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1,7-Electrocyclization Reactions of 2-Aza-4,5-benzoheptatrienyl- and 4-Aza-6,7-benzononatetraenyllithium Compounds: Synthesis of Novel 2-Benzazepines and (Benzocyclooctenyl)amines

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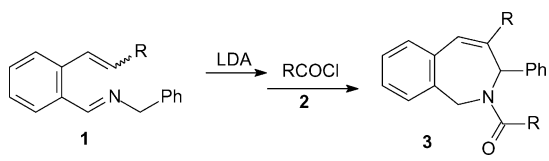
Deprotonation reactions of *N*-benzyl- and *N*-allylimines **1** and **4** led to benzo-annulated 2-azaheptatrienyl- and 4-azanonatetraenyllithium compounds, which underwent 1,7-electrocyclization reactions to yield the novel 2,3-dihydro-1*H*-benzo[*c*]azepines **3**, **5**, **11** and **13** or the (5,6-dihydrobenzocycloocten-5-yl)amines **6** after subsequent addition of acyl chlorides, carbamoyl chlorides, imidoyl chlorides or pivaldehyde, respectively. Acyl and carbamoyl chlorides reacted as electrophiles at the nitrogen atom, whereas imidoyl halides and pivaldehyde attacked position C-5 in the seven-membered ring. In the case of pivaldehyde, the final tricyclic product **13** is the result of a subsequent nucleophilic attack at the imine moiety after a proton shift. The temperature dependence of the reaction cascades was studied, allowing preferred formation either of the seven-membered heterocyclic systems **3** and **5** or of the eight-membered carbocycles **6**. All compounds were fully characterized, including by X-ray diffraction studies of **6c**, **6f**, **11a** and **13a**.

Introduction

Seven-membered heterocycles form an important class of compounds that has attracted the particular attention of medicinal chemists.[1,2] Benzo-annulated systems such as 2-benzazepines are of special interest for the pharmaceutical industry: capsazepine, for example, is a commercially available competitive agonist for the vanilloid receptor (VR1), used in the therapy of neurophatic pain.[3] In contrast, partially saturated benzazepines with only one unsaturated unit in the seven-membered ring, such as 2,3-dihydro-1*H*-benzazepines, are not very common in pharmaceutical applications, and we have found only a few examples of synthetic methods for their preparation. Kogen et al. published the synthesis of substituted 2,3-dihydro-1*H*-benzazepines by ring-closing metathesis (RCM) through reactions between styrenes and allylamines,[4] Dieltiens and Stevens[5] described a ring-closing enyne metathesis/cross metathesis procedure leading to 1-phosphonylated benzazepines, and van Otterlo et al. developed an isomerisation reaction followed by RCM for the preparation of substituted benzo-annulated heterocycles; one example is a single 2,3-dihydro-1*H*-benzazepine.[6] A further quite useful method for the synthesis of seven-membered rings is to be found in anionic electrocyclization reactions, several examples of which have been published.[7–11] Other examples of electrocyclization reactions that utilise 1,7-dipoles as isoelectronic species for the corresponding anions are known.[12–15]

We have recently published a synthetic approach leading to the formation of the partially unsaturated seven-membered nitrogen heterocycles **3** (Scheme 1, Table 1),[7] based on 1,7-electrocyclization reactions of azapolyenylmetal compounds.[8,9] The driving force for these orbital-symmetry-allowed processes is the formal transposition of the electronegative nitrogen atom from an unfavourable (even) nodal position of the HOMO in the unsaturated chain to a favourable (odd) coefficient position. According to quantum chemical calculations, only such processes are predicted to be exothermic. Azapolyenylmetal compounds were prepared by deprotonation of the *N*-benzylimines **1** to give lithium intermediates. After their electrocyclization, the cyclic intermediates were regioselectively trapped at the nitrogen atom by acyl halides **2** as electrophiles, presumably to give (not isolated) *o*-quinodimethane compounds. In the final reaction step a formal 1,5-hydrogen shift produced the stable amides **3** in moderate to good yields (see below).



Scheme 1.

Furthermore, we also reported on the synthesis of mixtures each consisting of a seven-membered benzazepine **5** and a benzo-annulated eight-membered carbocyclic ring **6**

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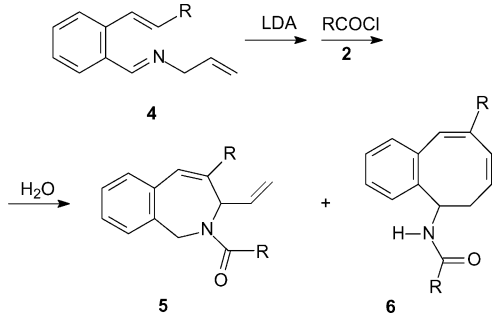
when starting from *N*-allylimines **4** (Scheme 2).[7] For the formation of the eight-membered ring the suggested reaction sequence consists of a deprotonation of **4**, an anionic 1,7-electrocyclization reaction, the addition of the electrophile **2**, a second deprotonation and a subsequent [2,3]-aza-Wittig rearrangement finally to produce **6** (Scheme 2 and below).



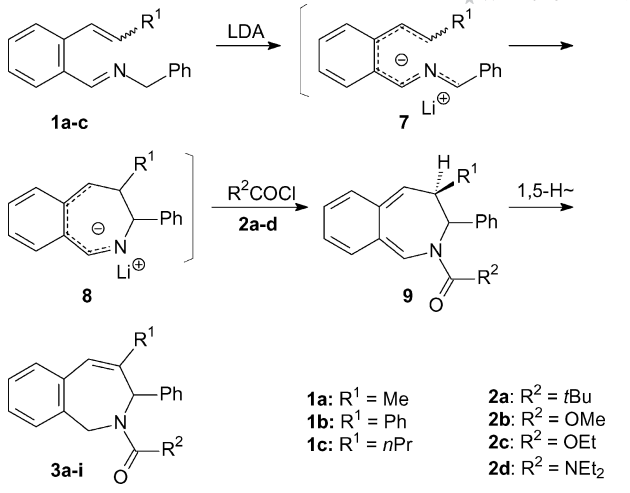
Scheme 2.

In this report we investigate the scope and limitations of these novel reaction sequences and extend our investigations to the synthesis of differently substituted 2-benzazepines by use of acyl chlorides, carbamoyl chlorides and imidoyl chlorides as electrophiles and of tricyclic benzo-annulated compounds with aldehydes as electrophiles. We further study the experimental preconditions for the more controlled synthesis either of the seven-membered- or of the eight-membered-ring compounds and investigate the stereochemical course of the rearrangements by a marker experiment.

Results and Discussion

Following our recently published procedure[7] we have now extended the series of reactions to the synthesis of the compounds **3f**–**i** (Scheme 3, Table 1). (Compounds **3a**–**e** had been reported previously.[7]) The lithiated annulated azapolyenes **7** were prepared by deprotonation of the benzylic aldimine compounds **1a**–**c** (*E*/*Z* mixtures; **1a**: 0.53:1, **1b**: 0.52:1, **1c**: 0.5:1) by treatment with lithium diisopropylamide (LDA) in tetrahydrofuran at –78 °C. The reaction mixtures were allowed to warm to 0 °C to achieve cyclization to compounds **8** and were then quenched with 2.0 equiv. of either the chloroformates **2b** or **2c** or the carbamoyl chloride **2d** as electrophiles. After the reaction mixture had warmed to room temperature and aqueous workup had been performed, the compounds **3f**–**i** were purified by column chromatography. The new 2-benzazepines **3f**–**i** with carbamoyl (**3f**–**h**) or urea (**3i**) moieties, resulting from hydrogen shifts in the intermediate *o*-quinodimethane compounds **9**, were isolated in moderate to good yields of 40–73%.

We next treated the 2-aza-4,5-benzoheptatrienes **1a** and **1c** with LDA as base and subsequently with an imidoyl chloride **10** as electrophile (Scheme 4). The only products were the 4,5-dihydro-3*H*-2-benzazepines **11a** and **11b**, isolated as single diastereomers by careful column chromatography in low yields of 29 and 21%. Unlike the acyl halides and carbamoyl halides, these electrophilic compounds show the same regioselectivity as alkyl halides,[9] with the reactions taking place at the C-5 positions in the cyclic intermediates. Obviously, imidoyl chlorides seem to be less prone than acyl halides to attack nitrogen atoms in preference to carbon atoms (less "azaphilic"). The imine moieties of these compounds are rather sensitive towards hydrolysis, explaining the low yields.



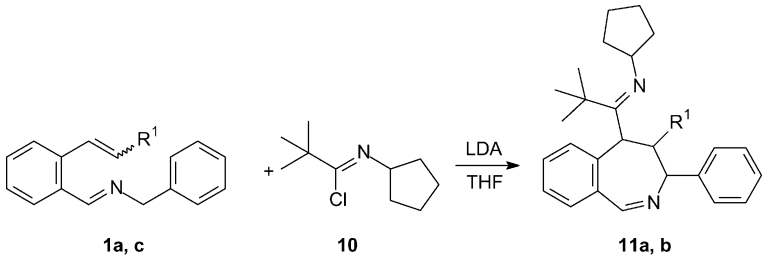
Scheme 3. Reaction pathway for the formation of the seven-membered ring systems **3** by deprotonation of the imines **1**.

Table 1. Substitution patterns and yields for compounds **3** (yields for **3a**–**e** are from ref.[7]).

	R^1	R^2	Yield (%)
3a	Me	*t*Bu	47
3b	Me	OMe	54
3c	Ph	*t*Bu	47
3d	*n*Pr	*t*Bu	68
3e	*n*Pr	OMe	79
3f	Me	OEt	62
3g	Ph	OMe	40
3h	*n*Pr	OEt	73
3i	*n*Pr	NEt_2	63

Compound **11a** was characterized by X-ray crystallography (Figure 1).[16,17] The heterocycle shows a boat-like conformation. The imino and the methyl groups are situated *trans*, indicating that the electrophile attacked the sterically less demanding side of the molecule. The sterically less favourable *cis* arrangement of the phenyl and methyl groups is an indication of the allowed conrotatory mode of the 8π electrocyclization mechanism of the ring-closure reaction, thus indicating that **11a** was formed from the major diastereomer (*Z*)-**1a**. Products resulting from the minor isomer (*E*)-**1a** could not be identified.

The two very interesting tricyclic compounds **13a** and **13b** were synthesized in 44 and 38% yields by treatment of the 2-aza-4,5-benzoheptatrienes **1a** and **1c**, respectively, with LDA and subsequently with pivaldehyde (**12**, Scheme 5). The aldehyde was found to react analogously to



Scheme 4.

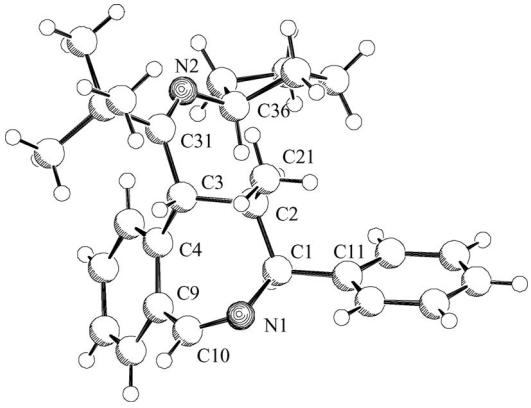
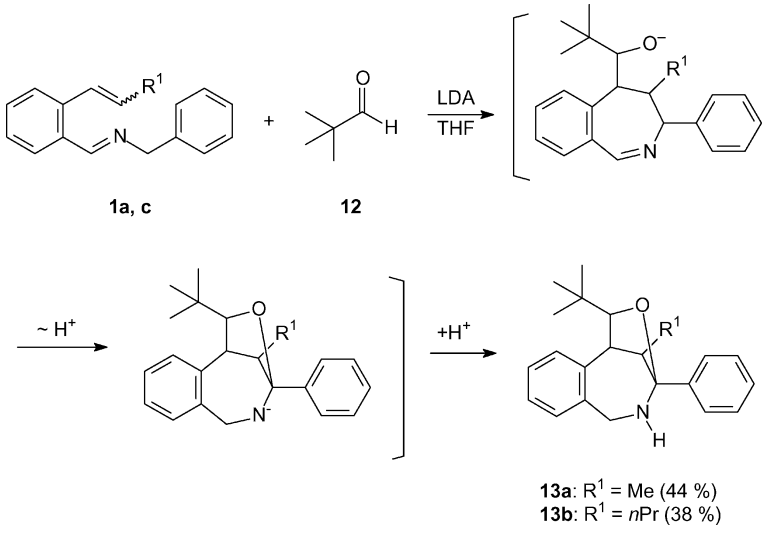


Figure 1. Molecular structure of **11a** in the crystalline state as determined by X-ray diffraction, together with crystallographic numbering.

the imidoyl chlorides and alkyl halides at the C-5 positions in the anionic heterocycles. However, the intermediate alkoxide ions attack the adjacent α-positions to the nitrogen atom at C-3 as strong nucleophiles, producing the tricyclic N,O-acetals. Additionally, tautomerism (base-induced proton shifts from C-3 to C-1, possibly involving intermediate 2-azaallyl anions) is necessary to explain the products observed. Only one diastereomer was detected by spectroscopic methods in each case, and no reversibility was observed. Reactions of benzaldehyde as electrophile gave only mixtures of compounds that could not be separated or characterized.

Compound **13a** could be characterized by X-ray crystallography (Figure 2).[16,17] The benzazepine ring is strongly folded, and the tetrahydrofuranyl subunit shows a half-chair conformation. The methyl group at C-2 (crystallographic numbering) adopts an *endo* position, the *t*Bu group an *exo* position. The diastereoselectivity observed may most probably be the result of lithium coordination and preorientation of the electrophile towards the cyclic intermediate. The aldehyde thus attacked the seven-membered ring intermediate from the less hindered side (*anti* to the methyl group in C-3 position).

In a second project, we investigated the previously observed unusual conversion of allyl imines **4** – *N*-allylaldimine analogues of the *N*-benzyl-substituted 2-azaheptatrienes **1** – into mixtures of seven-membered heterocycles **5** and eight-membered carbocycles **6** (Scheme 6) in more detail. In particular, we were interested in identifying appropriate reaction conditions that would allow the reaction cascades to be influenced in one or the other direction with better yields of the corresponding products **5** or **6**. Just careful



Scheme 5.

