4,5-Dihydro-3*H*-benzo[*c*]azepines from 1,7-Electrocyclization Reactions of 2-Aza-4,5-benzoheptatrienyllithium Compounds

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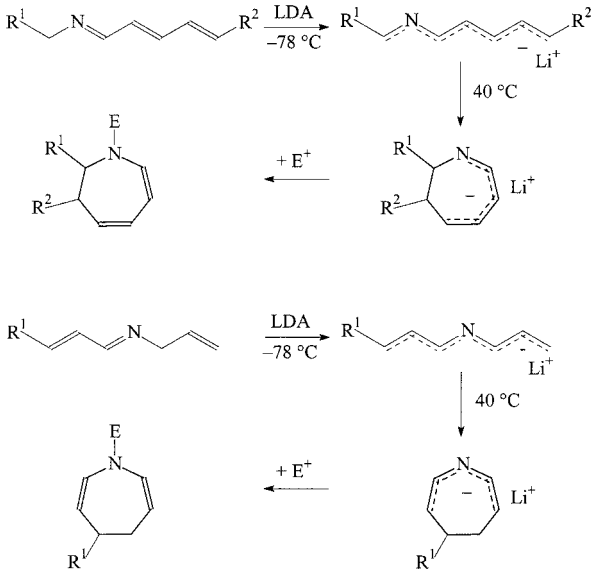
Various differently substituted (2-alkenylbenzylidene)amines **4b**–**d** gave, upon deprotonation with amide bases and addition of an electrophile, the respective 4,5-dihydro-3*H*-benzo[*c*]azepines **6a**–**k** in moderate to good yields. The imines **4** are easily accessible from 2-bromobenzaldehyde (**1**) by Wittig olefination, formylation with DMF, and subsequent condensation with benzylamine. The ring-closure reaction is interpreted as an anionic 1,7-electrocyclization reaction involving benzo-annulated 2-azaheptatrienyllithium compounds. This reaction, and the subsequent addition of the electrophiles, proceed with excellent diastereoselectivity, determined by the (*E*) or (*Z*) configuration of the imines **4b**–**d**. The corresponding allylimines **4e**,**f** do not give nine-membered heterocycles **7**, but rather the corresponding 3-vinyl-4,5-dihydro-3*H*-benzo[*c*]azepines **6l**,**m**. Molecular structures of several compounds **6** in the solid state were determined by X-ray crystallography, including the structure of a 14-membered ring dimer **8**. High-level quantum chemical calculations on model anions concerning structures and relative energies of possible intermediates and transition states support the pericyclic mechanism suggested for the ring-closure reaction.

Introduction

Seven-membered heterocycles constitute an important class of compounds that has found many applications in medicinal chemistry.[1,2] Of special interest within this class of compounds are benzo-annulated systems, among them dibenzoazepines (e.g. imipramine) and benzodiazepines (e.g. clonazepam, diazepam, chlordiazepoxide).[3] We have previously reported a new synthetic pathway to partially unsaturated seven-membered nitrogen heterocycles, based on an electrocyclization reaction of azapolyenylmetal compounds, where the nitrogen atoms are placed in even positions of the anionic chain (Scheme 1).[4,5] Only when this condition is fulfilled can facile ring-closure reactions by anionic electrocyclization take place; azapolyenylmetal compounds with nitrogen atoms in odd positions are thermodynamically stable and do not cyclize easily. These experimental observations were rationalized by molecular orbital arguments (topological charge stabilization[6]); since nitrogen atoms are electronegative, they strongly prefer the odd positions within an unsaturated hydrocarbon chain, as this is where the bigger coefficients in the HOMO are located. For the corresponding cations, the opposite rules apply (ring closure is favored when the nitrogen atoms are in the odd positions).



Scheme 1

In this report, we extend our studies from simple 2- or 4-azaheptatrienylmetal compounds to 2-aza-4,5-benzoheptatrienyllithium systems, in order to investigate the scope of the electrocyclic ring-closure reaction, and eventually gain access to differently substituted benzo-annulated seven-membered nitrogen heterocycles. Special emphasis in our

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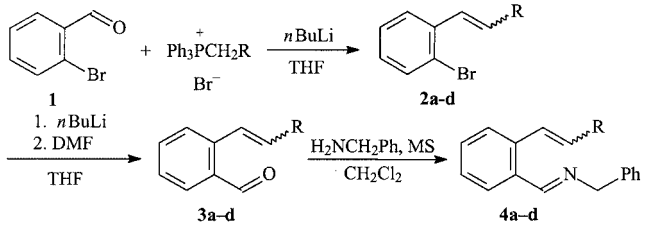
studies is directed towards the elucidation of the stereoelectronic properties of the ring-closure reaction and the subsequent electrophilic addition to the intermediate anionic species. For a more detailed discussion of the reaction mechanism, we include high level quantum chemical calculations in this study.

Anionic electrocyclization reactions to form seven-membered rings are rare.[4,5,7,8] However, many examples are known that involve neutral [1,7]-dipoles; these species are isoelectronic to the corresponding anions.[9−12]

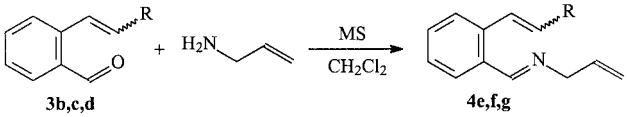
Results and Discussion

For the preparation of the anionic reactive intermediates by deprotonation, the corresponding 2-(alkenyl)benzaldimine derivatives **4** were synthesized using a three-step procedure starting from 2-bromobenzaldehyde (**1**). In the first step, the alkenyl moiety of the styrene derivatives **2** was established by a Wittig reaction as reported by Hibino et al.[13] (Scheme 2). This gave an (*E*)/(*Z*) mixture of **2** [(*Z*)/(*E*) = 1:0.5−0.7]. Pure **(*E*)-2b** was obtained by isomerization of the (*E*)/(*Z*) mixture using iodine.[14] Formylation of **2** to yield the 2-(alkenyl)benzaldehydes **3** was accomplished by metalation with *n*-butyllithium and subsequent addition of dimethylformamide, also according to a procedure given by Hibino et al.[13] In the third step, condensation with benzylamine in the presence of molecular sieves yielded the 2-(alkenyl)benzaldimines **4a−d** (Scheme 2).[15] Condensation with allylamine produced the imines **4e−g** (Scheme 3). The solid-state structure of derivative **4g** was determined by X-ray crystallography.[16] It shows the (*E*) configuration of the C=C bond, and a conformation of the imine moiety relative to the benzene ring resulting from rotation around the C−CN bond away from the stilbene part of the molecule (Figure 1).



2, 3, 4	R	Yield 2 (%)	Yield 3 (%)	Yield 4 (%)
a	H	44	66	64
b	CH_3	71	89	96
c	Pr	53	97	80
d	Ph	46	97	88

Scheme 2



	R	Yield (%)
4e	CH_3	96
4f	Pr	89
4g	Ph	88

Scheme 3

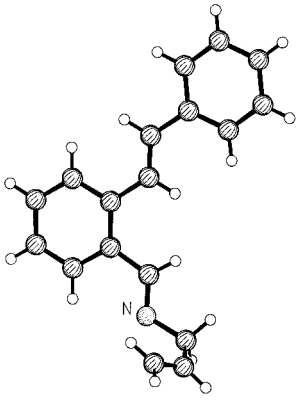
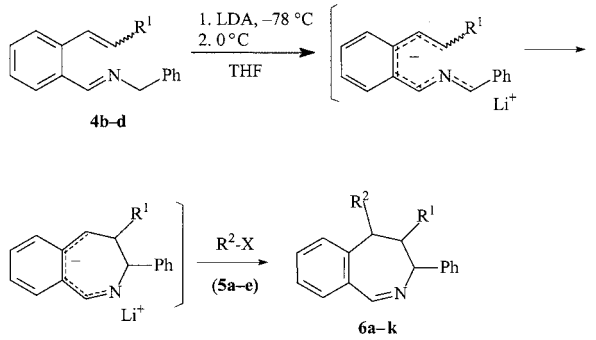


Figure 1. Molecular structure of compound **4g** in the solid state (X-ray diffraction)

The deprotonation of the imines **4** to generate the intermediate anions requires a carefully optimized protocol, which starts with the preparation of a small excess (ca. 20%) of lithium diisopropylamide (LDA) from *n*-butyllithium and diisopropylamine in THF at −40 °C, warming to room temperature and subsequent cooling to −78 °C. At this temperature, a solution of the imine **4b−d** in THF is added dropwise to the base over 30 min. The reaction is completed by warming the mixture to 0 °C and stirring at this temperature for 30 min before addition of the respective electrophile **5** and aqueous workup (Scheme 4). After column chromatography on silica gel, using petroleum ether/ethyl acetate (10:2 to 10:1) as eluent, the major component of the reaction mixture could be isolated as the first fraction.

In this way, the 4,5-dihydro-3*H*-benzo[*c*]azepines **6** were obtained in moderate to good isolated yields (Scheme 4), as oily or slowly crystallizing materials. They were fully characterized, and in some cases, X-ray analysis was obtained. For the preparation of **6k**, LiTMP (lithium 2,2,6,6-tetramethylpiperidide) proved to be superior to LDA. The reaction is interpreted as a 1,7-electrocyclic ring-closure reaction, as indicated above. The driving force of the reaction is the generation of the energetically favored bicyclic 1-azapentadienyl anion, in which the nitrogen atom is in a position with a large HOMO coefficient, from the disfavored 2-azaheptatrienyl anion, in which the nitrogen atom is in a nodal position of the HOMO.[4]

However, deprotonation of the styrene derivative **4a** and subsequent electrophilic addition does not lead to cyclic



4	6	R^1	R^2-X (**5**)	Yield (%)
(*E*,*Z*)-**4b**	(3*R**,4*S**,5*S**)-**6a**	CH_3	H-OH (**5a**)	42
(*E*,*Z*)-**4b**	(3*R**,4*S**,5*S**)-**6b**	CH_3	CH_3-I (**5b**)	48
	+ (3*R**,4*R**,5*R**)-**6b**	CH_3	CH_3-I (**5b**)	14
(*E*)-**4b**	(3*R**,4*R**,5*R**)-**6b**	CH_3	CH_3-I (**5b**)	68
(*E*)-**4b**	(3*R**,4*R**,5*R**)-**6c**	CH_3	C_2H_5-Br (**5c**)	66
(*E*,*Z*)-**4b**	(3*R**,4*S**,5*S**)-**6d**	CH_3	CH_2=CH-CH_2-Br (**5d**)	56
(*E*)-**4b**	(3*R**,4*R**,5*R**)-**6d**	CH_3	CH_2=CH-CH_2-Br (**5d**)	72
(*E*,*Z*)-**4b**	(3*R**,4*S**,5*S**)-**6e**	CH_3	$PhCH_2$-Br (**5e**)	56
(*E*,*Z*)-**4c**	(3*R**,4*S**)-**6f**	Pr	H-OH (**5a**)	51
(*E*,*Z*)-**4c**	(3*R**,4*S**,5*S**)-**6g**	Pr	CH_3-I (**5b**)	45
(*E*,*Z*)-**4c**	(3*R**,4*S**,5*S**)-**6h**	Pr	C_2H_5-Br (**5c**)	38
(*E*,*Z*)-**4c**	(3*R**,4*S**,5*S**)-**6i**	Pr	CH_2=CH-CH_2-Br (**5d**)	72[a]
(*E*,*Z*)-**4c**	(3*R**,4*S**,5*S**)-**6j**	Pr	$PhCH_2$-Br (**5e**)	29
(*E*)-**4d**	(3R*,4*R**)-**6k**	Ph	H-OH (**5a**)	29[b]

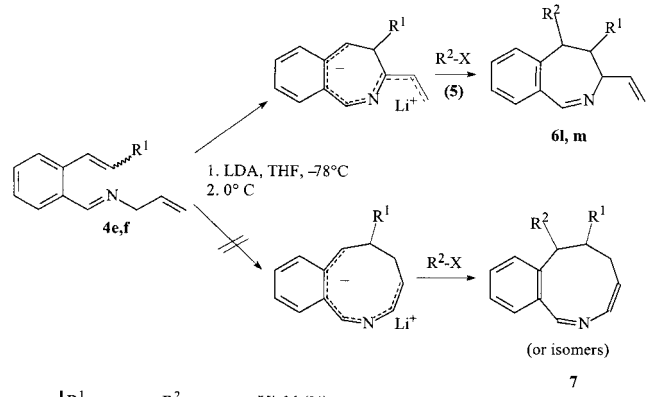
[a] Contains a second diastereomer of unknown configuration. [b] Purity 81 % (GC).

Scheme 4

products, presumably due to anionic polymerization. Similarly, **4g** decomposes on deprotonation to give polymers.

