The Dipolar Route to Azepin-3-one Derivatives by Heterocyclization of Linear and Monocyclic Enallenyl Nitrones as the Key Step

Karin Knobloch,[a,b] Joachim Koch,[a] Manfred Keller,[a][‡] and and Wolfgang Eberbach*[a]

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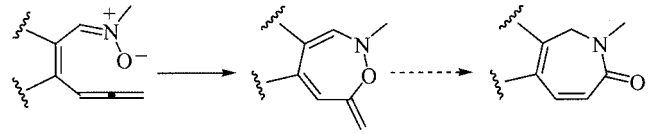
The recently discovered transformation of benzopentenynyl nitrones into 1,2-dihydrobenz[*c*]azepin-3-ones has been extended to the synthesis of structurally different systems including the monocyclic derivatives **17** and **18**, the bicyclic azepinones **10a–d**, and the tricyclic heterocycles **37–40**, **42**, **43**, **45**, **47**, and **48**. In addition, the applicability of the reaction principle was demonstrated through the preparation of the benzo-piperidino compound **52** which acts as a model compound for the alkaloid astrocasine (**53**). A multistep reaction mechanism is proposed that involves enallenyl nitrones as precursors of a 1,7-dipolar electrocyclization process followed by further bond reorganizations. The occurrence of cyclopropanones (type **E** and **H**) as intermediates is supported by the formation of isoindoles (**41**, **44**, and **46**) as minor products in some cases. Photochemical studies with selected dihydroazepinones gave different results: Whereas the monocyclic azepinone **17** reacted under both direct and sensitized excitation to form the bicyclic diastereomers **20** and **21**, the reactions of the bicyclic compounds **10** were more complicated. Only **10a**,**b** were observed to undergo the 4π-cyclization reaction upon direct irradiation, resulting, after CO extrusion and hydrolysis, in the formation of the aldehydes **22a**,**b**. Under triplet-sensitized conditions **10b–d** undergo a 1,5-phenyl shift to afford the isomers **25b–d**.

Introduction

Owing to the frequently observed biological activity of seven-membered azaheterocycles their synthesis remains an ongoing challenge. Of the wide range of structures that are known, the benzazepin-3-one system deserves particular attention because there are quite a number of its derivatives that have been used for pharmaceutical purposes, for instance, as adrenaline antagonists,[1] inflammation inhibitors,[2] as a drug with cholesterol-lowering properties,[3] or as a mediator in cellular adhesion events.[4] Until now only a few general syntheses of the system have been available.[5]

We have previously developed a novel methodology for the synthesis of this benzazepin-3-one system that is particularly simple, variable with respect to structural requirements, and can be executed under unusually mild conditions.[6] The procedure is based on the heterocyclization of conjugated penta-1,2,4-trienyl nitrones of general type **1** as the key step leading to intermediate oxazepine derivatives **2** which undergo a multistep rearrangement sequence to afford azepin-3-one products **3** in high overall yield (Scheme 1).[7] The reaction principle is a further example of the increasing number of successful applications of an allene unit in ring-forming procedures,[8] for example, in [2+2],[9,10] Diels–Alder,[11,12] and 1,3-dipolar cycloaddition reactions,[13,14] as well as in palladium-catalyzed transformations,[15] Pauson–Khand-type cyclization reactions,[16] and metathesis processes.[17]



1 **2** **3**

Scheme 1.

As a result of our work on the preparation of 1,2-dihydrobenzazepin-3-ones, it was the aim of this work to broaden the scope of the methodology by applying the same type of transformation to compounds with an alkeno-annulation of the double bond (see structure **9**), and also to the linear systems **14** and **16**.[18]

To construct the allene unit we took advantage of the base-catalyzed propargyl-allenyl isomerization of an appropriate precursor which could proceed by the formal migration of either an inner or an outer proton, that is, migration of the type **4** → **5** or **6** → **5** (Scheme 2), respectively. In contrast to our recent investigations[6,7] we used the latter alternative to generate an equilibrium concentration of the allene isomer, which was expected to undergo the required transformation under the same mild conditions.

[‡] Correspondence author for the crystal structure analyses.
[a] Institut für Organische Chemie und Biochemie der Universität Freiburg,
Albertstrasse 21, 79104 Freiburg, Germany
Fax: +49-(0)761/203-6085
E-mail: eberbach@organik.chemie.uni-freiburg.de
[b] Current address: Siegfried CMS Ltd., 4800 Zofingen, Switzerland

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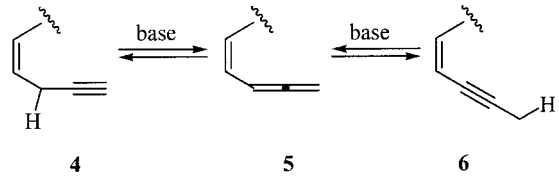


Scheme 2.

As a further test of the reaction principle of Scheme 1, the preparation of an analogue of astrocasine, a naturally occurring euphorbiaceae alkaloid, is described.[19] In addition, the photochemical reactivity of some dihydroazepinone derivatives will be briefly discussed.

Results and Discussion

Synthesis and Transformation of Cycloalkeno-Annulated Nitrone Systems

The annulated allene precursors **9** were prepared by following the general protocol applied earlier to related compounds (Scheme 3).[7] Sonogashira alkynylation of the known annulated bromo aldehydes **7**[20] produced the propargyl compounds **8** (89–98%) which were treated with methylhydroxylamine hydrochloride and sodium acetate in dichloromethane as solvent to give the conjugated nitrones **9a–d** in yields of 57–88% (Scheme 3).

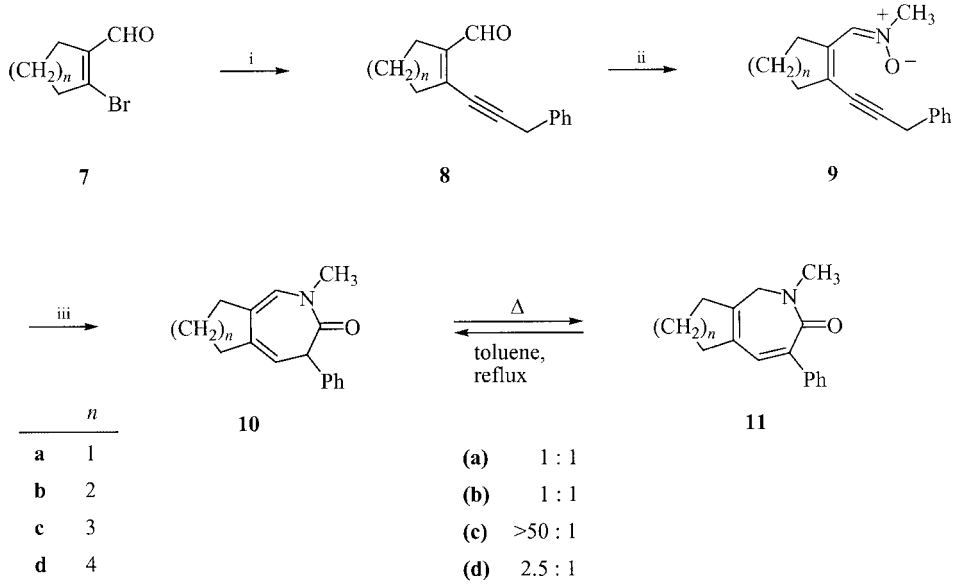
After treatment of 0.1 M solutions of the dipolar systems **9** in methanol with 0.5 equiv. of potassium hydroxide at room temperature complete consumption of the starting materials was attained after 1.5 h (**a**, **c**, **d**) and 3 h (**b**). Aqueous work up and chromatographic purification of the crude material afforded a crystalline product, which, in each case, had the structure of an annulated dihydroazepinone **10** (**a**: 79%, **b**: 88%, **c**: 46%, **d**: 65%). As found in our previous experiments, the formation of an allenic compound, supposedly the direct precursor of the 1,7-dipolar cyclization process, was not observed. The structures of the bicyclic lactams were unambiguously confirmed by elemental analyses and detailed spectroscopic investigations. Among other data the strong IR absorptions at 1670/1675 cm^{-1} as well as the ^{13}C NMR signals at about 166 ppm underline the presence of the lactam moiety.