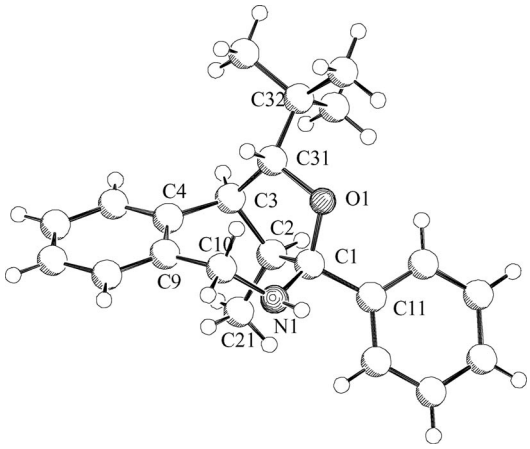
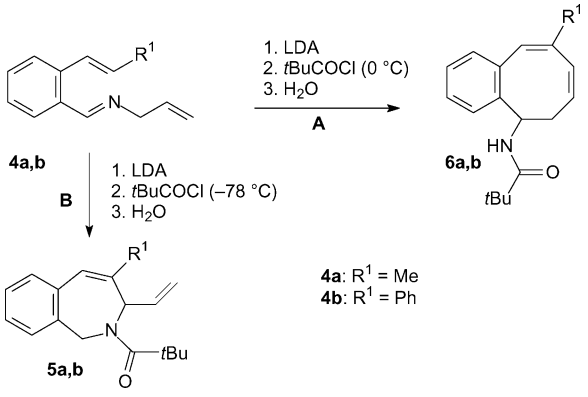


Figure 2. Molecular structure of **13a** in the crystalline state as determined by X-ray diffraction, together with crystallographic numbering.

temperature control came out to be an efficient measure. Thus, for the preferred formation of the eight-membered heterocycles **6a** and **6b** (reaction conditions A; see Experimental Section), treatment of the aldimine compounds **4a** and **4b** with LDA at –78 °C, warming to room temperature, then trapping with the electrophile at 0 °C and finally stirring at room temperature for several hours was advantageous. For better yields of the seven-membered heterocycles **5a** and **5b** (reaction conditions B; see Experimental Section), treatment of the aldimine compounds **4a** and **4b** with LDA, warming to 0 °C, renewed cooling to –78 °C and then addition of the electrophile turned out to be favourable (Table 2). In each case, the other isomer could not be observed or isolated after chromatographic workup. These observations indicate a somewhat higher activation barrier for the second part of the reaction cascade on the pathway to the compounds **6**, the [2,3]-aza-Wittig rearrangement.



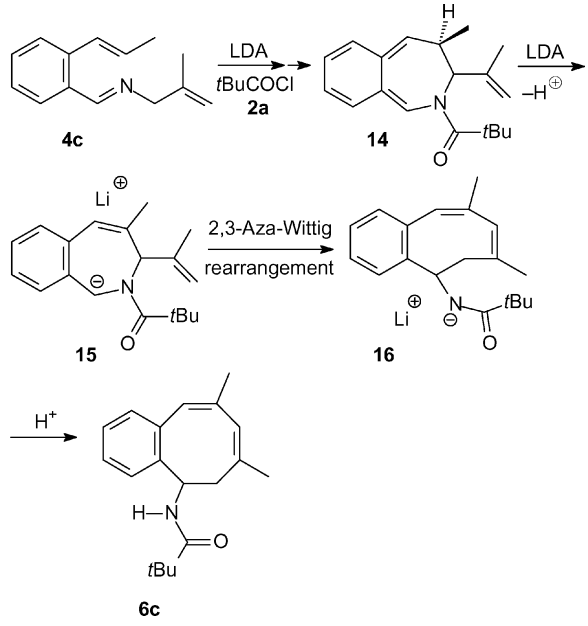
Scheme 6.

In order to supplement our published mechanism for the reaction cascade for the formation of the eight-membered rings[7,18] (Scheme 7), which was mainly based on quantum chemical calculations, we now reinvestigated it by a marker experiment (Scheme 8). This reaction cascade starts with the formation of intermediate **14**, its subsequent deprotonation by surplus base to afford **15** and an [2,3]-aza-Wittig

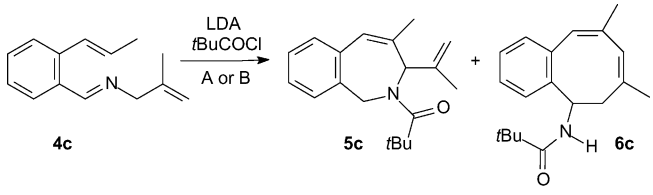
Table 2. Substitution patterns and isolated yields for compounds **5a**, **5b**, **6a**, and **6b** under reaction conditions A (addition of the electrophile after warming to 0 °C) or reaction conditions B (addition of the electrophile at low temperature).

	R^1	Yield (%)	Reaction conditions
5a	Me	51	B
6a	Me	62	A
5b	Ph	52	B
6b	Ph	49	A

rearrangement to provide **16**, to give **6** after protonation. A methyl group was therefore introduced as a marker in the *N*-allyl moiety of **4c** to find out the position of this group in the final (benzocyclooctenyl)amine **6c**. The isolated reaction products **5c** (reaction conditions B) and **6c** (reactions conditions A) are in good agreement with the previously postulated cascade mechanism (Scheme 7).[7] The structure of **6c** could also be confirmed by X-ray analysis. No product containing a dihydronaphthalene substructure as result of a [1,2]-rearrangement was ever observed.

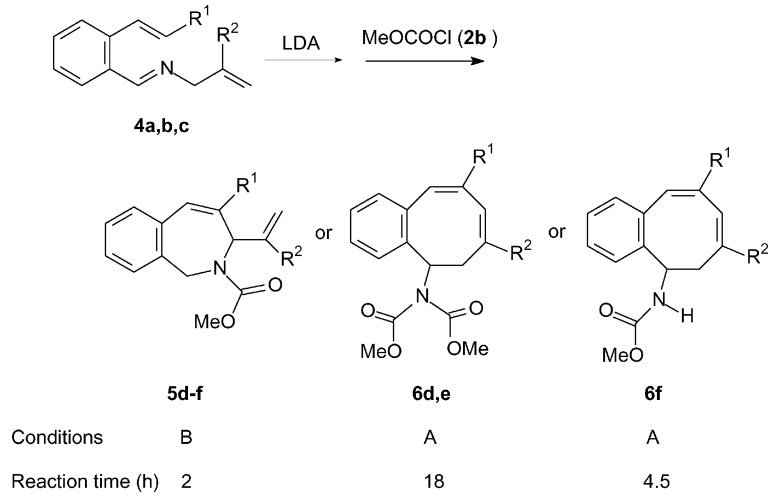


Scheme 7. Suggested reaction cascade for the methyl-marked compound **4c** to give **6c**.



Scheme 8.

The temperature dependence of the product formation was also utilized for quenching experiments by using 2 equiv. of methyl chloroformate (**2b**) as electrophile



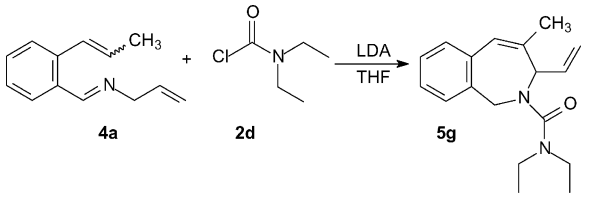
Scheme 9.

(Scheme 9, Table 3) for the synthesis either of the seven-membered ring systems **5** or of the eight-membered carbocycles **6**. Starting with the deprotonation of **4a**, **4b** or **4c**, we obtained the corresponding carbamates **5d**–**f** and the bis(carbamates) **6d**–**e** after the addition of the electrophile. In one case only a monosubstituted eight-membered carbocycle (**6f**) was isolated in a rather low yield of 10%.

Table 3. Substitution patterns and isolated yields for compounds **5d**–**f** and **6d**–**f**.

	R^1	R^2	Yield (%)	Reaction conditions
5d	Me	H	47	B
5e	Ph	H	20	B
5f	Me	Me	68	B
6d	Me	H	42	A
6e	Ph	H	55	A
6f	Ph	H	10	A

Finally, we investigated the same reaction sequence starting from **4a**, with diethylcarbamoyl chloride (**2d**) as electrophile. This electrophile reacts similarly to the acyl chlorides at the nitrogen atom of the cyclic anionic intermediates and provides access to the interesting asymmetric urea derivative **5g** (Scheme 10) in a yield of 71% without any indications of eight-membered carbocyclic products, even under forced conditions such as reactions conditions A. In view of the mechanism depicted in Scheme 7 the exclusive formation of the seven-membered compound **5g** from **4a** may be explained by the different acidity of the associated urea intermediate (like **14**) relative to those of the amide intermediates involved in the other reactions.



Scheme 10.

Conclusions

This report describes the synthesis of substituted 2-benzazepines and (benzocyclooctenyl)amines by 1,7-electrocyclization reactions of benzo-annulated 2-azaheptatrienyl- and 4-azanonatetraenyllithium compounds with subsequent addition of acyl chlorides or carbamoyl chlorides. The use of additional electrophiles such as imidoyl chlorides and aldehydes led to some interesting and novel 2-benzazepines, such as the imine-substituted 2-benzazepines **11** or the tricyclic reaction products **13**, in moderate to good yields. *N*-Allylimines **4** gave access to either seven-membered heterocycles **5** or, through a second deprotonation and an additional 2,3-aza-Wittig rearrangement, eight-membered carbocycles **6**. The different temperature dependence of the two competing reaction channels can be utilised to direct the reactions preferentially to either the seven-membered heterocyclic systems **5** or the eight-membered carbocyclic compounds **6**.

Experimental Section

Materials and Methods: IR: Nicolet FT-IR 5DXC. ^{1}H NMR: Bruker WM 300 (300.13 MHz), Varian INOVA 500 (500 MHz) and Varian Unity Plus (599.86 MHz), internal reference tetramethylsilane or solvent. ^{13}C NMR: Bruker WM (75.47 MHz), Varian INOVA (125 MHz), Varian Unity Plus (150.85 MHz), internal reference tetramethylsilane or solvent. In cases of broad signals due to hindered amide rotation at room temperature, high-temperature spectra were taken. GC/MS: Varian MAT CH7A with GC Varian 3400 plus data system SS 200; Varian MAT 8230 with GC Varian 3400 plus data system SS 300. HRMS: Bruker Micro TOF. CHN: Perkin–Elmer Dia CHN 240. Column chromatography: silica gel 60 (Merck), 0.063–0.200 mm. TLC: Aluminium sheets 5 × 7.5 cm, silica gel 60 F_{254} (Merck). Melting points (uncorrected): Büchi B-540. All solvents were rigorously dried by standard methods. All deprotonations and ring-closure reactions were carried out with complete exclusion of moisture (argon, modified Schlenk techniques). The aldimines **1a**–**c**, **4a** and **4b** were synthesized in accordance with literature procedures, from 2-alkenylbenzaldehydes and benzyl- or allylamine:[9,19,20] (*E*/*Z*)-2-(Alkenyl)bromobenzenes were

prepared by Wittig olefination of 2-bromobenzaldehyde; the 2-alkenylbenzaldehydes were obtained by formylation of these 2-(alkenyl)bromobenzenes with *n*-butyllithium and dimethylformamide. EA = ethyl acetate; P = pentane, PE = petroleum ether; TEA = triethylamine.

(*E*/*Z*)-(2-Methylallyl)[2-(prop-1-enyl)benzylidene]amine (4c): (*E*/*Z*)-2-(Prop-1-enyl)benzaldehyde (2.05 g, 14.06 mmol) was added to (2-methylallyl)amine (1.00 g, 14.06 mmol) in dichloromethane (30 mL) in the presence of molecular sieves (4 Å). After 16 h of stirring at room temperature, the molecular sieves were removed by filtration and washed with dichloromethane (25 mL). The solvent was then removed under reduced pressure. The product was purified by kugelrohr distillation and was isolated as a colourless oil. Yield 1.98 g (71%), b.p. 100 °C (0.016 mbar), *Z*/*E* ratio = 1:0.2. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.65 (dd, ^3J = 6.8, ^4J = 2.0 Hz, 3 H, CH_3, *Z*), 1.82 [s, 3 H, CH_3 (allyl)-*Z*], 1.83 [s, 3 H, CH_3 (allyl)-*E*], 1.91 (dd, ^3J = 6.8, ^4J = 2.0 Hz, 3 H, CH_3, *E*), 4.14 (s, 2 H, NCH_2, *Z*), 4.17 (s, 2 H, NCH_2, *E*), 4.89 (m, C=CH_2, 2H-*E*, 2H-*Z*), 5.92 (dq, ^3J = 7.2, ^3J = 11.2 Hz, 1 H, CH=C*H*CH$_3$, *Z*), 6.07 (dq, ^3J = 7.2, ^3J = 15.6 Hz, 1 H, CH=C*H*CH$_3$, *E*), 6.65 (d, ^3J = 11.2 Hz, 1 H, C*H*=CHCH$_3$, *Z*), 6.89 (d, ^3J = 15.6 Hz, 1 H, C*H*=CHCH$_3$, *E*), 7.18–7.40 (m, C$H_{arom.}$, 3H-*E*, 3H-*Z*), 7.91 (m, 1 H, C$H_{arom.}$, *E*), 8.05 (m, 1 H, C$H_{arom.}$, *Z*), 8.47 (s, 1 H, N=C*H*, *Z*), 8.61 (s, 1 H, N=C*H*, *E*) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.4 (*C*H$_3$, *Z*), 18.8 (*C*H$_3$, *E*), 21.1 (*C*H$_3$-allyl, *E*/*Z*), 67.4 (N*C*H$_2$, *Z*), 67.5 (N*C*H$_2$, *E*), 111.3 (CH=*C*H$_2$, *E*/*Z*), 126.7, 126.8, 126.9, 127.0, 127.3, 127.4, 127.6, 127.8, 129.0, 129.1, 129.6, 129.8, 129.9, 130.2 (*C*H$_{arom.}$), 132.7, 133.8 (C_{ipso}), 138.0, 138.4, 143.7 (C_{ipso}), 160.4 (N=*C*H, *Z*), 160.8 (N=*C*H, *E*) ppm. IR (film): $\tilde{\nu}$ = 3064 (m, $CH_{arom.,olef.}$), 3018 (m, $CH_{arom.,olef.}$), 2972 (m, $CH_{aliph.}$), 2935 (m, $CH_{aliph.}$), 2912 (m, $CH_{aliph.}$), 2877 (m, $CH_{aliph.}$), 2808 (m, $CH_{aliph.}$), 1639 (s, C=N), 1597 (m, C=C), 1477 (m), 1444 (m), 1400 (m), 1371 (m), 1319 (w), 1288 (m), 1238 (m), 1213 (w), 1157 (w), 1062 (w), 1039 (m), 1008 (m), 964 (m), 925 (w), 894 (m), 806 (m), 761 (s), 713 (m) cm^{-1}. MS (70 eV): *m*/*z* (%) = 199 (7) [M]$^+$, 184 (100) [M – CH_3]$^+$, 157 (4), 130 (15), 116 (12), 91 (4), 55 (41). $C_{14}H_{17}N$ (199.29): calcd. C 84.37, H 8.60, N 7.03; found C 84.15, H 8.64, N 7.01.