In order to investigate the possible extension of this synthetic method to nine-membered benzo-annulated heterocycles, the allylimine derivatives **4e**,**f** were synthesized and deprotonated (Scheme 5). However, after addition of the electrophiles, workup and characterization of the products, all spectroscopic and analytical evidence was in full agreement with the 4,5-dihydro-3*H*-benzo[*c*]azepine structures **6l**,**m** with vinyl groups in the 3-positions. There was no indication of the formation of nine-membered ring derivatives **7** with the structure shown (Scheme 5) or isomeric products resulting from electrophilic attack at any of the other positions.

After isolation by column chromatography and crystallization, we were able to obtain the molecular structures in the solid state of the main fractions of four 4,5-dihydro-3*H*-benzo[*c*]azepine derivatives **6b**,**c**,**d**,**f** by X-ray diffraction (see Figure 2 for the structures of **6b** and **6d**). This allowed an easy and unambiguous assignment of the relative configurations. Since we are dealing here with racemic compounds,



	R^1	R^2	Yield (%)
6l	CH_3	Et	47
6m	Pr	CH_3	26

Scheme 5

we use the Chemical Abstracts (*R**,*S**) system for the assignment of the relative configurations.[17] Compounds **6d** and **6f** show the same relative configuration at the carbon atoms C3 and C4 of the seven-membered ring [(3*R**,4*S**,5*S**) for **6d** and (3*R**,4*S**) for **6f**]. This is different from the configuration of **6b** and **6c**, which both have a (3*R**,4*R**,5*R**) configuration. On the basis of these crystal structures, the ^{1}H and ^{13}C NMR spectra of all compounds **6** could be clearly differentiated with respect to the relative configurations of the possible diastereomers. We found the X-ray diffraction study of one other example of a 4,5-dihydro-3*H*-benzo[*c*]azepine (dibromo derivative) in the literature.[18]

These crystal structures exemplify nicely how sensitively the conformations of such 4,5-dihydro-3*H*-benzo[*c*]azepines react to changes in substitution pattern and relative configuration. Table 1 summarizes the dihedral angles around the seven-membered rings (note that **6f** has no substituent at position 5).

Interestingly, in all cases, the successful reactions of the (*E*)/(*Z*) mixtures of **4** led to crude mixtures of products, from which pure diastereomers (with the exception of **6b** and **6i**) with relative (3*R**,4*S**) configuration could be separated by column chromatography (Scheme 6). From the yields obtained, one can trace back the formation of this particular diastereomer to the major isomer of **4**, which is the (*Z*) form **(*Z*)-4** (major isomer), as obtained from the Wittig reaction in the first step. In the case of **6b**, small

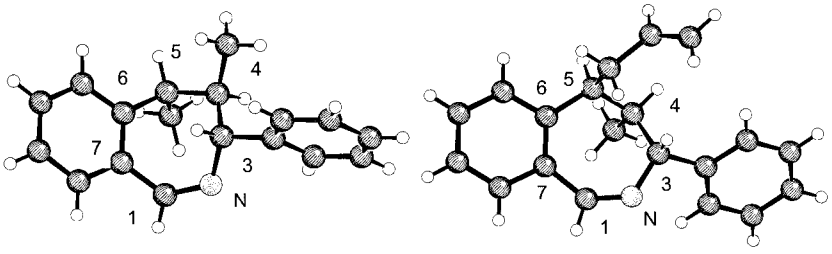
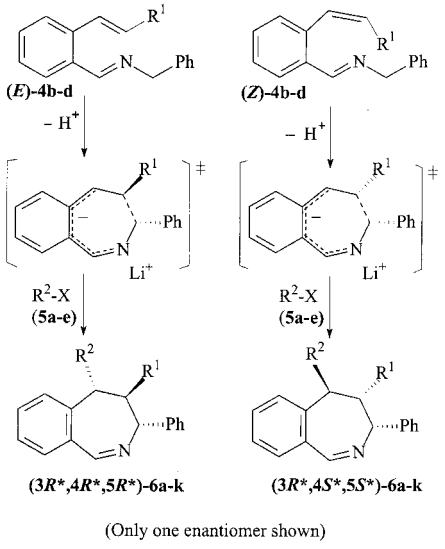


Figure 2. Molecular structure of compounds **(3*R**,4*R**,5*R**)-6b** (left) and **(3*R**,4*S**,5*S**)-6d** (right) in the solid state (X-ray analysis; only one enantiomer of each is shown)

Table 1. Dihedral angles [°] of the seven-membered ring of four 4,5-dihydro-3*H*-benzo[*c*]azepines **6**, as determined by X-ray crystallography

	(3*R**,4*R**,5*R**)-6b	(3*R**,4*R**,5*R**)-6c[a]	(3*R**,4*S**,5*S**)-6d	(3*R**,4*S**)-6f
C7−C1−N2−C3	−4.9(2)	4.5(8)	−1.8(3)	−4.76(19)
C1−N2−C3−C4	76.82(17)	−77.1(6)	31.3(2)	80.58(13)
N2−C3−C4−C5	−53.19(17)	54.0(6)	−71.35(16)	−53.44(12)
C3−C4−C5−C6	−28.75(18)	28.5(6)	74.25(15)	−33.61(14)
C4−C5−C6−C7	63.16(18)	−62.3(6)	−36.95(19)	67.27(15)
C5−C6−C7−C1	−7.3(2)	6.3(7)	3.3(2)	−4.80(17)
C6−C7−C1−N2	−41.7(2)	43.0(8)	1.2(3)	−45.05(19)

[a] One of two similar, independent molecules in the asymmetric unit cell.



Scheme 6

amounts of the minor isomer (ca. 14%) **(3*R**,4*R**,5*R**)-6b**, originating from **(*E*)-4b**, could be isolated and characterized. The fate of the minor isomers, originating from the other olefins **(*E*)-4**, could not be clarified in most cases, due to their less favorable chromatographic properties.

These observations are in agreement with an experiment in which pure **(*E*)-4b** was subjected to the conditions of the deprotonation reaction. In this case, diastereomer **6b**, with the relative (3*R**,4*R**,5*R**) configuration, was obtained exclusively in 68% yield.

Hence, the formation of the new C3−C4 single bond during the cyclization reaction is a highly diastereoselective process, which is in full agreement with a conrotatory electrocyclization mode, as predicted by the Woodward−Hoffmann rules for 8π systems.[19] Furthermore, the addition of the electrophile to position 5 of the intermediate anion obviously occurs with high diastereoselectivity, as the incoming electrophile is always found in the *trans* position to the substituent at center C4. In summary, of the four possible diastereomers of the (racemic) product, only one is formed during the reaction sequence, as determined by the stereochemistry of the ethenyl moiety of the starting material **4** and the subsequent stereoselective addition of the electrophile.

In one experiment (deprotonation of **4b** and quenching with water to form **6a**), a surprising dimeric compound **8** was isolated, in very low yield. Nevertheless, it was possible to characterize this compound by X-ray analysis (Figure 3). It crystallizes centrosymmetrically, forming an approximate rectangle with (*R**,*S**) configuration, as observed in the corresponding seven-membered ring **6a**. Acid-catalyzed equilibria between dimers and monomers of 4,5-dihydrobenzo[*c*]azepines have been reported previously by Goldman et al.[20]

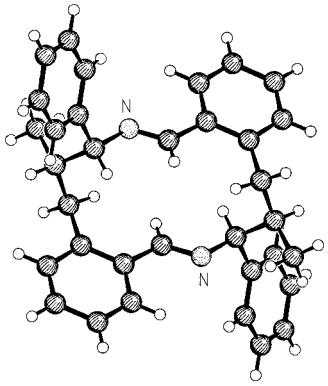


Figure 3. Molecular structure of the macrocycle **8** in the solid state (X-ray diffraction)

Using low-temperature ^{1}H NMR techniques (600 MHz), we were able to investigate the ring-closure reaction of the imine derivative **(*E*,*Z*)-4b** directly. The deprotonation using LDA was performed at −78 °C in [D_8]THF in an NMR tube. At −20 °C, two sets of signals (among others) could be identified; the more intense set was assigned to the predominant anion **Li-4b**, having a (*Z*) configuration at the C=C bond (Table 2). In comparison to the neutral starting material, a high-field shift of most of the signals was observed, which was particularly pronounced at the odd positions of the conjugated anionic system. This was as expected, given the electron distribution in the HOMO. This species may be considered as a benzo-annulated 2-azaheptatrienyl anion.

On warming of the sample to temperatures above −10 °C, new signals appeared. The new signals became more intense at 25 °C, and the initially observed signals disappeared. The two new sets of signals may be unambiguously

Table 2. Selected ^{1}H NMR chemical shifts [ppm] for starting material **(*Z*)-4b**, the corresponding lithium compound **Li-4b** at −20 °C, the resulting cyclic lithium compound **Li-6b** at 25 °C, and for the product **(3*R**,4*S**,5*S**)-6b** (after hydrolysis) (600 MHz); compounds **4** are numbered as 2-azaheptatrienyl anions; compounds **6** as 4,5-dihydro-3*H*-benzo[*c*]azepines

	H^1	H^3	H^6	H^7
(*Z*)-4b	4.79	8.58	6.65	5.92
Li-4b	6.62	7.58	6.28	5.38
	H^3	H^1	H^5	H^4
Li-6b	3.86	7.35	5.13	1.90
(3*R,4*S**,5*S**)-6b**	4.44	8.76	2.42/2.80	2.80

attributed to the bicyclic anion **Li-6b**, of which the more intense set was assigned to the (3*R**,4*S**) diastereomer. The most significant change in chemical shift was observed for the protons H^1 and H^7 of the open-chain anion, since the respective carbon atoms change their hybridization from sp^2 to sp^3, due to the formation of the new single bond. Interestingly, the protons of the benzo ring of the deprotonated starting material **(*E*,*Z*)-4b**, as well as of the bicyclic anion show alternately high and low relative shifts, indicating substantial involvement of these centers in the conjugation of the anion.

Quantum Chemical Calculations

In order to obtain an estimate of the thermodynamics and kinetics of the ring-closure reaction to form the seven-membered ring, quantum chemical model calculations on the RHF, MP2, SCS-MP2[21] and G3MP2[22] level were performed. Previous studies have shown that DFT calculations of the B3LYP/6-31G* level underestimate both barriers and products.[23] The program package GAUSSIAN98[24] was used throughout for the calculations. All stationary points were characterized by frequency calculations. All energies are given in kcal/mol, including zero point corrections (ZPE, unscaled for RHF, MP2 and SCS-MP2).

At first, we did a conformational search of the anionic imine derivative, using the 1-(2-ethenylphenyl)-2-azaallyl anion (**9**) as a simplified model for the experimentally studied lithium compounds. With the exception of **9e**, which is kept planar by an intramolecular hydrogen bond, all structures are more or less twisted with respect to the vinyl groups (**9a**,**b**,**c**) or to the vinyl- and 2-azaallyl moieties (**9d**,**f**,**g**). Structure **9a**, with the W-shape of the 2-azaallyl moiety, was found to be lowest in energy. It corresponds exactly to the structure of the imine precursor **4g**, as determined by X-ray crystallography (see Figure 1); **9b** and **9c** are only slightly more energy-rich. The formation of the cyclic structure **10** from the open-chain structures is significantly exothermic, indicating a gain of energy during the ring-closure reaction of 8−10 kcal/mol with respect to the best open-chain structure **9a**. The methods employed (RHF, MP2, SCS-MP2, G3MP2) produce quite similar data sets. Since MP2 values are already quite good, the performance of SCS-MP2 is not as superior as was observed earlier.[23]

Secondly, we looked for some relevant transition states, in order to obtain an estimate for the kinetics of the ring-closure reaction. Here, the methods disagree markedly over the existence of a U form and a related barrier for ring closure to form **10**. RHF finds a minium for such a U form ($E_{rel} \approx 14$ kcal/mol), and predicts a substantial barrier (ca. 23 kcal/mol). MP2 optimization (as integrated in the G3MP2 model chemistry) does not localize a U-shaped

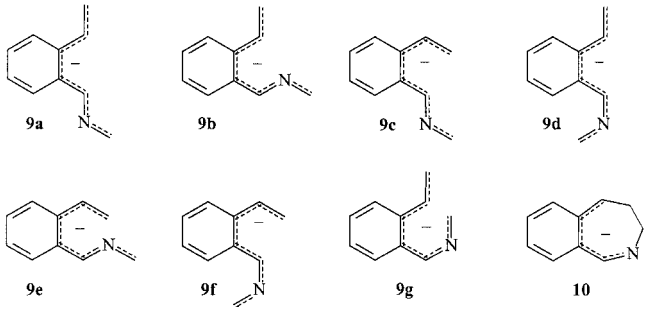


Figure 4. Conformations and configurations of the anions **9a**−**g** and **10**

Table 3. Relative energies of various structures of **9** and **10** and of some relevant transition states at different levels of theory [kcal/mol]

