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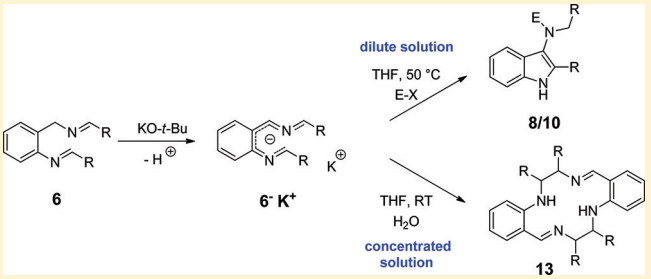
Ring Closure Reactions of 2,6-Diazaheptatrienyl Metal Compounds: Synthesis of 3-Aminoindole Derivatives and 14-Membered Macrocyclic Dimers

Benedikt Neue, Ralph Reiermann, Klaus Gerdes, Roland Fröhlich, Birgit Wibbeling, and Ernst-Ulrich Würthwein*

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Corrensstrasse 40, 48149 Münster, Germany

Supporting Information

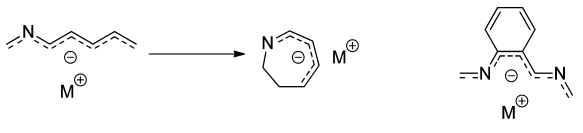
ABSTRACT: 2,6-Diazaheptatrienyl metal compounds **6**$^-$**K**$^+$ are easily accessible from the corresponding diimines **6** by deprotonation using KO-*t*-Bu as base. According to quantum chemical calculations, they are, in comparison to other isomeric species with nitrogen atoms in other positions, highly reactive intermediates, which undergo in dilute solution at 50 °C ring closure reactions to form 3-aminoindole derivatives **8**/**10**. In contrast, in more concentrated solution at room temperature, the formation of 14-membered macrocyclces **13** as a result of formal dimerization is observed. The 3-aminoindole derivatives obtained in this work possess rare substitution patterns, and the macrocyclic compounds are essentially unknown. Two-fold vinylogous derivatives **7** give rise to tricyclic systems with δ-carboline backbone **12**. The experimental results are interpreted using high-level DFT calculations with regard to the possible reaction mechanism and the nature of the transition state of the five-membered ring formation. The molecular structures in the solid state of all types of compounds were elucidated by X-ray diffraction.



INTRODUCTION

The tendency of 2-aza- and 2,4-diazapentadienyl metal compounds to undergo electrocyclic ring closure reactions[1] to form five-membered heterocycles containing one or two nitrogen atoms was reported first by Hunter et al.[2] In subsequent studies, we were able to explain this interesting chemical behavior by mechanistic and quantum chemical studies, to generalize its basic principles and to apply them in various ring forming reactions for five-, six-, and seven-membered ring systems[3] (**1**, Scheme 1). Thus, we learned

Scheme 1. Reaction of 2-Azaheptatrienyl Metal Compounds and Structure of Benzannulated 2,6-Diazaheptatrienyl Metal Compounds



1 **2** **3**

that within the classes of such nitrogen-containing polyenyl anions (metal compounds) and also of the corresponding cations the ability to undergo ring closure reactions strongly depends on the position of the—in comparison to carbon—more electronegative nitrogen within the unsaturated chain.[4] According to these findings ("ring closure rules"), we were able to predict that azaheptatrienyl metal compounds with nitrogen atoms in even positions of the chain (position 2 in structure **1**, Scheme 1) are destabilized and therefore prone to undergo thermodynamically favorable electrocyclic ring closure reactions to form the respective heterocyclic anions (compound **2** in Scheme 1). In contrast, anions with nitrogen atoms in odd positions (1- or 3-position) are more stable and do not undergo cyclization reactions.

The behavior of such nitrogen-substituted polyenyl metal compounds in regioselective reactions with carbonyl compounds and for the diastereoselective synthesis of alkyl-substituted *N*-allylimines at low temperature to prevent cyclization was also investigated in our group.[5]

Various applications of these principles allowed easy and straightforward access to a large number of N-heterocyclic systems just by appropriate positioning of the nitrogen atom in polyenylic anionic starting materials.[6] Besides linear examples, also benzannulated compounds react in the same manner.

In this study, we extend this concept to hitherto unknown benzannulated 2,6-diazaheptatrienyl metal compounds (**3**). In the following, we describe our motivation to study these special systems, their preparation, and the use of these metal organic compounds as easily accessible precursors for the efficient

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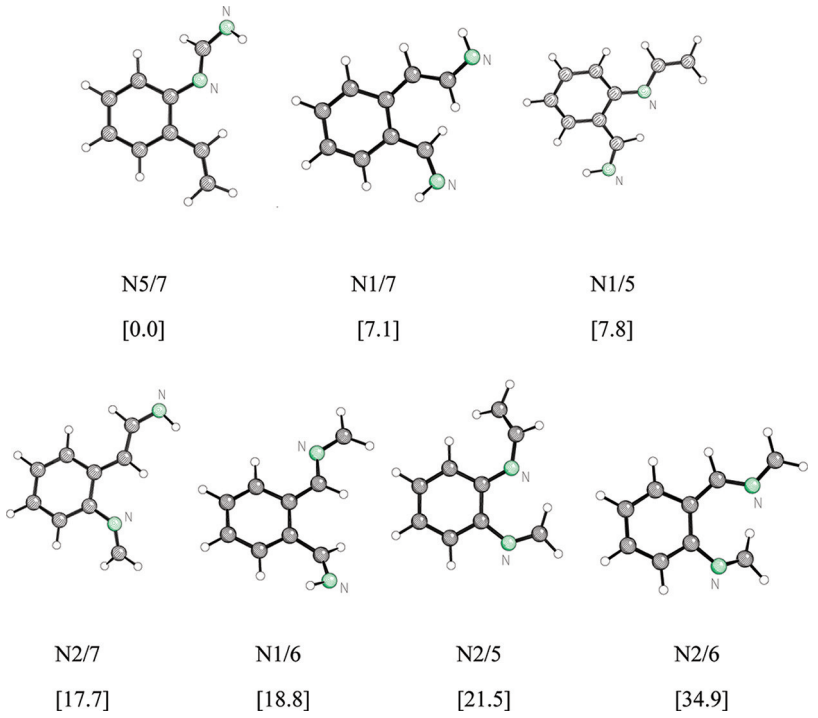


Figure 1. Optimized conformers with relative energies of 3,4-benzannulated diazaheptatrienyl anions with the two nitrogen atoms in different positions (energies in [kcal/mol], SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p)+ZPE).

synthesis of various 3-aminoindole derivatives and novel macrocyclic dimers.

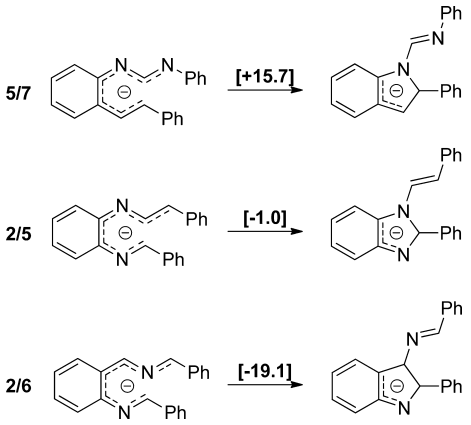
RESULTS AND DISCUSSION

Choice of the System. In order to identify benzannulated diazaheptatrienyl anions (metal compounds) capable for ring closure reactions, we have investigated by quantum chemical methods a number of anionic benzoheptatrienyl systems with the two nitrogen atoms in varying positions. On the SCS-MP2/6-311+G(d,p)//B3LYP/6-311+G(d,p)[7,8] level of theory (corrected for zero-point energies, calculations without countercation),[9] we determined the relative energies for the best conformers of benzannulated diazaheptatrienyl anions as given in Figure 1 (numbering in analogy to the 3,4-benzoheptatrienyl anion).

In accordance with the rules mentioned above, anionic compounds with both nitrogen atoms in odd positions of the chain are low in energy.[3] Here, the nitrogen atoms are located in coefficient positions of the HOMO with high electron density (5/7, 1/7, and 1/5, Scheme 2). Among these, the most stable is the anion with nitrogen atoms in 5- and 7-positions (0.0 kcal/mol). Changing the location of one of the two nitrogen atoms to an even position results in elevated relative energies for most of these compounds (examples 2/7, 1/6, and 2/5 in Scheme 2). In these anions, one heteroatom is positioned in a less favorable nodal position of the HOMO, which causes destabilization (for example structure 2/7, 17.7 kcal/mol). If both nitrogen atoms are located in even positions, the system is most destabilized (structure 2/6, 34.9 kcal/mol). Here both heteroatoms are located in electron-deficient nodal positions of the HOMO causing high reactivity (e.g., for ring forming reactions).

These relative energies are in excellent accordance with calculated reaction energies for the respective ring closure reactions to form five-membered ring systems. Hence, we compared the tendencies for 1,5-electrocyclization of three

Scheme 2. Calculated Cyclization Energies of Three Selected Diphenyldiazaheptatrienyl Anions (SCS-MP2/6-311+G(d,p)//B3LYP/6-31G(d)+ZPE [kcal/mol])



selected diphenyl-substituted diazaheptatrienyl metal compounds with two nitrogen atoms in 5/7-, 2/5- and 2/6-position (Scheme 2) (calculations peformed without metal countercation).

The anion with both nitrogen atoms in odd positions with high electron density (5/7) is low in energy and is not capable of undergoing an electrocyclic ring closure reaction (+15.7 kcal/mol). Cyclization of the 2,5-compound (one nitrogen in odd and one in even position) is approximately thermoneutral (−1.0 kcal/mol). In contrast, due to the destabilization of the open chain compound, the corresponding electrocyclic ring closure reaction of the benzannulated 2,6-diazaheptatrienyl anion is thermodynamically highly favored (−19.1 kcal/mol) since after the cyclization one nitrogen atom is in a favorable position with a large coefficient of the HOMO. Figure 2 shows

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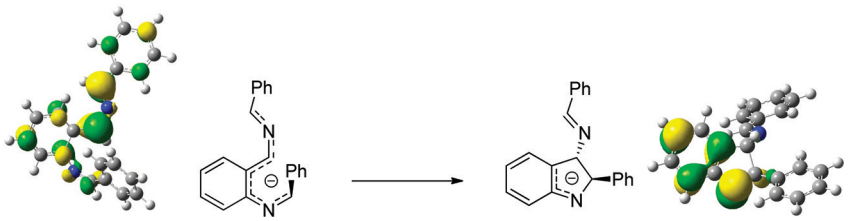


Figure 2. HOMOs of the open chain (left) and of the cyclic anion (right) of the 1,7-diphenyl-2,6-diaza-4,5-benzoheptatrienyl system (B3LYP/6-31G(d), isocontour value 0.04).

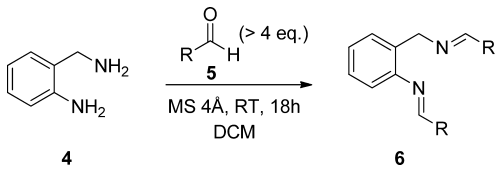
the electronic structures of the HOMO of the open chain and the cyclic compound.

On the basis of these quantum chemical predictions, we have chosen benzannulated 2,6-diazaheptatrienyl metal compounds as starting points for our experimental and theoretical investigation described in this work.

It should be mentioned that anionic systems with adjacent nitrogen atoms (not shown in Scheme 2) also show high reactivity. We have investigated the reactions of such hydrazone-derived compounds in another project.[10]

Synthesis of the Precursors. In previous studies, we had learned that deprotonation reactions using strong, sterically hindered bases are promising methods for the synthesis of such nitrogen-containing polyenyl anions (metal compounds). Thus, for the preparation of benzannulated diazaheptatrienyl anions $\mathbf{6}^-$, the corresponding 2,6-diazaheptatrienes (diimines) **6** are the starting materials of choice (Scheme 3).[11]

Scheme 3. Synthesis of Diaryldiazabenzoheptatrienes 6



The diimines **6** were synthesized from commercially available 2-aminobenzylamine **4** and various aromatic aldehydes **5**, which were used in at least four-fold excess, by a two-fold imine condensation reaction (Scheme 3, Table 1) in the presence of molecular sieves.[12] After removal of the excess of aldehyde by distillation and recrystallization, pure compounds **6** were obtained in good to excellent yields. They are sensitive toward moisture. Use of the aldehydes in less than 4.0 equiv resulted in the formation of six-membered aminals as side products.[13]

Table 1. Overview of the Synthesized Diazabenzoheptatrienes 6 and Isolated Yield

no.	R	yield (%)	no.	R	yield (%)
6a	Ph	91	**6i**	2-pyridyl	99
6b	4-Me-Ph	84	**6j**	2-NO_2-Ph	95
6c	4-Cl-Ph	63	**6k**	4-CF_3-Ph	99
6d	4-OMe-Ph	87	**6l**	anthracene-9-yl	86
6e	4-NEt_2-Ph	68	**6m**	naphthalene-2-yl	88
6f	thien-2-yl	89	**6n**	4-Br-Ph	56
6g	4-*t*-Bu-Ph	92	**6o**	2-Me-Ph	80
6h	4-CN-Ph	94			

Reactions of **4** with aliphatic aldehydes gave no satisfactory results but inseparable mixtures of various compounds. Thus, only aromatic aldehydes were used in this study.