General Procedure for the Synthesis of 2,3-Dihydro-1*H*-2-benzazepines 3f–i:[7] Lithium diisopropylamide (LDA) was freshly prepared under argon from *n*-butyllithium (1.6 M in *n*-hexane, 1.2 equiv.) at –78 °C in dry THF (30 mL) and diisopropylamine (1.1 equiv.). One of the benzaldimines **1a**–**c** (1.5 mmol, 1 equiv.) was dissolved in THF (10 mL), and the solution was added dropwise to the LDA solution over a period of 30 min. After 1.5 h of stirring at –78 °C, the reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was then treated with the appropriate electrophile (2 equiv.) and was again stirred at 0 °C for 30 min. The mixture was allowed to warm to room temperature and, after aqueous workup and extraction with diethyl ether, the combined organic layers were dried with magnesium sulfate. The solvent was evaporated under reduced pressure, and the product was purified by column chromatography (silica gel; P/EA, 10:1 to 5:1] and by subsequent recrystallisation (*n*-heptane/$CHCl_3$).

Ethyl 4-Methyl-3-phenyl-2,3-dihydro-1*H*-2-benzazepine-2-carboxylate (3f): This compound was synthesised from (benzyl){2-[(*E*/*Z*)-prop-1-enyl]benzylidene}amine (**1a**,[9] 352 mg, 1.50 mmol), LDA (1.65 mmol) and ethyl chloroformate (2.5 equiv., 3.75 mmol, 0.30 mL). The crude product was purified by column chromatography (silica gel; P/EA, 8:1). The compound was isolated as a colourless oil in a yield of 62% (286 mg, 0.93 mmol). R_f (TLC) = 0.40 (silica gel; PE/EA, 8:1). ^{1}H NMR (499.83 MHz, [D$_8$]toluene, 373 K): δ = 0.92 (br. s, CH_3, 3 H), 1.73 (s, 3 H, CH=CCH_3), 3.85 (q, ^3J = 7.0 Hz, 2 H, OCH_2), 4.02 (d, ^2J = 15.5 Hz, 1 H, CH*H*N), 4.20 (br. s, 1 H, C*H*HN), 6.26 (br. s, 1 H, *H*CC$_6$H$_5$), 6.36 (s, 1 H, *H*C=CCH$_3$), 6.88–7.11, 7.32–7.33 (m, 9 H, C$H_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, [D$_8$]toluene, 373 K): δ = 14.6 (CH$_2$*C*H$_3$), 24.9 (*C*H$_3$), 47.2 (*C*H$_2$N), 61.4 (O*C*H$_2$), 64.8 (H*C*C$_6$H$_5$), 126.5, 127.3, 127.9, 128.4, 128.9, 129.8, 130.2 (*C*H$_{arom.}$), 132.0 (H*C*=CCH$_3$), 135.5, 138.6, 139.6, 141.9 (C_{ipso}), 161.7 (*C*=O) ppm. IR (film): $\tilde{\nu}$ = 3055 (m, $CH_{arom.,olef.}$), 3030 (m, $CH_{arom.,olef.}$), 2983 (m, $CH_{arom.,olef.}$), 2931 (m, $CH_{aliph.}$), 1689 [vs, RO(CO)NR$_2$], 1602 (vw), 1490 (m), 1485 (m), 1456 (s), 1442 (m), 1417 (s), 1382 (m), 1326 (m), 1303 (m), 1265 (s), 1201 (m), 1180 (w), 1139 (w), 1118 (s), 1026 (m), 958 (vw), 896 (m), 831 (vw), 738 (vs), 705 (vs) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* = 307.3 [M]$^+$, 292.2 [M – CH_3]$^+$, 278.2 [M – C_2H_5]$^+$, 234.2 [M – $CH_3CH_2O(CO)$]$^+$, 218.2 [M – $H_2N(C=O)OCH_2CH_3$]$^+$, 204.2 [218 – CH_3]$^+$, 189.2, 178.2, 156.0, 143.2, 129.2, 115.2, 104.2 [PhCH=CH_2], 91.2, 77.2 [C_6H_5]$^+$, 65.2. MS (MicroTOF): calcd. 387.2795 [M + H]$^+$; found 387.2796 [M + H]$^+$. $C_{20}H_{21}NO_2$ (307.39): calcd. C 78.15, H 6.89, N 4.56; found C 77.89, H 6.85, N 4.39.

Methyl 3,4-Diphenyl-2,3-dihydro-1*H*-2-benzazepine-2-carboxylate (3g): This compound was synthesised from (benzyl)[(*E*/*Z*)-2-styrylbenzylidene]amine (**1b**,[9] 445 mg, 1.50 mmol), LDA (1.65 mmol) and methyl chloroformate (2.5 equiv., 3.75 mmol, 0.30 mL). The crude product was purified by column chromatography (silica gel; P/EA, 8:1, 6:1). The compound was isolated as a slowly crystallizing colourless oil in a yield of 40% (212 mg, 0.60 mmol). R_f (TLC) = 0.24 (silica gel; PE/EA, 8:1), m.p. 111–112 °C. ^{1}H NMR (499.83 MHz, [D$_8$]toluene, 348 K): δ = 3.41 (s, 3 H, CH_3), 4.08 (d, ^2J = 9.6 Hz, 1 H, CH*H*N), 4.24 (s, 1 H, CH*H*N), 6.81 (s, 1 H, *H*C=CC$_6$H$_5$), 6.87–7.00 (m, 8 H, C$H_{arom.}$), 7.06–7.08 (m, 2 H, C$H_{arom.}$), 7.17 (s, 1 H, *H*CC$_6$H$_5$), 7.32 (s, 2 H, C$H_{arom.}$), 7.44 (s, 2 H, C$H_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, [D$_8$]toluene, 348 K): δ = 47.5 (O*C*H$_3$), 52.5 (*C*H$_2$N), 63.4 (H*C*C$_6$H$_5$), 127.3, 127.4, 127.6, 127.7, 127.8, 128.71, 128.74, 128.8 (*C*H$_{arom.}$), 130.0 (C_{ipso}), 132.6 (H*C*=CCH$_3$), 133.6 (C_{ipso}), 139.7 (*C*H$_{arom.}$), 141.5 (C_{ipso}), 143.4 (HC=*C*C$_6$H$_5$), 156.3 (*C*=O) ppm. IR (KBr): $\tilde{\nu}$ = 3101 (vw, $CH_{arom.,olef.}$), 3078 (vw, $CH_{arom.,olef.}$), 3058 (w, $CH_{arom.,olef.}$), 3043 (w, $CH_{arom.,olef.}$), 3026 (m, $CH_{arom.,olef.}$), 2956 (w, $CH_{aliph.}$), 2923 (w, $CH_{aliph.}$), 2869 (w, $CH_{aliph.}$), 2852 (w, $CH_{aliph.}$), 1681 [vs, RO(CO)NR$_2$], 1598 (m), 1573 (m), 1492 (s), 1467 (vs), 1454 (s), 1433 (s), 1404 (s), 1377 (m), 1365 (m), 1321 (s), 1303 (m), 1278 (s), 1259 (s), 1232 (s), 1207 (s), 1191 (s), 1178 (s), 1155 (m), 1120 (s), 1074 (m), 1031 (m), 1016 (m), 1001 (m), 985 (w), 952 (m), 916 (m), 898 (m), 879 (w), 831 (m), 786 (w), 754 (vs), 738 (m), 702 (vs), 651 (m), 632 (m), 576 (m), 563 (m), 547 (m), 536 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 355 (100) [M]$^+$, 280 (40) [M – $NH_2(CO)OCH_3$]$^+$, 264 (24) [M – C_7H_7]$^+$, 207 (30), 178 (28), 82.9 (67), 57 (22). MS (MicroTOF): calcd. 378.1465 [M + Na]$^+$; found 378.1464 [M + Na]$^+$. $C_{24}H_{21}NO_2$ (355.43): calcd. C 81.10, H 5.96, N 3.94; found C 80.60, H 5.86, N 3.77.

Ethyl 3-Phenyl-4-propyl-2,3-dihydro-1*H*-2-benzazepine-2-carboxylate (3h): This compound was synthesised from (benzyl){2-[(*E*/*Z*)-pent-1-enyl]benzylidene}amine (**1c**,[9] 394 mg, 1.50 mmol), LDA (1.65 mmol) and ethyl chloroformate (2.5 equiv., 3.75 mmol, 0.30 mL). The crude product was purified by column chromatography (silica gel; P/EA, 8:1). The compound was isolated as a colourless oil in a yield of 73% (366 mg, 1.09 mmol). R_f (TLC) = 0.20 (silica gel; PE/EA, 8:1). ^{1}H NMR (499.83 MHz, [D$_8$]toluene, 348 K): δ = 0.85 (t, ^3J = 7.5 Hz, 3 H, CH$_2$CH$_2$CH_3), 1.12 (d, ^3J = 6.5 Hz, 3 H, CH_3CH$_2$O), 1.55 (m, 2 H, CH$_2$CH_2CH$_3$), 2.06 (m, 2 H, CH_2CH$_2$CH$_3$), 3.94 (q, ^3J = 6.5 Hz, 2 H, OCH_2), 4.03 (d, ^2J = 15.5 Hz, 1 H, CH*H*N), 4.19 (br. s, 1 H, C*H*HN), 6.44 (br. s, 1 H,

HCC_6H_5), 6.49 (s, 1 H, $HC{=}CCH_2$), 6.93–7.16, 7.37–7.38 (m, 9 H, $CH_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, [D$_8$]toluene, 348 K): δ = 14.6 ($CH_2CH_2CH_3$), 21.2 (CH_3CH_2O), 22.8 ($CH_2CH_2CH_3$), 40.5 ($CH_2CH_2CH_3$), 47.3 (CH_2N), 61.4 (OCH_2), 63.3 (HCC_6H_5), 126.5, 127.3, 127.8, 127.9, 128.4, 128.9, 129.6 ($CH_{arom.}$), 130.0 ($HC{=}C–CH_2$), 132.3 ($CH_{arom.}$), 135.4, 139.5, 141.9, 143.4 (C_{ipso}), 155.2 ($C{=}O$) ppm. IR (film): $\tilde{\nu}$ = 3060 (w, $CH_{arom.,olef.}$), 3028 (w, $CH_{arom.,olef.}$), 2962 (m, $CH_{arom.,olef.}$), 2931 (m, $CH_{aliph.}$), 2871 (w, $CH_{aliph.}$), 1739 (w), 1695 [s, RO(CO)NR$_2$], 1600 (vw), 1492 (m), 1454 (m), 1415 (m), 1373 (m), 1323 (m), 1307 (m), 1290 (m), 1275 (m), 1251 (m), 1201 (m), 1174 (w), 1159 (w), 1118 (m), 1029 (w), 960 (vw), 906 (w), 837 (vw), 754 (m), 707 (m) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* = 335.3 [M]$^+$, 306.2 [M – CH_2CH_3]$^+$, 292.2 [M – $CH_2CH_2CH_3$]$^+$, 278.2 [M – C_4H_9]$^+$, 262.3, 246.2 [278 – CH_4O]$^+$, 234.2, 217.2, 203.2, 189.2, 172.2, 170.2, 162.2, 142.2, 128.2, 115.2, 104.2 [PhCH=CH$_2$]$^+$, 91.2, 77.2. MS (MicroTOF): calcd. 358.1778 [M + Na]$^+$; found 358.1778 [M + Na]$^+$. $C_{22}H_{25}NO_2$ (335.44): calcd. C 78.77, H 7.51, N 4.18; found C 78.74, H 7.49, N 4.06.