	RHF//6-31G*//RHF/6-31G*+ZPE	MP2-Full/6-31G*//MP2/6-31G*+ZPE	SCS-MP2-Full/6-31G*//MP2/6-31G*+ZPE	MP2/GTMP2Large//MP2/6-31G*+ZPE	SCS-MP2/GTMP2Large//MP2/6-31G*+ZPE	G3MP2
9a	0.00	0.00	0.00	0.00	0.00	0.00
9b	2.36	1.73	1.86	1.98	2.11	1.98
9c	2.70	1.88	2.07	1.44	1.69	1.47
9d	8.07	6.19	6.77	5.08	5.72	5.51
9e	8.91	6.82	7.24	6.59	7.13	6.57
9f	11.38	8.37	9.18	7.04	7.97	7.53
9g	12.95	9.69	10.40	7.93	8.86	8.50
TS-9h	20.07	20.48	20.29	18.97	18.70	18.86
TS-9i	20.41	22.34	20.41	21.16	19.22	18.76
TS-9j	18.86	14.60	15.16	12.12	12.97	12.86
10	−12.49	−14.47	−13.92	−11.89	−11.55	−11.07

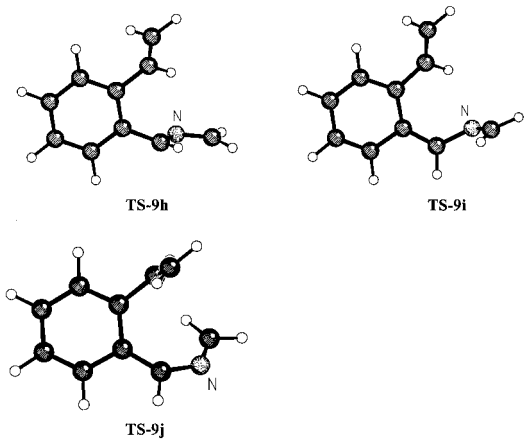


Figure 5. Calculated structures of three relevant transition states for internal rotation and ring closure [**9a** → **TS-9h** → **9b** (top left), **9b** → **TS-9i** → **9g** (top right) and **9g** → **TS-9j** → **10** (bottom) (MP2/6-31G*//MP2(6-31G*)]

structure at all, the small barrier towards cyclization **TS-9j** (12−13 kcal/mol) is connected to the internal rotation of **9g**, which is directly transformed into the cyclic form **10**. Similarly, other internal rotations also proceed without higher barriers (e.g. **TS-9h** for the conversion of **9a** into **9b**, and **TS-9i** for the conversion of **9b** into **9g**, both ca. 19 kcal/mol at G3MP2),[25] in agreement with the mild reaction conditions used experimentally. All these data fit well with a one-step pericyclic ring-closure reaction without involvement of intermediates.

Some additional calculations (on lower levels of theory) for the ring-closure reaction of the experimentally studied systems **(*E*)-4b** and **(*Z*)-4b** as anions, as well as neutral systems including lithium cations as counterions, came to similar conclusions as the model calculations described above.

Conclusion

In this report, we describe a novel, straightforward method for the preparation of various differently substituted 4,5-dihydro-3*H*-benzo[*c*]azepines **6a**−**k** by deprotonation of the corresponding [2-(alkenyl)benzylidene]amines **4b**−**d** with amide bases, and addition of electrophiles. The reaction proceeds smoothly on warming the lithiated imine **4** from −78 °C to room temperature. The imines **4** were prepared from 2-bromobenzaldehyde (**1**) by Wittig olefination, formylation using DMF, and subsequent condensation with benzylamine. The ring-closure reaction is interpreted in terms of an anionic 1,7-electrocyclization reaction involving benzo-annulated 2-azaheptatrienyllithium compounds. This reaction and the subsequent addition of the electrophile proceed with excellent diastereoselectivity, determined by the (*E*) or (*Z*) configuration of the imines **4a**−**d**. The corresponding allylimines **4e**,**f** do not give nine-membered heterocycles **7**, but rather the corresponding 3-vinyl-4,5-dihydro-3*H*-benzo[*c*]azepines **6l**,**m**. Structures of several compounds **6** in the solid state, as determined by X-ray crystallography, show variable ring conformations depending on the substitution pattern and relative configuration. A 14-membered ring dimer **8** was isolated in low yield, and characterized by X-ray crystallography. High-level quantum chemical calculations on model anions **9** and **10**, which serve as models of of possible intermediates and transition states, are in good agreement with the pericyclic mechanism suggested for the ring-closure reaction.

Experimental Section

Materials and Methods: IR: Nicolet FT-IR 5DXC, ^{1}H NMR: Bruker WM 300 (300.13 MHz), AMX 400 (400.13 MHz) and Varian Unity plus (599.86 MHz), internal reference tetramethylsilane. ^{13}C NMR: Bruker WM (75.47 MHz), Varian Unity Plus (150.85 MHz), internal reference tetramethylsilane or solvent. GC: Hewlett-Packard 6890 with HP5 quartz capillary (30 m). GC/MS: Varian MAT CH7A with GC Varian 3400 plus data system SS 200; Varian MAT 8230 with GC Varian 3400 plus data system SS300. CHN: Perkin-Elmer Dia CHN 240. Column chromatography: Silica gel 60 (Merck), 0.063−0.200 mm. Melting points (uncorrected): Büchi B-540. All solvents were rigorously dried by standard methods. When necessary, the experiments were carried out with complete exclusion of moisture (argon, septum-syringe technique) in glassware that had been thoroughly dried by repeated heating under argon and subsequent evacuation. The 2-(alkenyl)bromobenzenes **2a**,[13] **2b**, **2d**,[14] **2c**[26] were prepared by Wittig olefination of 2-bromobenzaldehyde (**1**) in accordance and analogy to literature procedures. Pure (*E*) isomer **(*E*)-2b** was obtained upon isomerization of **(*E*,*Z*)-2b** in the presence of iodine.[14] The 2-alkenylbenzaldehydes **3a**,[13] **3b**, **3d**,[14] **3c**[27] were prepared by formylation of the compounds **2a**−**d** using *n*-butyllithium and dimethylformamide according to a literature procedure.[13] For the preparation of **(*E*)-3b** pure **(*E*)-2b** was used.

General Procedure for the Synthesis of 4a−**d:** 1 equiv. of the 2-(alkenyl)benzaldehyde **3** was added to 1 equiv. of benzylamine in the presence of molecular sieves (4 Å) in 15 mL of dry dichloromethane in analogy to a published procedure.[15] After 16 h of stirring at room temperature, the molecular sieves were removed by filtration and carefully washed with 25 mL of dichloromethane. The solvent was removed under reduced pressure and the product, if necessary, was purified by kugelrohr distillation or crystallisation. Benzyl(2-vinylbenzylidene)amine (**4a**) was prepared form **3a** as reported in ref.[15]

(*E*,*Z*)-Benzyl(2-propenylbenzylidene)amine [(*E*,*Z*)-4b]: The imine was prepared from 1.17 g (8.0 mmol) of (*E*/*Z*)-2-(1-propenyl)benzaldehyde (**3b**) and 0.85 g (8.0 mmol) of benzylamine in dichloromethane. After removal of the molecular sieves, the solvent was evaporated under reduced pressure to give **4b** (1.83 g, 7.7 mmol, 96%) as a colorless liquid. (*Z*)/(*E*) ratio = 1:0.55. IR (film): $\tilde{\nu}$ = 3091 cm^{-1} (m, $CH_{arom.,olef.}$), 3070 (m, $CH_{arom.,olef.}$), 3021 (s, $CH_{arom.,olef.}$), 2940 (m, $CH_{aliph.}$), 2905 (m, $CH_{aliph.}$), 2878 (m, $CH_{aliph.}$), 2864 (m, $CH_{aliph.}$), 1632 (vs, C=N), 1590 (m), 1487 (m), 1473 (w), 1446 (s), 1370 (m), 1349 (w), 1281 (m), 1026 (m), 964 (m), 757 (s), 696 (s). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.65 (dd, ^3J = 6.92, ^4J = 1.91 Hz, 3 H, CH_3, *Z*), 1.91 (dd, ^3J = 6.67, ^4J = 1.90 Hz, 3 H, CH_3, *E*), 4.79 (d, ^4J = 1.43 Hz, 2 H, N−CH_2, *Z*), 4.83 (d, ^4J = 1.43 Hz, 2 H, N−CH_2, *E*), 5.92 (dq, ^3J = 6.92, ^3J = 11.21 Hz, 1 H, CH=C*H*−CH_3, *Z*), 6.06 (dq, ^3J = 6.68, ^3J = 15.49 Hz 1 H, CH=C*H*−CH_3, *E*), 6.65 (m, ^3J = 11.21 Hz, 1 H, C*H*=CH−CH_3, *Z*), 6.88 (m, ^3J = 15.50 Hz, 1 H, C*H*=CH−CH_3,

E), 7.16−7.40 (m, 8 H, $CH_{arom.}$, *E*/*Z*), 7.93 (m, 1 H, $CH_{arom.}$, *E*), 8.07 (m, 1 H, $CH_{arom.}$, *Z*), 8.58 (d, ^4J = 1.43 Hz, 1 H, N=CH, *Z*), 8.72 (t, ^4J = 1.43 Hz, 1 H, N=CH, *E*) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.48 (CH_3, *Z*), 19.25 (CH_3, *E*), 65.77 (N−CH_2, *Z*), 65.83 (N−CH_2, *E*), 122.77 (CH=*C*H−CH_3, *Z*), 127.26, 127.49, 127.83, 128.13, 128.34, 128.87, 129.58, 130.08, 130.42, 130.73 ($C_{arom.}$, *C*H=CHCH$_3$, *E*/*Z*), 133.20, 134.23, 138.53, 139.00, 140.01 (C_{ipso}, *E*/*Z*), 161.02 (N=CH, *Z*), 161.30 (N=CH, *E*) ppm. MS (70 eV): *m*/*z* (%) = 235 (2) [M^+], 220 (80) [M^+ − CH_3], 144 (3) [M^+ − $PhCH_2$], 129 (6), 115 (8), 91 (100) [$PhCH_2^+$], 65 (10). $C_{17}H_{17}N$ (235.3): calcd. C 86.77, H 7.28, N 5.95; found C 86.34, H 7.03, N 5.63.

(*E*)-Benzyl(2-propenylbenzylidene)amine [(*E*)-4b]: 0.73 g (5.0 mmol) of **(*E*)-3b**[14] and 0.53 g (5.0 mmol) of benzylamine were mixed together in dry dichloromethane (20 ml) and stirred in the presence of molecular sieves (4 Å) at room temperature for 16 h. The molecular sieves were removed by filtration and washed with dichloromethane (20 ml). The solvent was removed in vacuo to afford **(*E*)-4b** (1.10 g, 4.7 mmol, 95%) as brownish oil. IR (film): $\tilde{\nu}$ = 3014 cm^{-1}, 3000 (m, $CH_{arom.,olef.}$), 2867, 2850 (m, $CH_{aliph.}$), 1616 (vs, C=N), 1579 (m), 1475(m), 1428 (s), 1359 (s), 1326 (s), 1270 (s), 1014 (s), 950 (s), 742 (s), 725 (s), 688 (s). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.87 (dd, ^3J = 6.68, ^4J = 1.67 Hz, 3 H, CH_3), 4.80 (d, ^4J = 1.19 Hz, 2 H, N−CH_2), 6.02 (dq, ^3J = 6.68, ^3J = 15.73 Hz, 1 H, CH=CH−CH_3), 6.84 (m, ^3J = 15.74 Hz, 1 H, CH=CH−CH_3), 7.21−7.38 (m, 8 H, $CH_{arom.}$), 7.90 (m, 1 H, $CH_{arom.}$), 8.70 (s, 1 H, N=CH) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 18.71 (CH_3), 65.30 (N−CH_2), 126.78, 126.83 (CH=$CHCH_3$), 127.06, 127.63, 127.78, 127.81, 128.35, 129.80, 130.20, 132.68, 138.46, 139.47, 160.46 (N=CH) ppm. MS (70 eV): *m*/*z* (%) = 235, 220 (67), 144 (4), 129 (5), 115 (10), 91 (100), 77 (3), 65 (13) ppm. $C_{17}H_{17}N$ (235.32): calcd. C 86.77, H 7.28, N 5.95; found C 86.33, H 7.62, N 6.02.