In order to test the thermodynamic stability of the structures **10**, which contain two exocyclic double bonds that can be shifted by a sigmatropic 1,5-hydrogen migration to afford the seemingly more stable isomers **11**, the compounds were refluxed in toluene. After 2 h equilibrium concentrations were obtained that depend on the size of the carbocyclic ring: Whereas the ratio of the tautomeric compounds **10** and **11** was unity for derivatives **a** and **b**, structure **10** dominates by a factor of 2.5 in the case of **d**, with a ratio of >50:1 for **c**. With the exception of the cyclohepteno-annulated azepinone system, the thermodynamic stability of the double-bond isomers is, in contrast to expectation, not very different. In order to obtain more information about these systems, the thermochemical data is currently being evaluated, including the determination of the enthalpy of formation and the molecular strain.[21]

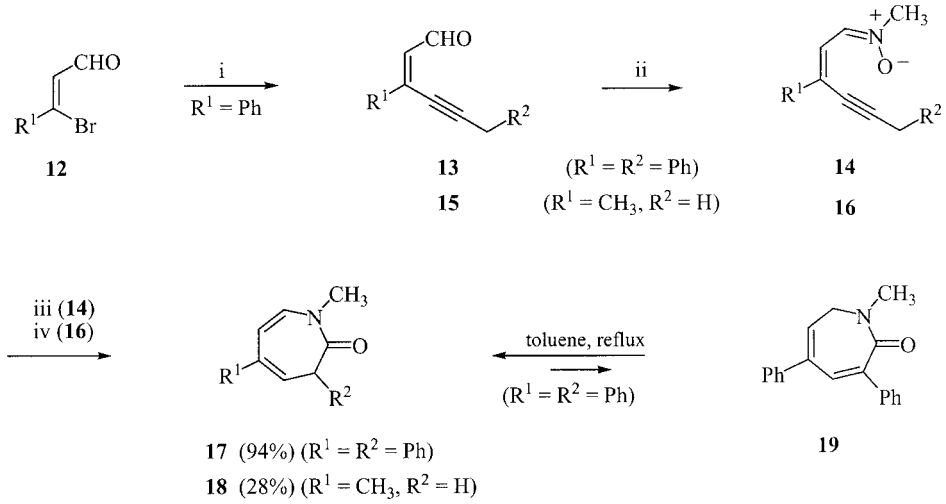
Synthesis and Transformation of Linear Nitrone Systems

Following the same procedure as described for the synthesis of compounds **9**, the linear phenyl-benzyl system **14** was obtained from (*Z*)-β-bromocinnamaldehyde (**12**)[22,23] via **13** in 36 and 86% yields for the two steps, respectively (Scheme 4). Dimethyl nitrone **16** was formed in 90% yield from the known 3-methylhexenynal **15**.[24]

Treatment of a methanolic solution of the benzyl derivative **14** with sodium methoxide at room temperature for



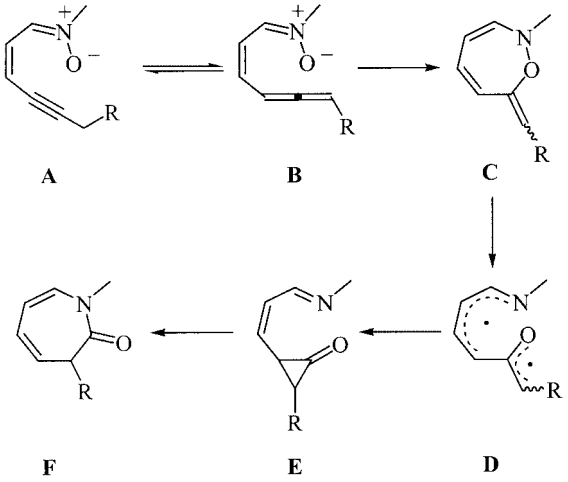
Scheme 3. Reagents and conditions: (i) $HC{\equiv}CCH_2Ph$, $PdCl_2(PPh_3)_2$, CuI, NEt_3, C_6H_6; (ii) $CH_3NHOH{\cdot}HCl$, NaOAc, CH_2Cl_2; (iii) KOH, MeOH, room temp.



Scheme 4. Reagents and conditions: (i) and (ii) as for Scheme 3; (iii) MeONa, MeOH, 30 min, room temp.; (iv) NaH, DMF, 22 h, 60 °C.

30 min gave **17** in almost quantitative yield (94%, m.p. 74–76 °C). In contrast, the conditions required for the reaction of compound **16** with a terminal methyl group turned out to be much harsher. Owing to the significantly lower acidity of the propargylic proton a stronger base for the induction of the essential propargyl-allenyl rearrangement was needed. Even with sodium hydride in DMF and at a temperature of 60 °C the reaction took 22 h for complete conversion (Scheme 4). It was a pleasant surprise that despite such conditions the expected dihydroazepinone **18** was formed at all, albeit in a lower yield (28%). Interestingly, both dihydroazepinones **17** and **18** have double bonds conjugated to the ring nitrogen. Experiments with derivative **17** in boiling toluene revealed the corresponding isomer with carbonyl and phenyl conjugation (**19**) to have an equilibration concentration of less than 3%.

The importance of the base strength on the reactivity of **14** and **16** lends further support to our mechanistic proposal for a multistep rearrangement with the formation of an allene in the first step (**A** → **B**) and subsequent 1,7-dipolar cyclization to methyleneoxazepine **C** (Scheme 5, general case). Cleavage of the notoriously weak NO bond[25] of **C** gives the diradical **D** which rebonds to give the azadienylcyclopropanone **E** and is followed by a one- or two-step cyclization reaction to produce **F**.[7]



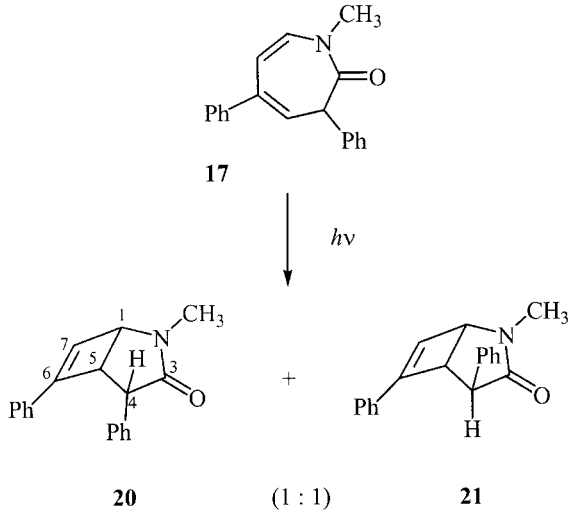
Scheme 5.

Photoreactivity of the Dihydroazepinones 10a–d and 17

The photochemistry of dihydroazepinones (the same is true for azepinones) has been studied in only a few cases.[26,27] In analogy with other 1,3-cycloheptadienes,[28] electrocyclic ring closure to the corresponding bicyclic isomers is observed as the main reaction. Owing to the limited knowledge of the photochemistry of such heterocycles, and with appropriate systems in hand, we have made some preliminary studies of the photochemistry of the monocyclic and bicyclic compounds **17** and **10a–d**, respectively.

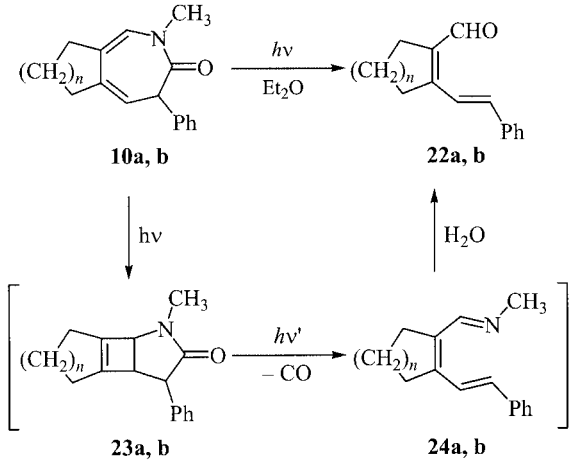
On irradiation of approximately 10^{-3} M solutions of the diphenyldihydroazepinone **17** under both direct (diethyl ether, $\lambda > 270$ nm, 30 min, 70% conversion) and triplet-sensitized excitation (acetone, $\lambda > 270$ nm, 15 min, 44% conversion), a bicyclization reaction took place to afford an approximate 1:1 mixture of the diastereomers **20** and **21** (Scheme 6) in 86 and 62% yields (related to conversion), respectively, which could be easily separated by flash chromatography; no other products were detectable. The structures of the isomers were differentiated on the basis of the magnitude of the ^{1}H NMR coupling constant $J_{4,5}$, which is 10.7 Hz for **20** and 2.7 Hz for **21**, which correspond to dihedral angles of about 0 and 120°, respectively.

In the case of the dihydroazepinones **10** the type of annulation has an important effect on the photochemical behavior. Whereas on direct excitation of **10a**,**b** (ca. 10^{-3} M in diethyl ether, $\lambda > 210$ nm, 1 h), reaction mixtures were formed which, after chromatographic work up, gave the known aldehydes **22a**,**b**[29] in 80 and 59% yields, no defined product could be detected after the photolysis of **10c**,**d**. Although there was no direct evidence for the formation of the tricyclic lactams **23a**,**b**, their intermediate formation



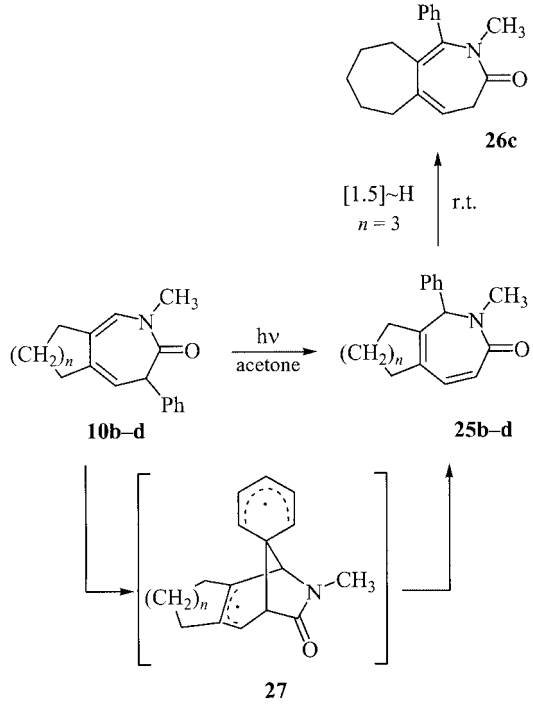
Scheme 6.

through a 4π-cyclization process seems likely (Scheme 7). Subsequent CO extrusion by a Norrish I reaction would then lead to the imines **24**, which are hydrolyzed during chromatographic purification.