***N*,*N*-Diethyl-3-phenyl-4-propyl-2,3-dihydro-1*H*-2-benzazepin-2-carboxamide (3i):** This compound was synthesised from (benzyl){2-[(*E*/*Z*)-pent-1-enyl]benzylidene}amine (**1c**,[9] 394 mg, 1.50 mmol), LDA (1.65 mmol) and *N*,*N*-diethylcarbamoyl chloride (1.5 equiv., 3.00 mmol, 0.38 mL). The crude product was purified by column chromatography (silica gel; P/EA, 8:1). The compound was isolated as a yellow oil in a yield of 63% (340 mg, 0.94 mmol). R_f (TLC) = 0.27 (silica gel; PE/EA, 8:1). ^1H NMR (499.83 MHz, $CDCl_3$, 298 K): δ = 0.96 (t, ^3J = 7.5 Hz, 3 H, $CH_2CH_2CH_3$), 1.0 [t, ^3J = 7.0 Hz, 6 H, (CO)NCH$_2$CH_3, (CO)NCH$_2$CH_3], 1.58 (m, 2 H, $CH_2CH_2CH_3$), 2.17 (t, ^3J = 7.5 Hz, 2 H, $CH_2CH_2CH_3$), 3.05 [dq, ^3J = 7.0, 14.0 Hz, 2 H, (CO)NCH_2], 3.27 [dq, ^3J = 7.0, 14.0 Hz, 2 H, (CO)NCH_2], 4.11 (d, ^2J = 16.0 Hz, 1 H, CH*H*N), 4.19 (d, ^2J = 16.0 Hz, 1 H, C*H*HN), 5.85 (s, 1 H, HCC_6H_5), 6.58 (s, 1 H, $HC{=}CCH_2$), 7.07–7.10, 7.23–7.40 (m, 9 H, $CH_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, $CDCl_3$, 298 K): δ = 13.2 [(CO)NCH$_2$CH_3], 14.0 ($CH_2CH_2CH_3$), 22.3 ($CH_2CH_2CH_3$), 39.9 ($CH_2CH_2CH_3$), 42.5 [(CO)NCH_2], 48.9 (CH_2N), 64.5 (HCC_6H_5), 125.9, 127.0, 127.4, 127.7, 128.3 ($CH_{arom.}$), 128.4 ($HC{=}C–CH_2$), 129.7, 131.8 ($CH_{arom.}$), 134.9, 138.4, 141.5, 143.3 (C_{ipso}), 164.1 [N(*C*O)N] ppm. IR (film): $\tilde{\nu}$ = 3058 (m, $CH_{arom.,olef.}$), 3026 (m, $CH_{arom.,olef.}$), 2962 (s, $CH_{arom.,olef.}$), 2931 (m, $CH_{aliph.}$), 2871 (w, $CH_{aliph.}$), 1739 (w), 1637 [s, NR$_2$(CO)NR$_2$], 1583 (w), 1492 (m), 1452 (s), 1409 (s), 1379 (s), 1357 (m), 1338 (m), 1317 (m), 1303 (m), 1271 (s), 1251 (s), 1209 (m), 1172 (m), 1110 (m), 1080 (m), 1029 (w), 1012 (w), 956 (w), 939 (w), 921 (vw), 894 (vw), 879 (vw), 864 (vw), 840 (vw), 754 (s), 736 (m), 702 (s) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* = 362.3 [M]$^+$, 347.3 [M – CH_3]$^+$, 333.3 [M – CH_2CH_3]$^+$, 319.3 [M – $CH_2CH_2CH_3$]$^+$, 289.2, 262.2 [M – (CO)N(CH_2CH_3)$_2$]$^+$, 260.2, 246.2 [262 – NH_2]$^+$, 230.2, 217.2 [246.2 – CH_2CH_3]$^+$, 203.2 [217 – CH_2]$^+$, 191.2, 178.2, 170.2, 165.2, 141.2, 129.2, 115.2, 100.2 [(CO)NCH$_2$CH$_3$]$^+$, 91.2, 72.2, 65.2, 58.2, 44.1. MS (MicroTOF): calcd. 363.2431 [M + H]$^+$; found 363.2418 [M + H]$^+$. $C_{24}H_{30}N_2O$ (362.51): calcd. C 79.52, H 8.34, N 7.73; found C 79.12, H 8.38, N 7.59.

General Procedure for the Synthesis of Compounds 11a, 11b, 13a and 13b: Lithium diisopropylamide (LDA) was freshly prepared at –78 °C under argon from *n*-butyllithium (1.6 M in *n*-hexane, 1.2 equiv.) in dry THF (30 mL) and diisopropylamine (1.1 equiv.). One of the benzaldimines (1 equiv., 1.5 mmol) was dissolved in THF (10 mL), and the solution was added dropwise over a period of 30 min to the LDA solution. After 1.5 h of stirring at –78 °C, the reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was then cooled to –78 °C and treated with the appropriate electrophile (2 equiv.). Stirring was then continued for 2 h. The mixture was allowed to warm to room temperature and stirred for 18 h, and after aqueous workup and extraction with diethyl ether, the combined organic layers were dried with magnesium sulfate. The solvent was evaporated under reduced pressure, and the product was purified by column chromatography (silica gel; P/EA, 10:1 to 5:1) and by subsequent recrystallisation (*n*-heptane/$CHCl_3$).

(Cyclopentyl)[2,2-dimethyl-1-(4-methyl-3-phenyl-4,5-dihydro-3*H*-2-benzazepin-5-yl)propylidene]amine (11a): This compound was synthesised from **1a**[9] (352 mg, 1.50 mmol), LDA (1.65 mmol) and *N*-cyclopentyl-2,2,2-trimethylacetimidoyl chloride (**10**,[21] 1.0 equiv., 1.45 mmol, 271 mg). The crude product was purified by column chromatography (silica gel; P/EA, 10:1). The compound was isolated as a yellow solid in a yield of 29% (160 mg, 0.41 mmol). R_f (TLC) = 0.45 (silica gel; PE/EA, 10:1), m.p. 96 °C. The solid should be stored under argon. ^1H NMR (600.14 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 7.2 Hz, 3 H, CH_3), 0.98 [s, 9 H, C(CH_3)$_3$], 1.43, 1.59–1.68, 1.75–1.99 [m, 8 H, (CH_2)$_4$], 3.25 (m, 1 H, $HCCH_3$), 3.68 [d, ^3J = 10.8 Hz, 1 H, $HCC(CH_3)_3$], 4.34 [q, ^3J = 5.4 Hz, 1 H, $HC(CH_2)_4$], 4.59 (dd, ^4J = 1.8, ^3J = 4.2 Hz, 1 H, HCC_6H_5), 7.07 (m, 1 H, $CH_{arom.}$), 7.21 (m, 1 H, $CH_{arom.}$), 7.31–7.36 (m, 5 H, $CH_{arom.}$), 7.48 (m, 2 H, $CH_{arom.}$), 8.77 (s, 1 H, $HC{=}N$) ppm. ^{13}C NMR (150.84 MHz, $CDCl_3$): δ = 14.7 (CH_3), 25.1 (CH_2), 28.9 [C(CH_3)$_3$], 33.8 (CH_2), 41.4 [$C(CH_3)_3$], 49.4 [$HCC(=N)C(CH_3)_3$], 53.4 ($HCCH_3$), 62.5 [$HC(CH_2)_4$], 65.9 (HCC_6H_5), 126.4, 126.7, 127.3, 128.0, 128.2, 128.3, 129.5 ($CH_{arom.}$), 134.2, 138.7, 142.6 (C_{ipso}), 163.2 ($HC{=}N$), 169.7 ($C{=}N$) ppm. IR (KBr): $\tilde{\nu}$ = 3055 (s, $CH_{arom.,olef.}$), 2964 (s, $CH_{aliph.}$), 2870 (m, $CH_{aliph.}$), 1732 (vw), 1627 (m, C=N), 1602 (w), 1492 (w), 1477 (m), 1450 (m), 1421 (m), 1392 (w), 1377 (w), 1365 (w), 1265 (vs), 1209 (vw), 1029 (vw), 1012 (vw), 968 (vw), 943 (vw), 896 (m), 738 (vs), 705 (vs) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* = 386.3 [M]$^+$, 371.3 [M – CH_3]$^+$, 355.3, 341.1, 329.3 [M – $(CH_3)_3$]$^+$, 312.3, 301.3 [M – $C_5H_9NH_2$]$^+$, 286.3, 261.2, 244.2, 234.2 [M –$(CH_3)_3CNC_5H_9$]$^+$, 219.2 [234 – CH_3]$^+$, 207.2, 196.2, 186.3, 170.2, 152.3 [$(CH_3)_3CNC_5H_9$]$^+$, 143.2, 129.2, 115.2, 104.2, 91.2, 84.2, 77.2 [C_6H_5]$^+$, 65.2 [C_5H_5]$^+$, 57.2 [$C(CH_3)_3$]$^+$, 41.1. MS (MicroTOF): calcd. 387.2795 [M + H]$^+$; found 387.2796 [M + H]$^+$. $C_{27}H_{34}N_2$ (386.58): calcd. C 83.89, H 8.86, N 7.25; found C 83.42, H 8.83, N 7.14.

X-ray Crystal Structure Analysis for 11a:[16,17] Formula $C_{27}H_{34}N_2$, M = 386.56, light yellow crystal 0.30 × 0.20 × 0.10 mm, a = 12.478(1), b = 14.463(1), c = 14.005(1) Å, β = 115.51(1)°, V = 2281.1(3) Å^3, $\rho_{calcd.}$ = 1.126 g cm^{-3}, μ = 0.490 mm^{-1}, empirical absorption correction ($0.867 \leq T \leq 0.953$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 17633 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 4016 independent (R_{int} = 0.069) and 3000 observed reflections [$I \geq 2\sigma(I)$], 266 refined parameters, R = 0.072, wR^2 = 0.240, max/min residual electron density 0.31/–0.28 e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

(Cyclopentyl)[2,2-dimethyl-1-(3-phenyl-4-propyl-4,5-dihydro-3*H*-2-benzazepin-5-yl)propylidene]amine (11b): This compound was synthesised from **1c**[9] (394 mg, 1.50 mmol), LDA (1.65 mmol) and *N*-cyclopentyl-2,2,2-trimethylacetimidoyl chloride (**10**,[21] 1.0 equiv., 1.45 mmol, 271 mg). The crude product was purified by column chromatography (silica gel; P/EA/TEA, 20:1:1). The compound was isolated as a yellow, viscous oil in a yield of 21% (128 mg, 0.31 mmol). R_f (TLC) = 0.63 (silica gel; PE/EA/TEA, 20:1:1). The oil should be stored under argon. ^1H NMR (600.14 MHz, [D$_6$]benzene): δ = 0.74 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.15 [s, 9 H, C(CH_3)$_3$], 1.44–1.52, 1.64–1.81, 1.93–2.10 [m, 12 H, CH_2CH_2, (CH_2)$_4$], 3.48 [m, 1 H, $HC(CH_2)_2CH_3$], 4.08 [d, ^3J = 10.2 Hz, 1 H, $HCC(=N)$-$C(CH_3)_3$], 4.42 [q, ^3J = 4.8 Hz, 1 H, $HC(CH_2)_4$], 4.91 (m, 1 H, HCC_6H_5), 6.97 (m, 1 H, $CH_{arom.}$), 7.05 (m, 1 H, $CH_{arom.}$), 7.13–

7.32 (m, 5 H, C$H_{arom.}$), 7.81 (m, 2 H, C$H_{arom.}$), 8.66 (s, 1 H, HC=N) ppm. ^{13}C NMR (150.84 MHz, [D$_6$]benzene): δ = 14.8 (CH$_3$), 22.3, 25.5, 25.6 (CH$_2$), 29.2 [C(CH$_3$)$_3$], 32.5, 34.6, 36.1 (CH$_2$), 41.7 [C(CH$_3$)$_3$], 48.4 [HC–C(=N)C(CH$_3$)$_3$], 58.7 [HC-(CH$_2$)$_2$CH$_3$], 62.8 [HC(CH$_2$)$_4$], 65.9 (HCC$_6$H$_5$), 126.7, 127.0, 127.6, 128.0, 128.3, 128.5, 128.6, 128.9, 129.4 (CH$_{arom.}$), 134.9, 139.2, 143.5 (C_{ipso}), 161.6 (HC=N), 170.8 (C=N) ppm. IR (film): $\tilde{\nu}$ = 3060 (m, CH$_{arom.,olef.}$), 3024 (m, CH$_{arom.,olef.}$), 2958 (s, CH$_{arom.,olef.}$), 2933 (vs, CH$_{arom.,olef.}$), 2870 (vs, CH$_{aliph.}$), 1674 (w), 1627 (s, C=N), 1600 (m), 1583 (w), 1571 (w), 1492 (m), 1475 (s), 1465 (s), 1450 (s), 1390 (m), 1377 (m), 1364 (m), 1288 (m), 1263 (w), 1224 (w), 1207 (m), 1176 (w), 1157 (w), 1072 (m), 1029 (m), 999 (w), 983 (vw), 952 (vw), 923 (w), 900 (w), 871 (vw), 840 (vw), 756 (s), 736 (m), 702 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 414 (49) [M]$^+$, 357 (80) [M – C(CH$_3$)$_3$]$^+$, 289 (99), 262 (51) [(M$^+$ – CH$_3$)$_3$CNC$_5$H$_9$]$^+$, 186 (17), 152 (69) [(CH$_3$)$_3$CNC$_5$H$_9$]$^+$, 83 (100). MS (MicroTOF): calcd. 415.3108 [M + H]$^+$; found 415.3106 [M + H]$^+$. C$_{29}$H$_{38}$N$_2$ (414.63): calcd. C 84.01, H 9.24, N 6.76; found C 83.82, H 9.40, N 6.55.