Configuration and conformation of diimine **6c** was determined by X-ray diffraction[14] (Figure 3). Compound **6c** shows *E*-configurations for both iminic bonds.

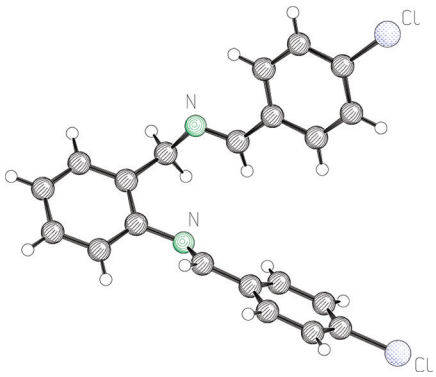
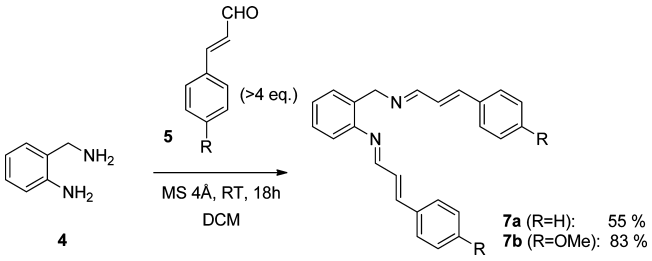


Figure 3. Molecular structure of compound **6c** (Schakal plot[15]).

To gain additional synthetic possibilities, the conjugated system was elongated by introduction of further double bonds to give the two-fold 1-azabutadiene derivatives **9**, which turned out to be thermolabile. For this reason, the distillation had to be performed very carefully, preferably under low pressure by using as low temperatures as possible (Scheme 4; see experimental details). Subsequent recrystallization after distillation was necessary to isolate the pure compounds in moderate to good yield.

Scheme 4. Synthesis of Diaryldiazabenzoundecapentaenes 7



The molecular structure of compound **7a** was determined by X-ray diffraction giving evidence for *E*-configurations for both the iminic C=N bonds as well as for the C=C double bonds (Figure 4).

Deprotonation Reactions, Formation of Monomeric Products. After treatment of compounds **6** (0.5–2.0 mmol in 150 mL of THF) with base (KO-*t*-Bu, 1.1 equiv) for the indicated period of time at elevated temperatures (50 °C), subsequent addition of trimethyl acetyl chloride (pivaloyl chloride, 4.0 equiv), and aqueous workup, 3-(*N*-acylamino)-indoles **8** were obtained in one case in low, but mostly in

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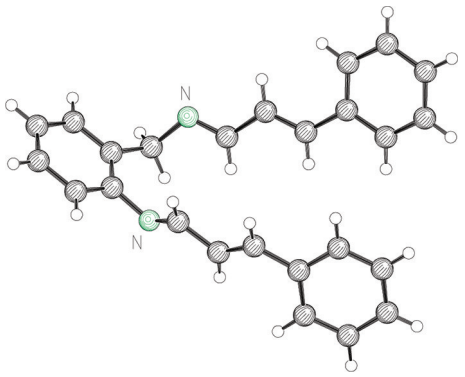


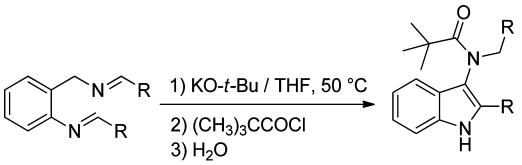
Figure 4. Molecular structure of compound **7a** (Schakal plot).

satisfying or good yield, respectively (Table 2, Scheme 5). In all cases, the crude products were purified by recrystallization. The formation of seven-membered heterocyclic compounds was not observed (see below).

Table 2. Reaction Times and Yields for Conversion of Diimines 6 into 3-(*N*-Pivaloylamino)indoles 8

no.	diimine	R	reaction time	isolated yield (%)
8a	**6a**	Ph	3 h	62
8b	**6b**	4-Me-Ph	15 min	64
8c	**6c**	4-Cl-Ph	4 h	74
8d	**6d**	4-OMe-Ph	10 min	86
8e	**6m**	naphthalen-2-yl	4 h	47
8f	**6f**	thien-2-yl	4 h	47
8g	**6g**	4-*t*-Bu-Ph	1 h	14
8h	**6o**	2-Me-Ph	2 h	41

Scheme 5. Deprotonation of Compounds 6, 1,5-Electrocyclic Reaction, and Subsequent Reaction with Trimethyl Acetyl Chloride To Form Compounds 8



6 **8**

As seen from Table 2, satisfactory yields were generally achieved after a few hours of stirring at 50 °C (**6a**, **6c**, **6m**, and **6g**) (TLC or NMR reaction control). As expected, significantly shorter reaction times were observed for diimines with electron-donating groups such as 4-Me-Ph (**6b**) and 4-MeO-Ph (**6d**). In the cases of **6j** (2-NO_2-Ph), **6k** (4-CF_3-Ph), and **6e** (4-NEt_2-Ph), no cyclization reactions took place or complex mixtures were obtained. Compound **6l** underwent an 1,5-electrocyclization but did not react with trimethyl acetyl chloride, but gave compound **11b** (see below, Table 3) upon aqueous workup. The molecular structure of compounds **8f** was determined by X-ray crystallographic analysis (Figure 5).

If the deprotonation of compound **6a** (1.0 mmol) was carried out using 2.0 equiv of KO-*t*-Bu in 150 mL of 1,4-dioxane at 90 °C with stirring for 4 h, the doubly acylated *N*-benzyl-*N*-(2-phenyl-1-pivaloyl-1*H*-indol-3-yl)pivalamide **9** was obtained in 32% yield after treatment with 4.0 equiv of

Table 3. Reaction Times and Isolated Yields for the Conversion of Compounds 6 into 3-(*N*-Benzylamino)indoles 10 and 3-(*N*-Benzylideneamino)indoles 11

product	diimine	R	reaction time	yield **10**	yield **11**
10a/11a	**6c**	4-Cl-Ph	4 h	**10a**/55%	**11a**/47%
11b	**6l**	anthracen-9-yl	3 h		**11b**/50%
11c	**6d**	4-OMe-Ph	10 min		**11c** / 34%

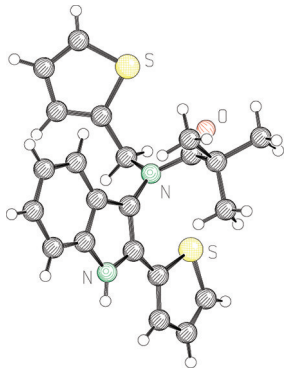
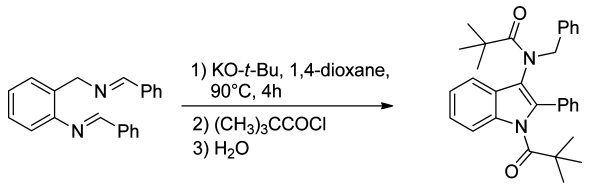


Figure 5. Molecular structure of compound **8f** (Schakal plot).

Scheme 6. Synthesis of Compound 9



6a **9**

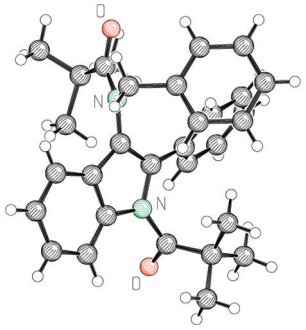


Figure 6. Molecular structure of compound **9** (Schakal plot).

trimethyl acetyl chloride, aqueous workup, and recrystallization (Scheme 6). The molecular structure of compound **9** was determined by X-ray diffraction (Figure 6). Obviously, the two-fold acylation reaction is the result of the harsh reaction conditions and the larger excess of electrophile.

In a second series of experiments (0.5−1.0 mmol of **6**, 65−150 mL of THF, 1.1 equiv of KO-*t*-Bu), the reaction mixtures were treated with water without any further electrophile after the indicated time of stirring at 50 °C. In these experiments, 3-(*N*-benzylamino)indole **10** and 3-(*N*-benzylideneamino)-indoles **11** were obtained (Scheme 7, Table 3 for yields and reaction times). Presumably, spontaneous oxidation by air converted during the workup the 3-(*N*-benzylamino)indoles **10**

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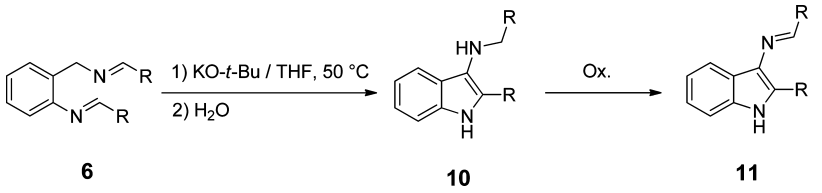
Scheme 7. Formation of Compounds 10 and 11



partially or completely to the 3-(*N*-benzylideneamino)indoles **11**. In case of the 4-chlorophenyl derivative **10a**/**11a**, the two products could be separated by recycling GPC using toluene as eluant. Spectroscopic analysis gave good evidence for the formation of **10a**, and the structure **11a** was proven by X-ray diffraction (Figure 7). The isolated compounds **10** and **11** are sensitive toward oxidation and/or hydrolysis.

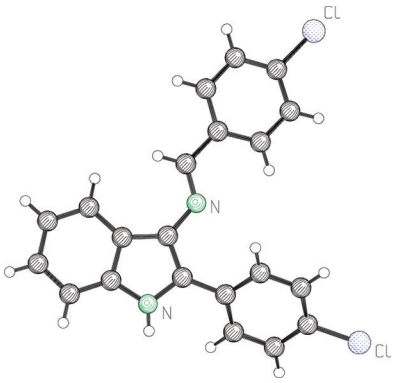


Figure 7. Molecular structure of compound **11a** (Schakal plot).

Reactions with electrophiles other than trimethyl acetyl chloride or water were studied, but the corresponding products could not be isolated in pure form.

3-Aminoindole derivatives **8**−**11** are of interest in pharmaceutical and medicinal chemistry.[16] Compounds with similar substitution patterns are rare in literature,[17] and the examples presented here are to our knowledge unknown.

Then, we used the diazabenzoundecapentaenes **7** to investigate the scope of the cyclization reaction with respect to this two-fold vinylogous system. Here, an anion might be formed with the negative charge delocalized over 11 atoms. After deprotonation of compound **7a** with KO-*t*-Bu (1.1 equiv), stirring for 4 h at 50 °C, and aqueous workup, compound **12a** was obtained. The X-ray diffraction study of **12a** (Figure 8) confirms the structure of a *δ*-carboline. Unfortunately, conversion was low, and it was not possible to isolate the product **12a** in pure form (Figure 7, Scheme 8). Similary,

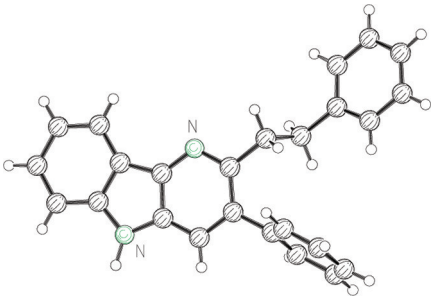
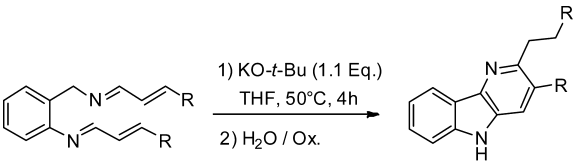


Figure 8. Molecular structure of compound **12a** (Schakal plot).

Scheme 8. Synthesis of Compounds 12



7a: R = Ph
7b: R = Ph-4OMe

12a: R = Ph
12b: R = Ph-4OMe

indications for the formation of **12b** in the reaction mixture were obtained by NMR spectroscopy and mass spectrometry. Reaction control experiments by NMR and GC revealed that the starting materials **9** polymerize very fast under these conditions. Reduction of temperature, variation of the concentrations, and use of different bases decrease the formation of polymers and also prevent the formation of the anion and/or the cyclization. The observed substitution patterns are hitherto unknown. *δ*-Carbolines are of biological and pharmaceutical importance but are rare in nature.[16,18,19] These additional examples underline the manifold possibilities of diazapolyenyl metal compounds for the synthesis of heterocyclic compounds to be studied in the future.

Formation of Dimers. During the optimization of the synthesis of compounds **8**-**11**, starting from **6**, a second product was found in some cases in the crude mixture. This compound could be identified by X-ray crystallographic analysis as a macrocyclic dimer with the racemic (all-*R* and all-*S*) structure **13** (Figure 9).