Scheme 7.

The acetone-sensitized photolysis of **10** produced quite different results. With the exception of the lowest homologue, **10a**, which gave no specific products, the dihydroazepinones were transformed upon irradiation (ca. 10^{-3} M in acetone; $\lambda > 270$ nm; **b**: 2 h, **c**: 1 h, **d**: 0.5 h) into the isomeric compounds **25b–d** in 42, 60 and 62% yields (Scheme 8). Among the new products, **25c** was thermally labile and rearranged even at room temperature by a 1,5-hydrogen shift to the isomer **26c** which has the double bonds in the same position as the starting compounds. The structures of the photoproducts are clearly supported by the spectroscopic data. For example, in the ^{1}H NMR spectra of **25b** and **25d**, the AB pattern of the olefinic protons at C-4 and C-5 with a coupling constant of $J_{4,5}$ = 12.2 Hz and the singlet signals of the benzylic 1-H (4.72/4.92 ppm) are convincing evidence for the particular functionalities of the lactam ring. In contrast, the ring protons of the secondary product **26c** form a three-spin system.



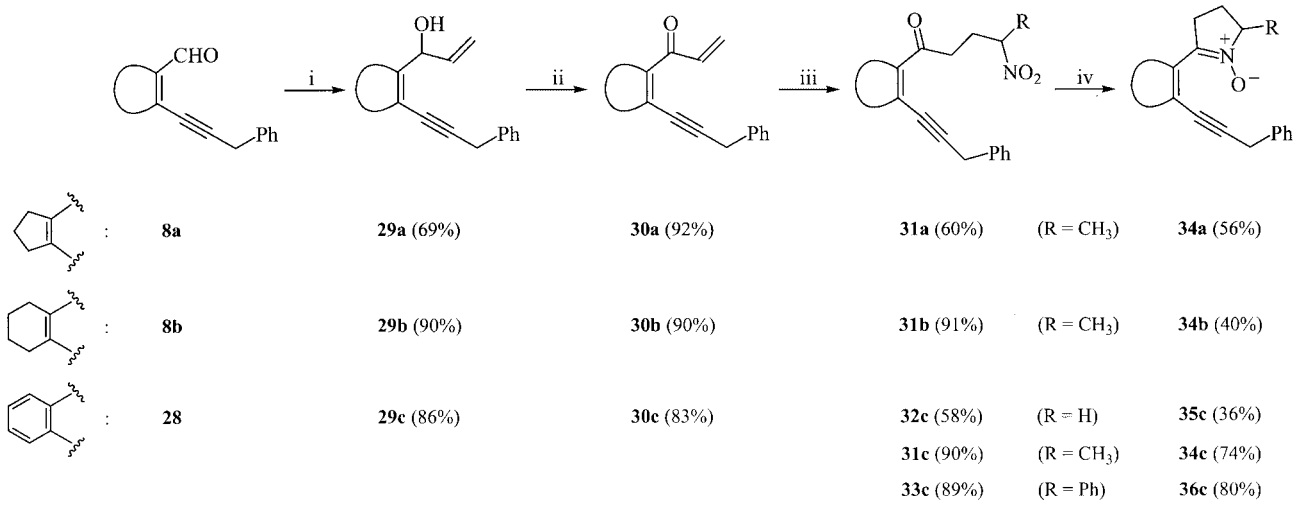
Scheme 8.

The conversion of the lactam **10** into the isomeric compound **25** is connected with a 1,5-migration of the phenyl group along the diene system. The spin-correlation effect, that is, the different result obtained under acetone-sensitized photolysis compared with the direct excitation modus is an indication of a triplet process and, consequently, not a concerted sigmatropic shift. If the possible 1,5-hydrogen migration did not take place, the special migratory ability of phenyl groups through the formation of bridged species must be recognized. Although a multistep walk process[30] would also be feasible, we prefer a mechanism through a bridged intermediate like **27** (Scheme 8).

Comparable phenyl migrations are very rare. Besides a report of the photochemical 1,5-phenyl shift in dibenzoylethenes,[31] which, however, happens along an ene-carbonyl unit to an oxygen terminus, we are aware of only the few examples detected by Uda and co-workers during studies on the photochemistry of phenyl-substituted oxepinones and cyclohepta-1,3-dienones.[32] As in our case, all these transformations take place from the excited triplet state.

Synthesis and Transformation of Pyrroline *N*-Oxide Systems[33]

In order to broaden the scope of the above reaction principle, the synthesis of pyrrolidino-annulated azepinones from the pyrroline *N*-oxides **34**–**36** was investigated.[34] The required dipolar precursors were prepared by following a procedure which was recently developed for the synthesis of 13-azasteroid analogues (see Scheme 9).[35] Thus, Grignard



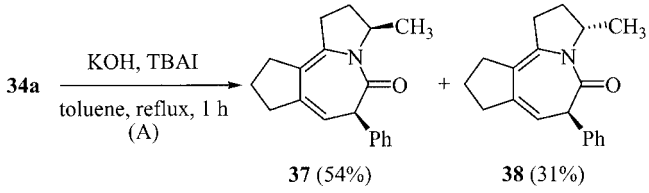
Scheme 9. Reagents and conditions: (i) vinylmagnesium bromide, THF; (ii) IBX, DMSO, room temp.; (iii) RCH_2NO_2, iPr_2NH, $CHCl_3$; (iv) Fe, HCl, EtOH, reflux.

reaction of the aldehydes **8a**,**b** and **28** with vinylmagnesium bromide gave the allylic alcohols **29a**–**c** (69–90%) and, after oxidation with IBX (*o*-iodoxybenzoic acid), the vinyl ketones **30a**–**c** (ca. 90%). Subsequent Michael addition with nitromethane, nitroethane, and phenylnitromethane, respectively, afforded the compounds **31a**–**c**, **32c**, and **33c** (58–91%), which were transformed into the pyrroline *N*-oxides **34a**–**c**, **35c**, and **36c** (36–80%) by reductive cyclization with Fe/HCl, according to a protocol of Black and Strauch.[36]

The cyclization experiments were typically carried out by refluxing solutions of the nitrones **34**–**36** in toluene with potassium hydroxide as base and catalytic amounts of tetra-*n*-butylammonium iodide (TBAI) to enhance the propargylallene isomerization process (procedure A) or, in some cases, by stirring methanolic solutions of the nitrones at room temperature with sodium methoxide as the base (procedure B).

The cyclopenteno-annulated nitrone system **34a** was refluxed in toluene according to procedure (A). After complete conversion (1 h, TLC) and work up, a 4:7 mixture of two products was obtained in 85% yield which could not be separated by chromatography. However, crystallization of an ethanolic solution of the mixture gave the major compound in the pure form. According to the analytical data the product was identified as an isomer of the starting compound **34a**, namely, the two-fold annulated dihydroazepinone **37**. The second product turned out to possess the isomeric structure **38** with the 3-methyl and 6-phenyl groups in a *trans* position (Scheme 10).

The identification of the products was mainly based on spectroscopic information, especially the ^1H and ^{13}C NMR data. In the case of **37**, the strong IR absorption at 1667 cm^{-1} and the ^{13}C NMR signal at δ = 163 ppm indicate the presence of the lactam moiety. Further support for the structure comes from the ^1H NMR signals at δ = 3.48 and 5.28 ppm which have been assigned to the protons at C-6 and C-7 (J = 5.2 Hz). The relatively high-field absorption of the olefinic 7-H is characteristic of an olefinic hydrogen



Scheme 10.

atom in the δ position to the dienamide unit. These assignments are unambiguously supported by the crystal structure analysis[37] of **37** which also confirmed the *cis* arrangement of the methyl and phenyl groups (Figure 1).

In a similar manner, the cyclohexeno-annulated nitrone **34b** was refluxed in toluene with KOH/TBAI for 1 h to give a mixture of the two diastereomers **39** and **40** in 40 and 16% yield, respectively (Scheme 11). The structural assignment of the major component to the *cis* component **39**, obtained as a colorless solid after flash chromatography of the reaction mixture and subsequent crystallization of the main fraction from ethanol, was mainly based on the almost identical ^1H NMR pattern of the 3-H, 6-H, and 7-H protons of the pyrrolidine-azepinone part of the molecule to that of the cyclopenteno derivative **37**. In contrast, the signals of 6-H and 7-H of **40** are shifted upfield by 0.85 and 0.24 ppm, respectively.