12-*tert*-Butyl-13-methyl-10-phenyl-11-oxa-9-azatricyclo[8.2.1.0^{2,7}]-trideca-2(7),3,5-triene (13a): This compound was synthesised from **1a**[9] (352 mg, 1.50 mmol), LDA (1.65 mmol) and pivaldehyde (**12**, 2.0 equiv., 3.00 mmol, 0.33 mL). The crude product was purified by column chromatography (silica gel; P/EA, 10:1). The compound was isolated as a colourless solid in a yield of 44% (120 mg, 0.37 mmol). R_f (TLC) = 0.42 (silica gel; PE/EA, 10:1), m.p. 129–130 °C. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 0.60 (d, ^3J = 6.9 Hz, 3 H, CH_3), 0.97 [s, 9 H, C(CH_3)$_3$], 2.07 (br. s, 1 H, NH), 2.17 (dt, ^3J = 7.2, 14.7 Hz, 1 H, HCCH$_3$), 3.12 [d, ^3J = 7.8 Hz, 1 H, HCCHC(CH$_3$)$_3$], 3.68 (d, ^2J = 14.5 Hz, 1 H, NHCHH), 4.16 [d, ^3J = 1.5 Hz, 1 H, HCCHC(CH$_3$)$_3$], 4.67 (d, ^2J = 14.5 Hz, 1 H, NHCHH), 6.96 (m, 1 H, C$H_{arom.}$), 7.07–7.08 (m, 3 H, C$H_{arom.}$), 7.17–7.26 (m, 3 H, C$H_{arom.}$), 7.60–7.63 (m, 2 H, C$H_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$, 298 K): δ = 10.6 (CH$_3$), 35.9 [C(CH$_3$)$_3$], 47.3 (CH$_2$N), 48.7 [HCCHC(CH$_3$)$_3$], 53.4 (HCCH$_3$), 92.2 [HCCHC(CH$_3$)$_3$], 99.5 (C$_q$C$_6$H$_5$), 125.0 (o-CH$_{arom.}$), 126.4 (4′-CH$_{arom.}$), 127.0 (3′-CH$_{arom.}$), 127.4 (p-CH$_{arom.}$), 128.1 (m-CH$_{arom.}$), 129.1 (2′-CH$_{arom.}$), 129.4 (5′-CH$_{arom.}$), 138.4 (6′-CH$_{arom.}$), 141.6 (1′-CH$_{arom.}$), 145.2 (C_{ipso}) ppm. IR (KBr): $\tilde{\nu}$ = 3394 (m, R$_2$NH), 3365 (s, R$_2$NH), 3078 (m, CH$_{arom.,olef.}$), 3028 (s, CH$_{arom.,olef.}$), 3008 (m, CH$_{arom.,olef.}$), 2987 (s, CH$_{arom.,olef.}$), 2950 (vs, CH$_{aliph.}$), 2912 (vs, CH$_{aliph.}$), 2868 (vs, CH$_{aliph.}$), 2841 (vs, CH$_{aliph.}$), 2727 (m, CH$_{aliph.}$), 2675 (m, CH$_{aliph.}$), 1982 (w), 1949 (m), 1911 (m), 1880 (m), 1836 (w), 1807 (m), 1774 (w), 1757 (w), 1737 (w), 1624 (m), 1602 (m), 1492 (s), 1477 (s), 1456 (vs), 1392 (s), 1373 (s), 1361 (vs), 1326 (s), 1303 (m), 1286 (s), 1267 (s), 1249 (m), 1205 (s), 1180 (s), 1161 (m), 1136 (vs), 1116 (vs), 1097 (vs), 1072 (s), 1031 (s), 1002 (vs), 956 (s), 921 (vs), 908 (vs), 885 (s), 877 (s), 823 (s), 796 (w), 752 (vs), 736 (vs), 705 (vs), 624 (s), 613 (s), 580 (s), 541 (s), 528 (s) cm^{-1}. GC-MS (EI, 70 eV): m/z = 321.3 [M]$^+$, 304.3 [M – OH]$^+$, 289.2, 265.2 [M – C(CH$_3$)$_3$]$^+$, 246.2, 235.2, 265.2 [M – CH$_2$O]$^+$, 220.2, 206.2, 187.3, 170.2, 157.2, 146.2, 144.2, 130.2, 115.2, 105.1, 91.2, 77.1, 65.2, 57.2, 41.1. MS (MicroTOF): calcd. 322.2165 [M + H]$^+$; found 322.2167 [M + H]$^+$. C$_{22}$H$_{27}$NO (321.46): calcd. C 82.20, H 8.47, N 4.36; found C 82.01, H 8.29, N 4.36.

X-ray Crystal Structure Analysis for 13a:[16,17] Formula C$_{22}$H$_{27}$NO, M = 321.45, colourless crystal 0.40 × 0.25 × 0.25 mm, a = 9.562(1), b = 9.898(1), c = 10.298(1) Å, α = 98.29(1), β = 110.47(1), γ = 94.44(1)°, V = 894.9(2) Å^3, $\rho_{calcd.}$ = 1.193 g cm^{-3}, μ = 0.553 mm^{-1}, empirical absorption correction ($0.809 \le T \le 0.874$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 10385 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 3133 independent (R_{int} = 0.036) and 2973 observed reflections [$I \ge 2\sigma(I)$], 225 refined parameters, R = 0.041, wR^2 = 0.112, max/min residual electron density 0.21/–0.15 e Å^{-3}, hydrogen atom at N1 from difference Fourier calculations, others calculated and refined as riding atoms.

12-*tert*-Butyl-10-phenyl-13-propyl-11-oxa-9-azatricyclo[8.2.1.0^{2,7}]-trideca-2(7),3,5-triene (13b): This compound was synthesised from **1c**[9] (394 mg, 1.50 mmol), LDA (1.65 mmol) and pivaldehyde (**12**, 2.0 equiv., 3.00 mmol, 0.33 mL). The crude product was purified by column chromatography (silica gel; P/EA, 10:1). The compound was isolated as a colourless oil in a yield of 38% (201 mg, 0.57 mmol). R_f (TLC) = 0.50 (silica gel; PE/EA, 10:1). ^{1}H NMR (499.83 MHz, CDCl$_3$, 298 K): δ = 0.61 (t, ^3J = 7.0 Hz, 3 H, CH_3), 0.93–1.32 (m, 4 H, CH$_2$CH_2CH$_3$, CH_2CH$_2$CH$_3$), 1.08 [s, 9 H, C(CH_3)$_3$], 2.12 (dt, ^3J = 8.0, 10.8, ^4J = 2.9 Hz, 1 H, HCCH$_2$CH$_2$CH$_3$), 2.18 (br. s, NH, 1 H), 3.34 [dd, ^3J = 8.0, 1.8 Hz, 1 H, HCCHC(CH$_3$)$_3$], 3.81 (d, ^2J = 14.5 Hz, 1 H, NHCHH), 4.24 [d, ^3J = 1.5 Hz, 1 H, HCCHC(CH$_3$)$_3$], 4.77 (d, ^2J = 14.5 Hz, 1 H, NHCHH), 7.08 (m, 1 H, 2′-C$H_{arom.}$), 7.17–7.20 (m, 3 H, 3′-,4′-,5′-C$H_{arom.}$), 7.27–7.30 (m, 1 H, p-C$H_{arom.}$), 7.33–7.36 (m, 2 H, m-C$H_{arom.}$), 7.74–7.76 (m, 2 H, o-C$H_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, CDCl$_3$, 298 K): δ = 14.1 (CH$_2$CH$_2$$CH_3$), 20.5 ($CH_2CH_3$), 26.0 [C($CH_3$)$_3$], 27.1 ($CH_2CH_2CH_3$), 35.9 [$C$(CH$_3$)$_3$], 48.7 ($CH_2$N), 51.01 [H$C$CHC(CH$_3$)$_3$], 53.3 (H$CCH_2CH_2CH_3$), 92.4 [HC$C$HC(CH$_3$)$_3$], 99.4 (C$_qC_6H_5$), 125.3 ($o$-$CH_{arom.}$), 126.4 (4′-$CH_{arom.}$), 126.9 (3′-$CH_{arom.}$), 127.4 ($p$-$CH_{arom.}$), 128.1 ($m$-$CH_{arom.}$), 129.3 (2′-$CH_{arom.}$), 129.4 (5′-$CH_{arom.}$), 138.5 (6′-$CH_{arom.}$), 141.1 (1′-$CH_{arom.}$), 145.3 ($C_{ipso}$) ppm. IR (film): $\tilde{\nu}$ = 3356 (w, R$_2$NH), 3053 (m, CH$_{arom.,olef.}$), 3030 (m, CH$_{arom.,olef.}$), 2958 (s, CH$_{aliph.}$), 2933 (s, CH$_{aliph.}$), 2871 (m, CH$_{aliph.}$), 1490 (m), 1477 (s), 1479 (m), 1465 (m), 1454 (m), 1421 (m), 1398 (w), 1361 (m), 1325 (w), 1265 (vs), 1217 (w), 1201 (w), 1182 (w), 1114 (m), 1083 (w), 1045 (m), 1026 (m), 1012 (m), 989 (m), 966 (w), 941 (w), 933 (w), 914 (m), 896 (m), 823 (vw), 740 (vs), 703 (s), 615 (vw), 586 (vw), 476 (vs) cm^{-1}. GC-MS (EI, 70 eV): m/z = 349.3 [M]$^+$, 332.2, 317.3, 292.3 [M – C(CH$_3$)$_3$]$^+$, 274.3, 262.3 [M – C(CH$_3$)$_3$ – CH$_2$O]$^+$, 246.3, 232.2, 220.2 [262 – CH$_2$CH$_2$CH$_3$]$^+$, 205.2, 184.2, 171.2, 158.2, 143.2, 129.2, 115.2, 105.2, 91.2, 77.2, 57.2, 41.1. MS (MicroTOF): calcd. 350.2478 [M + H]$^+$; found 350.2483 [M + H]$^+$. C$_{24}$H$_{31}$NO (349.51): calcd. C 82.48, H 8.94, N 4.01; found C 82.18, H 8.65, N 3.83.

General Procedure B for the Synthesis of 2,3-Dihydro-1*H*-2-benzazepines 5a–g: Lithium diisopropylamide (LDA) was freshly prepared at –78 °C under argon from *n*-butyllithium (1.6 M in *n*-hexane, 1.2 equiv.) in dry THF (30 mL) and diisopropylamine (1.1 equiv.). One of the *N*-allylimines **4a**–**c** (1 equiv., 1.5 mmol) was dissolved in THF (10 mL) and added to the LDA solution dropwise over a period of 30 min. After 1.5 h of stirring at –78 °C, the reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was then cooled to –78 °C and treated with the appropriate electrophile (2 equiv.). It was again stirred for 2 h. The mixture was allowed to warm quickly to room temperature and, after aqueous workup and extraction with diethyl ether, the combined organic layers were dried with magnesium sulfate. The solvent was evaporated under reduced pressure, and the product was purified by column chromatography (silica gel; P/EA, 10:1 to 5:1) and by subsequent recrystallisation (*n*-heptane/CHCl$_3$). For the synthesis of **5a**, see ref.[7]

2,2-Dimethyl-1-(4-phenyl-3-vinyl-2,3-dihydro-1*H*-2-benzazepin-2-yl)propan-1-one (5b): This compound was synthesised from **4b**[9] (370 mg, 1.50 mmol), LDA (1.65 mmol) and pivaloyl chloride (1.5 equiv., 3.00 mmol, 0.37 mL). The crude product was purified by column chromatography (silica gel; P/EA, 8:1). The compound was isolated as a colourless solid in a yield of 52% (258 mg,

0.78 mmol). R_f (TLC) = 0.35 (silica gel; PE/EA, 8:1), m.p. 135–136 °C. ^{1}H NMR (499.83 MHz, [D$_8$]toluene, 348 K): δ = 1.21 [s, 9 H, C(CH_3)$_3$], 4.16 (d, ^2J = 15.0 Hz, 1 H, NCHH), 4.92 (d, ^2J = 15.0 Hz, 1 H, NCHH), 5.00 (d, ^3J = 10.5 Hz, 1 H, CHCH=CHH), 5.03 (d, ^3J = 17.0 Hz, 1 H, CHCH=CHH), 5.70 (m, 1 H, CHCH=CH$_2$), 6.27 (s, 1 H, HCCHCH$_2$), 6.70 (s, 1 H, HC=CC$_6$H$_5$), 6.98–7.26, 7.42–7.44 (m, 9 H, C$H_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, [D$_8$]toluene, 348 K): δ = 28.9 [C(CH_3)$_3$], 39.2 [C(CH$_3$)$_3$], 49.2 (CH_2), 63.0 (HCCHCH$_2$), 118.4 (CHCH=CHH), 127.2, 127.4, 127.7, 127.8, 127.9, 128.7, 128.9, 129.4, 132.7 (C$H_{arom.}$), 132.0 (CH=CC$_6$H$_5$), 134.9, 137.1, 139.8, 142.9, 143.6 (C_{ipso}, CHCH=CH$_2$), 176.0 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3053 (s, CH$_{arom.,olef.}$), 3026 (s, CH$_{arom.,olef.}$), 2979 (vs, CH$_{aliph.}$), 2931 (s, CH$_{aliph.}$), 2908 (s, CH$_{aliph.}$), 2871 (m, CH$_{aliph.}$), 1625 [vs, (CO)NR$_2$], 1595 (vs), 1573 (s), 1494 (vs), 1477 (vs), 1442 (vs), 1409 (vs), 1387 (s), 1367 (vs), 1332 (s), 1311 (vs), 1284 (vs), 1199 (vs), 1182 (vs), 1155 (s), 1114 (s), 1078 (s), 1043 (s), 1033 (s), 997 (s), 983 (s), 960 (s), 943 (s), 931 (vs), 908 (m), 883 (m), 856 (w), 835 (w), 786 (s), 756 (vs), 736 (s), 696 (vs), 634 (s), 595 (m), 570 (s), 540 (s), 520 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z = 331.3 [M]$^+$, 316.3 [M – CH$_3$]$^+$, 302.3 [M – C$_2$H$_5$]$^+$, 298.3, 287.3, 274.2 [M – tBu]$^+$, 246.2 [274 – C$_2$H$_4$]$^+$, 230.2 [M – HN(C=O)C(CH$_3$)$_3$]$^+$, 218.2, 204.2, 191.2, 178.2, 165.2, 152.2, 140.2, 128.2, 115.2, 90.2, 57.2. MS (MicroTOF): calcd. 354.1828 [M + Na]$^+$; found 354.1830 [M + Na]$^+$. C$_{23}$H$_{25}$NO (331.45): calcd. C 83.34, H 7.60, N 4.23; found C 83.15, H 7.42, N 4.12.