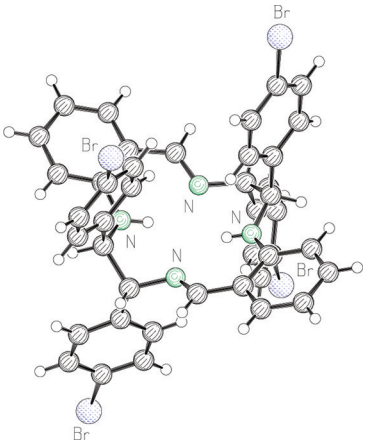


Figure 9. X-ray structure of compound **13c**.

We were able to modify the procedure to obtain compounds **13** in higher yields. By use of a larger excess of base and more

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concentrated solutions (1.0−25.0 mmol of **6**, 2.0 equiv of KO-*t*-Bu, 60 mL of dry THF), stirring for 24−48 h at rt (see Table 4)

Table 4. Yields of Tetraazadibenzocyclotetradecatetraenes 13/14

no.	diimine	R	isolated yield (%)
13a	**6a**	Ph	38
13b	**6c**	4-Cl-Ph	50
13c	**6n**	4-Br-Ph	99
13d	**6i**	2-pyridyl	49
13e	**6f**	thien-2-yl[a]	14
14	**6h**	4-CN-Ph	21

[a]Mixture of diastereomers or configurational isomers.

and subsequent quenching with water, the tetraazadibenzocyclotetradecatetraenes **14** could be isolated in moderate to good yields.

From compounds **6b**, **6d**, **6j**, and **6k**, the formation of products **13** was not observed, and in the cases of **6b,d**, the indole derivatives **8b** and **8d/11d** were formed exclusively. In the case of diimine **6l**, a product of type **11** could be identified in the crude mixture, but isolation was not possible. In the case of compound **13e**, which was isolated by column chromatography, two sets of signals were seen in the NMR spectra. Probably due to the purification method (the other compounds were purified by crystallization or washing), an additional diastereomer or configurational isomer was detected but could not be separated.

The formation of the dimeric, macrocyclic compounds **13/14** may possibly be explained by a template effect,[20,21] exerted by the potassium counterion (Scheme 9). During the reaction a 2,6-diazaheptatrienyl potassium compound ($\mathbf{6}^-\mathbf{K}^+$) might react as a nucleophile with a molecule of **6**, which acts as an electrophile.

Interestingly, starting from compound **6h**, an oxidative process, probably by air, lead to compound **14**. This compound is poorly soluble but easy to purify by washing with DCM and DMSO (Scheme 9). The ^{1}H NMR and ^{13}C NMR spectra of compound **14f** were found to be very similar to the ones of compound **13a−d**, except for the absence of the signals for the four CH groups. The mass spectroscopic analysis also coincides with the proposed structure.

Macrocyclic compounds of type **13/14** are to the best of our knowledge rare. We could only trace a few examples with related structures in the literature.[22] They show some analogy to porphyrins,[23] which makes these compounds, especially compound **14** with its fully conjugated system, interesting for further investigations. Obviously, these 14-membered ring systems offer the preconditions for metal complexation and might be used as a new class of ligands in coordination chemistry.

Mechanism. The formation of the observed 3-aminoindolyl compounds **8/11**, the macrocyclic compounds **13/14**, and also of the expected, but not observed, benzodiazepine derivative **15** may be rationalized by the following mechanism (Scheme 10).

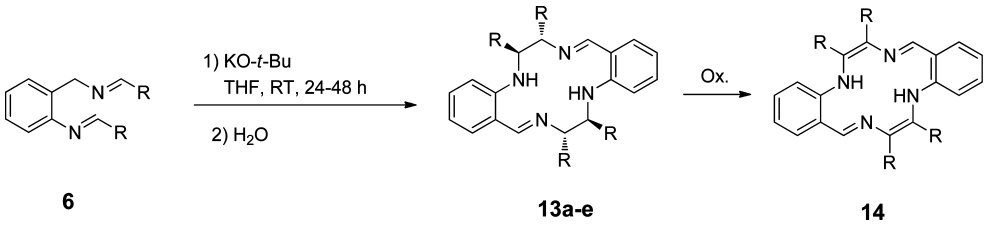
We assume that, in the first step, the diimine **6** is deprotonated by KO-*t*-Bu, forming the potassium compound $\mathbf{6}^-\mathbf{K}^+$. The electrocyclization step may either lead to the seven-membered intermediate $\mathbf{15}^-\mathbf{K}^+$ or to the five-membered intermediate $\mathbf{16}^-\mathbf{K}^+$. In comparison to KO-*t*-Bu, these potassium compounds themselves might be considered, on the one hand, to be strong bases, which may also deprotonate starting material **6**, while being converted into the protonated forms **15**, **16**, **17**, and **10** (E = H). These, on the other hand, with regard to the structure of the product obtained, may be the subject of further tautomerization steps, triggered by the mutual presence of excess KO-*t*-Bu, the basic potassium compounds, as well as *tert*-butyl alcohol. With regard to these various equilibria, taking place over the long period of time and elevated temperature, the final quenching reaction with the electrophile may eventually lead to the experimentally observed 3-aminoindole derivatives **8/10**. These latter tautomerization steps obviously benefit energetically greatly from the aromaticity of the final product **8/10**. This is indicated by a very low calculated relative energy of about −19 kcal/mol of **10** in comparison to the various other protonated intermediates including the not observed seven-membered ring system **15**. Of course, solvent and counterion effects may also influence the reaction pathway. Finally, aqueous workup or reaction with pivaloyl chloride leads to the observed products **8** and **10**. Air oxidation of **10** gives rise to the formation of compound **11**.

We furthermore studied the nature of the ring forming reaction starting from deprotonated $\mathbf{6}^-$ to give the five-membered intermediate $\mathbf{16}^-$ via transition state $\mathbf{TS\text{-}6}^-\mathbf{-16}^-$. Here, anions in the gas phase without counterions were calculated (Scheme 11).

Thus, the calculated structure of $\mathbf{6}^-$ and the transition structure $\mathbf{TS\text{-}6}^-\mathbf{-16}^-$ are in accordance with a disrotatory cyclization mode, which is reasonable for an electrocyclization involving 6π electrons (Figure 10).

For the almost planar 6π transition structure, a minimal NICS value of −6.7 ppm (B3LYP/6-311G+(d,p); see Supporting Information) was calculated along an axis perpendicular to the center of the forming ring.[24,25] Together with the small charge separation of 0.16e (NBO,[26] 6-31+G(d)), the characteristics of a Hückel-type aromatic transition state of an electrocyclic reaction are given.

Scheme 9. Formation of Compounds 13a−e (Only One Enantiomer Shown) and Oxidation to Compound 14



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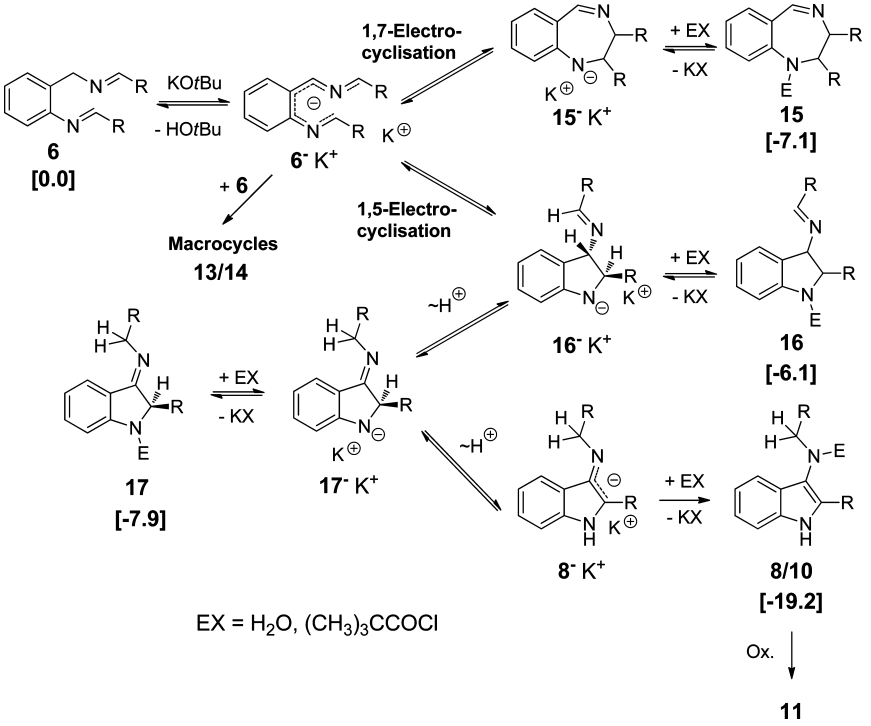
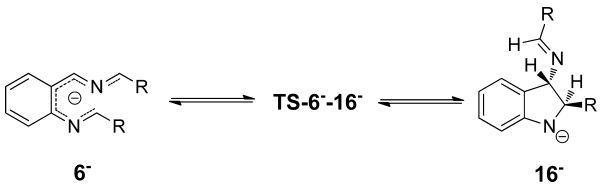
Scheme 10. Proposed Reaction Mechanism for the Formation of Five- and Seven-Membered Ring Compounds with Relative Energies for the Protonated Species (E = H, R = Ph) ([kcal/mol], SCS-MP2/6-311+G(d,p)//B3LYP/6-31G(d)+ZPE)



Scheme 11. Formation of the Five-Membered Ring Compound 16^-



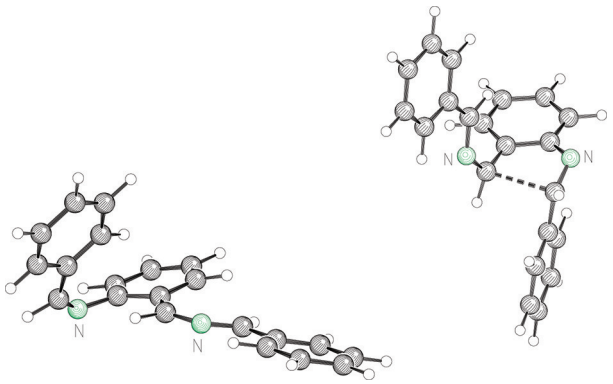


Figure 10. Calculated structures of compound 6^- (left) and transition structure **TS-6$^-$−16$^-$** (right) (B3LYP/6-31G(d)//B3LYP/6-31G(d)).

CONCLUSION

As shown by high-level quantum chemical calculations, topology and relative electronegativity of nitrogen in comparison to carbon are the principal properties in the chemistry of isomeric cationic or anionic azapolyenyl derivatives, which control the reactivity, for example, toward ring closure reactions to form heterocyclic systems. In continuation of our previous work on such charged intermediates, we now studied the generation and reactivity of benzannulated 2,6-diazaheptatrienyl metal compounds. At 50 °C in dilute solution, 3-(*N*-acylamino)indoles **8** and their oxidation products 3-(benzylideneamino)indoles **11** were found to be the major products; the formation of seven-membered ring systems was not observed. In contrast, reaction in concentrated solution at room temperature leads to the formation of macrocyclic dimers of type **13** with novel substitution patterns. Such 14-membered heterocyclic systems are promising as ligands for metal complexation. The elongated systems **7** are shown to be useful precursors for the synthesis of tricyclic compounds (**12**) with hitherto unknown structural motifs. Quantum chemical calculations again came out to be very valuable for the choice of the system under study and for the interpretation of the experimental results with regard to the reaction mechanism.

EXPERIMENTAL SECTION

Melting points are uncorrected. ^{1}H, ^{13}C, ^{19}F NMR spectroscopy: TMS (^{1}H) (0.00 ppm), CD_2Cl_2 (^{1}H) (5.32 ppm), $CDCl_3$ (^{1}H) (7.26 ppm), C_6D_6 (^{1}H) (7.16 ppm), THF-d_8 (^{1}H) (1.72/3.58 ppm), CD_2Cl_2 (^{13}C) (53.8 ppm), $CDCl_3$ (^{13}C) (77.0 ppm), C_6D_6 (^{13}C) (128.1 ppm), THF-d_8 (^{13}C) (25.3/67.2 ppm), $CFCl_3$ (^{19}F) (0.0 ppm) were used as external reference. NMR spectra of indoles were measured in $CDCl_3$ containing one drop of TFA (trifluoroacetic acid). If necessary, the experiments were carried out with complete exclusion of moisture. Abbreviations: DE diethylether, EA ethyl acetate, TEA triethylamine, DCM dichloromethane, DCE dichloroethane.

General Procedure for the Synthesis of 2,6-Diaza-4,5-benzoheptatrienes (6a−o). The compounds were synthesized using the molecular sieves method.[12] In a Schlenk flask, 2-aminobenzylamine (1 equiv) was dissolved in dry DCM. Subsequently, the aldehyde (4 equiv) in pure or dissolved in dry DCM was added to the mixture while stirring. The solution was stirred for 18 h and filtered through a pad of Celite which was washed three times with DCM (3 × 50 mL). The solvent was removed under reduced

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pressure. In order to purify the diimine, the excess of aldehyde was either removed by Kugelrohr distillation or the crude product was purified by recrystallization.