After the reaction of **34b** with sodium methoxide in methanol for 5 h at room temperature, a mixture of three compounds was obtained after work up. Besides the 6,7,5-ring systems **39** and **40**, the isomeric 6,5,5-product **41** was isolated (Scheme 11). The formation of this type of compound was recently observed in an analogous heterocyclization reaction.[7] Important structural indications are the ^1H NMR signals of the proton at C-3′ (m, δ = 5.00 ppm, $J_{3',CH3}$ = 6.5 Hz), the benzylic methylene protons at C-2 (s, δ = 3.98 ppm), and, in addition, the ^{13}C signal at δ = 185 ppm as well as the 1619 cm^{-1} IR absorption of the keto

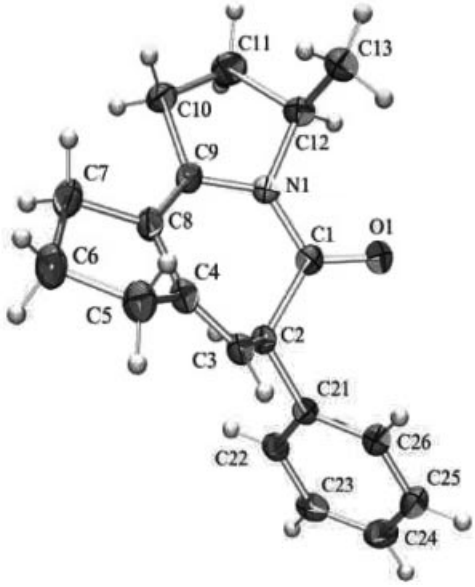
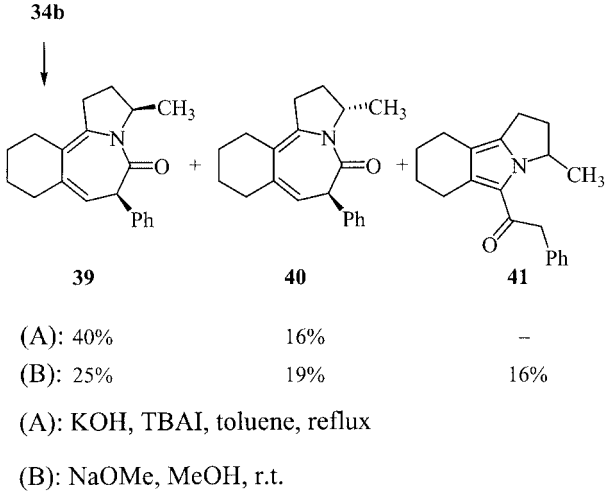


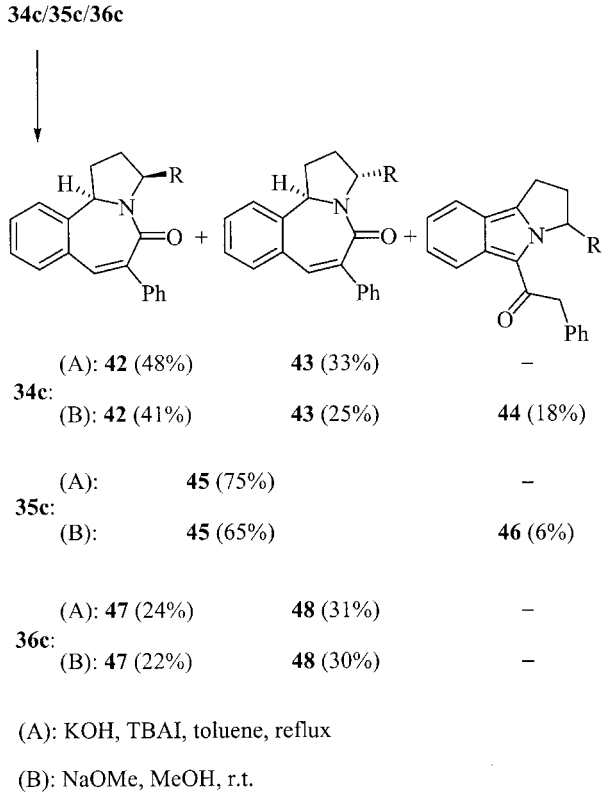
Figure 1. ORTEP plot of the crystal structure of the bis-annulated dihydroazepinone **37** (hydrogen atoms omitted for clarity; the numbering does not correspond to the correct nomenclature); selected bond lengths [Å] and torsion angles [°]: C1–C2 1.531, C1–O1 1.223, C2–C3 1.515, C3–C4 1.341, C4–C5 1.513, C4–C8 1.456, C8–C7 1.520, C8–C9 1.353, C9–N1 1.408, C9–C10 1.508, C12–N1 1.484, C1–N1 1.371; N1–C1–C2–C3 74.0, C1–C2–C3–C4 –70.4, C2–C3–C4–C8 6.0, C3–C4–C8–C9 33.2, C4–C8–C9–N1 –1.4, C8–C9–N1–C1 –26.7.



Scheme 11.

group. Hence, the compound does not contain an amide function.

The base-catalyzed transformation of the benzo-annulated nitrone derivative **34c** proceeded in the same general way generating the corresponding tricyclic heterocycles **42** and **43** (Scheme 12) upon application of procedure A, and, additionally, the isoindole **44** after reacting **34c** under conditions B; in both cases overall yields of about 80% were obtained. Attempts were made to separate the products by flash chromatography and crystallization, however, only **43** (as crystals) and **44** (as an oil) were obtained in their pure form, whereas **42** had to be analyzed as a crystalline mixture with **43**.



Scheme 12.

Although much structural information was obtained for the dihydroazepinones **42** and **43**, including the relative stereochemistry at C-3 and C-11b, from inspection of their NMR spectra, crystallographic analysis of **43** confirmed its structure and the *cis* geometry of the methyl group and the 11b-H proton (Figure 2).

With the pyrroline *N*-oxides **35c** and **36c** it was shown that a methyl group in the α′-position to the ring nitrogen of the nitrone systems is not mandatory. Reaction of **35c** according to procedure A resulted in the formation of the dihydroazepinone **45** (R = H); again, an isoindole (**46**) was identified after treatment of a methanolic solution of **35c** with sodium methoxide at room temperature. In contrast, the reaction of the phenyl-substituted nitrone **36c** gave a 3:4 mixture of the 6,7,5-ring isomers **47** and **48** as the only products under both conditions. It is no surprise that in the case of the benzo-annulated nitrones (unlike the alkeno-annulated systems, see Schemes 3 and 10) the isolated heterocycles are those which are formed by a final hydrogen shift, that is, after reestablishment of the aromaticity of the six-membered rings.

The stereochemical assignment of structure **47** to the minor component, isolated as colorless crystals, with *trans* geometry of the phenyl group at C-3 and the 11b-H atom was tentatively derived from the fact that 3-H (δ = 5.21 ppm) is coupled with both vicinal protons 2α-H and 2β-H (J = 7.5 Hz) and not with only one hydrogen as in

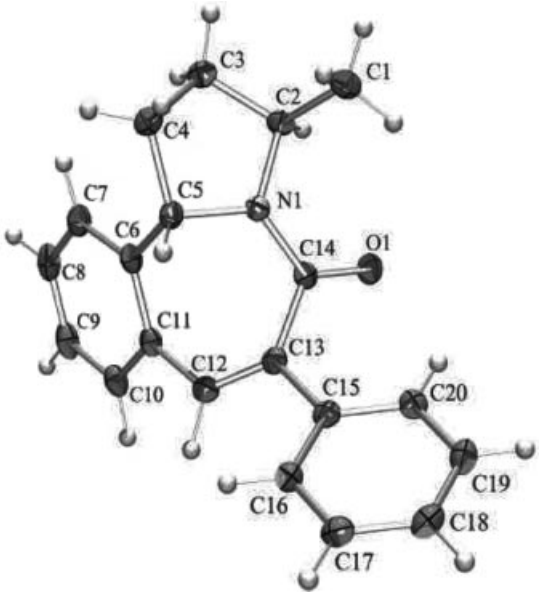


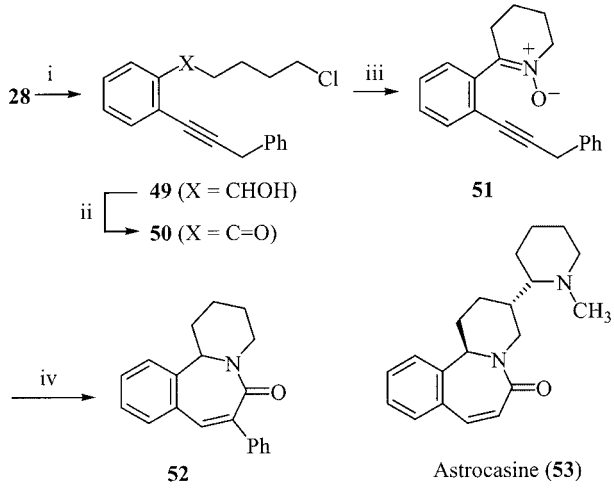
Figure 2. ORTEP plot of the crystal structure of the dihydrobenzoazepinone **43** (hydrogen atoms omitted for clarity; the numbering does not correspond to the correct nomenclature); selected bond lengths [Å] and torsion angles [°]: C2–N1 1.4825, C4–C5 1.5246, C5–N1 1.4772, C5–C6 1.5222, C6–C11 1.4097, C11–C12 1.4733, C12–C13 1.3462, C13–C14 1.5134, C14–N1 1.3454, C14–O1 1.2350; N1–C14–C13–C12 –59.16, C14–C13–C12–C11 9.98, C13–C12–C11–C6 40.74, C12–C11–C6–C5 –2.14, C11–C6–C5–N1 –66.61, C6–C5–N1–C14 63.52, C5–N1–C14–C13 14.66.