(*E*,*Z*)-Benzyl(2-pent-1-enylbenzylidene)amine [(*E*,*Z*)-4c]: The imine was prepared from 1.74 g (10.0 mmol) of **(*E*,*Z*)-3c** and 1.07g (10.0 mmol) of benzylamine in dichloromethane. After removal of the molecular sieves, the solvent was evaporated under reduced pressure to give **3c** (2.12 g, 8.0 mmol, 80%) as a colorless liquid. (*Z*)/(*E*) ratio = 1:0.5. IR (film): $\tilde{\nu}$ = 3085 cm^{-1} (w, $CH_{arom.,olef.}$), 3062 (m, $CH_{arom.,olef.}$), 3026 (m, $CH_{arom.,olef.}$), 2958 (s, $CH_{aliph.}$), 2929 (m, $CH_{aliph.}$), 2871 (m, $CH_{aliph.}$), 1637 (vs, C=N), 1596 (m), 1494 (m), 1452 (s), 1377 (m), 1342 (w), 1286 (m), 1226 (w), 1028 (m), 964 (m), 798 (w), 754 (s), 696 (s). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.85 (t, ^3J = 8.83 Hz, 3 H, CH_3, *Z*), 0.97 (t, ^3J = 7.40 Hz, 3 H, CH_3, *E*), 1.38 (m, 2 H, CH_2, *Z*), 1.52 (m, 2 H, CH_2, *E*), 2.00 (m, ^3J = 7.39 Hz, 2 H, CH_2, *Z*), 2.22 (m, ^3J = 6.91 Hz, 2 H, CH_2, *E*), 4.80 (s, 2 H, N−CH_2, *Z*), 4.83 (s, 2 H, N−CH_2, *E*), 5.83 (dt, ^3J = 7.39, ^3J = 11.44 Hz, 1 H, CH=C*H*−CH_3, *Z*), 6.05 (dt, ^3J = 6.91, ^3J = 15.50 Hz, 1 H, CH=C*H*−CH_3, *E*), 6.63 (d, ^3J = 11.45 Hz, C*H*=CH−CH_3, 1 H, *Z*), 6.86 (d, ^3J = 15.49 Hz, C*H*=CH−CH_3, 1 H, *E*), 7.10−7.40 (m, 8 H, $CH_{arom.}$, *E*/*Z*), 7.92 (d, 1 H, $CH_{arom.}$, *E*), 8.06 (d, 1 H, $CH_{arom.}$, *Z*), 8.61 (s, 1 H, N=CH, *Z*), 8.72 (s, 1 H, N=CH, *E*) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.48 (CH_3, *Z*), 19.25 (CH_3, *E*), 65.77 (N−CH_2, *Z*), 65.83 (N−CH_2, *E*), 122.77 (CH=*C*H−CH_3), 127.26, 127.49, 127.83, 128.13, 128.34, 128.87, 129.58, 130.08, 130.42, 130.73 ($C_{arom.}$), 133.20, 134.23, 138.53, 139.00, 140.01 (C_{ipso}), 161.02 (N=CH, *Z*), 161.30 (N=CH, *E*) ppm. GC-MS (70 eV): *m*/*z* (%) = 263 (2) [M^+], 248 (5) [M^+ − CH_3], 220 (35) [M^+ − $C_2H_5^+$], 172 (30) [M^+ − $PhCH_2$], 129 [M^+ − $PhCH_2$ − C_2H_5], 115 (8), 91 (100) [$PhCH_2^+$], 65 (12). $C_{19}H_{21}N$ (263.3). C 86.65, H 8.04, N 5.32; found C 86.33, H 8.20, N 5.00.

(*E*)-Benzyl(2-styrylbenzylidene)amine [(*E*)-4d]: The imine was prepared from 1.04 g (5.0 mmol) of **3d** and 0.53 g (5.0 mmol) of benzylamine in dichloromethane. After removal of the molecular sieves, the solvent was evaporated under reduced pressure to give **(*E*)-4d** (1.34 g, 4.5 mmol, 90%) as a yellow solid. M.p. 115 °C. IR (film): $\tilde{\nu}$ = 3091 cm^{-1} (m, $CH_{arom.,olef.}$), 3070 (m, $CH_{arom.,olef.}$), 3021 (s, $CH_{arom.,olef.}$), 2940 (m), 2905 (m, $CH_{aliph.}$), 2878 (m, $CH_{aliph.}$), 2864 (m, $CH_{aliph.}$), 1632 (vs, C=N), 1590 (m), 1487 (m), 1473 (w), 1446 (s), 1370 (m), 1349 (w), 1281 (m), 1026 (m), 964 (m), 757 (s), 696 (s). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 4.77 (s, 2 H, N−CH_2), 6.85 (d, ^3J = 16.22 Hz, 1 H, PhC*H*), 7.10−7.40 (m, 12 H, $CH_{arom.}$, PhCH) 7.50 (m, 1H , $CH_{arom.}$), 7.65 (m, 1 H, $CH_{arom.}$), 7.80 (m, 1 H, $CH_{arom.}$), 8.68 (s, 1 H, N=CH) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 65.55 (N−CH_2), 125.97, 126.70, 126.80, 127.60, 127.83, 128.00, 128.48, 128.64, 128.73, 129.09, 130.28, 132.24, ($C_{arom.}$), 133.48, 137.32, 137.82, 139.44, (C_{ipso}), 160.64 (N=CH) ppm. MS (70 eV): *m*/*z* (%) = 297 (10) [M^+], 220 (75) [M^+ − Ph], 208 (32), 178 (34) 165 (10), 128 (6), 91 (100) [$PhCH_2^+$], 65 (10). $C_{22}H_{19}N$ (297.3): calcd. C 88.85, H 6.44, N 4.71; found C 88.69, H 6.07, N 4.66.

(*E*,*Z*)-Allyl(2-propenylbenzylidene)amine [(*E*,*Z*)-4e]: The imine was prepared from 1.17 g (8.0 mmol) of **(*E*,*Z*)-3b** and 0.46 g (8.0 mmol) of allylamine in dichloromethane. After removal of the molecular sieves, the solvent was evaporated under reduced pressure. The crude product was purified by kugelrohr distillation (80 °C/3 × 10^{-3} mbar) to give **(*E*,*Z*)-4e** (1.42 g, 7.7 mmol, 96%) as a colorless liquid. (*Z*)/(*E*) ratio = 1:0.5. IR (film): $\tilde{\nu}$ = 3070 cm^{-1} (m, $CH_{arom.,olef.}$), 3050 (m, $CH_{arom.,olef.}$), 2974 (m, $CH_{aliph.}$), 2919 (m, $CH_{aliph.}$), 2878 (s, $CH_{aliph.}$), 2816 (m, $CH_{aliph.}$), 1652 (vs, C=N), 1597 (m), 1473 (m), 1446 (s), 1356 (s), 1315 (w), 1288 (m), 1033 (m), 1012 (m), 971 (m), 923 (s), 813 (w), 764 (s), 716 (m). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.63 (dd, ^3J = 6.92, ^4J = 1.91 Hz, 3 H, CH_3, *Z*), 1.91 (dd, ^3J = 6.67, ^4J = 1.90 Hz, 3 H, CH_3, *E*), 4.25 (m, ^4J = 1.67 Hz, 2 H, N−CH_2, *E*/*Z*), 5.20 (m, ^2J = 1.91, ^3J = 10.26, ^3J = 17.24 Hz, 2 H, CH=C*H*$_2$, *E*/*Z*), 5.92 (dq, ^3J = 7.15, ^3J = 11.44 Hz, 2 H, CH=C*H*−CH_3, *Z*, C*H*=CH_2), 6.07 (m, 2 H, CH=C*H*−CH_3, *E*, C*H*=CH_2), 6.65 (d, ^3J = 11.44 Hz, 1 H, C*H*=CH−CH_3, *Z*), 6.88 (m, ^3J = 15.50 Hz, 1 H, C*H*=CH−CH_3, *E*), 7.10−7.41 (m, 3 H, $CH_{arom.}$, *E*/*Z*), 7.90 (m, 1 H, $CH_{arom.}$, *E*), 8.02 (m, 1 H, $CH_{arom.}$, *Z*), 8.48 (s, 1 H, N=CH, *Z*), 8.63 (s, 1 H, N=CH, *E*) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.95 (CH_3, *Z*), 14.25 (CH_3, *E*), 63.80 (N−CH_2, *Z*), 63.87 (N−CH_2, *E*), 115.84 (CH=*C*H$_2$) 126.65, 126.80, 126.90, 126.96, 127.06, 127.40, 127.48, 127.77, 128.92, 129.13, 129.64, 129.94, 129.26, ($C_{arom.}$), 133.80, (C_{ipso}), 136.13 (*C*H=CH_2), 138.00, 138.48, (C_{ipso}), 160.53 (N=CH, *Z*), 160.88 (N=CH, *E*) ppm. MS (EI): *m*/*z* (%) = 185 (68) [M^+], 171 (12), 158 (20), 157 (18), 144 (43), 131 (100). $C_{13}H_{15}N$ (185.3): calcd. C 84.28, H 8.16, N 7.56; found C 83.77, H 8.45, N 7.24.

(*E*,*Z*)-Allyl(2-pent-1-enylbenzylidene)amine [(*E*,*Z*)-4f]: The imine was prepared from 1.74 g (10.0 mmol) of **(*E*,*Z*)-3c** and 0.57g (10.0 mmol) of allylamine in dichloromethane. After removal of the molecular sieves, the solvent was evaporated under reduced pressure to give **4f** (1.93 g, 9.0 mmol, 90%) as a colorless liquid. (*Z*)/(*E*) ratio = 1:0.4. IR (film): $\tilde{\nu}$ = 3062 cm^{-1} (m, $CH_{arom.,olef.}$), 3014 (s, $CH_{arom.,olef.}$), 2933 (s, $CH_{aliph.}$), 2912 (m, $CH_{aliph.}$), 2875 (m, $CH_{aliph.}$), 2817 (m, $CH_{aliph.}$), 1641 (vs, C=N), 1596 (m), 1477 (m), 1444 (s), 1375 (m), 1315 (m), 1288 (m), 1107 (w), 1022 (m), 991 (m), 964 (m), 918 (s), 810 (w), 761 (s), 713 (w). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.85 (t, ^3J = 7.39 Hz, 3 H, CH_3, *Z*), 0.97 (t, ^3J = 7.40 Hz, 3 H, CH_3, *E*), 1.38 (m, ^3J = 7.39 Hz, 2 H, CH_2, *Z*), 1.52 (m, ^3J = 7.40 Hz, 2 H, CH_2, *E*), 2.02 (m, ^3J = 7.39, ^4J = 1.67 Hz, 2 H, CH_2, *Z*), 2.22 (m, ^3J = 7.16, ^4J = 1.67 Hz, 2 H, CH_2,

E), 4.25 (m, 2 H, N−CH_2, *E*/*Z*), 5.15 (m, ^2J = 1.67, ^3J = 10.25 Hz, 1 H, CH=CH_{cis}, *E*/*Z*), 5.25 (m, ^2J = 1.67, ^3J = 17.16 Hz, 1 H, CH=CH_{trans}, *E*/*Z*), 5.83 (dt, ^3J = 7.39, ^3J = 11.44 Hz, 1 H, CH=C*H*−CH_2, *Z*), 6.05 (m, 1 H, CH=C*H*−CH_2, *E*, and 1 H, C*H*=CH_2, *E*/*Z*), 6.63 (m, ^3J = 11.45 Hz, 1 H, C*H*=CH−CH_3, *Z*), 6.86 (m, ^3J = 15.49 Hz, 1 H, C*H*=CH−CH_3, *E*), 7.10−7.43 (m, 3 H, $CH_{arom.}$, *E*/*Z*), 7.90 (m, 1 H, $CH_{arom.}$, *E*), 8.03 (m, 1 H, $CH_{arom.}$, *Z*), 8.50 (s, 1 H, N=CH, *Z*), 8.63 (s, 1 H, N=CH, *E*) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.12 (CH_3, *Z*), 14.35 (CH_3, *E*), 22.86 (CH_2), 23.34 (CH_2), 30.91 (CH_2, *Z*), 35.79 (CH_2, *E*), 64.17 (N−CH_2, *Z*), 64.26 (N−CH_2, *E*), 116.25 (CH=*C*H_2), 126.82, 126.92, 127.02, 127.45, 127.88, 128.39, 130.02, 130.35, 130.63 ($C_{arom.}$, *E*/*Z*), 133.29 (C_{ipso}), 134.19 (C_{ipso}), 135.42, 135.76, 136.50 ($C_{arom.}$, *E*/*Z*), 138.80, 138.97, (C_{ipso}), 160.98 (N=CH, *Z*), 161.27 (N=CH, *E*) ppm. MS (70 eV): *m*/*z* (%) = 213 (10) [M^+], 198 (7) [$M^+ - CH_3$], 183 (23) [$M^+ - C_2H_5^+$], 170 (100) [$M^+ - C_3H_7^+$], 130 (35), 113 (28), 91 (8), 77 (10). $C_{15}H_{19}N$ (213.3): calcd. C 84.46, H 8.98, N 6.57; found C 84.03, H 9.12, N 6.47.