*1,7-Diphenyl-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6a**):* From 12.53 mL (124.09 mmol) of benzaldehyde and a solution of 3.79 g (31.02 mmol) of 2-aminobenzylamine dissolved in 100 mL of dry DCM. The excess of aldehyde was removed by distillation at 60 °C (9.0×10^{-3} mbar): A yellowish oil was obtained which solidifies after 2 days of drying in vacuo to give a colorless solid: 8.42 g (28.22 mmol, 91%), mp 48−49 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 4.79 ppm (s, 2H), 6.45−7.50 (m, 14H), 7.73 (s, 1H), 7.86 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 61.4 ppm, 117.7, 126.0, 126.2, 126.6, 127.3, 128.1, 128.2, 128.5, 128.9, 129.0, 129.8, 130.6, 132.8, 136.3, 136.3, 150.5, 159.9, 162.4; IR (KBr) $\tilde{\nu}$ = 1641 (C═N), 1634 (C═N); HRMS (ESI) calcd for $C_{21}H_{18}N_2H$ 299.1543, found 299.1545. Anal. Calcd for $C_{21}H_{18}N_2$ (298.38): C, 84.53; H, 6.08; N, 9.39. Found: C, 84.38; H, 6.10; N, 9.29.

*1,7-Bis(4-methylphenyl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6b**):* From 27.66 mL (0.24 mol) of 4-methylbenzaldehyde and a solution of 7.32 g (0.06 mol) of 2-aminobenzylamine in 100 mL of dry DCM. The resulting diimine was purified by removing the aldehyde by distillation at 70 °C (9.0×10^{-3} mbar): 16.45 g (0.05 mol, 84%) was obtained as a yellow oil; ^{1}H NMR (C_6D_6, 400 MHz) δ = 2.02 ppm (s, 3H), 2.06 (s, 3H), 5.12 (s, 2H), 6.92 (d, 2H, J = 7.6 Hz), 7.00 (d, 2H, J = 7.6 Hz), 7.13−7.16 (m, 4H), 7.69 (d, 2H, J = 7.6 Hz), 7.76 (d, 2H, J = 7.6 Hz), 8.08 (s, 1H), 8.20 (s, 1H); ^{13}C NMR (C_6D_6, 100 MHz) δ = 21.3 ppm, 21.4, 61.4, 118.0, 126.0, 127.1, 128.3, 128.6, 128.6, 129.2, 129.3, 129.3, 129.4, 129.5, 129.6, 134.1, 134.6, 134.7, 140.5, 141.5, 151.1, 159.6, 161.8; IR (neat) $\tilde{\nu}$ = 1626 cm^{-1} (C═N), 1609 (C═N); HRMS (ESI) calcd for $C_{23}H_{22}N_2H$ 327.1856, found 327.1854. Anal. Calcd for $C_{23}H_{22}N_2$ (326.43): C, 84.63; H, 6.79; N, 8.58. Found: C, 84.39; H, 6.76; N, 8.49.

*1,7-Bis(4-chlorophenyl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6c**):* From 3.67 g (30.00 mmol) of 2-aminobenzylamine, dissolved in 50 mL of dry DCM, and 14.42 g (120.00 mmol) of 4-chlorobenzaldehyde, dissolved in 50 mL of dry DCM. The excess of aldehyde was removed by distillation at 95 °C (9.0×10^{-3} mbar): 7.00 g (19.00 mmol, 63%), as a colorless solid; mp 102−103 °C; ^{1}H NMR (C_6D_6, 300 MHz) δ = 5.00 ppm (s, 2H), 6.71−7.55 (m, 12H), 7.84 (s, 1H), 7.94 (s, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ = 61.3 ppm, 117.9, 126.5, 128.3, 129.0, 129.2, 129.5, 129.7, 130.2, 133.8, 135.3, 135.4, 136.6, 137.4, 150.5, 158.3, 160.5; IR (KBr) $\tilde{\nu}$ = 1638 cm^{-1} (C═N), 1626 (C═N); HRMS (ESI) calcd for $C_{21}H_{16}Cl_2N_2H$ 367.0763, found 367.0767. Anal. Calcd for $C_{21}H_{16}Cl_2N_2$ (367.27): C, 68.68; H, 4.39; N, 7.63. Found: C, 68.50; H, 4.25; N, 7.55. X-ray crystal structure data of **6c** can be found in the Supporting Information.

*1,7-Bis(4-methoxyphenyl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6d**):* From 7.33 g (0.06 mol) of 2-aminobenzylamine, dissolved in 100 mL of dry DCM, and 26.98 mL (0.24 mol) of 4-methoxybenzaldehyde. The crude product was purified by Kugelrohr distillation (80 °C, 9.0×10^{-3} mbar): 18.65 g (0.05 mmol, 87%) of a yellow oil was obtained; ^{1}H NMR (C_6D_6, 300 MHz) δ = 3.19 ppm (s, 3H), 3.23 (s, 3H), 5.16 (s, 2H), 6.76 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 6.89−6.91 (m, 1H), 7.22−7.24 (m, 2H), 7.72−7.74 (m, 1H), 7.78 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.8 Hz, 2H), 8.08 (s, 1H), 8.21 (s, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ = 54.7 ppm, 54.9, 61.5, 114.0, 114.2, 114.4, 118.1, 125.9, 127.3, 128.0, 128.3, 129.4, 130.1, 130.9, 131.8, 134.2, 151.3, 159.1, 161.9, 162.6, 161.2; IR (neat) $\tilde{\nu}$ = 1639 cm^{-1} (C═N), 1607 (C═N); HRMS (ESI) calcd for $C_{23}H_{22}N_2O_2H$ 359.1754, found 359.1752. Anal. Calcd for $C_{23}H_{22}N_2O_2$ (358.43): C, 77.07; H, 6.19; N, 7.82. Found: C, 76.99; H, 6.27; N, 7.78.

*1,7-Bis(4-diethylaminophenyl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6e**):* From 1.22 g (10.00 mmol) of 2-aminobenzylamine, dissolved in 50 mL of dry DCM, and 7.09 g (40.00 mmol) of 4-diethylaminobenzaldehyde, dissolved in 50 mL of dry DCM. The excess of aldehyde was removed by distillation (139 °C, 1.4×10^{-2} mbar): 2.98 g (6.77 mmol, 68%) as a red-brown oil was obtained; ^{1}H NMR (C_6D_6, 300 MHz) δ = 0.81 ppm (q, J = 6.9 Hz, 12H), 2.83−2.91 (m, J = 6.9 Hz, 8H) 5.23 (s, 2H), 6.48 (t, J = 9.0 Hz, 4H), 6.93−6.96 (m, 1H), 7.18−7.22 (m, 3H), 7.79−7.82 (m, 2H), 7.91 (d, J = 9.0 Hz, 2H), 8.23 (s, 1H), 8.36 (s, 1H); ^{13}C NMR (C_6D_6, 100 MHz) δ = 12.8 ppm, 44.3, 61.6, 111.4, 118.3, 125.2, 125.3, 125.4, 129.2, 130.4, 131.23, 134.9, 149.5, 150.1, 152.0, 159.4, 161.7; IR (neat) $\tilde{\nu}$ = 1599 cm^{-1} (C═N), 1584 (C═N); HRMS (ESI) calcd for $C_{29}H_{36}N_4H$ 441.3013, found 441.3020.

*1,7-Di(thien-2-yl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6f**):* From 1.22 g (10.00 mmol) of 2-aminobenzylamine, dissolved in 100 mL of dry DCM, and 3.74 mL (40.00 mmol) of 2-thiophenecarbaldehyde. In order to purify the crude product, the excess of aldehyde was removed by distillation in a Kugelrohr oven (120 °C, 2.2×10^{-2} mbar): 2.80 g (8.87 mmol, 89%) was obtained as a yellow-brown oil; ^{1}H NMR (C_6D_6, 400 MHz) δ = 5.01 ppm (s, 2H), 6.81−6.63 (m, 1H), 6.65−6.67 (m, 1H), 6.68−6.72 (m, 1H), 6.77 (dt, J = 5.2 Hz, J = 1.2 Hz, 1H), 6.86 (dd, J = 3.6 Hz, J = 1.2 Hz, 1H), 6.89 (dt, J = 4.8 Hz, J = 1.2 Hz, 1H), 6.94 (dd, J = 3.6 Hz, J = 1.2 Hz, 1H), 7.06−7.11 (m, 2H), 7.56−7.60 (m, 1H), 8.00 (s, 1H), 8.22 (s, 1H); ^{13}C NMR (C_6D_6, 100 MHz) δ = 61.1 ppm, 118.0, 126.4, 127.1, 127.7, 128.8, 129.6, 130.1, 130.2, 134.0, 143.8, 143.9, 150.2, 152.6, 155.4; IR (neat) $\tilde{\nu}$ = 1630 cm^{-1} (C═N), 1614 (C═N); HRMS (ESI) calcd for $C_{17}H_{14}N_2S_2H$ 311.0671, found 311.0666. Anal. Calcd for $C_{17}H_{14}N_2S_2$ (310.44): C, 65.77; H, 4.55; N, 9.02. Found: C, 65.51; H, 4.81; N, 9.19.

*1,7-Bis(4-tert-butylphenyl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6g**):* From 6.69 mL (40.00 mmol) of 4-*tert*-butylbenzaldehyde, dissolved in 50 mL of dry DCM, and 1.22 g (10.00 mmol) of 2-aminobenzylamine, dissolved in 50 mL of dry DCM. The crude product was purified by Kugelrohr distillation (120 °C, 6.0×10^{-2} mbar): 3.79 g (9.23 mmol, 92%) was obtained as a brown oil; ^{1}H NMR (C_6D_6, 300 MHz) δ = 1.15 ppm (s, 9H), 1.20 (s, 9H), 5.18 (s, 2H), 6.79−6.85 (m, 1H), 7.12−7.18 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.65−7.68 (m, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H), 8.14 (s, 1H), 8.27 (s, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ = 31.2 ppm, 34.8, 34.9, 61.6, 118.1, 125.7, 125.9, 126.1, 128.6, 129.2, 129.4, 134.1, 134.7, 134.8, 151.3, 153.6, 154.7, 159.8, 161.9; IR (neat) $\tilde{\nu}$ = 1641 cm^{-1} (C═N), 1628 (C═N); HRMS (ESI) calcd for $C_{29}H_{34}N_2H$ 411.2795, found 411.2783.

*1,7-Bis(4-cyanophenyl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6h**):* From 5.25 g (40.00 mmol) of 4-cyanobenzaldehyde, dissolved in 50 mL of dry DCM, and 1.22 g (10.00 mmol) of 2-aminobenzylamine, dissolved in 50 mL of dry DCM. The product was purified by Kugelrohr distillation (140 °C, 4.1×10^{-2} mbar): 3.28 g (9.42 mmol, 94%) was obtained as a yellow-brown solid; mp 139−140 °C; ^{1}H NMR (C_6D_6, 300 MHz) δ = 5.05 ppm (s, 2H), 6.80 (m, 1H), 7.04 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.24−7.27 (m, 4H), 7.38 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.54−7.57 (m, 1H), 7.87 (s, 1H), 7.93 (s, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ = 61.2 ppm, 114.3, 114.9, 117.7, 118.4, 118.5, 127.2, 128.5, 128.5, 129.0, 129.6, 132.3, 132.4, 133.7, 149.8, 157.8, 160.2; IR (neat) $\tilde{\nu}$ = 1672 cm^{-1} (C═N), 1649 (C═N); HRMS (ESI) calcd for $C_{23}H_{16}N_4H$ 349.1448, found 349.1441. Anal. Calcd for $C_{23}H_{16}N_4$ (348.40): C, 79.29; H, 4.63; N, 16.08. Found: C, 79.14; H, 4.32; N, 16.00.

*1,7-Di(2-pyridyl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6i**):* From 1.22 g (10.00 mmol) of 2-aminobenzylamine, dissolved in 100 mL dry DCM, and 3.80 mL (40.00 mmol) of 2-pyridinecarbaldehyde. The excess of aldehyde was removed by Kugelrohr distillation (60 °C, 2.3×10^{-2} mbar): 2.99 g (9.96 mmol, 99%) was obtained as a dark purple oil; ^{1}H NMR (C_6D_6, 400 MHz) δ = 5.06 ppm (s, 2H), 6.59 (m, 1H), 6.65 (m, 1H), 6.78 (d, J = 7.6 Hz, 1H), 6.97−7.14 (m, 4H), 7.44 (m, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.44 (d, J = 4.8 Hz, 1H), 8.48 (d, J = 4.8 Hz, 1H), 8.69 (s, 1H), 8.71 (s, 1H); ^{13}C NMR (C_6D_6, 100 MHz) δ = 61.1 ppm, 117.9, 121.0, 121.5, 124.4, 124.9, 126.9, 129.5, 133.9, 136.0, 136.2, 149.5, 149.8, 149.8, 155.6, 155.8, 161.1, 163.7; IR (neat) $\tilde{\nu}$ = 1645 cm^{-1} (C═N), 1630 (C═N); HRMS (ESI) calcd for $C_{19}H_{16}N_4H$ 301.1447, found 301.1435.