case of the major compound **48** ($\delta_{3\text{-H}}$ = 5.37 ppm, J = 7.9 Hz) and the related product **43** with clearly proven stereochemistry. The structure of **47** was later unambiguously confirmed by crystallography.[37]

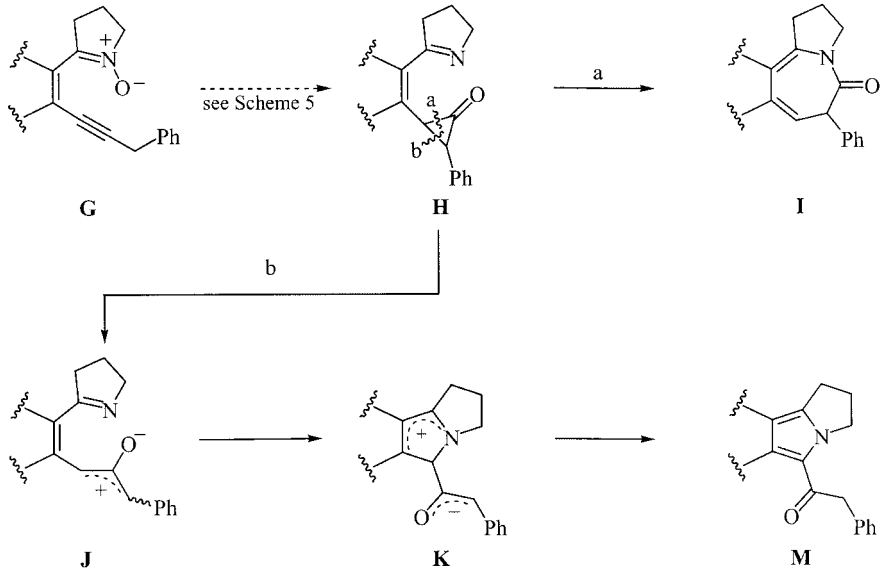
Mechanistically, the formation of the new bis-annulated dihydroazepinones of type **I** (Scheme 13) can be explained by the same general route as sketched in Scheme 5 for the transformation **A**→**F**. The additional occurrence of the isoindole derivatives **41**, **44**, and **46** (general structure **M**, Scheme 13) lends further support to a cyclopropanone of structure **H** as a key intermediate within the proposed reaction cascade. Besides the rearrangement of **H** to a dihydroazepinone **I** by cleavage of bond a, the alternative opening of bond b would lead to an oxallyl species **J** which, after nucleophilic attack of the imine nitrogen with formation of the isomeric dipole **K**, produces the isoindole **M** by simple tautomerization.

Synthesis of Astrocasine Analogue 52

The structure and absolute configuration of the alkaloid astrocasine (**53**, Scheme 14), isolated from *Astrocasia phyllantoides*,[19] was determined by Silverton and co-workers by crystallography.[38] The main part of the molecule con-



Scheme 14. Reagents and conditions: (i) $BrMg(CH_2)_4Cl$, THF, –40 °C; (ii) IBX, DMSO, room temp.; (iii) $NH_2OH{\cdot}HCl$, K_2CO_3, $EtOH/H_2O$, reflux; (iv) KOH, TBAI, toluene, reflux.



Scheme 13.

sists of a benzopiperidinoazepin-3-one system with 6,7,6-ring annulation, which is homologous to the 6,7,5-systems **42**, **43**, **45**, **47**, and **48** described above, and the question arose as to whether the former system would be available by the same general route. Therefore preliminary studies toward the preparation of the azepinone derivative **52**, envisaged as a model of the naturally occurring compound **53**, were made.

The synthesis of the dipolar precursor **51** is shown in Scheme 14. Grignard reaction of **28** with 4-chlorobutylmagnesium bromide, prepared in situ from 4-chlorobutyl bromide and magnesium in THF, afforded the alcohol **49**,[39] which was transformed into the corresponding ketone **50** by oxidation with IBX. In a variation of the dipole-forming step, **50** was treated according to a procedure of Brandman and Conley[40] with hydroxylamine hydrochloride and potassium carbonate in a 1:1 mixture of ethanol and water to give the required nitrone **51** in 42% yield. Further transformation of **51** was accomplished under our standard conditions with potassium hydroxide and TBAI in refluxing toluene to deliver the desired benzopiperidinoazepinone **52** as a crystalline compound (52%).

Conclusions

The synthetic scope and generality of the recently discovered multistep transformation of benzopentenynyl nitrones into 1,2-dihydrobenz[*c*]azepin-3-ones has been extended to structurally different systems including monocyclic and alkeno-annulated systems as well as to dihydrobenzazepinones with an additional annulation in the 1,2-position. The applicability of this methodology was further demonstrated by the preparation of a piperidino derivative of the latter series, which can be used as a model compound of the alkaloid astrocasine. Despite the complexity of the overall reaction sequence the transformations take place in mostly good yields and under unusually mild conditions at room temperature, albeit boiling toluene is preferable in the synthesis of the tricyclic heterocycles. Photochemical studies of some azepinone derivatives revealed, among other results, examples of hitherto rarely observed 1,5-phenyl migration processes.

Experimental Section

General: Melting points are uncorrected. IR: Perkin–Elmer 257 Infracord spectrometer. ^{1}H NMR: Bruker WM 250 (250 MHz), WM 400 (400 MHz), and DRX 500 (500 MHz) spectrometers. ^{13}C NMR: Bruker WM 400 (100 MHz) and DRX 500 (125 MHz) spectrometers. $CDCl_3$ as solvent and TMS as internal standard. MS: Finnigan MAT 44 S spectrometer (70 eV) with Datasystem MAT SS 200. Elemental analyses: Perkin–Elmer Elemental Analyzer 240. Flash chromatography: silica gel (silica 32–36, ICN Biomedicals). TLC: SiO_2 60 F-254, 0.2 mm (Merck).

General Procedure for the Sonogashira Reaction of the Bromo Aldehydes 7 with 3-Phenylprop-1-yne: A degassed (argon) 0.2 M solution of **7** in dry benzene was stirred with $PdCl_2(PPh_3)_2$ (5 mol%), CuI (0.05–0.1 mol%) and 3-phenylprop-1-yne (1.5 equiv.) for 15 min at room temperature, and then treated with dry triethylamine (1.1 equiv.). After completion of the reaction (TLC) the red-brown mixture was filtered and the solution was concentrated in vacuo. The crude material was purified by flash chromatography on silica gel.

2-(3′-Phenylprop-1′-ynyl)cyclopent-1-ene-1-carbaldehyde (8a): Treatment of **7a** (880 mg, 5.03 mmol, 4.5 h) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 60:1), gave **8a** (1.04 g, 98%) as a dark-yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3030, 2960, 2820, 2215 (C≡C), 1675 (C=O), 1600 (C=C), 1495, 1455, 1355, 1250, 1225, 1030 cm^{-1}. ^{1}H NMR (250 MHz): δ = 1.95 (dddd, $^3J_{4,3a/3b/5a/5b}$ = 7.6 Hz, 2 H, 4-H), 2.61 (m_c, 2 H, 3-/5-H), 2.72 (m_c, 2 H, 3-/5-H), 7.27–7.36 (m, 5 H, Ar-H), 10.07 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz): δ = 22.1 (C-4), 22.2/29.5 (C-3/-5), 39.2 (C-3′), 76.9 (C-1′), 100.0 (C-2′), 127.0 (C-Ar), 127.9 (C-Ar), 128.8 (C-Ar), 135.8 (C-1′′), 143.9/147.7 (C-1/-2), 189.0 (CHO) ppm. MS (EI, 70 eV): *m/z* (%) = 210 (91) $[M]^+$, 209 (100), 181 (15) $[M - CHO]^+$, 165 (29), 153 (25), 115 (16), 91 (11) $[CH_2Ph]^+$, 77 (11) $[C_6H_5]^+$. HRMS ($C_{15}H_{14}O$): calcd. 210.1045; found 210.1045.

2-(3′-Phenylprop-1′-ynyl)cyclohex-1-ene-1-carbaldehyde (8b): Treatment of **7b** (2.00 g, 10.6 mmol, 4 h) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 60:1), gave **8b** (3.31 g, 97%) as a pale-red oil. IR (CCl_4): $\tilde{\nu}$ = 3065, 3030, 2940, 2865, 2215 (C≡C), 1675 (C=O), 1605 (C=C), 1495, 1455, 1365, 1275, 1230, 1170 cm^{-1}. ^{1}H NMR (250 MHz): δ = 1.65 (m_c, 4 H, 4-H, 5-H), 2.20–2.29 (m, 2 H, 3-/6-H), 2.38–2.47 (m, 2 H, 3-/6-H), 3.82 (s, 2 H, 3′-H), 7.21–7.35 (m, 5 H, Ar-H), 10.21 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz): δ = 21.2 (C-4/-5), 21.9 (C-4/-5), 22.0/26.1 (C-3/-6), 32.7 (C-3′), 79.9 (C-1′), 97.6 (C-2′), 126.9 (C-Ar), 127.9 (C-Ar), 128.8 (C-Ar), 136.1 (C_q), 140.6 (C_q), 142.4 (C_q), 193.1 (CHO) ppm. MS (EI, 70 eV): *m/z* (%) = 224 (82) $[M]^+$, 209 (100), 195 (76) $[M - CHO]^+$, 181 (49), 167 (73), 163 (43), 153 (41).