2,2-Dimethyl-1-(4-methyl-3-prop-1-enyl-2,3-dihydro-1*H*-2-benzazepin-2-yl)propan-1-one (5c): This compound was synthesised from (2-methylallyl){2-[(*E*/*Z*)-prop-1-enyl]benzylidene}amine (**4c**, 299 mg, 1.50 mmol), LDA (1.65 mmol) and pivaloyl chloride (3.00 mmol, 0.37 mL). The crude product was purified by column chromatography (silica gel; P/EA, 6:1). The compound was isolated as a colourless oil in a yield of 64% (272 mg, 0.96 mmol). R_f (TLC) = 0.60 (silica gel; PE/EA, 7:1). ^{1}H NMR (499.83 MHz, [D$_8$]toluene, 373 K): δ = 1.18 [s, 9 H, C(CH_3)$_3$], 1.66 (s, 3 H, CH_3C=CH$_2$), 1.88 (s, 3 H, CH_3), 4.39 (d, ^2J = 16.0 Hz, 1 H, NCHH), 4.75 (d, ^2J = 16.0 Hz, 1 H, NCHH), 4.84 [s, 1 H, CHCH=C(CH$_3$)H], 5.07 [s, 1 H, CHC(CH$_3$)=CHH], 5.54 (m, 1 H, CHC=CH$_2$), 6.25 (s, 1 H, HC=CCH$_3$), 6.91–7.09 (m, 4 H, C$H_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, [D$_8$]toluene, 373 K): δ = 20.8 (CH_3C=CH$_2$), 25.1 (CH_3), 29.4 [C(CH_3)$_3$], 39.7 [C(CH$_3$)$_3$], 48.4 (CH_2), 66.4 (HCC=CH$_2$), 118.3 [CHC(CH$_3$)=CHH], 126.6, 127.1, 128.9 (C$H_{arom.}$), 129.9 (CH=C–CH$_3$), 132.5 (C$H_{arom.}$), 135.2, 139.2, 139.5 (C_{ipso}, CH=CCH$_3$), 144.0 (CH$_3$C=CH$_2$), 176.0 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3055 (s, CH$_{arom.,olef.}$), 3020 (m, CH$_{arom.,olef.}$), 2977 (s, CH$_{aliph.}$), 2937 (m, CH$_{aliph.}$), 2975 (m, CH$_{aliph.}$), 1622 [vs, (CO)NR$_2$], 1575 (vw), 1492 (m), 1477 (s), 1438 (s), 1406 (s), 1379 (m), 1365 (m), 1305 (m), 1265 (vs), 1199 (m), 1174 (s), 1139 (w), 1110 (w), 1053 (vw), 1033 (vw), 1010 (w), 974 (w), 954 (vw), 918 (m), 896 (m), 875 (vw), 846 (vw), 738 (vs), 704 (vs) cm^{-1}. MS (EI, 70 eV): m/z (%) = 283 (52) [M]$^+$, 268 (28) [M – CH$_3$]$^+$, 255 (8), 226 [(CH$_3$)$_3$C=O]$^+$ (76), [M – C(CH$_3$)$_3$]$^+$ 198 [M – C]$^+$ (21), 183 [M – HN(C=O)C(CH$_3$)$_3$]$^+$ (31), 167 (22), 142 (20), 129 (11), 102 (2), 83 (37), 57 (100) [C(CH$_3$)$_3$]$^+$. MS (MicroTOF): calcd. 306.1828 [M + H]$^+$; found 306.1827 [M + H]$^+$. C$_{19}$H$_{25}$NO (283.41): calcd. C 80.52, H 8.89, N 4.94; found C 80.09, H 9.01, N 4.69.

Methyl 4-Methyl-3-vinyl-2,3-dihydro-1*H*-2-benzazepine-2-carboxylate (5d): This compound was synthesised from (allyl){2-[(*E*/*Z*)-prop-1-enyl]benzylidene}amine (**4a**,[9] 278 mg, 1.50 mmol), LDA (1.65 mmol) and methyl chloroformate (2.5 equiv., 3.75 mmol, 0.30 mL). The crude product was purified by column chromatography (silica gel; P/EA, 8:1, 6:1). The compound was isolated as a colourless oil in a yield of 47% (174 mg, 0.72 mmol). R_f (TLC) = 0.25 (silica gel; PE/EA, 8:1). ^{1}H NMR (499.83 MHz, [D$_8$]toluene, 348 K): δ = 1.76 (s, 3 H, CH_3), 3.36 (s, 3 H, OCH_3), 4.06 (d, ^2J = 15.0 Hz, 1 H, NCHH), 4.38 (s, 1 H, NCHH), 5.11 (m, 2 H, CHCH=CH_2), 5.57 (s, 1 H, CHCH=CH$_2$), 5.76 (m, 1 H, CHCH=CH$_2$), 6.23 (m, 1 H, HC=CCH$_3$), 6.93–7.09 (m, 4 H, C$H_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, [D$_8$]toluene, 348 K): δ = 24.8 (CH_3), 47.7 (CH_2), 52.2 (OCH_3), 63.5 (HCCHCH$_2$), 118.3 (CHCH=CH$_2$), 126.5, 127.6, 128.3 (C$H_{arom.}$), 128.7 (CH=CCH$_3$), 129.3 (C$H_{arom.}$), 131.6, 135.5, 139.0 (C_{ipso}), 136.7 (CHCH=CH$_2$), 156.0 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3076 (w, CH$_{arom.,olef.}$), 3058 (m, CH$_{arom.,olef.}$), 3020 (m, CH$_{arom.,olef.}$), 2976 (m, CH$_{aliph.}$), 2954 (s, CH$_{aliph.}$), 2920 (m, CH$_{aliph.}$), 2856 (w, CH$_{aliph.}$), 1703 [vs, RO(CO)NR$_2$], 1637 (m), 1575 (w), 1490 (m), 1461 (s), 1406 (s), 1382 (s), 1326 (s), 1309 (s), 1276 (s), 1255 (s), 1205 (s), 1159 (w), 1120 (s), 1072 (m), 1051 (w), 1014 (m), 993 (s), 962 (m), 950 (m), 933 (m), 894 (m), 871 (vw), 844 (m), 767 (s), 754 (s), 657 (m), 646 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 243 (100) [M]$^+$, 228 (99) [M – CH$_3$]$^+$, 184 (71) [M – (CO)OCH$_3$]$^+$, 168 (34), 157 (20), 142 (18), 115 (21). MS (MicroTOF): calcd. 266.1151 [M + H]$^+$; found 266.1148 [M + H]$^+$. C$_{15}$H$_{17}$NO$_2$ (243.30): calcd. C 74.05, H 7.04, N 5.76; found C 73.71, H 6.98, N 5.60.

Methyl 4-Phenyl-3-vinyl-2,3-dihydro-1*H*-2-benzazepine-2-carboxylate (5e): This compound was synthesised from **4b**[9] (370 mg, 1.50 mmol), LDA (1.65 mmol) and methyl chloroformate (2.5 equiv., 3.75 mmol, 0.30 mL). The crude product was purified by column chromatography (silica gel; P/EA, 6:1). The compound was isolated as a colourless oil in a yield of 20% (89 mg, 0.29 mmol). R_f (TLC) = 0.40 (silica gel; PE/EA, 6:1). ^{1}H NMR (499.83 MHz, [D$_8$]toluene, 348 K): δ = 3.41 (s, 3 H, CH_3), 4.26 (d, ^2J = 15.5 Hz, 1 H, NCHH), 4.46 (br. s, 1 H, NCHH), 4.97 (d, ^3J = 10.0 Hz, 1 H, CHCH=CHH), 5.05 (d, ^3J = 17.0 Hz, 1 H, CHCH=CHH), 5.69 (m, 1 H, CHCH=CH$_2$), 6.36 (s, 1 H, HCCHCH$_2$), 6.61 (s, 1 H, HC=CC$_6$H$_5$), 6.98–7.14 (m, 7 H, C$H_{arom.}$), 7.41–7.43 (m, 2 H, C$H_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, [D$_8$]toluene, 348 K): δ = 48.1 (CH_2), 52.4 (OCH_3), 61.9 (HCCHCH$_2$), 118.9 (CHCH=CH$_2$), 126.4, 127.1, 127.3, 127.5, 127.7, 128.3, 128.8 (C$H_{arom.}$), 131.7 (CH=CC$_6$H$_5$), 136.9, 137.4, 139.4, 143.7 (C_{ipso}, CHCH=CH$_2$), 157.8 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3055 (s, CH$_{arom.,olef.}$), 3028 (m, CH$_{arom.,olef.}$), 2985 (s, CH$_{aliph.}$), 2956 (m, CH$_{aliph.}$), 2931 (m, CH$_{aliph.}$), 2871 (m, CH$_{aliph.}$), 2856 (m, CH$_{aliph.}$), 1697 [vs, (CO)NR$_2$], 1645 (w), 1598 (m), 1573 (w), 1548 (w), 1494 (m), 1450 (s), 1421 (s), 1411 (s), 1379 (s), 1340 (m), 1326 (m), 1311 (m), 1265 (vs), 1213 (m), 1193 (m), 1159 (m), 1124 (m), 1093 (m), 1078 (m), 1047 (m), 1033 (m), 1008 (m), 997 (m), 966 (m), 935 (m), 896 (m), 871 (w), 842 (w), 740 (vs), 703 (vs), 659 (w), 597 (vw), 588 (w), 472 (vs) cm^{-1}. GC-MS (EI, 70 eV): m/z = 305.2 [M]$^+$, 290.2 [M – CH$_3$]$^+$, 278.2, 272.2, 258.2, 246.2 [M – (CO)OCH$_3$]$^+$, 230.2 [M – H$_2$N(CO)OCH$_3$]$^+$, 215.2, 204.2, 191.2, 176.2, 165.2, 152.2, 128.2, 115.2, 101.2, 91.2, 77.2, 59.1. MS (MicroTOF): calcd. 328.1308 [M + Na]$^+$; found 328.1308 [M + Na]$^+$. C$_{20}$H$_{19}$NO$_2$ (305.37): calcd. C 78.66, H 6.27, N 4.59; found C 78.42, H 6.65, N 4.34.

Methyl 4-Methyl-3-(prop-1-en-1-yl)-2,3-dihydro-1*H*-2-benzazepine-2-carboxylate (5f): This compound was synthesised from **4c** (299 mg, 1.50 mmol), LDA (1.65 mmol) and methyl chloroformate (2.5 equiv., 3.75 mmol, 0.30 mL). The crude product was purified by column chromatography (silica gel; P/EA, 7:1). The compound was isolated as a colourless solid in a yield of 68% (263 mg, 1.02 mmol). R_f (TLC) = 0.48 (silica gel; PE/EA 7:1), m.p. 74 °C. ^{1}H NMR (499.83 MHz, [D$_8$]toluene, 348 K): δ = 1.71 (s, 3 H, CH_3CCH$_2$), 1.81 (s, 3 H, CH_3), 3.36 (s, 3 H, OCH_3), 4.19 (d, ^2J = 15.5 Hz, 1 H, NCHH), 4.40 (s, 1 H, NCHH), 4.83 [s, 1 H, CHC(CH$_3$)=CHH], 5.05 [s, 1 H, CHC(CH$_3$)=CHH], 5.40 [s, 1 H,

C*H*C(CH$_3$)=CH$_2$], 6.26 (m, 1 H, *H*C=CCH$_3$), 6.92–7.09 (m, 4 H, C*H*$_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, [D$_8$]toluene, 348 K): δ = 20.9 (*C*H$_3$CCH$_2$), 24.9 (*C*H$_3$), 47.0 (*C*H$_2$), 52.3 (O*C*H$_3$), 66.2 [H*C*C(CH$_3$)=CH$_2$], 117.4 [CHC(CH$_3$)=*C*H$_2$], 125.8, 126.5, 127.3 (*C*H$_{arom.}$), 129.7 (*C*H=CCH$_3$), 132.1 (*C*H$_{arom.}$), 135.2, 135.4, 139.3, 144.3 (*C*$_{ipso}$), 156.6 (*C*=O) ppm. IR (KBr): $\tilde{\nu}$ = 3076 (m, CH$_{arom.,olef.}$), 3055 (m, CH$_{arom.,olef.}$), 3020 (m, CH$_{arom.,olef.}$), 2954 (s, CH$_{aliph.}$), 2918 (m, CH$_{aliph.}$), 2856 (m, CH$_{aliph.}$), 1703 [vs, RO(CO)NR$_2$], 1649 (m), 1492 (m), 1461 (vs), 1406 (s), 1386 (s), 1375 (s), 1332 (s), 1274 (s), 1255 (s), 1226 (s), 1197 (m), 1139 (m), 1120 (s), 1041 (m), 1016 (m), 997 (s), 974 (m), 956 (m), 912 (m), 875 (w), 842 (w), 800 (w), 769 (vs), 754 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 257 (100) [M]$^+$, 242 [M – CH$_3$]$^+$, 216 (84), 198 [M – CO$_2$CH$_3$]$^+$, 176 (34), 156 (27), 144 (14), 129 (24), 102 (14), 91 (8), 59 (10). MS (MicroTOF): calcd. 280.1308 [M + Na]$^+$; found 280.1315 [M + Na]$^+$. C$_{16}$H$_{19}$NO$_2$ (257.33): calcd. C 74.68, H 7.44, N 5.44; found C 74.50, H 7.43, N 5.24.