(*E*)-Allyl(2-styrylbenzylidene)amine [(*E*)-4g]: The imine was prepared from 1.04 g (5.0 mmol) of **(*E*)-3d** and 0.28 g (5.0 mmol) of allylamine in dichloromethane. After removal of the molecular sieves, the solvent was evaporated under reduced pressure to give **(*E*)-4g** (1.13 g, 4.5 mmol, 88%) as a yellow solid. M.p. 88 °C. IR (KBr): $\tilde{\nu}$ = 3091 cm^{-1} (m, $CH_{arom.,olef.}$), 3070 (m, $CH_{arom.,olef.}$), 3021 (s, $CH_{arom.,olef.}$), 2940 (m, $CH_{aliph.}$), 2905 (m, $CH_{aliph.}$), 2878 (m, $CH_{aliph.}$), 2864 (m, $CH_{aliph.}$), 1632 (vs, C=N), 1590 (m), 1487 (m), 1473 (w), 1446 (s), 1370 (m), 1349 (w), 1281 (m), 1026 (m), 964 (m), 757 (s), 696 (s). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 4.30 (m, ^4J = 1.43 Hz, 2 H, N−CH_2), 5.19 (m, ^2J = 1.91, ^3J = 10.25 Hz, 1 H, CH=CH_{cis}), 5.21 (m, ^2J = 1.91, ^3J = 17.17 Hz, 1 H, CH=CH_{trans}), 6.10 (m, ^3J = 10.25, ^3J = 17.17 Hz, 1 H, C*H*=CH_2), 6.95 (d, ^3J = 16.21 Hz, 1 H, PhCH), 7.25−7.90 (m, 10 H, $CH_{arom.}$, PhCH), 8.68 (s, 1 H, N=CH) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 63.95 (N−CH_2), 115.91 (CH=*C*H_2), 125.72, 126.69, 126.80, 127.57, 127.88, 128.31, 128.68, 130.30, 132.48, ($C_{arom.}$, PhCH), 133.50 (C_{ipso}), 136.00 ($C_{arom.}$), 137.31, 137.88 (C_{ipso}), 160.51 (CH=N) ppm. MS (70 eV): *m*/*z* (%) = 235 (2) [M^+], 220 (80) [$M^+ - CH_3$], 144 (3) [$M^+ - PhCH_2$], 129 (6), 115 (8), 91 (100) [$PhCH_2^+$], 65 (10). $C_{18}H_{17}N$ (247.3): calcd. C 87.41, H 6.93, N 5.66; found C 86.80, H 6.93, N 5.22.

X-ray Crystal Structure Analysis of (*E*)-4g:[16] Formula $C_{18}H_{17}N$, *M* = 247.33, colorless crystal, 0.25 × 0.10 × 0.05 mm, *a* = 5.586(1), *b* = 8.654(1), *c* = 14.630(1) Å, β = 99.47(1)°, *V* = 697.6(2) $Å^3$, $\rho_{calcd.}$ = 1.177 g·cm^{-3}, μ = 0.68 cm^{-1}, empirical absorption correction (0.983 ≤ *T* ≤ 0.997), *Z* = 2, monoclinic, space group $P2_1$ (No. 4), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 7140 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.65 $Å^{-1}$, 3144 independent (R_{int} = 0.052) and 1901 observed reflections [$I \geq 2\sigma(I)$], 172 refined parameters, *R* = 0.063, wR^2 = 0.124, max. residual electron density 0.20 (−0.26) e·$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

General Procedure for the Synthesis of 4,5-Dihydro-3*H*-benzo[*c*]-azepines 6: For the deprotonation of the benzaldimines **4** the septum-syringe technique was applied. Lithium diisopropylamide (LDA) was freshly prepared under argon from 1.2 equiv. (1−2 mmol) of diisopropylamine and 1.1 equiv. of *n*-butyllithium (1.6 M in *n*-hexane) at −40 °C in dry THF; 1 equiv. of the benzaldimines **4** was dissolved in 10 mL of THF and added dropwise over a period of 30 min to the LDA solution at −78 °C. After 1 h of stirring at −78 °C, the reaction mixture was warmed up to 0 °C and was kept at this temperature for another 30 min. The reaction mixture was then treated with a surplus of the respective electrophile. After aqueous work up and extraction with diethyl ether, the combined organic layers were dried with magnesium sulfate. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography [silica gel; petroleum ether (PE)/ethyl acetate (EA), 5:1 to 10:1].

(3*R,4*S**)-4-Methyl-3-phenyl-4,5-dihydro-3*H*-benzo[*c*]azepine [(3*R**,4*S**)-6a]:** The imine **(*E*,*Z*)-4b** (352 mg, 1.50 mmol) was deprotonated with 1.07 equiv. of LDA (1.60 mmol) in 30 mL of THF. After warming to 0 °C, the reaction mixture was poured into a sodium bicarbonate solution (10%; 200 ml). After extraction with diethyl ether and evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1). **(3*R**,4*S**)-6a** (147 mg, 0.62 mmol, 42%) was isolated as a colorless powder. R_f = 0.15 (silica gel; PE/EA, 10:1). M.p. 85 °C. IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (m, $CH_{arom.}$), 3024 (m, $CH_{arom.}$), 2956 (s, $CH_{aliph.}$), 2927 (s, $CH_{aliph.}$), 2869 (m, $CH_{aliph.}$), 2850 (m), 1693 (w), 1620 (s, C=N), 1600 (m), 1571 (m), 1492 (m), 1450 (s), 1375 (m), 1311 (w), 1218 (m), 1191 (m), 1112 (w), 1074 (w), 1029 (w), 964 (m), 943 (m), 923 (m), 896 (m), 848 (w), 752 (s), 725 (s), 702 (s), 657 (w), 648 (m), 601 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.86 (d, ^3J = 6.52 H, 3 Hz, $PhCH_2CHCH_3$), 2.42 (dd, ^3J = 2.82, ^2J = 12.50 Hz, 1 H, $PhCH_2$), 2.80 (m, ^3J = 6.63 Hz, 2 H, $PhCH_2$, CH_2CH-CH_3), 4.44 (d, ^3J = 3.16 Hz, 1 H, PhCH−N), 7.20−7.50 (m, 9 H, $CH_{arom.}$), 8.76 (s, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 18.02 (CH_3), 41.45 (CH_2), 49.12 (*C*H−CH_3), 68.53 (PhCH), 120.50−130.78 ($C_{arom.}$), 136.52, 140.24, 142.77 (C_{ipso}), 164.52 (CH=N) ppm. MS (70 eV): *m*/*z* (%) = 235 (90) [M^+], 206 (5) [$M^+ - C_2H_5$], 165 (5), 131 (100) [$C_9H_9N^+$], 115 (22) [$C_8H_8N^+$], 91 (28) [$C_7H_7^+$], 77 (8). $C_{17}H_{17}N$ (235.3): calcd. C 86.77, H 7.28, N 5.95; found C 86.34, H 7.03, N 5.63.

As a byproduct in very little yield crystals of 6,13-dimethyl-7,14-diphenyl-3,4;10,11-dibenzo-1,8-diazacyclotetradeca-1,3,8,10-tetraene (**8**) were isolated.

X-ray Crystal Structure Analysis of 8:[16] Formula $C_{34}H_{34}N_2$, *M* = 470.63, colorless crystal, 0.60 × 0.40 × 0.25 mm, *a* = 12.465(1), *b* = 9.641(1), *c* = 21.937(1) Å, *V* = 2636.3(4) $Å^3$, $\rho_{calcd.}$ = 1.186 g cm^{-3}, μ = 5.20 cm^{-1}, empirical absorption correction with ψ-scan data (0.746 ≤ *T* ≤ 0.881), *Z* = 4, orthorhombic, space group *Pbca* (No. 61), λ = 1.54178 Å, *T* = 223 K, ω/2θ scans, 2679 reflections collected (−*h*, −*k*, +*l*), [(sinθ)/λ] = 0.62 $Å^{-1}$, 2679 independent and 2224 observed reflections [$I \geq 2\sigma(I)$], 165 refined parameters, *R* = 0.039, wR^2 = 0.117, max. residual electron density 0.17 (−0.15) e·$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

4,5-Dimethyl-3-phenyl-4,5-dihydro-3*H*-benzo[*c*]azepines [(3*R,4*S**,5*S**)-6b) and [(3*R**,4*R**,5*R**)-6b]:** From **(*E*,*Z*)-4b** (252 mg, 1.1 mmol), LDA (1.18 mmol) and methyl iodide (340 mg, 2.4 mmol). The crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1). Two diastereomeric isomers **(3*R**,4*S**,5*S**)-6b** (120 mg, 48%) and **(3*R**,4*R**,5*R**)-6b** (35 mg, 0.14 mmol, 13%) were isolated as colorless oils. R_f = 0.23, 0.15 (silica gel; PE/EA, 10:1). Analytical data for **(3*R**,4*S**,5*S**)-6b**: IR (film): $\tilde{\nu}$ = 3062 cm^{-1} (m, $CH_{arom.}$), 3026 (m, $CH_{arom.}$), 2968 (s, $CH_{aliph.}$), 2929 (s, $CH_{aliph.}$), 2879 ($CH_{aliph.}$), 1770 (w), 1712 (m), 1654 (s, C=N), 1622 (s), 1571 (m), 1533 (w), 1492 (m), 1450 (s), 1380 (m), 1272 (m), 1215 (m), 1188 (m), 1126 (w), 1101 (w), 1060 (w), 1029 (m), 975 (w), 945 (m), 898 (m), 757 (s), 725 (s), 702 (s), 667 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.89 [d, ^3J = 6.68 Hz, 3 H, $PhCH(CH_3)CHCH_3$], 1.41 [d, ^3J = 6.68 Hz, 3 H, $PhCH(CH_3)CHCH_3$], 2.30 [m, ^3J = 2.15, ^3J = 6.68 Hz, 1 H,

PhCH(CH_3)C*H*CH_3], 2.58 [m, ^3J = 6.67, ^3J = 2.14 Hz, 1 H, PhC*H*(CH_3)CHCH_3] 4.48 (m, ^3J = 2.14 Hz, 1 H, PhCH−N), 7.10−7.55 (m, 9 H, $CH_{arom.}$), 8.65 (d, ^3J = 2.15 Hz, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.48 [PhCH(CH_3)CH*C*H_3] 17.64 [PhCH(*C*H_3)CHCH_3], 41.82 [PhCH(CH_3)*C*H], 54.92 [Ph*C*H(CH_3)CH], 68.37 (PhCH−N), 126.56, 126.62, 127.30, 127.83, 128.47, 128.71, 130.36, ($C_{arom.}$), 135.06, 143.21, 144.11 (C_{ipso}), 162.88 (CH=N) ppm. MS (70 eV): *m*/*z* (%) = 249 (50) [M^+], 213 (18), 145 (50) [$C_{11}H_{13}^+$], 127 (100), 115 (10) [$C_8H_8N^+$], 91 (28) [$C_7H_7^+$], 77 (8), 57 (44). $C_{18}H_{19}N$ (249.3): calcd. C 86.70, H 7.68, N 5.62; found C 85.94, H 7.66, N 5.50. For analytical data of **(3*R**,4*R**,5*R**)-6b** see below.

(3*R,4*R**,5*R**)-4,5-Dimethyl-3-phenyl-4,5-dihydro-3*H*-benzo[*c*]-azepine [(3*R**,4*R**,5*R**)-6b]:** From **(*E*)-4b** (235 mg, 1.00 mmol), LDA (1.10 mmol), and methyl iodide (300 mg, 2.00 mmol). The crude product was purified by flash chromatography (pentane/ethyl acetate, 10:1) to give **(3*R**,4*R**,5*R**)-6b** (169 mg, 0.68 mmol, 68%) as colorless solid, m.p. 113 °C, R_f = 0.31 (pentane/EA, 10:1). IR (KBr): $\tilde{\nu}$ = 3050 (w), 3030 (m, $CH_{arom.,olef.}$), 2929 (w), 2906 (w), 2873 (m, $CH_{aliph.}$), 1596 (s, C=N), 1469 (m), 1428 (s), 1346 (s), 1184 (s), 1051 (s), 987 (m), 941 (s), 919 (s), 883 (s), 754 (s), 690 (s). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ= 0.81 [d, ^3J = 7.12 Hz, 3 H, PhCH(CH_3)CHC*H*$_3$], 1.31 [d, ^3J = 7.37 Hz, 3 H, PhCH(C*H*$_3$)CHCH$_3$], 2.50 [m, ^3J = 1.52, ^3J = 7.12, ^3J = 11.19 Hz, 1 H, PhCH(CH_3)C*H*CH_3], 2.74 [m, ^3J = 7.4, ^3J = 1.53 Hz, 1 H, PhC*H*(CH_3)CHCH$_3$], 3.80 (m, ^4J = 2.29, ^3J = 11.19 Hz, 1 H, PhC*H*−N=CH), 7.21−7.35 (m, 9 H, $CH_{arom.}$), 8.60 (d, ^4J = 2.29 Hz, 1 H) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 20.69 [PhCH(CH_3)CH*C*H_3], 24.84 [PhCH(*C*H_3)CHCH$_3$], 47.08 [PhCH(CH_3)*C*H], 54.58 [Ph*C*H(CH_3)CH], 71.71 (Ph*C*H−N), 126.54, 126.73, 128.17, 128.19, 128.71, 130.05, 130.08, 132.73 ($C_{arom.}$), 144.27 (C_{ipso}), 145.33 (C_{ipso}), 163.05 (CH=N) ppm. MS (70 eV): *m*/*z* (%) = 249 (53), 213 (27), 145 (49), 127 (100), 91 (29). $C_{18}H_{19}N$ (249.35): calcd. C 86.70, H 7.68, N 5.62; found C 85.76, H 7.73, N 5.92.