*1,7-Bis(2-nitrophenyl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6j**):* From 6.83 g (45.20 mmol) of 2-nitrobenzaldehyde, dissolved in 50 mL of dry DCM, and 1.38 g (11.30 mmol) of 2-aminobenzylamine, dissolved in 50 mL of dry DCM. The crude product was purified by Kugelrohr distillation at 110 °C (7.3×10^{-2} mbar): 4.17 g (10.74 mmol, 95%)

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was obtained as a yellow solid; mp 120−121 °C; ^{1}H NMR (C_6D_6, 300 MHz) δ = 4.99 ppm (s, 1H, CH_2), 6.61 ppm (t, J = 8.4 Hz, 1H), 6.70 (t, J = 8.4 Hz, 1H), 6.82 (t, J = 7.5 Hz, 1H), 6.89−6.92 (m, 1H), 7.01 (t, J = 7.5 Hz, 1H), 7.05−7.12 (m, 2H), 7.36 (d, J = 8.1 Hz, 1H), 7.41−7.46 (m, 2H), 8.00 (d, J = 7.9 Hz, 1H), 8.09 (d, J = 7.9 Hz, 1H), 8.63 (br s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 61.0 ppm, 124.3, 124.8, 127.2, 128.7, 129.5, 129.9, 130.0, 130.8, 131.1, 131.3, 131.4, 132.8, 133.5, 133.7, 149.0, 149.4, 149.6, 155.8, 158.0; IR (neat) $\tilde{\nu}$ = 1641 cm^{-1} (C═N), 1628 (C═N); HRMS (ESI) calcd for $C_{21}H_{16}N_4O_4H$ 389.1244, found 389.1260. Anal. Calcd for $C_{21}H_{16}N_4O_4$ (388.38): C, 64.94; H, 4.15; N, 14.43. Found: C, 64.93; H, 3.83; N, 14.45.

*1,7-Bis(4-trifluoromethylphenyl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6k**):* From 1.22 g (10.00 mmol) of 2-aminobenzylamine, dissolved in 100 mL of dry DCM, and 5.35 mL (40.00 mmol) of 4-trifluoromethylbenzaldehyde. The excess of aldehyde was removed by Kugelrohr distillation at 100 °C (2.2×10^{-2} mbar): 4.33 g (9.97 mmol, 99%) was obtained as a light yellow solid; mp 67−68 °C; ^{1}H NMR (C_6D_6, 300 MHz) δ = 5.02 ppm (s, 2H), 6.72−6.75 (m, 1H), 7.18−7.21 (m, 1H), 7.27 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.48−7.56 (m, 6H), 7.87 (s, 1H), 7.97 (s, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ = 61.4 ppm, 117.9, 125.6, 125.7, 125.8, 125.8, 128.5, 128.6 129.2, 129.6, 133.7, 139.7, 139.8, 150.2, 158.2, 160.5; ^{19}F NMR (C_6D_6, 300 MHz) δ = −62.43 ppm, −62.37; IR (neat) $\tilde{\nu}$ = 1647 cm^{-1} (C═N), 1632 (C═N); HRMS (ESI) calcd for $C_{23}H_{16}F_6N_2H$ 435.1290, found 435.1298. Anal. Calcd for $C_{23}H_{16}F_6N_2$ (434.38): C, 63.60; H, 3.71; N, 6.45. Found: C, 63.23; H, 3.65; N, 6.26.

*1,7-Di(anthracen-9-yl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6l**):* From 8.25 g (40.00 mmol) of anthracene-9-carbaldehyde, dissolved in 50 mL of dry DCM, and 2.44 g (20.00 mmol) of 2-aminobenzylamine, dissolved in 50 mL of dry DCM. The crude product was recrystallized from DCE: 8.60 g (17.25 mmol, 86%) was obtained as a yellow solid; mp 179−180 °C; ^{1}H NMR (THF-d_8, 400 MHz) δ = 5.38 ppm (s, 2H), 7.21−7.26 (m, 2H), 7.26−7.29 (m, 9 H), 7.69 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 8.8 Hz, 2H), 8.07 (d, J = 7.6 Hz, 2H), 8.49 (s, 1H), 8.64 (s, 1H), 8.65 (d, J = 8.8 Hz, 2H), 8.99 (d, J = 8.8 Hz, 2H), 9.63 (s, 1H), 9.81 (s, 1H); ^{13}C NMR (THF-d_8, 100 MHz) δ = 63.8 ppm, 119.0, 126.0, 126.2, 126.3, 127.1, 127.3, 128.0, 128.4, 129.11 129.2, 129.6, 129.9, 130.2, 130.3, 131.4, 131.8, 132.0, 132.5, 132.6, 134.8, 152.8, 160.8, 161.8; IR (neat) $\tilde{\nu}$ = 1624 cm^{-1} (C═N), 1593 (C═N); HRMS (ESI) calcd for $C_{37}H_{26}N_2H$ 499.2169, found 499.2167. Anal. Calcd for $C_{37}H_{26}N_2$ (498.62): C, 89.13; H, 5.26; N, 5.62. Found: C, 89.16; H, 5.29; N, 5.63.

*1,7-Di(naphthalen-2-yl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6m**):* From 1.48 g (12.12 mmol) of 2-aminobenzylamine, dissolved in 50 mL of dry DCM, and 7.57 g (48.49 mmol) of naphthalene-2-carbaldehyde, dissolved in 50 mL of dry DCM. The excess of aldehyde was removed by distillation at 160 °C (4.5×10^{-2} mbar): 4.27 g (10.72 mmol, 88%) was obtained as a light brown solid; mp 130−131 °C; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ = 5.09 ppm (s, 1H), 7.10 (d, J = 7.5 Hz, 1H), 7.27−7.64 (m, 7H), 7.71 (d, J = 7.5 Hz, 1H), 7.81−7.85 (m, 3H), 7.91−8.03 (m, 4H), 8.18 (s, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.55 (s, 1H), 8.58 (s, 1H); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ = 61.8 ppm, 118.3, 124.2, 124.4, 126.5, 126.7, 127.2, 127.6, 128.2, 128.3, 128.4, 128.7, 128.8, 129.0, 129.1, 129.3, 129.7, 130.5, 131.9, 133.6, 133.6, 133.7, 134.7, 134.7 135.1, 135.6, 151.3, 160.6, 162.8; IR (neat) $\tilde{\nu}$ = 1634 cm^{-1} (C═N), 1618 (C═N); HRMS (ESI) calcd for $C_{29}H_{22}N_2H$ 399.1856, found 399.1846. Anal. Calcd for $C_{29}H_{22}N_2$ (398.50): C, 87.41; H, 5.56; N, 7.03. Found: C, 87.04; H, 5.66; N, 7.04.

*1,7-Bis(4-bromophenyl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6n**):* From 3.67 g (30.00 mmol) of 2-aminobenzylamine, dissolved in 50 mL of dry DCM, and 22.20 g (120.00 mmol) of 4-bromobenzaldehyde, dissolved in 50 mL of dry DCM. The excess of aldehyde was removed by distillation in a Kugelrohr oven (95 °C, 1.4×10^{-2} mbar): 7.70 g (16.88 mmol, 56%) was obtained as a light yellow solid; mp 117−118 °C; ^{1}H NMR (C_6D_6, 300 MHz) δ = 4.98 ppm (s, 2H), 6.69−6.74 (m, 1H), 7.10−7.20 (m, 4H), 7.25−7.34 (m, 4H), 7.36−7.40 (m, 2H), 7.50−7.56 (m, 1H), 7.82 (s, 1H), 7.92 (s, 1H); ^{13}C NMR (C_6D_6, 100 MHz) δ = 61.4 ppm, 117.9, 125.1, 126.0, 126.6, 129.5, 129.9, 130.4, 132.0, 132.2, 133.7, 135.7, 135.8, 150.5, 158.4, 160.6; IR (neat) $\tilde{\nu}$ = 1645 (C═N), 1628 (C═N); HRMS (ESI) calcd for $C_{21}H_{16}Br_2N_2H$ 456.9734, found 456.9732. Anal. Calcd for $C_{21}H_{16}Br_2N_2$ (456.17): C, 55.29; H, 3.54; N, 6.14. Found: C, 55.44; H, 3.52; N, 5.96.

*1,7-Bis(2-methylphenyl)-2,6-diaza-4,5-benzo-1,4,6-heptatriene (**6o**):* From 5.00 g (40.90 mmol) of 2-aminobenzylamine, dissolved in 100 mL of dry DCM, and 18.90 mL (164.00 mmol) of 2-methylbenzaldehyde. The excess of aldehyde was removed by Kugelrohr distillation (75 °C, 1.5×10^{-2} mbar) to give 10.70 g (32.78 mmol, 80%) of **6o** as a yellow oil: ^{1}H NMR (C_6D_6, 300 MHz) δ = 2.19 ppm (s, 3H), 2.22 (s, 3H), 6.80 (s, 2H), 6.80−6.86 (m, 1H), 6.89−6.93 (m, 2H), 7.03−7.06 (m, 2H), 7.07−7.10 (m, 2H), 7.15−7.21 (m, 2H), 7.64−7.69 (m, 1H), 8.10−8.16 (m, 1H), 8.16−8.22 (m, 1H), 8.48 (s, 1H), 8.56 (s, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ = 19.5 ppm, 62.3, 118.1, 126.2, 126.3, 126.5, 128.2, 128.4, 128.7, 129.0, 129.4, 130.2, 131.0, 131.0, 131.3, 134.1, 134.8, 134.9, 138.0, 138.9, 151.7, 158.9, 160.7; IR (neat) $\tilde{\nu}$ = 1624 (C═N), 1601 (C═N); HRMS (ESI) calcd for $C_{23}H_{22}N_2H$ 327.1856, found 327.1857. Anal. Calcd for $C_{23}H_{22}N_2$ (326.43): C, 84.63; H, 6.79; N, 8.58. Found: C, 84.42; H, 6.77; N, 8.35.

Synthesis of 4,8-Diaza-6,7-benzoundeca-1,3,6,8,10-pentaene (7a,b). The synthesis of compounds **7a,b** was performed analogously to compounds **6a−o**.

*1,11-Diphenyl-4,8-diaza-6,7-benzoundeca-1,3,6,8,10-pentaene (**7a**):* From 3.05 g (25.00 mmol) of 2-aminobenzylamine, dissolved in 20 mL of dry DCM, and 12.59 mL (100.00 mmol) of *trans*-cinnamylaldehyde. The solution was stirred for 18 h at rt. The excess of aldehyde was removed by Kugelrohr distillation at 60 °C (1.5×10^{-2} mbar), and the crude product was subsequently purified by recrystallization from toluene: 4.80 g (13.70 mmol, 55%) was obtained as colorless crystals; mp 113−114 °C; ^{1}H NMR (C_6D_6, 300 MHz) δ = 5.16 ppm (s, 1H), 6.58 (d, J = 15.0 Hz, 1H), 6.69 (d, J = 15.0 Hz, 1H), 6.85−6.88 (m, 1H), 6.99−7.08 (m, 7H), 7.11−7.22 (m, 7H), 7.65−7.68 (m, 1H), 7.94 (d, J = 8.7 Hz, 1H), 8.02 (d, J = 8.7 Hz, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ = 61.6 ppm, 117.9, 126.3, 127.4, 127.7, 128.4, 128.9, 129.0, 129.4, 129.5, 134.3, 136.1, 136.4, 141.1, 143.4, 151.2, 161.4, 163.4; IR (neat) $\tilde{\nu}$ = 1630 cm^{-1} (C═N), 1611 (C═N); HRMS (ESI) calcd for $C_{25}H_{22}N_2H$ 351.1856, found 351.1858. Anal. Calcd for $C_{25}H_{22}N_2$ (350.46): C, 85.68; H, 6.33; N, 7.99. Found: C, 85.56; H, 6.41; N, 7.71. X-ray crystal structure data of **7a** can be found in the Supporting Information.

