcd for $C_{17}H_{23}N_3$ (269.38): C, 75.80; H, 8.61; N, 15.60. Found: C, 75.81; H, 8.84; N, 15.32.

1-Amino-4-spiro[cyclopentan]-4H-isoquinolin]-3-on (**13**). During the purification of **12e** a side product, generated by hydrolysis, was observed, which could be enriched by crystallization from acetone/water. The impure compound could be characterized by X-ray diffraction to be **13**. Yield: 0.21 g (1.0 mmol, 5%), colorless solid, impure. HRMS (ESI) m/z: $[M + CH_3]^+$ Calcd for $C_{14}H_{17}N_2O$ 229.1336. Found 229.1338. For X-ray crystal structure data see the Supporting Information.

1-Piperidyl-spiro[cyclopentane-1′,4-4H-isoquinolin]-3-one (**14**). **14** was obtained from a solution of piperidine (0.59 mL, 0.51 g, 6.0 mmol) in 10 mL of tetrahydrofuran, *n*-butyllithium (3.80 mL, 6.0 mmol), and a solution of **9b** (1.08 g, 5.0 mmol) in 5 mL of tetrahydrofuran according to the general procedure. Instead of the usual workup, the reaction was quenched by adding 1 equiv of water (0.33 mL, 0.33 mg, 6.0 mmol) and filtered over Celite. Subsequent flash chromatography (pentane/ethyl acetate = 3:1 + 10% triethylamine) gave 0.83 g (2.9 mmol, 58%) of **14** as a colorless oil. R_f = 0.17 (pentane/ethyl acetate = 3:1 + 10% triethylamine). IR: $\tilde{\nu}$ = 671 (vw), 689 (m), 733 (vw), 760 (vs), 795 (vw), 829 (vw), 853 (w), 885 (w), 908 (vw), 951 (vw), 1005 (m), 1022 (m), 1078 (vw), 1113 (m), 1136 (vw), 1159 (m), 1211 (w), 1258 (m), 1279 (vs), 1304 (s), 1368 (w), 1433 (vs), 1468 (s), 1514 (vs), 1582 (s), 1599 (m), 1665 (s), 1695 (w), 2857 (w), 2938 (m) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.65−1.96 (m, 12 H, CH_2), 2.40−2.60 (m, 2 H, CH_2), 3.81−4.00 (m, 4 H, NCH_2), 7.22−7.32 (m, 1 H, CH_{ar}), 7.37−7.66 (m, 3 H, CH_{ar}) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 24.7, 25.4, 26.6, 37.1 (CH_2), 49.2 (C_q), 55.6 (NCH_2), 124.3 (CH_{ar}), 125.5 (CH_{ar}, C_{ipso}), 126.9 (CH_{ar}), 131.0 (CH_{ar}), 148.3 (C_{ipso}), 167.2 (C═N), 187.0 (C═O) ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}N_2O$ 283.1805. Found 283.1800. Anal. Calcd for $C_{18}H_{22}N_2O$ (282.38): C, 76.56; H, 7.85; N, 9.92. Found: C, 76.90; H, 7.91; N, 9.69

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00126.

Crystallographic data for **8** (CIF)
Crystallographic data for **10a** (CIF)
Crystallographic data for **10b** (CIF)
Crystallographic data for **10c** (CIF)
Crystallographic data for **11b** (CIF)
Crystallographic data for **11c** (CIF)
Crystallographic data for **12a** (CIF)
Crystallographic data for **12b** (CIF)
Crystallographic data for **12c** (CIF)
Crystallographic data for **12d** (CIF)
Crystallographic data for **12e** (CIF)
Crystallographic data for **12f** (CIF)
Crystallographic data for **13** (CIF)
Experimental details (NMR spectra and detailed X-ray data) and quantum chemical DFT results (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Dr. Günter Haufe at the occasion of his 65th birthday.

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