X-ray Crystal Structure Analysis of (3*R,4*R**,5*R**)-6b:**[16] Formula $C_{18}H_{19}N$, M = 249.34, colorless crystal, 0.40 × 0.25 × 0.20 mm, a = 10.623(1), b = 12.487(1), c = 11.036(1) Å, β = 107.85(1)°, V = 1393.4(2) Å^3, $\rho_{calcd.}$ = 1.189 g·cm^{-3}, μ = 0.68 cm^{-1}, no absorption correction (0.973 ≤ T ≤ 0.986), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 5550 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 3306 independent (R_{int} = 0.044) and 2236 observed reflections [$I \geq 2\ \sigma(I)$], 174 refined parameters, R = 0.057, wR^2 = 0.114, max. residual electron density 0.22 (−0.17) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

(3*R,4*R**,5*R**)-5-Ethyl-4-methyl-3-phenyl-4,5-dihydro-3*H*-benzo-[*c*]azepine [(3*R**,4*R**,5*R**)-6c]:** From **(*E*)-4b** (235 mg, 1.00 mmol), LDA (1.10 mmol), and ethyl bromide (220 mg, 2.00 mmol). The crude product was purified by flash chromatography (pentane/ethyl acetate, 10:1) to give **(3*R**,4*R**,5*R**)-6c** (173 mg, 0.66 mmol, 66%) as colorless solid, m.p. 100 °C, R_f = 0.24 (pentane/EA, 10:1). IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3050 (m, $CH_{arom.}$), 2881 (m), 2854 (m, $CH_{aliph.}$), 1608 (s, C=N), 1467 (s), 1436 (s), 1349(s), 1182(s), 1058 (w), 1018 (w), 933 (w), 873 (w), 746 (s), 692 (s). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.56 (t, ^3J = 14.79 Hz, 3 H, CH_2CH_3), 0.72 (d, ^3J = 7.15 Hz, 3 H, CH_3), 1.64 (m, 2 H, CH_2CH$_3$), 2.33 (m, 1 H, CH_3CH_2CH), 2.49 [m, 1 H, PhC*H*(CH_3)CHCH_2CH_3], 3.75 (m, ^4J = 1.9 Hz, 1 H, PhC*H*−N), 7.10−7.30 (m, 9 H, $CH_{arom.}$), 8.50 (d, ^4J = 1.9 Hz, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.25 (CH_3), 21.51 (CH_3), 31.74 (*C*H_2CH_3), 53.86 [PhCH(CH_3)*C*HCH_2CH_3], 55.56 [Ph*C*H(CH_3)CHCH_2CH_3], 71.99 (Ph*C*H−N), 127.05, 127.21, 128.67, 128.67, 128.95, 130.12, 131.67, 133.35, 144.15, 144.85, 163.55 (CH=N) ppm. MS (70 eV): *m*/*z* (%) = 263 (100), 234 (7), 220 (16), 193 (3), 159 (44), 117 (50), 91 (44), 77 (8), 57 (2). $C_{19}H_{21}N$ (263.38): calcd. C 86.65, H 8.04, N 5.32; found C 86.46, H 7.92, N 5.15.

X-ray Crystal Structure Analysis of (3*R,4*R**,5*R**)-6c:**[16] Formula $C_{19}H_{21}N$, M = 263.37, colorless crystal, 0.40 × 0.20 × 0.10 mm, a = 11.676(2), b = 11.250(1), c = 23.090(2) Å, β = 99.36(1)°, V = 2992.6(6) Å^3, $\rho_{calcd.}$ = 1.169 g·cm^{-3}, μ = 5.07 cm^{-1}, no absorption correction (0.823 ≤ T ≤ 0.951), Z = 8, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 5357 reflections collected (+h, +k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 5086 independent (R_{int} = 0.038) and 2208 observed reflections [$I \geq 2\ \sigma(I)$], 366 refined parameters, R = 0.077, wR^2 = 0.168, crystals are weakly diffracting, leading to limited quality of data set and analysis, asymmetric unit contains two nearly identical independent molecules, max. residual electron density 0.25 (−0.25) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

(3*R,4*S**,5*S**)-5-Allyl-4-methyl-3-phenyl-4,5-dihydro-3*H*-benzo-[*c*]azepine [(3*R**,4*S**,5*S**)-6d]:** From **(*E*,*Z*)-4b** (235 mg, 1.00 mmol), LDA (1.10 mmol) and allyl bromide (242 mg, 2.00 mmol). The crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1) **(3*R**,4*S**,5*S**)-6d** (155 mg, 0.56 mmol, 56%) was isolated as yellow solid, m.p. 88 °C. R_f = 0.20 (silica gel; PE/EA, 10:1). IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (s, $CH_{arom.,olef.}$), 3024 (m, $CH_{arom.}$), 2972 (s, $CH_{aliph.}$), 2927 (s, $CH_{aliph.}$), 2877 (s, $CH_{aliph.}$), 1645 (s, C=N), 1622 (s), 1571 (m), 1492 (m), 1450 (s), 1415 (w), 1379 (m), 1342 (m), 1313 (m), 1267 (m), 1211 (m), 1178 (m), 1124 (w), 1076 (w), 1053 (w), 995 (m), 970 (m), 950 (m), 914 (s), 850 (w), 810 (w), 757 (s), 730 (s), 702 (s), 665 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.75 (d, ^3J = 6.96 Hz, 3 H, CH_3), 2.42 [m, ^3J = 7.04 Hz, 1 H, PhC*H*($CH_2CH=CH_2$)CH], 2.58 (m, 2 H, CH_2−CH=CH_2), 2.75 [dt, ^3J = 6.41, ^3J = 7.86 Hz, 1 H, PhCH($CH_2CH=CH_2$)C*H*], 4.76 (d, ^3J = 6.41 Hz, 1 H, PhCH−N), 5.10 (m, 2 H, CH=CH_2), 5.82 (m, 1 H, C*H*=CH_2), 7.20−7.24 (m, 1 H, $CH_{arom.}$), 7.31−7.46 (m, 8 H, $CH_{arom.}$), 8.69 (s, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.02 (CH_3), 38.03 (*C*H_2−CH=CH_2), 46.97 (*C*H−CH_3), 48.70 [Ph*C*H($CH_2CH=CH_2$)], 65.31 (PhCH−N), 116.83 (CH=*C*H_2),126.22, 126.45, 127.37, 128.03, 128.70, 130.04, 131.15, ($C_{arom.}$), 133.84 (*C*H=CH_2), 142.43 (C_{ipso}), 143.45 (C_{ipso}), 162.00 (CH=N) ppm. MS (70 eV): *m*/*z* (%) = 275 (15) [M^+], 274 (35) [M^+ − H], 260 (40) [M^+ − CH_3], 232 (15), 218 (20) [M^+ − CH_3 − H − C_3H_5], 172(18), 143 (85), 129 (100) [M^+ − C_5H_9 − Ph], 115 (50) [$C_8H_8N^+$], 91 (30) [$C_7H_7^+$], 77 (9). $C_{20}H_{21}N$ (275.4): calcd. C 87.23, H 7.69, N 5.09; found C 86.58, H 7.01, N 4.85.

X-ray Crystal Structure Analysis of (3*R,4*S**,5*S**)-6d:**[16] Formula $C_{20}H_{21}N$, M = 275.38, colorless crystal, 0.30 × 0.15 × 0.15 mm, a = 6.705(1), b = 7.419(1), c = 16.359(1) Å, α = 79.39(1), β = 79.84(1), γ = 77.84(1)°, V = 773.9(2) Å^3, $\rho_{calcd.}$ = 1.182 g·cm^{-3}, μ = 5.13 cm^{-1}, no absorption correction (0.861 ≤ T ≤ 0.927), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223 K, ω and φ scans, 5434 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 2615 independent (R_{int} = 0.028) and 2115 observed reflections [$I \geq 2\ \sigma(I)$], 192 refined parameters, R = 0.039, wR^2 = 0.100, max. residual electron density 0.17 (−0.15) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

(3*R,4*R**,5*R**)-5-Allyl-4-methyl-3-phenyl-4,5-dihydro-3*H*-benzo-[*c*]azepine [(3*R**,4*R**,5*R**)-6d]:** From **(*E*)-4b** (235 mg, 1.00 mmol), LDA (1.10 mmol), and allyl bromide (240 mg, 2.00 mmol). The crude product was purified by flash chromatography (pentane/ethyl

acetate, 100:8) to yield **(3*R**,4*R**,5*R**)-6d** (198 mg, 0.72 mmol, 72%) as colorless viscous oil; R_f = 0.20 (pentane/EA, 10:1). IR (film): $\tilde{\nu}$ = 3080 (w), 3000 (m, $CH_{arom.}$), 2915 (w), 2892 (m, $CH_{aliph.}$), 1687 (s), 1625 (s, C=N), 1535 (w), 1471 (w), 1438 (w), 1346 (w), 1278 (w), 1070 (w), 1006 (w), 975 (s), 906 (w), 750 (s), 696 (s). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.71 (d, ^3J = 6.92 Hz, 3 H, CH_3), 2.30 [m, 1 H, PhCH($CH_2CH{=}CH_2$)C*H*], 2.50 (m, 2 H, CH_2−CH=CH_2), 2.65 [m, 1 H, PhC*H*($CH_2CH{=}CH_2$)CH], 3.72 (d, ^3J = 11.2 Hz, 1 H, PhCH−N), 4.79 (m, 2 H, CH=CH_2), 5.40 (m, 1 H, C*H*=CH_2), 7.10−7.26 (m, 9 H, $CH_{arom.}$), 8.52 (s, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 20.79 (CH_3), 42.27 (CH_2−CH=CH_2), 52.21 (*C*H−CH_3), 52.73 [Ph*C*H($CH_2CH{=}CH_2$], 71.60 (PhCH−N), 116.22 (CH=*C*H_2), 126.78, 127.37, 128, 128.23, 128.54, 129.88, 130.88, 133.09 ($C_{arom.}$), 136.66 (*C*H=CH_2), 143.19, 144.24, 163.26 (CH=N) ppm. MS (70 eV): *m*/*z* (%) = 275 (36), 260 (39), 232 (14), 218 (15), 193 (7), 146 (17), 129 (100), 115 (50), 91 (61), 77 (13), 55 (8). $C_{20}H_{21}N$ (275.39): calcd. C 87.23, H 7.69, N 5.09; found C 86.83, H 7.83, N 5.14.

(3*R,4*S**,5*S**)-5-Benzyl-4-methyl-3-phenyl-4,5-dihydro-3*H*-benzo[*c*]azepine [(3*R**,4*S**,5*S**)-6e]:** From **(*E*,*Z*)-4b** (235 mg, 1.00 mmol), LDA (1.10 mmol) and benzyl bromide (340 mg, 2.00 mmol). The crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1). **(3*R**,4*S**,5*S**)-6e** (155 mg, 0.56 mmol, 56%) was isolated as yellow oil, which contains small amounts of a diastereomeric compound of unkown configuration. R_f = 0.12 (silica gel; PE/EA, 10:1). IR (film): $\tilde{\nu}$ = 3105 cm^{-1} (sh, $CH_{arom.}$), 3085 (m, $CH_{arom.}$), 3032 (s, $CH_{arom.}$), 2973 (s, $CH_{aliph.}$), 2933 (s, $CH_{aliph.}$), 1663 (s, C=N), 1630 (s), 1492 (m), 1453 (m), 1380 (m), 1308 (w), 1262 (w), 1189 (m), 1025 (m), 952 (m), 906 (m), 762 (m), 709 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.59 (d, ^3J = 6.92 Hz, 3 H, CH_3), 2.33 [m, 1 H, PhCH($PhCH_2$)C*H*CH_3], 3.02 [m, 3 H, PhC*H*($PhCH_2$)CH], 4.89 (m, 1 H, PhCH−N), 7.10−7.40 (m, 14 H, $CH_{arom.}$), 8.62 (s, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.07 (CH_3), 41.25 [PhCH(Ph*C*H_2)CH], 44.71 [PhCH($PhCH_2$)*C*H−CH_3], 50.84 [Ph*C*H($PhCH_2$)CH], 65.20 (PhCH−N), 126.16, 126.54, 126.87, 127.35, 128.00, 128.11, 128.24, 128.55, 129.53, 129.96, 131.04, 132.31 ($C_{arom.}$, C_{ipso}), 161.40 (CH=N) ppm. MS (70 eV): *m*/*z* (%) = 325 (100) [M^+], 234 (22) [$M^+ - C_7H_7$], 205 (10), 193 (8), 165(5), 129 (25) [$M^+ - C_5H_9$,−Ph], 115 (13) [$C_8H_8N^+$], 91 (68) [$C_7H_7^+$]. $C_{24}H_{23}N$ (325.4): calcd. C 88.57, H 7.12, N 4.30; found C 87.56, H 7.42, N 4.07.