*1,11-Bis(4-methoxyphenyl)-4,8-diaza-6,7-benzoundeca-1,3,6,8,10-pentaene (**7b**):* From 1.15 g (9.43 mmol) of 2-aminobenzylamine, dissolved in 50 mL of dry DCM, and 6.12 g (37.72 mmol) of 4-methoxycinnamylaldehyde, dissolved in 50 mL of dry DCM. The compound was purified by recrystallization from toluene/DCM (1:1): 3.20 g (7.80 mmol, 83%) was obtained as a yellow solid; mp 140−141 °C; ^{1}H NMR (C_6D_6, 300 MHz) δ = 3.22 ppm (s. 3H), 3.24 (s, 3H), 5.21 (s, 2H), 6.56−6.78 (m, 6H), 6.89−6.92 (m, 1H), 7.05−7.24 (m, 8H), 7.69−7.72 (m, 1H), 8.00 (d, J = 9.0 Hz, 1H), 8.09 (d, J = 9.0 Hz, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ = 54.8 ppm, 54.8, 114.5, 114.6, 127.4, 127.4, 117.9, 126.1, 128.4, 128.9, 129.0, 129.2, 129.3, 129.4, 134.4, 140.8, 143.3, 151.5, 160.7, 161.2, 161.6, 163.6; IR (neat) $\tilde{\nu}$ = 1632 cm^{-1} (C═N), 1620 (C═N); HRMS (ESI) calcd for $C_{27}H_{26}N_2O_2H$ 411.2067, found 411.2049. Anal. Calcd for $C_{27}H_{26}N_2O_2$ (410.51): C, 79.00; H, 6.38; N, 6.82. Found: C, 78.82; H, 6.34; N, 6.83.

General Procedure for the Synthesis of 3-(*N*-Acylamino)-indoles (8a−h). In a Schlenk flask, a solution of KO-*t*-Bu (1.1 equiv, 1 M in THF or solid) in dry THF was heated to 50 °C. Then 1.0 equiv of **6** in dry THF was added in portions within 15 min. An intense color appeared. The reaction mixture was stirred at 50 °C for a definite period of time. After addition of trimethyl acetyl chloride (2.0 equiv), the solution immediately decolorized. Then the mixture was stirred for 15−30 min, 50 mL of DE was added, and the organic layer was washed with saturated $NaHCO_3$ solution (3 × 50 mL) and dried over Mg_2SO_4. The solvent was removed in vacuo. The crude products were purified by recrystallization.

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*N-Benzyl-N-(2-phenyl-1H-indol-3-yl)pivalamide (**8a**):* From 0.46 g (1.54 mmol) of **6a** in 20 mL of dry THF, added to a stirred solution of 0.19 g (1.69 mmol) of KO-*t*-Bu, dissolved in 130 mL of dry THF, and after 3 h, 0.38 mL (3.08 mmol) of trimethyl acetyl chloride. The crude product was purified by recrystallization from DCE: 0.37 g (0.95 mmol, 62%) of compound **8a** was obtained as colorless crystals; mp 260−261 °C; ^{1}H NMR ($CDCl_3$/TFA, 400 MHz) δ = 0.94 ppm (s, 9H), 4.51 (d, J = 13.5 Hz, 1H), 5.49 (d, J = 13.5 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 7.12−7.21 (m, 6H), 7.34−7.38 (m, 2H), 7.40−7.46 (m, 4H), 8.36 (br s, 1H); ^{13}C NMR ($CDCl_3$/TFA, 100 MHz) δ = 28.9 ppm, 41.4, 57.6, 110.3, 111.3, 113.2, 116.0, 117.1, 118.8, 119.3, 121.1, 123.7, 126.0, 126.7, 128.1, 128.4, 128.8, 129.6, 130.1, 130.3, 131.9, 134.0, 136.5, 182.8; IR (neat) $\tilde{\nu}$ = 1601 cm^{-1} (C═O); HRMS (ESI) calcd for $C_{26}H_{26}N_2ONa$ 405.1937, found 405.1945. Anal. Calcd for $C_{26}H_{26}N_2O$ (382.50): C, 81.64; H 6.85; N, 7.23. Found: C, 81.48; H, 6.71; N, 7.52. X-ray crystal structure data of **8a** can be found in the Supporting Information.

*N-(4-Methylbenzyl)-N-(2-p-methylphenyl-1H-indol-3-yl)-pivalamide (**8b**):* A solution of 0.55 mL (0.55 mmol) of KO-*t*-Bu (1 M solution in THF) in 130 mL of dry THF was heated to 50 °C. Subsequently, 0.16 g (0.50 mmol) of **6b**, dissolved in 20 mL of dry THF, was slowly added. The color of the solution immediately turned to deep orange. After 10 min, the reaction mixture was quenched with 0.12 mL (1.00 mmol) of trimethyl acetyl chloride. The product was recrystallized from DCE: 0.13 g (0.32 mmol, 64%) of compound **8b** was obtained as a yellow solid; mp 240−241 °C; ^{1}H NMR ($CDCl_3$/TFA, 400 MHz) δ = 0.92 ppm (s, 9H), 2.26 (s, 3H), 2.37 (s, 3H), 4.32 (d, 1H, J = 15.0 Hz), 5.44 (d, 1H, J = 15.0 Hz), 6.88−6.95 (m, 4H), 7.10−7.19 (m, 5H), 7.33 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 8.44 (br s, 1H); ^{13}C NMR ($CDCl_3$/TFA, 100 MHz) δ = 20.1 ppm, 20.2, 29.0, 41.0, 56.1, 110.9, 118.0, 120.0, 120.3, 122.8, 125.7, 127.2, 127.9, 128.7, 129.8, 129.9, 131.7, 133.8, 135.1, 136.8, 138.1, 179.6; IR (neat) $\tilde{\nu}$ = 1599 cm^{-1} (C═O); HRMS (ESI) calcd for $C_{28}H_{30}N_2ONa$ 433.2250, found 433.2260. Anal. Calcd for $C_{28}H_{30}N_2O$ (410.55): C, 81.91; H, 7.37; N, 6.82. Found: C, 81.51; H, 7.06; N, 6.75.

*N-(4-Chlorbenzyl)-N-(2-p-chlorphenyl-1H-indol-3-yl)-pivalamide (**8c**):* A solution of 2.08 mL (2.08 mmol) of KO-*t*-Bu (1 M solution in THF) in 130 mL of dry THF was warmed to 50 °C. Subsequently, 0.69 g (1.89 mmol) of **6c** dissolved in 20 mL dry THF was added slowly to the stirred mixture. The color of the solution immediately turned to dark red. After 4 h of stirring, 0.47 mL (3.78 mmol) of trimethyl acetyl chloride was added. The crude product was purified by recrystallization from DCE: 0.63 g (1.40 mmol, 74%) of compound **8c** was obtained as yellow crystals; mp 275−276 °C; ^{1}H NMR ($CDCl_3$/TFA, 400 MHz) δ = 0.94 ppm (s, 9H), 4.45 (d, J = 14.0 Hz, 1H), 4.49 (d, J = 14.0 Hz, 1H), 6.95−7.38 (m, 12H), 8.15 (br s, 1H); ^{13}C NMR ($CDCl_3$/TFA, 100 MHz) δ = 28.9 ppm, 41.7, 56.8, 108.8, 111.5, 112.6, 116.4, 119.0, 120.1, 121.6, 124.2, 127.1, 128.5, 129.8, 131.6,134.3, 134.6, 134.9, 183.0; IR (KBr) $\tilde{\nu}$ = 1593 cm^{-1} (C═O); HRMS (ESI) calcd for $C_{26}H_{24}Cl_2N_2ONa$ 473.1158, found 473.1159. Anal. Calcd for $C_{26}H_{24}Cl_2N_2O$ (451.39): C, 69.18; H, 5.36; N, 6.21. Found: C, 69.34; H, 4.99; N, 5.99.

*N-(4-Methoxybenzyl)-N-(2-p-methoxyphenyl-1H-indol-3-yl)-pivalamide (**8d**):* A solution of 2.03 mL (2.03 mmol) of KO-*t*-Bu (1 M solution in THF) in 130 mL of dry THF was heated to 50 °C: 0.66 g (1.85 mmol) of diimine **6d**, dissolved in 20 mL of dry THF, was added slowly to the stirred mixture. The color of the solution turned to dark red. The anionic intermediates were quenched with 0.46 mL (3.70 mmol) of trimethyl acetyl chloride. Recrystallization from DCE afforded the product: 0.70 g (1.59 mmol, 86%) of compound **8d** was obtained as light yellow crystals; mp 224−225 °C; ^{1}H NMR ($CDCl_3$/TFA, 400 MHz) δ = 0.93 ppm (s, 9H), 3.73 (s, 3H), 3.83 (s, 3H), 4.39 (d, J = 13.2 Hz, 1H), 5.33 (d, J = 13.2 Hz, 1H), 6.64 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 9.0 Hz, 3H), 6.96 (t, J = 7.9 Hz, 1H), 7.12 (d, J = 8.5 Hz, 3H), 7.31 (d, J = 8.1 Hz, 1H), 7.41 (d, J = 8.9 Hz, 2H), 8.40 (br s, 1H); ^{13}C NMR ($CDCl_3$/TFA, 100 MHz) δ = 29.0 ppm, 41.0, 55.2, 55.3, 55.6, 110.8, 113.3, 114.5, 117.3, 119.3, 120.3, 122.6, 123.3, 127.2, 127.2, 130.4, 131.3, 131.7, 133.8, 158.9, 159.4, 179.68; IR (KBr) $\tilde{\nu}$ = 3217 cm^{-1} (NH), 1612 (C═O); HRMS (ESI) calcd for $C_{28}H_{30}N_2O_3Na$ 465.2149, found 465.2149. Anal. Calcd for $C_{28}H_{30}N_2O_3$ (442.55): C, 75.99; H, 6.83; N, 6.33. Found: C, 75.69; H, 6.82; N, 6.27. X-ray crystal structure data of **8d** can be found in the Supporting Information.

*N-(2-(Naphthalen-2-yl)-1H-indol-3-yl)-N-(naphthalen-2-ylmethyl)pivalamide (**8e**):* A solution of 1.10 mL (1.10 mmol) of KO-*t*-Bu (1 M solution in THF) in 130 mL of dry THF was warmed to 50 °C. Subsequently, 0.40 g (1.00 mmol) of diimine **6m** dissolved in 20 mL of dry THF was added slowly. The color of the solution changed to dark red. After 4 h at this temperature, 0.25 mL (2.00 mmol) of trimethyl acetyl chloride was added. The crude product was purified by recrystallization from DCM: 0.23 g (0.47 mmol, 47%) of compound **8e** was obtained as a light brown solid; mp 237−238 °C; ^{1}H NMR ($CDCl_3$/TFA, 300 MHz) δ = 1.00 ppm (s, 9H), 4.99 (d, J = 13.5 Hz, 1H), 5.41 (d, J = 13.5 Hz, 1H), 6.96−7.08 (m, 2H), 7.19−7.24 (m, 1H), 7.31−7.67 (m, 12H), 7.72−7.76 (m, 3H), 8.46 (br s, 1H); ^{13}C NMR ($CDCl_3$/TFA, 75 MHz) δ = 29.0 ppm, 41.8, 57.8, 108.8, 111.4, 112.6, 116.4, 119.1, 121.3, 123.2, 123.8, 125.4, 126.0, 126.1, 126.6, 127.0, 127.5, 127.5, 127.8, 128.0, 128.0, 128.4, 129.1, 129.6, 132.2, 132.9, 133.0, 133.2, 133.3, 133.7, 134.2, 182.9; IR (neat) $\tilde{\nu}$ = 1612 cm^{-1} (C═O); HRMS (ESI) calcd for $C_{34}H_{30}N_2OH$ 483.2431, found 483.2438. Anal. Calcd for $C_{34}H_{30}N_2O$ (482.61): C, 84.61; H, 6.27; N, 5.80. Found: C, 84.28; H, 6.26; N, 5.71.

*N-(2-(Thien-2-yl)-1H-indol-3-yl)-N-(thien-2-yl-methyl)-pivalamide (**8f**):* Diimine **6f** (0.43 g, 1.39 mmol) was dissolved in 20 mL of dry THF. Subsequently, the mixture was added slowly to a solution of KO-*t*-Bu (1.53 mL, 1.53 mmol, 1 M solution in THF) in 130 mL of dry THF at 50 °C. The solution immediately turned to dark purple. After 4 h, 0.34 mL (2.78 mmol) of trimethyl acetyl chloride was added: 0.25 g (0.64 mmol, 46%) of compound **8f** was obtained as a light yellow crystals; mp 218−219 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.87 ppm (s, 9H), 4.19 (d, J = 14.4 Hz, 1H), 5.61 (d, J = 14.4 Hz, 1H), 6.57−6.58 (m, 1H), 6.64−6.68 (m, 2H), 6.84 (t, J = 7.8 Hz, 1H), 6.99−7.02 (m, 1H), 7.02−7.11 (m, 2H), 7.13−7.17 (m, 2H), 7.22−7.25 (m, 1H), 8.36 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 28.6 ppm, 41.3, 51.9, 111.1, 113.0, 116.5, 116.8, 119.0, 121.2, 123.7, 124.3, 126.3, 126.6, 126.7, 128.1, 128.8, 132.0, 134.0, 138.8, 182.1; IR (neat) $\tilde{\nu}$ = 1601 cm^{-1} (C═O); HRMS (ESI) calcd for $C_{22}H_{22}N_2OS_2Na$ 417.1066, found 417.1071. Anal. Calcd for $C_{22}H_{22}N_2OS_2$ (394.55): C, 66.97; H, 5.62; N, 7.10. Found: C, 66.77; H, 5.39; N, 6.99. X-ray crystal structure data of **8f** can be found in the Supporting Information.