***N*,*N*-Diethyl-4-methyl-3-vinyl-2,3-dihydro-1*H*-2-benzazepin-2-carboxamide (5g):** This compound was synthesised from (allyl){2-[(*E*/*Z*)-prop-1-enyl]benzylidene}amine (**4a**,[9] 278 mg, 1.50 mmol), LDA (1.65 mmol) and *N*,*N*-diethylcarbamoyl chloride (1.5 equiv., 3.00 mmol, 0.38 mL). The crude product was purified by column chromatography (silica gel; P/EA, 5:1). The compound was isolated as a yellow oil in a yield of 71% (302 mg, 1.06 mmol). R_f (TLC) = 0.28 (silica gel; PE/EA, 5:1). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 0.96 [t, ^3J = 7.2 Hz, 6 H, (CO)NCH$_2$C*H*$_3$, (CO)NCH$_2$C*H*$_3$], 1.99 (s, 3 H, C*H*$_3$), 3.02 [dq, ^3J = 7.2, 14.1 Hz, 2 H, (CO)NC*H*$_2$], 3.18 [dq, ^3J = 7.2, 14.1 Hz, 2 H, (CO)NC*H*$_2$], 4.34 (s, 2 H, C*H*$_2$N), 5.03 (d, ^3J = 5.7 Hz, 1 H, *H*CC$_2$H$_3$), 5.21 (ddd, ^2J = 1.5, ^3J = 17.1, ^4J = 1.5 Hz, 1 H, CHCH=CH*H*$_E$), 5.39 (ddd, ^2J = 1.5, ^3J = 10.5, ^4J = 1.5 Hz, 1 H, CHCH=CH*H*$_Z$), 5.98 (ddd, ^3J = 5.7, ^3J = 10.2, ^3J = 17.4 Hz, 1 H, CHC*H*=CH$_2$), 6.40 (s, 1 H, *H*C=CCH$_3$), 7.05–7.17 (m, 4 H, C*H*$_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 13.2 [(CO)NCH$_2$*C*H$_3$], 25.0 (*C*H$_3$), 42.3 [(CO)N*C*H$_2$], 49.1 (*C*H$_2$N), 64.5 (H*C*C$_2$H$_3$), 119.3 (CHCH=*C*H$_2$), 125.9, 127.0, 127.6 (*C*H$_{arom.}$), 128.4 (H*C*=CCH$_3$), 131.4 (*C*H$_{arom.}$), 134.9, 136.7, 138.4, 138.6 (*C*$_{ipso}$, CH*C*H=CH$_2$), 164.0 [N(*C*O)N] ppm. IR (film): $\tilde{\nu}$ = 3076 (w, CH$_{arom.,olef.}$), 3057 (m, CH$_{arom.,olef.}$), 3018 (m, CH$_{arom.,olef.}$), 2968 (s, CH$_{arom.,olef.}$), 2929 (s, CH$_{aliph.}$), 2871 (m, CH$_{aliph.}$), 1699 (w), 1639 [s, NR$_2$(CO)NR$_2$], 1575 (w), 1446 (s), 1409 (s), 1379 (s), 1357 (m), 1337 (m), 1319 (m), 1305 (m), 1271 (s), 1251 (s), 1211 (m), 1170 (m), 1136 (w), 1110 (m), 1070 (m), 1010 (w), 954 (m), 933 (m), 893 (w), 867 (w), 848 (w), 796 (m), 754 (s), 730 (m), 719 (w) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* = 284.2 [M]$^+$, 269.2 [M – CH$_3$]$^+$, 255.2 [M – CH$_2$CH$_3$]$^+$, 240.2 [255.2 – CH$_3$]$^+$, 225.2, 211.2, 185.2 [M – (CO)N(CH$_2$CH$_3$)$_2$]$^+$, 170.2, 156.2, 141.2, 129.2, 115.2, 100.2 [(CO)NCH$_2$CH$_3$]$^+$, 89.2, 77.2, 72.1, 58.2, 44.1. MS (MicroTOF): calcd. 285.1961 [M + H]$^+$; found 285.1959 [M + H]$^+$. C$_{18}$H$_{24}$N$_2$O (284.40): calcd. C 76.02, H 8.51, N 9.85; found C 75.90, H 8.71, N 9.63.

General Procedure A for the Synthesis of *N*-[(7*Z*,9*Z*)-5,6-Dihydrobenzocycloocten-5-yl]propionamides 6b–e: LDA was freshly prepared at –78 °C under argon from *n*-butyllithium (1.6 M in *n*-hexane, 2 equiv.) in dry THF (30 mL) and diisopropylamine (1.1 equiv.). One of the (allyl){[(*E*/*Z*)-alkenyl]benzylidene}amines **4a**–**c** (1 equiv.) was dissolved in THF (10 mL), and the solution was added to the LDA solution dropwise over a period of 30 min. After 1.5 h of stirring at –78 °C, the reaction mixture was stirred at 0 °C for 2 h. The reaction mixture was then treated with electrophile **2a** or **2b** (2 equiv.) and was again stirred at 0 °C for 1 h. The mixture was allowed to warm to room temperature and stirred for 4.5 h and, after aqueous workup and extraction with diethyl ether, the combined organic layers were dried with magnesium sulfate. The solvent was evaporated under reduced pressure, and the product was purified by column chromatography (silica gel; P/EA, 5:1) and by subsequent recrystallisation. For the synthesis of **6a**, see ref.[7]

2,2-Dimethyl-*N*-[(7*Z*,9*E*)-9-phenyl-5,6-dihydrobenzocycloocten-5-yl]propionamide (6b): This compound was synthesised from **4b**[9] (1 equiv., 370 mg, 1.50 mmol), LDA (1.65 mmol) and pivaloyl chloride (2.0 equiv., 3.00 mmol, 0.37 mL). The crude product was purified by column chromatography (silica gel; P/EA, 8:1). The compound was isolated as a colourless solid in a yield of 49% (243 mg, 0.74 mmol). R_f (TLC) = 0.23 (silica gel; PE/EA, 8:1), m.p. 154–155 °C. ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 1.15 [s, 9 H, C(C*H*$_3$)$_3$], 2.53 (m, ^2J = 17.0 Hz, 1 H, CH*H*), 2.94 (m, ^2J = 17.0 Hz, 1 H, C*H*H), 5.68 (dq, ^4J = 3.0, ^3J = 12.0 Hz, 1 H, CH$_2$C*H*=CHCC$_6$H$_5$), 5.78 (dq, ^4J = 2.4, ^3J = 12.6 Hz, 1 H, CH$_2$CH=C*H*CC$_6$H$_5$), 5.97 (m, 1 H, C*H*NHCO), 6.12 (d, ^3J = 7.2 Hz, 1 H, N*H*), 7.04 (s, 1 H, *H*C=CCC$_6$H$_5$), 7.23–7.39, 7.55–7.58 (m, 9 H, C*H*$_{arom.}$) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 27.4 [C(*C*H$_3$)$_3$], 37.9 (*C*H$_2$), 38.4 [*C*(CH$_3$)$_3$], 49.5 (H*C*NH), 124.9 (*C*H$_{arom.}$), 125.9 (H*C*=C*C*$_6$H$_5$), 126.2 (*C*H$_{arom.}$), 126.7 (CH$_2$*C*H=CH*C*C$_6$H$_5$), 127.6, 127.7, 127.9 (*C*H$_{arom.}$), 128.3 (CH$_2$CH=*C*HCC$_6$H$_5$), 128.7, 128.8 (*C*H$_{arom.}$), 137.1, 140.7, 141.1, 141.2 (C$_{ipso}$, HC=*C*C$_6$H$_5$), 177.1 (*C*=O) ppm. IR (KBr): $\tilde{\nu}$ = 3357 (s, CN–H), 3055 (m, CH$_{arom.,olef.}$), 3022 (m, CH$_{arom.,olef.}$), 2964 (s, CH$_{aliph.}$), 2927 (m, CH$_{aliph.}$), 2906 (m, CH$_{aliph.}$), 2885 (m, CH$_{aliph.}$), 2868 (m, CH$_{aliph.}$), 1637 [vs, (CO)NH], 1581 (w), 1531 [vs, (CO)-NH], 1494 (s), 1481 (m), 1448 (m), 1429 (m), 1400 (m), 1365 (m), 1301 (m), 1251 (m), 1209 (m), 1193 (m), 1161 (w), 1118 (m), 1078 (m), 1066 (m), 1047 (w), 1031 (w), 1004 (w), 894 (w), 856 (w), 806 (w), 783 (w), 758 (vs), 721 (m), 696 (s), 640 (m) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* = 331.3 [M]$^+$, 247.3 [M – C(CH$_3$)$_3$C=O]$^+$, 244.2, 230.2 [M – H$_2$N(C=O) C(CH$_3$)$_3$]$^+$, 217.2 [230 – CH$_3$]$^+$, 191.2, 168.2, 156.2, 141.2, 130.2, 129.2, 115.2, 91.2, 85.2, 57.2. MS (MicroTOF): calcd. 354.1828 [M + Na]$^+$; found 354.1832 [M + Na]$^+$. C$_{23}$H$_{25}$NO (331.45): calcd. C 83.34, H 7.60, N 4.23; found C 83.32, H 7.56, N 4.10.

2,2-Dimethyl-*N*-[(7*Z*,9*Z*)-7,9-dimethyl-5,6-dihydrobenzocycloocten-5-yl]propionamide (6c): This compound was synthesised from **4c** (299 mg, 1.50 mmol), LDA (1.65 mmol) and pivaloyl chloride (2.0 equiv., 3.00 mmol, 0.37 mL). The crude product was purified by column chromatography (silica gel; P/EA, 8:1). The compound was isolated as a colourless solid in a yield of 52% (221 mg, 0.78 mmol). R_f (TLC) = 0.35 (silica gel; PE/EA, 7:1), m.p. 134–136 °C. ^{1}H NMR (499.83 MHz, [D$_8$]toluene, 298 K): δ = 1.18 [s, 9 H, C(C*H*$_3$)$_3$], 1.69 (s, 3 H, HCCC*H*$_3$), 1.96 (s, 3 H, C*H*$_3$CCH$_2$), 2.40 (dd, ^3J = 12.0, ^2J = 16.5 Hz, 1 H, C*H*H), 2.76 (dd, ^3J = 2.0, ^2J = 16.5 Hz, 1 H, CH*H*), 5.46 (s, 1 H, CH$_2$C=C*H*CCH$_3$), 5.62 (m, 1 H, C*H*NHCO), 6.10 (s, 1 H, N*H*), 6.40 (s, 1 H, *H*C=CCH$_3$), 7.08–7.26 (m, 4 H, C*H*$_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, [D$_8$]-toluene, 298 K): δ = 25.3 (*C*H$_3$CCH$_2$), 26.8 (HCC*C*H$_3$), 27.5 [C(*C*H$_3$)$_3$], 38.5 [*C*(CH$_3$)$_3$], 43.1 (*C*H$_2$), 49.2 (H*C*NH), 124.2 (H*C*CCH$_3$), 125.1 (*C*H$_{arom.}$), 125.5 (CH$_2$C=*C*HCCH$_3$), 126.1 127.0, 128.8 (*C*H$_{arom.}$), 134.5, 137.2, 137.9, 140.8 (*C*$_{ipso}$), 177.1 (*C*=O) ppm. IR (KBr): $\tilde{\nu}$ = 3332 (s, CN–H), 3051 (m, CH$_{arom.,olef.}$), 3024 (m, CH$_{arom.,olef.}$), 2964 (s, CH$_{aliph.}$), 2931 (s, CH$_{aliph.}$), 2871 (m, CH$_{aliph.}$), 1718 (m), 1637 (vs, C=O), 1535 (vs, C=O), 1479 (s), 1458 (m), 1434 (m), 1398 (m), 1365 (s), 1309 (m), 1288 (m), 1265 (m), 1217 (s), 1199 (m), 1155 (m), 1105 (m), 1070 (m), 1031 (m), 995 (w), 943 (w), 904 (w), 854 (vw), 815 (m), 754 (s), 651 (m), 607 (m), 576 (m), 545 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 283 (11) [M]$^+$, 272 (3) [M – CH$_3$]$^+$, 242 (5), 213 (8), 182 (100) [M – HN(C=O)C(CH$_3$)$_3$]$^+$, 167 (36), 127 (34), 113 (4), 85 (11), 57 (54) [C(CH$_3$)$_3$]. MS (MicroTOF): calcd. 306.1822 [M + Na]$^+$; found

306.1828 [M + Na]$^+$. $C_{19}H_{25}NO$ (283.41): calcd. C 80.52, H 8.89, N 4.94; found C 80.33, H 8.98, N 4.81.

X-ray Crystal Structure Analysis for 6c:[16,17] Formula $C_{19}H_{25}NO$, M = 283.40, colourless crystal 0.30 × 0.20 × 0.10 mm, a = 9.831(1), b = 19.192(1), c = 19.404(1) Å, β = 90.39(1)°, V = 3661.0(5) Å^3, $\rho_{calcd.}$ = 1.028 g cm^{-3}, μ = 0.481 mm^{-1}, empirical absorption correction (0.869 ≤ T ≤ 0.954), Z = 8, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 293(2) K, ω and ϕ scans, 12013 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6381 independent (R_{int} = 0.028) and 4051 observed reflections [$I \geq 2\sigma(I)$], 387 refined parameters, R = 0.078, wR^2 = 0.255, max/min residual electron density 0.54/–0.16 e Å^{-3}; two almost identical molecules in the asymmetric unit, hydrogen atom at N1 from difference Fourier calculations, others calculated and refined as riding atoms.

General Procedure for the Synthesis of Compounds 6d–f: LDA was freshly prepared at –78 °C under argon from *n*-butyllithium (1.6 M in *n*-hexane, 2 equiv.) in dry THF (30 mL) and diisopropylamine (1.1 equiv.). One of the (allyl){[(*E*/*Z*)-alkenyl]benzylidene}amines **4a** and **4b** (1 equiv.) was dissolved in THF (10 mL), and the solution was added dropwise over a period of 30 min to the LDA solution. After 1.5 h of stirring at –78 °C, the reaction mixture was stirred at 0 °C for 2 h. It was then treated with electrophile **2b** (2 equiv.) and was again stirred at 0 °C for 1 h. The mixture was allowed to warm to room temperature and stirred for the indicated number of hours, and after aqueous workup and extraction with diethyl ether, the combined organic layers were dried with magnesium sulfate. The solvent was evaporated under reduced pressure, and the product was purified by column chromatography (silica gel; P/EA) and by subsequent recrystallisation.