2-(3′-Phenylprop-1′-ynyl)cyclohept-1-ene-1-carbaldehyde (8c): Treatment of **7c** (2.21 g, 10.9 mmol, 9 h) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 60:1), gave **8c** (2.30 g, 89%) as a dark-yellow oil. IR (CCl_4): $\tilde{\nu}$ = 2925, 2855, 2205 (C≡C), 1675 (C=O), 1595, 1495, 1455, 1255, 1180, 950 cm^{-1}. ^{1}H NMR (250 MHz): δ = 1.53–1.71 (m, 4 H, 4-/5-/6-H), 1.74–1.87 (m, 2 H, 4-/5-/6-H), 2.49 (m_c, 2 H, 3-/7-H), 2.62 (m_c, 2 H, 3-/7-H), 3.85 (s, 2 H, 3′-H), 7.19–7.36 (m, 5 H, Ar-H), 10.17 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz): δ = 24.1/25.7/25.8 (C-4/-5/-6), 26.3/32.2 (C-3/-7), 37.8 (C-3′), 81.3 (C-1′), 99.4 (C-2′), 126.9 (C-Ar), 127.9 (C-Ar), 128.8 (C-Ar), 126.1 (C_q-Ar), 146.4 (C_q), 148.1 (C_q), 192.5 (CHO) ppm. MS (EI, 70 eV): *m/z* (%) = 238 (13) $[M]^+$, 163 (57), 105 (51), 91 (100) $[CH_2Ph]^+$, 77 (45) $[C_6H_5]^+$.

2-(3′-Phenylprop-1′-ynyl)cyclooct-1-ene-1-carbaldehyde (8d): Treatment of **7d** (1.30 g, 6.00 mmol, 5 h) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 100:1), gave **8d** (1.41 g, 94%) as a dark-yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3030, 2930, 2855, 2215 (C≡C), 1675 (C=O), 1595, 1495, 1455, 1300, 1215, 1030 cm^{-1}. ^{1}H NMR (250 MHz): δ = 1.42–1.59 (m, 4 H, 5-H, 6-H), 1.72–1.84 (m, 4 H, 4-H, 7-H), 2.45 (m_c, 2 H, 3-/8-H), 2.59 (m_c, 2 H, 3-/8-H), 7.23–7.36 (m, 5 H, Ar-H), 10.22 (s, 1 H, CHO) ppm. ^{13}C NMR (100 MHz): δ = 23.5/26.0/26.2/26.6 (C-4/-5/-6/-7), 28.9/29.9 (C-3/-8), 34.4 (C-3′), 80.4 (C-1′), 98.1 (C-2′), 126.9 (C-Ar), 127.9 (C-Ar), 128.8 (C-Ar), 136.1 (C-1′′), 143.6/145.7 (C-1/-2), 192.8 (CHO) ppm. MS (EI, 70 eV): *m/z* (%) = 252 (30) $[M]^+$, 251 (38), 237 (100), 223 (23) $[M - CHO]^+$, 209 (89), 181 (47), 165 (51), 141 (38), 115 (50), 91 (81) $[CH_2Ph]^+$. HRMS ($C_{18}H_{20}O$): calcd. 252.1514; found 252.1515.

General Procedure for Formation of the Nitrones 9: Sodium acetate (3 equiv.) and, after 15 min, the aldehyde **8** (1 equiv.) were added to a stirred suspension of *N*-methylhydroxylamine hydrochloride (0.25 M, 1.3 equiv.) in dry CH_2Cl_2 at room temperature. After completion of the reaction (TLC), the mixture was hydrolyzed with water and extracted 2–3 times with CH_2Cl_2. The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel.

Methyl{[2′-(3′′-phenylprop-1′′-ynyl)cyclopent-1′-en-1′-yl]methylene}amine *N*-Oxide (9a): Treatment of **8a** (710 mg, 3.38 mmol, 6 h) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 2:1), gave **9a** (700 mg, 88%) as beige crystals, m.p. 63 °C (ethanol). IR (CCl_4): $\tilde{\nu}$ = 3025, 2945, 2845, 1550, 1495, 1415, 1295, 1165 cm^{-1}. ^1H NMR (250 MHz): δ = 1.92 (m_c, 2 H, 4′-H), 2.51 (t, $^3J_{3',4'}$ = 7.6 Hz, 2 H, 3′-H), 3.16 (m_c, 2 H, 5′-H), 3.70 (s, 3 H, NCH_3), 3.84 (s, 2 H, 3′′-H), 7.21–7.38 (m, 6 H, Ar-H, 1-H) ppm. ^{13}C NMR (100 MHz): δ = 23.2 (C-4′), 26.3/33.7 (C-3′/-5′), 36.8 (C-3′′), 53.7 (NCH_3), 78.6 (C-1′′), 98.2 (C-2′′), 126.9 (C-Ar), 127.9 (C-Ar), 128.7 (C-Ar), 129.9 (C_q-Ar), 133.1 (C-1), 136.5/140.8 (C-1′/-2′) ppm. MS (EI, 70 eV): *m/z* (%) = 239 (18) $[M]^+$, 148 (66), 120 (32), 103 (23), 91 (43) $[CH_2Ph]^+$, 77 (38) $[C_6H_5]^+$, 51 (29), 42 (100). HRMS ($C_{16}H_{17}NO$): calcd. 239.1310; found 239.1311. $C_{16}H_{17}NO$ (239.3): calcd. C 80.30, H 7.16, N 5.85; found C 79.78, H 7.31, N 5.80.

Methyl{[2′-(3′′-phenylprop-1′′-ynyl)cyclohex-1′-en-1′-yl]methylene}amine *N*-Oxide (9b): Treatment of **8b** (4.55 g, 20.3 mmol, 22 h) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 2:1, 1:2), gave **9b** (3.73 g, 72%) as a colorless oil. IR (CCl_4): $\tilde{\nu}$ = 3030, 2940, 2860, 1535, 1495, 1450, 1420, 1245, 1175, 1160 cm^{-1}. ^1H NMR (250 MHz): δ = 1.62 (m_c, 4 H, 4′-H, 5′-H), 2.31 (br. s, 2 H, 3′-H), 2.88 (br. s, 2 H, 6′-H), 3.66 (s, 3 H, NCH_3), 3.81 (s, 2 H, 3′′-H), 7.22–7.37 (m, 5 H, Ar-H), 7.51 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz): δ = 21.7/22.1 (C-4′/-5′), 26.2/26.6 (C-3′/-6′), 31.6 (C-3′′), 54.3 (NCH_3), 82.2 (C-1′′), 95.8 (C-2′′), 125.3 (C_q), 126.9 (C-Ar), 127.9 (C-Ar), 128.7 (C-Ar), 136.4 (C_q), 138.7 (C-1), 138.8 (C_q) ppm. MS (EI, 70 eV): *m/z* (%) = 253 (46) $[M]^+$, 234 (29), 224 (13), 162 (100) $[M - CH_2Ph]^+$, 134 (23), 115 (22), 91 (24) $[CH_2Ph]^+$, 42 (25). HRMS ($C_{17}H_{19}NO$): calcd. 253.1467; found 253.1465.

Methyl{[2′-(3′′-phenylprop-1′′-ynyl)cyclohept-1′-en-1′-yl]methylene}amine *N*-Oxide (9c): Treatment of **8c** (500 mg, 2.00 mmol, 7 h) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 2:1, 1:2), gave **9c** (300 mg, 57%) as a dark-yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3025, 2925, 2850, 1550, 1495, 1450, 1415, 1165, 1130 cm^{-1}. ^1H NMR (250 MHz): δ = 1.52–1.64 (m, 4 H, 4′-/5′-/6′-H), 1.73–1.84 (m, 2 H, 4′-/5′-/6′-H), 2.49 (m_c, 2 H, 3′-H), 2.97 (m_c, 2 H, 7′-H), 3.66 (s, 3 H, NCH_3), 3.81 (s, 2 H, 3′′-H), 7.22–7.37 (m, 5 H, Ar-H), 7.42 (s, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz): δ = 26.1/26.2/26.3 (C-4′/-5′/-6′), 27.4/32.4 (C-3′/-7′), 35.6 (C-3′′), 54.1 (NCH_3), 83.5 (C-1′′), 97.1 (C-2′′), 126.8 (C-Ar), 127.9 (C-Ar), 128.7 (C-Ar), 132.4 (C_q), 136.9 (C_q), 137.3 (C-1), 142.2 (C_q) ppm. MS (EI, 70 eV): *m/z* (%) = 267 (10) $[M]^+$, 176 (68) $[M - CH_2Ph]^+$, 91 (67) $[CH_2Ph]^+$, 77 (26) $[C_6H_5]^+$, 65 (27), 57 (27), 42 (100). HRMS ($C_{18}H_{21}NO$): calcd. 267.1623; found 267.1625.