*N-(4-tert-Butylbenzyl)-N-(2-p-tert-butylphenyl-1H-indol-3-yl)-pivalamide (**8g**):* A solution of 1.10 mL (1.10 mmol) of KO-*t*-Bu (1 M solution in THF) in 130 mL of dry THF was prepared. Subsequently, 0.41 g (1.00 mmol) of **6g**, dissolved in 20 mL of dry THF, was slowly added to the stirred mixture. The color of the solution turned to dark red. After 1 h at 50 °C, 0.25 mL (2.00 mmol) of trimethyl acetyl chloride was added: 0.08 g (0.15 mmol, 15%) of compound **8g** was obtained as light yellow crystals from DE; mp 101−102 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.94 ppm (s, 9H), 1.26 (s, 9H), 1.33 (s, 9H), 4.37 (d, J = 15.0 Hz, 1H), 5.48 (d, J = 15.0 Hz, 1H), 6.79−6.82 (m, 1H), 6.89 (t, J = 6.0 Hz, 1H), 7.10−7.17 (m, 4H), 7.32−7.46 (m, 6H), 8.57 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 29.1 ppm, 31.3, 31.5, 34.5, 34.8, 41.2, 55.8, 110.9, 117.9, 119.6, 120.3, 122.8, 125.0, 125.7, 126.1, 127.4, 127.9, 129.9, 131.9, 134.0, 135.3 150.4, 151.3, 179.8; IR (neat) $\tilde{\nu}$ = 1599 cm^{-1} (C═O); HRMS (ESI) calcd for $C_{34}H_{42}N_2OH$ 495.3370, found 495.3366. Anal. Calcd for $C_{34}H_{42}N_2O$ (494.71): C, 82.55; H, 8.56; N, 5.66. Found: C, 82.00; H, 8.71; N, 5.57.

*N-(2-Methylbenzyl)-N-(2-o-methylphenyl-1H-indol-3-yl)-pivalamide (**8h**):* A solution of 1.10 mL (1.10 mmol) of KO-*t*-Bu (1 M solution in THF) in 130 mL dry THF was warmed to 50 °C. Subsequently, 0.33 g (1.00 mmol) of **6o**, dissolved in 20 mL dry THF, was added slowly. The color of the solution changed to dark red. After 2 h at this temperature, 0.25 mL (2.00 mmol) of trimethyl acetyl chloride was added. The crude product was purified by recrystallization from DE: 0.17 g (0.41 mmol, 41%) of compound **8h** was obtained as a colorless solid; mp 102−103 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.98 ppm (s, 9H), 1.95 (s, 3H), 2.20 (s, 3H), 4.75−4.99 (m, 2H), 6.86−6.92 (m, 2H), 6.97−7.04 (m, 3H), 7.08−7.17 (m, 5H), 7.20−7.29 (m, 2H), 8.21 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 19.2 ppm, 21.0, 29.3, 41.3, 53.7, 111.1, 119.0, 119.5, 120.5, 122.8, 125.7,

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126.1, 126.3, 126.9, 128.9, 130.0, 130.3, 130.4, 131.3, 132.9, 133.8, 136.1, 136.2, 136.6, 180.0; IR (neat) $\tilde{\nu}$ = 1630 cm^{-1} (C═O); HRMS (ESI) calcd for $C_{28}H_{30}N_2ONa$ 433.2250, found 433.2248.

*N-Benzyl-N-(2-phenyl-1-pivaloyl-1H-indol-3-yl)pivalamide (**9**):* KO-*t*-Bu (0.22 g, 2.00 mmol) was dissolved in 130 mL of 1,4-dioxane and heated to 90 °C. Then, 0.29 g (1.00 mmol) of diimine **6a** in 20 mL of 1,4-dioxane was added slowly. The color of the reaction mixture turned to dark red. After 4 h at 90 °C, 0.49 mL (4.00 mmol) of trimethyl acetyl chloride was added. The workup was performed analogously to the synthesis of compounds **8**. The crude product was recrystallized from 1,4-dioxane: 0.15 g (0.32 mmol, 32%) of compound **9** was obtained as colorless crystals; mp 148−149 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 0.90 ppm (s, 9H), 0.92 (s, 9H), 4.52 (d, J = 12.0 Hz, 1H), 5.23 (d, J = 12.0 Hz, 1H), 7.00−7.08 (m, 2H), 7.13−7.25 (m, 8H), 7.29−7.33 (m, 1H), 7.31−7.38 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 28.1 ppm, 29.2, 41.3, 45.1, 56.6, 111.4, 119.4, 121.2, 122.0, 124.5, 126.0, 127.7, 128.3, 128.8, 128.9, 129.4, 130.1, 131.6, 133.5, 134.5, 137.9, 179.6, 186.6; IR (neat) $\tilde{\nu}$ = 1713 cm^{-1} (C═O), 1638 (C═O); HRMS (ESI) calcd for $C_{31}H_{34}N_2O_2Na$ 489.2512, found 489.2519. Anal. Calcd for $C_{31}H_{34}N_2O_2$ (466.61): C, 79.79; H, 7.34; N, 6.00. Found: C, 79.36; H, 7.46; N, 5.92. X-ray crystal structure data of **9** can be found in the Supporting Information.

General Procedure for the Synthesis of 3-Aminoindole Derivatives (10a/11a−c). A solution of 1.1 equiv of KO-*t*-Bu (1.0 M in THF or solid) in dry THF was prepared and heated to 50 °C. Then, 1.0 equiv of diimine **6**, dissolved in dry THF, was added slowly. Immediately an intense color appeared, and the solution was stirred for a definite period of time. The reactive anionic intermediates were quenched by addition of 10 mL of distilled water. Immediately, the intense color of the solution faded. The organic phase was washed with saturated NaCl solution and dried over $MgSO_4$. Afterward, the solvent was removed in vacuo and the product was purified by column chromatography, recycling GPC (in toluene), and/or recrystallization.

*N-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-indol-3-amine (**10a**):* Diimine **6c** (0.37 g, 1.00 mmol) was dissolved in 20 mL of dry THF and added slowly to a stirred mixture of 1.10 mL (1.10 mmol) of KO-*t*-Bu (1.0 M in THF) in 130 mL of dry THF at 50 °C. The reaction mixture was stirred for 4 h and subsequently quenched with distilled water. The color of the solution turned to yellow. The crude product was purified by recycling GPC (toluene) to give 0.20 g (0.55 mmol, 55%) as a yellow solid: mp 147−148 °C; ^{1}H NMR (C_6D_6, 400 MHz) δ = 3.51 ppm (s, 1H), 3.89 (s, 2H), 6.68 (br s, 1H), 6.73 (d, J = 7.6 Hz, 1H), 6.80 (d, ^3J = 7.2 Hz, 2H), 6.96−7.07 (m, 4H), 7.17−7.18 (m, 2H), 7.22−7.26 (m, 1H), 7.43−7.48 (m, 2H); ^{13}C NMR (C_6D_6, 100 MHz) δ = 53.1 ppm, 111.6, 118.7, 119.9, 123.2, 124.2, 125.2, 125.6, 127.9, 128.2, 128.7, 129.0, 129.0, 129.1, 130.1, 131.1, 131.2, 131.5, 133.1, 135.5, 139.2; IR (neat) $\tilde{\nu}$ = 3063 cm^{-1} (NH); HRMS (ESI) calcd for $C_{21}H_{16}Cl_2N_2H$ 367.0763, found 367.0762.

*(E)-N-(4-Chlorobenzylidene)-2-(4-chlorophenyl)-1H-indol-3-amine (**11a**):* Obtained in a mixture with compound **10a** and could be separated by recycling GPC (toluene) and subsequent recrystallization from 1,4-dioxane to give 0.17 g (0.47 mmol, 47%) of compound **11a** as yellow crystals: mp 159−160 °C; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ = 7.19−7.23 ppm (m, 1H), 7.26−7.30 (m, 1H), 7.44−7.50 (m, 5H), 8.47 (br s, 1H), 9.12 (s, 1H); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ = 112.2 ppm, 120.4, 121.8, 122.1, 124.0, 126.3, 129.3, 129.5, 129.6, 129.8, 130.8, 132.1, 134.1, 136.2, 136.5, 137.0, 155.3; IR (neat) $\tilde{\nu}$ = 1622 cm^{-1} (C═N); HRMS (ESI) calcd for $C_{21}H_{14}Cl_2N_2Na$ 387.0426, found 387.0432. Anal. Calcd for $C_{21}H_{14}Cl_2N_2$ (365.26): C, 69.05; H, 3.86; N, 7.67. Found: C, 68.69; H, 4.00; N, 7.40. X-ray crystal structure data of **11a** can be found in the Supporting Information.

*(E)-2-(Anthracen-9-yl)-N-(anthracen-9-yl-methylene)-1H-indol-3-amine (**11b**):* Diimine **6l** (0.25 g, 0.50 mmol) was dissolved in 10 mL of dry THF and added slowly to a stirring mixture of 0.55 mL (0.55 mmol) of KO-*t*-Bu in 65 mL of dry THF at 50 °C. Immediately a dark red color appeared. The reaction mixture was stirred for 4 h and subsequently quenched with distilled water. The color of the solution turned to yellow. After addition of TEA, the yellow solid precipitate was purified by recrystallization from DCM/DE to give 0.12 g (0.25 mmol, 50%) of compound **11b**, cocrystallizing with triethyl ammonium chloride (yellow crystals): mp 239−240 °C; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ = 1.34 ppm (t, J = 7.3 Hz, 9H), 3.03 (q, J = 7.3 Hz, 6H), 7.10−7.16 (m, 2H), 7.31−7.61 (m, 9H), 7.88 (d, J = 8.4 Hz, 2H), 8.01 (t, J = 9.1 Hz, 4H), 8.15 (d, J = 8.4 Hz, 2H), 8.27−8.30 (m, 1H), 8.34 (s, 1H), 8.64 (br s, 1H), 8.71 (s, 1H), 9.67 (s, 1H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ = 9.0 ppm, 46.3, 112.1, 120.2, 121.6, 123.7, 125.6, 126.2, 126.8, 127.0, 127.3, 129.2, 129.8, 130.5, 131.8, 132.1, 132.3, 156.5; IR (neat) $\tilde{\nu}$ = 1603 cm^{-1} (C═N); HRMS (ESI) calcd for $C_{37}H_{24}N_2H$ 497.2012, found 497.2015. X-ray crystal structure data of **11b** can be found in the Supporting Information.

*(E)-N-(4-Methoxybenzylidene)-2-(4-methoxyphenyl)-1H-indol-3-amine (**11c**):* For the synthesis of compound **6d**, 0.36 g (1.00 mmol) of diimine **6d** was dissolved in 20 mL of dry THF. The solution was slowly added to a mixture of 1.10 mL (1.10 mmol) of KO-*t*-Bu (1.0 M in THF) in 130 mL of dry THF. After stirring for 2 h at 50 °C, 10 mL of distilled H_2O was added to quench the reactive intermediates. The product was purified by recycling GPC (toluene) and subsequent recrystallization from toluene: 0.12 g (0.34 mmol, 34%) of compound **11c** was obtained as a yellow solid; mp 156−157 °C; ^{1}H NMR (C_6D_6, 400 MHz) δ = 3.20−3.27 ppm (m, 1H), 3.30 (s, 3H), 3.31 (s, 3H), 6.26 (d, J = 12.0 Hz, 1H), 6.45−6.51 (m, 2H), 6.77−6.81 (m, 4H), 6.94−7.00 (m, 1H), 7.35−7.40 (m, 2H), 7.69−7.75 (m, 2H), 8.38 (s, 1H); ^{13}C NMR (C_6D_6, 100 MHz) δ = 54.7 ppm, 54.8, 114.1, 114.3, 115.8, 116.1, 117.0, 118.0, 129.2, 130.6, 131.2, 132.1, 132.8, 134.9, 148.4, 149.7, 158.9, 160.0, 166.6; IR (neat) $\tilde{\nu}$ = 1605 cm^{-1} (C═N) HRMS (ESI) calcd for $C_{23}H_{20}N_2O_2H$ 357.1598, found 357.1578. Anal. Calcd for $C_{23}H_{20}N_2O_2$ (356.42): C, 77.51; H, 5.66; N, 7.84. Found: C, 77.54; H, 5.31; N, 7.66.