(3*R,4*S**)-3-Phenyl-4-propyl-4,5-dihydro-3*H*-benzo[*c*]azepine [(3*R**,4*S**)-6f]:** **(*E*,*Z*)-4c** (263mg, 1.00 mmol) was deprotonated with 1.10 equiv. of LDA (1.10 mmol) in 30 mL of dry THF. After warming to 0 °C, the reaction mixture was poured into sodium bicarbonate solution (10%; 200 ml). After extraction with diethyl ether and evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1). **(3*R**,4*S**)-6f** (200 mg, 0.51 mmol, 51%) was isolated as a colorless powder. R_f = 0.27 (silica gel; PE/EA, 10:1). M.p. 90 °C. IR (KBr): $\tilde{\nu}$ = 3051 cm^{-1} (m, $CH_{arom.}$), 3026 (m, $CH_{arom.}$), 2956 (s, $CH_{aliph.}$), 2925 (s, $CH_{aliph.}$), 2856 (m, $CH_{aliph.}$), 1704 (m), 1689 (m), 1625 (m), 1608 (s, C=N), 1577 (m), 1512 (s), 1496 (m), 1456 (m), 1379 (m), 1330 (w), 1307 (m), 1263 (w), 1209 (m), 1170 (m), 1109 (m), 1043 (m), 1020 (m), 973 (w), 846 (w), 811 (m), 750 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.77 (t, ^3J = 7.16 Hz, 3 H, CH_3), 1.05 (m, 1 H, CHCH_2), 1.21−1.40 (m, 3 H, $CH_2CH_2CH_3$, C$H_2CH_2CH_3$), 2.38 (dd, ^2J = 13.95, ^3J = 10.89 Hz, 1 H, PhCH_2CH), 2.69 (m, ^3J = 10.89, ^3J = 6.30, ^3J = 5.63 Hz, 1 H, $PhCH_2CH$), 2.84 (dd, ^2J = 13.95, ^3J = 6.49 Hz, 1 H, PhCH_2CH), 4.50 (d, ^3J = 3.73 Hz, 1 H, PhCH−N), 7.20 (m, 1 H, $CH_{arom.}$), 7.26−7.38 (m, 6 H, $CH_{arom.}$), 7.46 (m, 2 H, $CH_{arom.}$), 8.66 (s, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.01 (CH_3), 20.04 (*C*H_2CH_3), 31.87 (CH*C*H_2), 37.71 ($PhCH_2$*C*H), 53.35 (Ph*C*H_2CH), 67.00 (PhCH−N), 126.20, 126.46, 127.51, 128.03, 128.18, 129.06, 129.79, 134.79 ($C_{arom.}$), 140.37, 142.48 (C_{ipso}), 162.77 (CH=N) ppm. MS (70 eV): *m*/*z* (%) = 263 (52) [M^+], 220 (100) [$M^+ - C_3H_7$], 206 (10), 159 (28), 129 (58) [$C_9H_9N^+$], 117 (69), 106 (10), 91 (52) [$C_7H_7^+$], 77 (10), 65 (5). $C_{19}H_{21}N$ (263.3): calcd. C 86.65, H 8.04, N 5.32; found C 86.19, H 7.93, N 4.98.

X-ray Crystal Structure Analysis of (3*R,4*S**)-6f:**[16] Formula $C_{19}H_{21}N$, M = 263.37, colorless crystal, 0.50 × 0.40 × 0.20 mm, a = 7.599(1), b = 19.064(1), c = 10.413(1) Å, β = 94.73(1)°, V = 1503.4(3) Å^3, $\rho_{calcd.}$ = 1.164 g·cm^{-3}, μ = 5.04 cm^{-1}, no absorption correction (0.787 ≤ T ≤ 0.906), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223 K, ω and φ scans, 4351 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 2537 independent (R_{int} = 0.022) and 2253 observed reflections [$I \geq 2\,\sigma(I)$], 183 refined parameters, R = 0.036, wR^2 = 0.089, max. residual electron density 0.15 (−0.13) e·Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

(3*R,4*S**,5*S**)-5-Methyl-3-phenyl-4-propyl-4,5-dihydro-3*H*-benzo[*c*]azepine [(3*R**,4*S**,5*S**)-6g]:** From **(*E*,*Z*)-4c** (263 mg, 1.00 mmol), LDA (1.10 mmol) and methyl iodide (284 mg, 2.00 mmol). The crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1). **(3*R**,4*S**,5*S**)-6g** (136 mg, 0.49 mmol, 49%) was isolated as a colorless solid. R_f = 0.22 (silica gel; PE/EA, 10:1). M.p. 92−94 °C. IR (KBr): $\tilde{\nu}$ = 3060 (m, $CH_{arom.}$), 3024 (m, $CH_{arom.}$), 2958 (s, $CH_{aliph.}$), 2929 (s, $CH_{aliph.}$), 2869 (s, $CH_{aliph.}$), 1645 (m), 1622 (s, C=N), 1571 (m), 1492 (m), 1450 (s), 1377 (m), 1340 (m), 1303 (m), 1290 (m), 1213 (w), 1176 (w), 1101 (w), 1070 (w), 1029 (m), 983 (w), 952 (w), 916 (m), 898 (m), 759 (s), 736 (m), 702 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.55 (t, ^3J = 7.29 Hz, 3 H, $CH_2CH_2CH_3$), 0.78 (m, 1 H, $CH_2CH_2CH_3$), 0.93 (m, 1 H, $CH_2CH_2CH_3$), 1.02 (m, 1 H, $CH_2CH_2CH_3$) 1.34 [d, ^3J = 6.93 Hz, 3 H, PhCH(CH_3)CH], 1.36 (m, 1 H, $CH_2CH_2CH_3$), 2.10 [m, ^3J = 6.93 Hz, 1 H, PhC*H*(CH_3)CH], 2.85 [m, ^3J = 14.22, ^3J = 7.11 Hz, 1 H, PhCH(CH_3)C*H*], 4.65 (m, 1 H, PhCH−N), 7.17 (m, 1 H, $CH_{arom.}$), 7.22−7.35 (m, 6 H, $C_{arom.}$), 7.42 (m, 2 H, $C_{arom.}$), 8.54 (s, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.18 (CH_2CH_2*C*H_3), 20.64 (CH_2), 20.84 [PhCH(*C*H_3)CH], 29.56 (CH_2), 40.25 [Ph*C*H(CH_3)CH], 55.76 [PhCH(CH_3)*C*H], 65.49 (PhCH−N), 126.14, 126.24, 127.34, 128.03, 128.08, 130.13, 130.80, 133.80 ($C_{arom.}$), 143.96 (C_{ipso}), 144.42, 161.65 (CH=N) ppm. MS (70 eV): *m*/*z* (%) = 277 (43) [M^+], 219 (35), 205 (5), 171 (10), 132 (100), 117 (5), 106 (18) 91 (28) [$C_7H_7^+$]. $C_{20}H_{23}N$ (277.3): calcd. C 86.59. H 8.36, N 5.05; found C 86.19, H 7.93, N 4.98.

(3*R,4*S**,5*S**)-5-Ethyl-3-phenyl-4-propyl-4,5-dihydro-3*H*-benzo[*c*]azepine [(3*R**,4*S**,5*S**)-6h]:** From **(*E*,*Z*)-4c** (263 mg, 1.00 mmol), LDA (1.10 mmol) and ethyl bromide (284 mg, 2.00 mmol). The crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1). **(3*R**,4*S**,5*S**)-6h** (110 mg, 0.38 mmol, 38%) was isolated as a colorless oil. R_f = 0.15 (silica gel; PE/EA, 10:1). IR (film): $\tilde{\nu}$ = 3062 (m, $CH_{arom.}$), 3026 (m, $CH_{arom.}$), 2964 (s, $CH_{aliph.}$), 2931 (s, $CH_{aliph.}$), 2873 (s, $CH_{aliph.}$), 1710 (m), 1650 (s, C=N), 1602(m), 1575 (m), 1492 (m), 1450 (s), 1379 (m), 1342 (m), 1294 (m), 1253 (m), 1180 (w), 1116 (w), 1074 (w), 1029 (m), 986 (w), 958 (w), 916 (m), 892 (w), 829 (w), 757 (s), 727 (m), 702 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.57 (t, ^3J = 7.12 Hz, 3 H, $CH_2CH_2CH_3$), 0.82 (m, 2 H, $CH_2CH_2CH_3$), 1.03 (t, ^3J = 7.40 Hz, 3 H, CH_2CH_3), 1.04 (m, 1 H, C$H_2CH_2CH_3$) 1.16

(m, 1 H, CH_2CH$_2$CH$_3$), 1.78 (m, 2 H, CH$_2$CH$_3$), 2.25 [m, 1 H, PhC*H*(CH$_2$CH$_3$)CH$_2$], 2.83 [dt, ^3J = 14.52, ^3J = 8.06 Hz, 1 H, PhCH(CH$_2$CH$_3$)C*H*], 5.05 (m, ^3J = 3.28 Hz, 1 H, PhCH−N), 7.24 (m, 1 H, CH$_{arom.}$), 7.28−7.46 (m, 7 H, CH$_{arom.}$), 7.51 (m, 1 H, CH$_{arom.}$), 8.54 (d, ^3J = 3.28 Hz, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 12.19 (CH$_2$CH$_2$*C*H$_3$), 13.95 (CH$_2$*C*H$_3$), 20.34 (CH$_2$), 28.11 (CH$_2$), 29.47 (CH$_2$), 46.71 [PhCH(CH$_2$CH$_3$)*C*H], 48.99 [Ph*C*H(CH$_2$CH$_3$)−CH(CH$_2$CH$_2$CH$_3$)], 64.97 (PhCH−N), 126.11, 126.43, 127.44, 128.02, 128.08, 128.29, 130.22, 130.54, (C$_{arom.}$), 132.86 (C$_{ipso}$), 134.08 (C$_{arom.}$), 143.50, 144.10 (C$_{ipso}$), 160.94 (CH=N). MS (70 eV): *m*/*z* (%) = 291 (43) [M$^+$], 219 (35), 205 (5), 171 (10), 132 (100), 117 (5), 106 (18) 91 (28) [C$_7$H$_7^+$]. C$_{21}$H$_{25}$N (291.4): calcd. C 86.55, H 8.65, N 4.81; found C 85.98, H 8.81, N 4.70.