Methyl{[2′-(3′′-phenylprop-1′′-ynyl)cyclooct-1′-en-1′-yl]methylene}amine *N*-Oxide (9d): Treatment of **8d** (550 mg, 2.58 mmol, 22 h) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 2:1), gave **9d** (501 mg, 82%) as a yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3025, 2925, 2855, 1550, 1450, 1225, 1165, 1030 cm^{-1}. ^1H NMR (250 MHz): δ = 1.40–1.55 (m, 4 H, 4′-/5′-/6′-/7′-H), 1.59–1.80 (m, 4 H, 4′-/5′-/6′-/7′-H), 2.47 (m_c, 2 H, 3′-H), 2.92 (m_c, 2 H, 8′-H), 3.67 (s, 3 H, NCH_3), 3.82 (s, 2 H, 3′′-H), 7.23–7.37 (m, 5 H, Ar-H), 7.55 (s, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz): δ = 25.3/26.0/26.2/26.5 (C-4′/-5′/-6′/-7′), 28.9/30.2 (C-3′/-8′), 32.7 (C-3′′), 54.5 (NCH_3), 82.8 (C-1′′), 96.0 (C-2′′), 126.8 (C-Ar), 127.8 (C-Ar), 128.6 (C-Ar), 129.2 (C_q-Ar), 136.8 (C_q), 136.9 (C-1), 138.9 (C_q) ppm. MS (EI, 70 eV): *m/z* (%) = 281 (39) $[M]^+$, 238 (17), 224 (21), 190 (100) $[M - CH_2Ph]^+$, 162 (30), 115 (36), 91 (70) $[CH_2Ph]^+$, 77 (19) $[C_6H_5]^+$, 42 (59). HRMS ($C_{19}H_{23}NO$): calcd. 281.1780; found 281.1780.

General Procedure for the Base-Catalyzed Transformation of the Nitrones 9 into 10: A 0.1 M solution of the nitrone **9** in dry methanol was treated with base (0.5 equiv.) and stirred at room temperature until completion of the reaction (TLC). The mixture was hydrolyzed with water and extracted with CH_2Cl_2. The combined organic phases were washed with saturated aqueous NH_4Cl and with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by flash chromatography on silica gel.

2-Methyl-4-phenyl-4,6,7,8-tetrahydrocyclopenta[*c*]azepin-3(2*H*)-one (10a): Treatment of **9a** (155 mg, 0.65 mmol, KOH, 1.5 h) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 3:1), gave **10a** (123 mg, 79%) as a colorless solid, m.p. 167–168 °C (ethanol). IR (CCl_4): $\tilde{\nu}$ = 3025, 2960, 2850, 1670 (C=O), 1375, 1260, 1220, 1100 cm^{-1}. ^1H NMR (250 MHz): δ = 1.86 (m_c, 2 H, 7-H), 2.42–2.63 (m, 4 H, 6-H, 8-H), 3.18 (s, 3 H, NCH_3), 3.74 (md, $^3J_{4,5}$ = 5.5 Hz, 1 H, 4-H), 5.48 (md, $^3J_{5,4}$ = 5.5 Hz, 1 H, 5-H), 6.11 (s, 1 H, 1-H), 7.23–7.39 (m, 5 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 24.7 (C-7), 31.0/31.1 (C-6/-8), 37.0 (NCH_3), 52.9 (C-4), 118.5/124.3 (C-5/-4′), 127.0 (C-1), 128.2 (C-Ar), 129.3 (C-Ar), 130.7 (C_q), 138.7/143.3 (C-5a/-8a), 164.9 (C-3) ppm. UV (CH_3CN): λ_{max} = 287 nm (ε = 4900 $dm^3 mol^{-1} cm^{-1}$). MS (EI, 70 eV): *m/z* (%) = 239 (100) $[M]^+$, 238 (54), 210 (18) $[M - NCH_3]^+$, 182 (10) $[M - CONCH_3]^+$, 134 (42), 77 (9) $[C_6H_5]^+$. $C_{16}H_{17}NO$ (239.32): calcd. C 80.30, H 7.16, N 5.85; found C 79.95, H 7.36, N 5.80.

2-Methyl-4-phenyl-2,4,6,7,8,9-hexahydro-3*H*-2-benzazepin-3-one (10b): Treatment of **9b** (100 mg, 0.39 mmol, KOH, 3 h) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 30:1), gave **10b** (88 mg, 88%) as a colorless solid, m.p. 94–95 °C (ethanol). IR (CCl_4): $\tilde{\nu}$ = 2935, 2860, 1675 (C=O), 1600 (C=C), 1445, 1380, 1260, 1220, 1085 cm^{-1}. ^1H NMR (250 MHz): δ = 1.47–1.71 (m, 2 H, 7-/8-H), 1.79–1.96 (m, 2 H, 7-/8-H), 2.18–2.44 (m, 4 H, 6-H, 9-H), 3.13 (s, 3 H, NCH_3), 3.74 (br. s, 1 H, 4-H), 5.45 (d, $^3J_{5,4}$ = 6.1 Hz, 1 H, 5-H), 6.01 (s, 1 H, 1-H), 7.23–7.40 (m, 5 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 25.9/26.0 (C-7/-8), 31.6/32.1 (C-6/-9), 35.7 (NCH_3), 51.4 (C-4), 123.6 (C-5), 126.0 (C-Ar), 126.9 (C-Ar), 127.6 (C_q), 128.2 (C-Ar), 129.4 (C-1), 137.2 (C_q), 138.4 (C_q), 167.4 (C-3) ppm. UV (CH_3CN): λ_{max} = 258 nm (ε = 5090 $dm^3 mol^{-1} cm^{-1}$). MS (EI, 70 eV): *m/z* (%) = 253 (100) $[M]^+$, 224 (25) $[(M - NCH_3) + 1]^+$, 196 (23) $[(M - CONCH_3) + 1]^+$, 176 (18) $[M - C_6H_5]^+$, 148 (40), 115 (27), 77 (16) $[C_6H_5]^+$. $C_{17}H_{19}NO$ (253.34): calcd. C 80.60, H 7.56, N 5.53; found C 80.15, H 7.62, N 5.43.

2-Methyl-4-phenyl-4,6,7,8,9,10-hexahydrocyclohepta[*c*]azepin-3(2*H*)-one (10c): Treatment of **9c** (105 mg, 0.39 mmol, KOH, 1.5 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 2:1) gave **10c** (48 mg, 46%) as a colorless solid, m.p. 128–129 °C (ethanol). IR (CCl_4): $\tilde{\nu}$ = 2925, 2850, 1675 (C=O), 1585, 1495, 1455, 1380, 1260, 1115, 1085 cm^{-1}. ^1H NMR (250 MHz): δ = 1.47–1.74 (m, 6 H, 7-H, 8-H, 9-H), 2.28–2.51 (m, 4 H, 6-H, 10-H), 3.13 (s, 3 H, NCH_3), 3.56 (d, $^3J_{4,5}$ = 6.1 Hz, 1 H, 4-H), 5.53 (d, $^3J_{5,4}$ = 6.1 Hz, 1 H, 5-H), 6.13 (s, 1 H, 1-H), 7.28–7.41 (m, 5 H, Ar-H) ppm. ^{13}C NMR (100 MHz): δ = 30.0/30.2/31.9

(C-7/-8/-9), 35.2/35.7 (C-6/-10), 35.8 (NCH_3), 51.8 (C-4), 124.4/127.0 (C-5/-4′), 127.5 (C-1), 128.3 (C-Ar), 129.6 (C-Ar), 132.2 (C_q), 138.6 (C_q), 142.0 (C_q), 166.9 (C-3) ppm. UV (CH_3CN): λ_{max} = 266 nm (ε = 5500 $dm^3 mol^{-1} cm^{-1}$). MS (EI, 70 eV): *m/z* (%) = 267 (100) $[M]^+$, 252 (23) $[M - CH_3]^+$, 238 (35) $[M - NCH_3]^+$, 210 (11) $[M - CONCH_3]^+$, 176 (30). $C_{18}H_{21}NO$ (267.37): calcd. C 80.88, H 7.71, N 5.13; found C 80.86, H 7.92, N 5.24.

2-Methyl-4-phenyl-2,4,6,7,8,9,10,11-octahydro-3*H*-cycloocta[*c*]-azepin-3-one (10d): Treatment of **9d** (200 mg, 0.71 mmol, KOH, 1.5 h) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 20:1), gave **10d** (130 mg, 65%) as a colorless solid, m.p. 121–123 °C (ethanol). IR (CCl_4): $\tilde{\nu}$ = 2930, 2855, 1675 (C=O), 1580, 1455, 1380, 1305, 1260, 1220, 1120, 1080 cm^{-1}. ^1H NMR (250 MHz): δ = 1.14–1.51 (m, 3 H, 8-/9-H), 1.55–1.85 (m, 5 H, 7-/8-/9-/10-H), 2.15–2.29 (m, 2 H, 6-/11-H), 2.41–2.54 (m, 1 H, 6-/11-H), 2.57–2.72 (m, 1 H, 6-/11-H), 3.15 (s, 3 H, NCH_3), 3.49 (d, $^3J_{4,5}$ = 6.1 Hz, 1 H, 4-H), 5.53 (d, $^3J_{5,4}$ = 6.1 Hz, 1 H, 5-H), 6.15 (s, 1 H, 1-H), 7.26–7.42 (m, 5 H, Ar-H) ppm. ^{13}C NMR (100 MHz): δ = 25.1/25.7 (C-8/-9), 30.1/31.9 (C-7/-10), 33.1/33.2 (C-6/-11), 35.7 (NCH_3), 51.8 (C-4), 124.6/128.0 (C-5/-4′), 127.0 (C-Ar), 128.3 (C-Ar), 129.7 (C-1), 131.0 (C_q-Ar), 138.7 (C_q), 141.6 (C_q), 166.8 (C-3) ppm. UV (CH_3CN): λ_{max} = 264 nm (ε = 3830 $dm^3 mol^{-1} cm^{-1}$). MS (EI, 70 eV): *m/z* (%) = 281 (100) $[M]^+$, 266 (16) $[M - CH_3]^+$, 252 (48) $[M - NCH_3]^+$, 238 (30), 224 (36) $[M - CONCH_3]^+$, 190 (34). $C_{19}H_{23}NO$ (281.40): calcd. C 81.10, H 8.24, N 4.98; found C 80.96, H 8.42, N 4.89.