Procedure for the Synthesis of 2-Phenethyl-3-phenyl-5*H*-pyrido[3,2-*b*]indole (12a). Following the procedure for the synthesis of compounds **8a−h**, 0.35 g (1.00 mmol) of compound **7a** was dissolved in 20 mL of dry THF. The mixture was added slowly to a stirring mixture of 0.12 g (1.10 mmol) of KO-*t*-Bu in 80 mL of dry THF and heated to 50 °C. Immediately, the colorless to light yellow solution turned to dark red. The crude product was recrystallized from DCM/PE: 0.07 g (0.20 mmol, 20%) of compound **12a** was obtained as a brown oil which was not pure; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ = 3.01−3.07 ppm (m, 2H), 3.19−3.24 (m, 2H), 6.99−7.59 (m, 14H), 7.54 (s, 1H), 8.38 (m, 1H), 8.98 (br s, 1H); HRMS (ESI) calcd for $C_{25}H_{20}N_2H$ 349.1699, found 349.1690. X-ray crystal structure data of **12a** can be found in the Supporting Information.

General Procedure for the Synthesis of Tetraazadibenzocyclotetradecaenes (13/14). Under an inert argon atmosphere, a Schlenk flask was charged with KO-*t*-Bu (1.0 M solution in THF or solid) and dry THF. At room temperature, a solution of the diimine **6** in dry THF was slowly added over a period of 30 min. The solution immediately adopted an intense color. The mixture was stirred for 48 h. Subsequently, 10 mL of distilled water was added, and the color of the solution faded within seconds. Fifty milliliters of DE was added, and the organic phase was washed with distilled water (3 × 50 mL). The solvent was removed in vacuo, and the product was purified by column chromatography or recrystallization.

*(R,R,R,R)- and (S,S,S,S)-2,3,9,10-Tetraphenyldibenzo[e,l]-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene (**13a**):* A solution of 25.48 mL (25.48 mmol) of KO-*t*-Bu (1.0 M solution in THF) in 40 mL of dry THF was prepared. The solution immediately turned deep red when 3.80 g (12.74 mmol) of diimine **6a**, dissolved in 20 mL of dry THF, was added slowly at rt. The mixture was stirred for 24 h. Distilled water was added to quench the reactive intermediates, and the solution immediately turned yellow. The crude product was purified by recrystallization from DE: 1.45 g (2,43 mmol, 38%) was obtained as light yellow crystals; mp 286−287 °C; ^{1}H NMR (C_6D_6, 400 MHz) δ = 4.56 ppm (s, 2H), 5.32 (d, J = 7.2 Hz, 2H), 6.33 (td, J = 7.2 Hz, J = 0.8 Hz, 2H), 6.44 (d, J = 8.0 Hz, 2H), 6.71 (dd, J = 7.6 Hz, J = 1.6 Hz, 2H), 6.08−6.85 (m, 2H), 6.97−7.01 (m, 2H), 7.11−7.20 (m, 10H), 7.43 (d, J = 7.6 Hz, 4H), 7.67 (d, J = 7.2 Hz, 4H), 7.81 (s, 2H), 11.52 (d, J = 7.2 Hz, 2H); ^{13}C NMR (C_6D_6, 100 MHz) δ = 63.0 ppm, 80.3, 112.1, 115.0, 118.0, 127.4, 127.5, 127.7, 128.4, 128.8, 128.9, 132.0, 134.9, 142.7, 143.3, 148.9, 165.9; IR (neat) $\tilde{\nu}$ = 1626 cm^{-1} (C═N); HRMS (ESI) calcd for $C_{42}H_{36}N_4H$ 597.3013, found 597.3016.

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Anal. Calcd for $C_{42}H_{36}N_4$ (596.76): C, 84.53; H, 6.08; N, 9.39. Found: C, 84.56; H, 6.05; N, 9.38. X-ray crystal structure data of **13a** can be found in the Supporting Information.

*(R,R,R,R)- and (S,S,S,S)-2,3,9,10-Tetrakis-(4-chlorophenyl)-dibenzo[e,l]-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene (**13b**):* A solution of 0.89 g (8.00 mmol) of KO-*t*-Bu in 40 mL of dry THF was prepared. Subsequently, 1.47 g (4.00 mmol) of compound **6c**, dissolved in 20 mL of dry THF, was added slowly. The color of the solution immediately turned dark purple and changed to yellow after quenching with distilled water. The crude product was purified by recrystallization from DCE: 0.52 g (0.72 mmol, 36%) of compound **13b** was obtained as colorless crystals; mp 230−231 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 4.57 ppm (br s, 2H), 5.19 (d, J = 7.2 Hz, 2H), 6.33 (d, J = 8.4 Hz, 2H), 6.53 (t, J = 7.8 Hz, 2H), 7.04 (t, J = 8.4 Hz, 2H), 7.07 (d, J = 7.8 Hz, 2H), 7.19−7.23 (m, 4H), 7.26−7.29 (m, 8H), 7.43 (d, J = 8.4 Hz, 4H), 8.09 (br s, 2H), 11.02 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 61.8 ppm, 78.9, 111.7, 115.3, 117.3, 128.4, 128.5, 128.7, 129.0, 132.2, 133.2, 133.4, 134.8, 140.2, 140.7, 148.0, 166.1; IR (neat) $\tilde{\nu}$ = 1622 cm^{-1} (C═N); HRMS (ESI) calcd for $C_{42}H_{32}Cl_4N_4Na$ 755.1273, found 755.1293. Anal. Calcd for $C_{42}H_{32}Cl_4N_4$ (734.54): C, 68.68; H, 4.39; N, 7.63. Found: C, 68.53; H, 4.23; N, 7.49. X-ray crystal structure data of 13b can be found in the Supporting Information.

*(R,R,R,R)- and (S,S,S,S)-2,3,9,10-Tetrakis-(4-bromophenyl)-dibenzo[e,l]-1,4,8,11- tetraazacyclotetradeca-4,6,11,13-tetraene (**13c**):* A solution of 7.63 mL (7.63 mmol) of KO-*t*-Bu (1.0 M solution in THF) in 40 mL of dry THF was prepared. Then, 1.74 g (3.81 mmol) of compound **6n** in 20 mL of dry THF was added slowly. Recrystallization from DCM afforded 1.74 g (1.91 mmol, 99%) of the product as yellow crystals: mp 291−292 °C; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ = 4.63 ppm (d, J = 0.9 Hz, 2H), 5.23 (d, J = 7.8 Hz, 2H), 6.36 (d, J = 8.4 Hz, 2H), 6.55 (td, J = 7.5 Hz, J = 0.9 Hz, 2H), 7.03−7.08 (m, 2H), 7.11 (dd, J = 7.8 Hz, J = 1.50, 2H), 7.26−7.29 (m, 4H), 7.40−7.44 (m, 8H), 7.46−7.49 (m, 4H), 8.14 (s, 1H), 11.03 (d, J = 7.8 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ = 62.1 ppm, 79.0, 112.0, 115.8, 117.9, 121.6, 121.7, 129.3, 129.4, 132.0, 132.2, 132.6, 135.3, 141.2, 141.8, 148.5, 166.8; IR (neat) $\tilde{\nu}$ = 1622 cm^{-1} (C═N); HRMS (ESI) calcd for $C_{42}H_{32}Br_4N_4Na$ 934.9212, found 934.91291. Anal. Calcd for $C_{42}H_{32}Br_4N_4$ (912.35): C, 55.29; H, 3.54; N, 6.14. Found: C, 55.44; H, 3.61; N, 6.01. X-ray crystal structure data of **13c** can be found in the Supporting Information.

*(R,R,R,R)- and (S,S,S,S)-2,3,9,10-Tetra-(2-pyridyl)-dibenzo[e,l]-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene (**13d**):* KO-*t*-Bu (2.74 mL, 2.74 mmol, 1.0 M solution in THF) was dissolved in 40 mL of dry THF. Subsequently, 0.41 g (1.37 mmol) of diimine **6i** in 20 mL of dry THF was added slowly to the stirred mixture. The reaction mixture was stirred overnight at room temperature. Distilled water was added to quench the reactive anionic species. After adding EA, a yellow solid precipitate was washed with EA: 0.20 g (0.34 mmol, 49%) of compound **13d** was obtained as a yellow solid; mp >350 °C; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ = 5.13 ppm (s, 2H), 5.89 (d, J = 8.4 Hz, 2H), 6.49 (t, J = 8.4 Hz, 4H), 7.00−7.06 (m, 4H), 7.11−7.17 (m, 4H), 7.22−7.26 (m, 2H), 7.38 (d, J = 7.7, 2H), 7.53 (td, J = 7.7 Hz, J = 1.7 Hz, 2H), 7.61 (td, J = 7.7 Hz, J = 1.7 Hz, 2H), 8.14 (s, 2H), 8.69 (d, J = 4.1 Hz, 4H), 11.07 (d, J = 8.4 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ = 63.4 ppm, 79.4, 112.1 115.4, 117.9, 121.5, 122.5, 122.6, 122.8, 132.5, 135.1, 136.5, 136.6, 149.3, 149.8, 150.4, 161.7, 161.8, 167.6; IR (neat) $\tilde{\nu}$ = 1626 cm^{-1} (C═N); HRMS (ESI) calcd for $C_{38}H_{32}N_8H$ 601.2823, found 601.2821. Anal. Calcd for $C_{38}H_{32}N_8$ (600.71): C, 75.98; H, 5.37; N, 18.65. Found: C, 76.01; H, 5.46; N, 18.20.

*2,3,9,10-Tetra-(thien-2-yl)-dibenzo[e,l]-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene (**13e**):* A solution of 2.32 mL (2.32 mmol) of KO-*t*-Bu (1.0 M solution in THF) in 40 mL of dry THF was prepared. The solution directly turned deep red when 0.36 g (1.16 mmol) of diimine **6f**, dissolved in 20 mL of dry THF, was added slowly at rt. The mixture was stirred for 24 h. Distilled water was added to quench the reactive intermediates, and the solution immediately turned to yellow. The crude product was purified by column chromatography. Two diastereomers Dia1 and Dia2 (1:0.3) were obtained which could not be separated by column chromatography: 0.05 g (0.08 mmol, 14%) of compound **13e** was obtained as a light yellow solid; mp 227−228 °C; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ = 4.96 ppm (s, 2H, Dia1), 5.12 (s, 2H, Dia2), 5.50 (d, J = 7.6 Hz, 2H, Dia1+Dia2), 6.56−6.72 (m, 4H, Dia1+Dia2), 6.86−6.94 (m, 4H, Dia1+Dia2), 7.01−7.09 (m, 4H, Dia1+Dia2), 7.12−7.26 (m, 8H, Dia1+Dia2), 8.30 (s, 2H, Dia1), 8.39 (s, 2H, Dia2), 11.08 (d, J = 7.6 Hz, 2H, Dia1+Dia2); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ = 58.7 ppm, 59.3, 74.9, 76.0, 111.1, 111.7, 115.7, 115.8, 118.0, 118.0, 124.9, 125.0, 125.2, 125.4, 125.5, 125.7, 126.6, 126.9, 127.1, 127.2, 128.7, 129.5, 132.6, 132.7, 135.2, 135.3, 145.4, 146.0, 146.6, 146.9, 148.7, 149.1, 166.9, 167.3; IR (neat) $\tilde{\nu}$ = 1605 cm^{-1} (C═N); HRMS (ESI) calcd for $C_{34}H_{28}N_4S_4H$ 621.1270, found 621.1274.

*2,3,9,10-Tetrakis-(4-cyanophenyl)-dibenzo[e,l]-1,4,8,11-tetraaza-cyclotetradeca-2,4,6,9,11,13-hexaene (**14**):* A solution of 1.39 g (4.00 mmol) of compound **6h** in 20 mL of dry THF was prepared. The solution was added slowly to a stirred mixture of 8.00 mL (8.00 mmol) of KO-*t*-Bu (1.0 M solution in THF) in 40 mL of dry THF. After 24 h, 10 mL of distilled water was added and the dark purple color of the solution changed to red. The resulting orange solid was washed with DCM and toluene: 0.29 g (0.41 mmol, 21%) of compound **14** was obtained; mp 301−302 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 7.19 ppm (t, J = 6.8 Hz, 2H), 7.29 (t, J = 7.2 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.95−8.00 (m, 8H), 8.12−8.16 (m, 6H), 8.27−8.30 (m, 4H), 9.26 (s, 2H), 12.03 (br s, 2H); ^{13}C NMR ppm (DMSO-d_6, 100 MHz) δ = 109.6 ppm, 111.9, 112.4, 118.9, 119.0, 120.3, 120.6, 121.3, 123.9 126.1, 128.3, 128.6, 131.9, 132.3, 132.7, 135.9, 136.3, 141.7, 153.7; IR (neat) $\tilde{\nu}$ = 2236 (C≡N), 1603 cm^{-1} (C═N); HRMS (ESI) calcd for $C_{46}H_{28}N_8Na$ 715.2329, found 715.2337.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C spectra for the new compounds; optimized Cartesian coordinates (B3LYP/6-31G(d,p) and SCS-MP2/6-311+G(d,p)//B3LYP/6-31G(d,p)+ZPE energies for the calculated structures; graphics of the crystal structures showing thermal ellipsoids with 50% probability. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wurthwe@uni-muenster.de. Fax: +49-251-83-39772.

Dedication

Dedicated to Prof. Dr. Gerhard Erker at the occasion of his 65th birthday.

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