Dimethyl (7*Z*,9*Z*)-9-Methyl-5,6-dihydrobenzocycloocten-5-ylimidodicarbonate (6d): This compound was synthesised from **4a**[9] (278 mg, 1.50 mmol), LDA (1.65 mmol) and methyl chloroformate (3.75 mmol, 0.29 mL) with stirring at room temperature for 18 h. The crude product was purified by column chromatography (silica gel; P/EA, 10:1, 8:1). The compound was isolated as a yellow oil in a yield of 42% (153 mg, 0.63 mmol). R_f (TLC) = 0.27 (silica gel; PE/EA, 10:1). ^{1}H NMR (600.14 MHz, $CDCl_3$, 298 K): δ = 1.97 (s, 1 H, CH_3), 2.49 (dt, ^2J = 14.0, ^3J = 5.4 Hz, 1 H, C*H*H), 3.46 (dt, ^2J = 14.0, ^3J = 9.0 Hz, 1 H, CH*H*), 3.73 (s, 6 H, OCH_3), 5.73 (ddd, ^3J = 4.8, ^3J = 7.2, ^3J = 11.4 Hz, 1 H, CH_2CH=CHCCH$_3$), 5.81 (d, ^3J = 12.0 Hz, 1 H, CH_2CH=C*H*CCH$_3$), 5.91 (dd, ^3J = 4.2, ^3J = 12.0 Hz, 1 H, C*H*NR_2), 6.45 (s, 1 H, *H*C=CCH$_3$), 7.04–7.06 (m, 1 H, C$H_{arom.}$), 7.14–7.16 (m, 2 H, C$H_{arom.}$), 7.45–7.46 (m, 1 H, C$H_{arom.}$) ppm. ^{13}C NMR (150.84 MHz, $CDCl_3$, 298 K): δ = 24.3 (*C*H$_3$), 33.1 (*C*H$_2$), 53.7 (O*C*H$_3$), 58.2 (H*C*NR_2), 126.2, 126.4 (*C*H$_{arom.}$), 126.8 (H*C*=CCH$_3$), 128.0 (CH_2*C*H=CHCCH$_3$), 129.4 130.0 (*C*H$_{arom.}$), 131.4 (CH_2CH=*C*HCCH$_3$), 135.5, 137.6, 137.7 (*C*$_{ipso}$), 154.5 (*C*=O) ppm. IR (film): $\tilde{\nu}$ = 3055 (s, $CH_{arom.,olef.}$), 2987 (m, $CH_{arom.,olef.}$), 2958 (m, $CH_{aliph.}$), 2929 (m, $CH_{aliph.}$), 2854 (m, $CH_{aliph.}$), 1782 [m, $(ROCO)_2N$], 1747 [s, $(ROCO)_2N$], 1708 [s, $(ROCO)_2N$], 1652 (w), 1600 (w), 1550 (w), 1488 (w), 1438 (s), 1421 (m), 1392 (m), 1340 (m), 1265 (vs), 1240 (s), 1195 (m), 1116 (m), 1103 (m), 1014 (m), 933 (w), 894 (m), 869 (w), 850 (w), 804 (m), 736 (vs), 705 (vs), 648 (vw) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* = 301.2 [M]$^+$, 286.2 [M – CH_3]$^+$, 242.2 [M – $OCOCH_3$]$^+$, 226.2, 211.2, 196.2, 182.2, 168.2 [M – $HN(OCOCH_3)_2$]$^+$, 153.2 [168.2 – CH_3]$^+$, 141.1, 128.2, 115.2, 102.2, 89.2, 83.2, 70.1, 59.1 [$OCOCH_3$]. MS (MicroTOF): calcd. 324.1211 [M + Na]$^+$; found 324.1204 [M + Na]$^+$.

Dimethyl (7*Z*,9*Z*)-9-Phenyl-5,6-dihydrobenzocycloocten-5-ylimidodicarbonate (6e): This compound was synthesised from **4b**[9] (1 equiv., 370 mg, 1.50 mmol), LDA (1.65 mmol) and methyl chloroformate (3.75 mmol, 0.29 mL) with stirring at room temperature for 18 h. The crude product was purified by column chromatography (silica gel; P/EA, 6:1). The compound was isolated as a yellow oil in a yield of 55% (251 mg, 0.83 mmol). R_f (TLC) = 0.28 (silica gel; PE/EA, 6:1). ^{1}H NMR (499.83 MHz, $CDCl_3$): δ = 2.59 (dt, ^2J = 12.5, ^3J = 5.5 Hz, 1 H, C*H*H), 3.65 (m, 1 H, CH*H*), 3.75 (s, 6 H, OCH_3), 5.95 (dd, ^3J = 4.5, ^3J = 12.5 Hz, 1 H, C*H*NR_2), 6.14 (ddd, ^3J = 6.0, ^3J = 9.0, ^3J = 11.0 Hz, 1 H, CH_2C*H*=CHC$_6$H$_5$), 6.22 (d, ^3J = 11.0 Hz, 1 H, CH_2CH=C*H*C$_6$H$_5$), 7.12 (s, 1 H, *H*C=C$_6$H$_5$), 7.20–7.28 (m, 4 H, C$H_{arom.}$), 7.35–7.38 (m, 1 H, C$H_{arom.}$), 7.41–7.47 (m, 2 H, C$H_{arom.}$), 7.57–7.59 (m, 2 H, C$H_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, $CDCl_3$): δ = 31.8 (*C*H$_2$), 53.6 (O*C*H$_3$), 58.7 (H*C*NR_2), 126.4, 126.8, 127.0, 127.7, 127.8 (*C*H$_{arom.}$), 128.4 (H*C*=C$_6$H$_5$), 130.1 (CH_2*C*H=CHC$_6$H$_5$), 130.4, 130.6 (*C*H$_{arom.}$), 131.1 (CH_2CH=*C*HC$_6$H$_5$), 136.9, 137.5, 137.7, 140.3 (C$_{ipso}$), 154.3 (*C*=O) ppm. IR (film): $\tilde{\nu}$ = 3057 (m, $CH_{arom.,olef.}$), 3022 (m, $CH_{arom.,olef.}$), 2954 (s, $CH_{arom.,olef.}$), 2927 (m, $CH_{aliph.}$), 2871 (w, $CH_{aliph.}$), 2852 (m, $CH_{aliph.}$), 1786 [m, $(ROCO)_2N$], 1751 [vs, $(ROCO)_2N$], 1708 [vs, $(ROCO)_2N$], 1598 (m), 1573 (w), 1494 (m), 1436 (vs), 1388 (s), 1313 (s), 1290 (vs), 1255 (s), 1228 (vs), 1191 (s), 1164 (m), 1118 (s), 1105 (s), 1078 (m), 1031 (m), 987 (m), 964 (m), 933 (w), 889 (vw), 869 (vw), 856 (vw), 842 (vw), 802 (m), 759 (s), 738 (s), 698 (s), 671 (w), 648 (w) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* = 363.2 [M]$^+$, 304.2 [M – $OCOCH_3$]$^+$, 273.2 [M – CHC_6H_5]$^+$, 244.2, 230.2 [M – $HN(OCOCH_3)_2$]$^+$, 215.2, 203.2, 182.2, 169.2, 153.2 [230.2 – C_6H_5], 141.2, 128.2, 115.2, 101.2, 70.1. MS (MicroTOF): calcd. 386.1368 [M + Na]$^+$; found 386.1363 [M + Na]$^+$.

Methyl *N*-[(7*Z*,9*Z*)-9-Phenyl-5,6-dihydrobenzocycloocten-5-yl]carbamate (6f): This compound was synthesised from **4b**[9] (1 equiv., 370 mg, 1.50 mmol), LDA (1.65 mmol) and methyl chloroformate (3.75 mmol, 0.29 mL) with stirring at room temperature for 4.5 h. The crude product was purified by column chromatography (silica gel; P/EA, 9:1). The compound was isolated as a colourless solid in a yield of 10% (46 mg, 0.15 mmol). R_f (TLC) = 0.13 (silica gel; PE/EA, 9:1), m.p. 120–121 °C. ^{1}H NMR (499.83 MHz, $CDCl_3$): δ = 2.48 (br. s, 1 H, C*H*H), 2.97 (d, ^2J = 16.0 Hz, 1 H, CH*H*), 3.60 (s, 3 H, OCH_3), 5.08 (br. s, 1 H, N*H*), 5.51 (m, 1 H, C*H*NHCO), 5.75 (m, 1 H, CH_2C*H*=CHC$_6$H$_5$), 5.95 (m, 1 H, CH_2CH=C*H*C$_6$H$_5$), 7.01 (s, 1 H, *H*C=C$_6$H$_5$), 7.21–7.40, 7.56–7.58 (m, 9 H, C$H_{arom.}$) ppm. ^{13}C NMR (125.70 MHz, $CDCl_3$): δ = 38.4 (*C*H$_2$), 51.1 (H*C*NH), 52.1 (O*C*H$_3$), 124.7 (*C*H$_{arom.}$), 125.8 (H*C*=C$_6$H$_5$), 126.3, 126.7 (*C*H$_{arom.}$), 127.7 (CH_2*C*H=CHC$_6$H$_5$), 127.8, 128.2, 128.4 (*C*H$_{arom.}$), 128.5 (CH_2CH=*C*HC$_6$H$_5$), 137.1, 140.8, 141.4 (*C*$_{ipso}$), 155.9 (*C*=O) ppm. IR (KBr): $\tilde{\nu}$ = 3437 (w, CN–H), 3055 (m, $CH_{arom.,olef.}$), 3026 (w, $CH_{arom.,olef.}$), 2987, 2960 (w, $CH_{aliph.}$), 2837 (m, $CH_{aliph.}$), 1724 [m, RO(CO)NH], 1598 (vw), 1508 (m), 1448 (w), 1421 (w), 1357 (m), 1299 (w), 1265 (vs), 1191 (w), 1157 (vw), 1099 (w), 1078 (w), 1039 (w), 896 (w), 738 (vs), 705 (vs) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* = 305.2 [M]$^+$, 290.2 [M – CH_3]$^+$, 274.2, 246.2 [M – $(CO)OCH_3$]$^+$, 230.2 [M – $N(CO)OCH_3$]$^+$, 218.2, 204.2, 191.2, 168.2, 154.2, 141.2, 128.2, 115.2, 102.2, 91.2, 77.2, 63.1, 59.1, 44.1. MS (MicroTOF): calcd. 328.1308 [M + Na]$^+$; found 328.1310 [M + Na]$^+$. $C_{20}H_{19}NO_2$ (305.37): calcd. C 78.66, H 6.27, N 4.59; found C 78.13, H 6.54, N 4.27.

X-ray Crystal Structure Analysis for 6f:[16,17] Formula $C_{20}H_{19}NO_2$, M = 305.36, colourless crystal 0.15 × 0.10 × 0.02 mm, a = 8.534(1), b = 9.409(1), c = 41.291(1) Å, V = 3315.5(5) Å^3, $\rho_{calcd.}$ = 1.223 g cm^{-3}, μ = 0.625 mm^{-1}, empirical absorption correction (0.912 ≤ T ≤ 0.988), Z = 8, orthorhombic, space group *Pbca* (No. 61), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 22894 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 2793 independent (R_{int} = 0.056) and 1741 observed reflections [$I \geq 2\sigma(I)$], 213 refined pa-

rameters, $R = 0.046$, $wR^2 = 0.119$, max/min residual electron density 0.12/–0.14 e Å^{-3}, hydrogen atom at N1 from difference Fourier calculations, others calculated and refined as riding atoms.

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[1] R. K. Smalley, "Azepines: Benzo-, Dibenzo- and Tribenzoazepines" in *Methods Org. Chem. (Houben-Weyl)*, **1997**, vol. E9d ("Hetarenes IV: Six-Membered and Larger Hetero Rings with Maximum Unsaturation"), pp. 207–298.
[2] D. O'Hagan, *Nat. Prod. Rep.* **1997**, *14*, 637–651.
[3] J. Lee, J. Lee, T. Szabo, A. F. Gonzales, J. D. Welter, P. M. Blumberg, *Bioorg. Med. Chem. Lett.* **2001**, *9*, 1713–1720.
[4] a) H. Kogen, N. Toda, K. Tago, S. Marumoto, K. Takami, M. Ori, N. Yamada, K. Koyama, S. Naruto, K. Abe, R. Yamazaki, T. Hara, A. Aoyagi, Y. Abe, T. Kaneko, *Org. Lett.* **2002**, *4*, 3359–3362; b) N. Toda, K. Tago, S. Marumoto, K. Takami, M. Ori, N. Yamada, K. Koyama, S. Naruto, K. Abe, R. Yamazaki, T. Hara, A. Aoyagi, Y. Abe, T. Kaneko, H. Kogen, *Bioorg. Med. Chem.* **2003**, *11*, 4389–4415.
[5] N. Dieltiens, C. V. Stevens, *Synlett* **2006**, 2771–2776.
[6] W. A. L. van Otterlo, R. Pathak, C. B. de Koning, *Synlett* **2003**, 1859–1861.
[7] M. Sajitz, R. Fröhlich, K. Salorinne, E.-U. Würthwein, *Synthesis* **2006**, *13*, 2183–2190.
[8] a) S. Klötgen, E.-U. Würthwein, *Tetrahedron Lett.* **1995**, *36*, 7065–7068; b) S. Klötgen, R. Fröhlich, E.-U. Würthwein, *Tetrahedron* **1996**, *52*, 14801–14812.
[9] K. Gerdes, P. Sagar, R. Fröhlich, B. Wibbeling, E.-U. Würthwein, *Eur. J. Org. Chem.* **2004**, 3465–3476.
[10] H. Kloosterziel, J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1084–1087.
[11] R. B. Bates, S. Brenner, C. M. Cole, *J. Am. Chem. Soc.* **1972**, *94*, 2130–2132.
[12] K. Hassenrück, H. D. Martin, *Synthesis* **1988**, 569–586.
[13] P. W. Groundwater, M. Nyerges, *Adv. Heterocycl. Chem.* **1999**, *73*, 97–129.
[14] W. Friebolin, W. Eberbach, *Tetrahedron* **2001**, *57*, 4349–4358.
[15] K. Marx, W. Eberbach, *Chem. Eur. J.* **2000**, *6*, 2063–2068.
[16] Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (B. V. Nonius, **1998**), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, *A59*, 228–234), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473), structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122), graphics SCHAKAL (University of Freiburg, **1997**).
[17] CDCC-713242 (**6a**), -713243 (**6f**), -713246 (**11a**) and -713245 (**13a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[18] The quantum chemical model calculations of the anions without counterion or solvent indicated a stepwise [2,3]-aza-Wittig rearrangement with a benzo-annulated *N*-acyl-1-aza-nonatetraenyl anion as intermediate, see ref.[7]
[19] K. Sato, K. Taguchi, Y. Adahi, K. Nomi, *Heterocycles* **1998**, *28*, 275–282.
[20] D. P. Munro, J. T. Sharp, *J. Chem. Soc. Perkin Trans. 1* **1984**, 849–858.
[21] N. Hesse, Dissertation, University of Münster, **2004**.

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