(3*R,4*S**,5*S**)-5-Allyl-3-phenyl-4-propyl-4,5-dihydro-3*H*-benzo[*c*]azepine [(3*R**,4*S**,5*S**)-6i]:** From **(*E*,*Z*)-4c** (394 mg, 1.50 mmol), LDA (1.50 mmol) and allyl bromide (363 mg, 3.00 mmol). The crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1). **(3*R**,4*S**,5*S**)-6i** (330 mg, 1.08 mmol, 72%) was isolated as a colorless solid, containing a second diastereoemer of unknown configuration. R_f = 0.12 (silica gel; PE/EA, 10:1). M.p. 97 °C. IR (KBr): $\tilde{\nu}$ = 3062 (m, CH$_{arom.}$), 3026 (m, CH$_{arom.}$), 2964 (s, CH$_{aliph.}$), 2931 (s, CH$_{aliph.}$), 2873 (s, CH$_{aliph.}$), 1710 (m), 1650 (s, C=N), 1602(m), 1575 (m), 1492 (m), 1450 (s), 1379 (m), 1342 (m), 1294 (m), 1253 (m), 1180 (w), 1116 (w), 1074 (w), 1029 (m), 986 (w), 958 (w), 916 (m), 892 (w), 829 (w), 757 (s), 727 (m), 702 (s). ^{1}H NMR (600 MHz, CDCl$_3$): δ = 0.57 (t, ^3J = 7.30 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 0.85 (m, 2 H, CH$_2$C*H*$_2$CH$_3$), 1.12 (m, 2 H, C*H*$_2$CH$_2$CH$_3$), 2.28 [m, 1 H, C*H*(CH$_2$CH$_2$CH$_3$)], 2.52 [m, 2 H, PhCH(C*H*$_2$CH=CH$_2$)], 3.08 [m, ^3J = 13.25, ^3J = 7.40 Hz, 1 H, PhCH(CH$_2$CH=CH$_2$)C*H*], 5.07 (m, 1 H, PhCH−N), 5.15 (m, 2 H, CH=C*H*$_2$), 5.88 (m, 1 H, C*H*=CH$_2$) 7.24 (m, 2 H, CH$_{arom.}$), 7.30−7.40 (m, 5 H, CH$_{arom.}$), 7.44 (d, ^3J = 7.20 Hz, 1 H, C$_{arom.}$), 7.50 (m, 1 H, CH$_{arom.}$), 8.59 (s, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 13.94 (CH$_2$CH$_2$*C*H$_3$), 20.32 (CH$_2$), 27.99 (CH$_2$), 41.19 (*C*H$_2$CH=CH$_2$), 46.40 [Ph*C*H(CH$_2$CH=CH$_2$)CH], 46.87 [PhCH(CH$_2$CH=CH$_2$)*C*H], 64.41 (PhCH−N), 117.19 (CH=*C*H$_2$), 126.11−144.20 (C$_{arom.}$, C$_{ipso}$), 136.12 (*C*H=CH$_2$), 160.82 (CH=N) ppm. GC-MS (70 eV): *m*/*z* (%) = 303 (10) [M$^+$], 274 (45) [M$^+$ − C$_2$H$_5$], 260 (60) [M$^+$ − C$_3$H$_7$], 220 (75) [C$_{16}$H$_{14}$N$^+$], 158 (56), 143 (90), 129 (100) [C$_9$H$_7$N$^+$], 115 (80), 91 (83) [C$_7$H$_7^+$]. C$_{22}$H$_{25}$N (303.4): calcd. C 87.08, H 8.30, N 4.62; found C 86.10, H 8.32, N 4.31.

(3*R,4*S**,5*S**)-5-Benzyl-3-phenyl-4-propyl-4,5-dihydro-3*H*-benzo[*c*]azepine [(3*R**,4*S**,5*S**)-6j]:** From **(*E*,*Z*)-4c** (406 mg, 1.60 mmol), LDA (1.60 mmol) and benzyl bromide (513 mg, 3.00 mmol). The crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1). **(3*R**,4*S**,5*S**)-6j** (155 mg, 0.44 mmol, 27%) was isolated as a yellow oil. R_f = 0.17 (silica gel; PE/EA, 10:1). IR (film): $\tilde{\nu}$ = 3085 cm^{-1} (m, CH$_{arom.}$), 3062 (s, CH$_{arom.}$), 3028 (m, CH$_{arom.}$) 2958 (s, CH$_{aliph.}$), 2929 (s, CH$_{aliph.}$), 2871(s), 1739 (w), 1649 (s, C=N), 1602 (m), 1575 (m), 1494 (s), 1456 (m), 1379 (m), 1340 (m), 1292 (m), 1259 (w), 1178 (m), 1114 (w), 1076 (w), 1029 (w), 983 (w), 956 (w), 916 (m), 892 (w), 844 (w), 759 (m), 721 (m), 700 (s), 657 (m). ^{1}H NMR (600 MHz, CDCl$_3$): δ = 0.59 (m, 3 H, CH$_2$CH$_2$C*H*$_3$), 0.80 (m, 2 H, CH$_2$C*H*$_2$CH$_3$), 1.05 (m, 2 H, C*H*$_2$CH$_2$CH$_3$), 2.15 [m, 1 H, PhCH(PhCH$_2$)C*H*], 3.02 [m, 2 H, PhCH(PhC*H*$_2$)CH], 3.35 (m, 1 H, PhC*H*(PhCH$_2$)CH), 4.89 (m, 1 H, PhCH−N), 7.10−7.40 (m, 14 H, CH$_{arom.}$), 8.62 (s, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 13.78 (CH$_3$), 20.19 (CH$_2$CH$_2$CH$_3$), 27.88 (*C*H$_2$CH$_2$CH$_3$), 43.56 [PhCH(Ph*C*H$_2$)CH], 45.14 [PhCH(PhCH$_2$)*C*H], 48.74 [Ph*C*H(PhCH$_2$)CH], 64.55 (PhCH−N), 126.05, 126.38, 126.68, 127.39, 127.93, 128.47, 129.04, 130.30, 131.00 (C$_{arom.}$), 132.82 (C$_{ipso}$), 134.77 (C$_{arom.}$), 139.09, 142.72, 144.10 C$_{ipso}$), 160.69 (CH=N) ppm. MS (70 eV): *m*/*z* (%) = 353 (45) [M$^+$], 310 (10) [M$^+$ − C$_3$H$_7$], 262 (13), 220 (100) [C$_{16}$H$_{14}$N$^+$], 193 (6), 129 (15), 115 (13) [C$_8$H$_8$N$^+$], 91 (72) [C$_7$H$_7^+$].

(3*R,4*R**)-3,4-Diphenyl-4,5-dihydro-3*H*-benzo[*c*]azepine [(3*R**,4*R**)-6k]: (*E*)-4d** (297 mg, 1.00 mmol) was deprotonated with lithium 2,2,6,6-tetramethylpiperidide (TMP; 1.00 mmol) in 40 mL of dry THF at −78 °C. To the reaction mixture were added some drops of water at −78 °C. After aqueous workup and evaporation of solvents, the crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1). Small amounts of remaining tetramethylpiperidine could not be separated from the product **(3*R**,4*R**)-6k** (GC purity ca. 81%, 155 mg, 29%). R_f = 0.17 (silica gel; PE/EA, 10:1). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 2.77 ppm (dd, ^2J = 14.07, ^3J = 1.43 Hz, 1 H, H^1), 3.22 (dd, ^2J = 14.07, ^3J = 8.34 Hz, 1 H, H^2), 3.71 (ddd, ^3J = 1.43, ^3J = 8.34, ^3J = 11.68 Hz, 1 H, H^3), 4.33 (dd, ^3J = 11.68, ^4J = 2.14 Hz, 1 H, H^4), 6.75 (m, 2 H, CH$_{arom.}$), 7.00 (m, 9 H, CH$_{arom.}$), 7.18 (m, 1 H, CH$_{arom.}$), 7.33 (m, 2 H, CH$_{arom.}$), 8.62 (d, ^4J = 2.14 Hz, 1 H, CH=N) ppm.

(3*R,4*S**,5*S**)-5-Ethyl-4-methyl-3-vinyl-4,5-dihydro-3*H*-benzo[*c*]azepine [(3*R**,4*S**,5*S**)-6l]:** From **(*E*,*Z*)-4e** (278 mg, 1.60 mmol), LDA (1.70 mmol) and ethyl bromide (327 mg, 3.00 mmol). The crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 5:1) and **(3*R**,4*S**,5*S**)-6l** (151 mg, 0.71 mmol, 44%) was isolated as a yellow oil. R_f = 0.23 (silica gel; PE/EA, 5:1). IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (s, CH$_{arom.,olef.}$), 3024 (m, CH$_{arom.}$), 2972 (s, CH$_{aliph.}$), 2927 (s, CH$_{aliph.}$), 2877 (s, CH$_{aliph.}$), 1645 (s, C=N), 1622 (s), 1571 (m), 1492 (m), 1450 (s), 1415 (w), 1379 (m), 1342 (m), 1313 (m), 1267 (m), 1211 (m), 1178 (m), 1124 (w), 1076 (w), 1053 (w), 995 (m), 970 (m), 950 (m), 914 (s), 850 (w), 810 (w), 757 (s), 730 (s), 702 (s), 665 (m). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 0.92 (m, 6 H, CH$_2$C*H*$_3$, CH$_3$), 1.74 (m, 2 H, C*H*$_2$CH$_3$), 2.23 (m, 1 H, H^2), 2.43 (m, 1 H, H^1), 4.04 (m, ^3J = 3.17, ^4J = 2.61 Hz, 1 H, H^3), 5.18 (m, ^2J = 1.59, ^3J = 10.44, ^3J = 3.17 Hz, 1 H, CH=C*H*$_{cis}$), 5.30 (m, ^3J = 17.16, ^3J = 3.36 Hz, 1 H, CH=C*H*$_{trans}$), 6.12 (m, ^3J = 10.45, ^3J = 17.16 Hz, 1 H, C*H*=CH$_2$), 7.28−7.40 (m, 4 H, CH$_{arom.}$), 8.69 (d, ^4J = 2.61 Hz, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 12.38 (CH$_2$C*H*$_3$), (13.80 (CH$_3$), 26.00 (C*H*$_2$CH$_3$), 45.74 (CH), 50.73 (CH), 64.26 (CH), 114.92 (CH=*C*H$_2$), 126.19, 128.30, 130.04, 131.22, (C$_{arom.}$), 133.15 (C$_{ipso}$), 139.99 (*C*H=CH$_2$), 142.77 (C$_{ipso}$), 161.85 (CH=N) ppm. MS (70 eV): *m*/*z* (%) = 213 (10) [M$^+$], 212 (22) [M$^+$ − H], 198 (100) [M$^+$ − CH$_3$], 184 (95) [M$^+$ − 2CH$_3$], 168 (33), 159 (25), 143 (68), 129 (60), 115 (50) [C$_8$H$_8$N$^+$], 91 (13) [C$_7$H$_7^+$]. C$_{15}$H$_{19}$N (213.2): calcd. C 84.46, H 8.98, N 6.57; found C 84.43, H 9.25, N 6.66.

(3*R,4*S**,5*S**)-5-Methyl-4-propyl-3-vinyl-4,5-dihydro-3*H*-benzo[*c*]azepine [(3*R**,4*S**,5*S**)-6m]:** From **(*E*,*Z*)-4f** (213 mg, 1.00 mmol), LDA (1.10 mmol) and methyl iodide (284 mg, 2.00 mmol). The crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 10:1) and **(3*R**,4*S**,5*S**)-6m** (30 mg, 0.13 mmol, 13%) was isolated as a yellow oil. R_f = 0.28 (silica gel; PE/EA, 10:1). IR (film): $\tilde{\nu}$ = 3057 cm^{-1} (m, CH$_{arom.,olef.}$), 2974 (s, CH$_{aliph.}$), 2933 (s, CH$_{aliph.}$), 2843 (m, CH$_{aliph.}$), 1728(m), 1639 (s, C=N), 1487 (m), 1473 (s), 1377 (s), 1342 (m), 1313 (m), 1170 (m), 1129 (w), 1109 (s), 1033 (m), 930 (m), 914 (s), 757 (s). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 0.83 (t, ^3J = 7.27 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 1.18 (m, 1 H, C*H*$_2$CH$_2$CH$_3$), 1.25−1.36 (m, 5 H, CH$_2$C*H*$_2$CH$_3$, CH$_3$), 1.56 (m, 1 H, C*H*$_2$CH$_2$CH$_3$), 2.01 (m, 1 H),

2.85 (m, 1 H), 4.04 (m, 1 H), 5.18 (m, ^2J = 1.59, ^3J = 10.44, ^3J = 3.17 Hz, 1 H, CH=CH_{cis}), 5.30 (m, ^3J = 17.16, ^3J = 3.36 Hz, 1 H, CH=CH_{trans}), 6.12 (m, ^3J = 10.45, ^3J = 17.16 Hz, 1 H, CH=CH_2) 7.28−7.40 (m, 4 H, $CH_{arom.}$), 8.69 (d, ^4J = 2.61 Hz, 1 H, CH=N) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.42 ($CH_2CH_2CH_3$), 20.37 (CH_3), 21.32 ($CH_2CH_2CH_3$), 30.42 ($CH_2CH_2CH_3$), 40.19 (CH), 53.94 (CH), 64.21 (CH), 114.59 (CH=CH_2), 126.09, 127.91, 130.05, 130.65, ($C_{arom.}$), 133.87 (C_{ipso}), 140.60 (CH=CH_2), 144.45 (C_{ipso}), 161.36 (CH=N) ppm. MS (70 eV): *m/z* (%) = 227 (60) [M^+], 212 (22) [$M^+ - CH_3$], 198 (25) [$M^+ - C_2H_5$], 184 (100) [$M^+ - C_3H_7$], 170 (95) [$M^+ - C_3H_7 - CH_2$], 159 (30), 143 (72), 127 (53), 117 (32), 91 (13) [$C_7H_7^+$].

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