2-Methyl-4-phenyl-1,6,7,8-tetrahydrocyclopenta[*c*]azepin-3(2*H*)-one (11a): A solution of **10a** (330 mg, 1.38 mmol) in dry toluene (70 mL) was refluxed for 2 h and then concentrated in vacuo. Separation of the isomers by flash chromatography (cyclohexane/ethyl acetate, 10:1, 3:1) gave, besides **10a** (170 mg, 52%), **11a** (145 mg, 44%) as colorless crystals, m.p. 109–110 °C (ethanol). IR (CCl_4): $\tilde{\nu}$ = 2960, 2890, 2835, 1630 (C=O), 1440, 1395, 1225, 1160, 1065 cm^{-1}. ^1H NMR (500 MHz): δ = 2.01 (m_c, 2 H, 7-H), 2.52–2.58 (m, 2 H, 6-/8-H), 2.61–2.67 (m, 2 H, 6-/8-H), 3.11 (s, 3 H, NCH_3), 3.78 (s, 2 H, 1-H), 6.69 (s, 1 H, 5-H), 7.26 (m_c, 1 H, Ar-H), 7.31–7.35 (m, 2 H, Ar-H), 7.52–7.56 (m, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 23.4 (C-7), 34.3/36.2 (C-6/-8), 35.8 (NCH_3), 47.7 (C-1), 127.5 (C-Ar), 128.0 (C-Ar), 128.3 (C-Ar), 128.7 (C-Ar), 139.5 (C_q), 139.6 (C_q), 139.8 (C_q), 142.6 (C_q), 168.2 (C-3) ppm. MS (EI, 70 eV): *m/z* (%) = 239 (100) $[M]^+$, 210 (33) $[M - NCH_3]^+$, 183 (54), 182 (17) $[M - CONCH_3]^+$, 134 (29). $C_{16}H_{17}NO$ (239.32): calcd. C 80.30, H 7.16, N 5.85; found C 79.93, H 7.28, N 5.78.

2-Methyl-4-phenyl-1,2,6,7,8,9-hexahydro-3*H*-2-benzazepin-3-one (11b): A solution of **10b** (500 mg, 1.97 mmol) in dry toluene (100 mL) was refluxed for 2 h and then concentrated in vacuo. Separation of the isomers by flash chromatography (cyclohexane/ethyl acetate, 10:1, 3:1) gave, besides **10b** (239 mg, 48%), **11b** (251 mg, 50%) as a colorless oil. IR (CCl_4): $\tilde{\nu}$ = 2935, 2860, 1635 (C=O), 1440, 1395, 1220, 1145, 1000 cm^{-1}. ^1H NMR (250 MHz): δ = 1.67 (m_c, 4 H, 7-H, 8-H), 2.20 (m_c, 2 H, 6-/9-H), 2.33 (m_c, 2 H, 6-/9-H), 3.13 (s, 3 H, NCH_3), 3.65 (s, 2 H, 1-H), 6.57 (s, 1 H, 5-H), 7.25–7.38 (m, 3 H, Ar-H), 7.52–7.58 (m, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz): δ = 22.3/22.5 (C-7/-8), 28.4/31.0 (C-6/-9), 35.4 (NCH_3), 53.6 (C-1), 127.5 (C-Ar), 128.1 (C-Ar), 128.2 (C-Ar), 133.5 (C_q), 134.2 (C-5), 136.3 (C_q), 138.5 (C_q), 139.3 (C_q), 167.5 (C-3) ppm. MS (EI, 70 eV): *m/z* (%) = 253 (100) $[M]^+$, 252 (44), 224 (46) $[M - NCH_3]^+$, 197 (20), 196 (54) $[M - CONCH_3]^+$, 136 (49), 77 (22) $[C_6H_5]^+$. HRMS ($C_{17}H_{19}NO$): calcd. 253.1467; found 253.1470. $C_{17}H_{19}NO$ (253.34): calcd. C 80.60, H 7.56, N 5.53; found C 80.00, H 7.46, N 5.37.

2-Methyl-4-phenyl-1,2,6,7,8,9,10,11-octahydro-3*H*-cycloocta[*c*]-azepin-3-one (11d): A solution of **10d** (300 mg, 1.07 mmol) in dry toluene (50 mL) was refluxed for 2 h and then concentrated in vacuo. Separation of the isomers by flash chromatography (cyclohexane/ethyl acetate, 10:1, 3:1) gave, besides **10d** (212 mg, 71%), **11d** (85 mg, 28%) as a colorless oil. IR (CCl_4): $\tilde{\nu}$ = 2925, 2855, 1640 (C=O), 1470, 1445, 1395, 1225, 1115, 1005 cm^{-1}. ^1H NMR (250 MHz): δ = 1.43–1.76 (m, 8 H, 7-H, 8-H, 9-H, 10-H), 2.30–2.47 (m, 4 H, 6-H, 11-H), 3.12 (s, 3 H, NCH_3), 3.74 (br. s, 2 H, 1-H), 6.64 (s, 1 H, 5-H), 7.22–7.39 (m, 3 H, Ar-H), 7.52–7.60 (m, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz): δ = 26.0/26.4/28.6/29.6/31.0/32.7 (C-6/-7/-8/-9/-10/-11), 35.1 (NCH_3), 53.8 (C-1), 127.5 (C-Ar), 128.1 (C-Ar), 128.2 (C-Ar), 129.6 (C_q), 134.8 (C-5), 136.9 (C_q), 139.0 (C_q), 139.3 (C_q), 167.1 (C-3) ppm. MS (EI, 70 eV): *m/z* (%) = 281 (100) $[M]^+$, 252 (44) $[M - NCH_3]^+$, 224 (37) $[M - CONCH_3]^+$, 190 (32), 91 (23), 42 (34). HRMS ($C_{19}H_{23}NO$): calcd. 281.1780; found 281.1780.

(*Z*)-3,6-Diphenylhex-2-en-4-ynal (13): A degassed and stirred solution of **12** (R^1 = Ph) (1.60 g, 7.58 mmol) in dry benzene was treated with $PdCl_2(PPh_3)_2$ (260 mg, 0.37 mmol), CuI (ca. 10 mg), 3-phenylprop-1-yne (1.15 g, 9.86 mmol) and, after 15 min, with dry triethylamine (849 mg, 8.34 mmol). The reaction mixture was stirred for 1.5 h under argon at room temperature. After filtration and concentration of the solution in vacuo, purification of the reddish-brown residue by flash chromatography (cyclohexane/ethyl acetate, 20:1) afforded **13** (668 mg, 36%) as a dark-yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3065, 3030, 2830, 2225 (C≡C), 1675 (C=O), 1565, 1495, 1450, 1340, 1140 cm^{-1}. ^1H NMR (250 MHz): δ = 3.97 (s, 2 H, 6-H), 6.76 (d, $^3J_{2,1}$ = 7.9 Hz, 1 H, 2-H), 7.26–7.47 (m, 8 H, Ar-H), 7.75–7.81 (m, 2 H, Ar-H), 10.29 (d, $^3J_{1,2}$ = 7.9 Hz, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz): δ = 26.3 (C-2), 77.8 (C-4), 101.6 (C-5), 127.1 (C-Ar), 127.1 (C-Ar), 128.0 (C-Ar), 128.8 (C-Ar), 128.9 (C-Ar), 131.0 (C-Ar), 131.5 (C-2), 135.5 (C_q-Ar), 136.0 (C_q-Ar), 142.9 (C-3), 193.4 (C-1) ppm. MS (EI, 70 eV): *m/z* (%) = 246 (66) $[M]^+$, 245 (100), 217 (85) $[M - CHO]^+$, 215 (85), 202 (96), 155 (87) $[M - CH_2Ph]^+$, 139 (33), 115 (42). HRMS ($C_{18}H_{14}O$): calcd. 246.1045; found 246.1039.

Methyl{[(*Z*)-3,6-diphenylhex-2-en-4-ynyl]methylene}amine *N*-Oxide (14): Treatment of **13** (668 mg, 2.71 mmol, 8 h) according to the general procedure, and subsequent purification by flash chromatography (cyclohexane/ethyl acetate, 1:2), gave **14** (643 mg, 86%) as a yellow, viscous oil which was crystallized from ethanol, m.p. 101–102 °C (ethanol; decomp.). IR (CCl_4): $\tilde{\nu}$ = 3065, 3025, 2945, 2225 (C≡C), 1535, 1495, 1410, 1340, 1170 cm^{-1}. ^1H NMR (250 MHz): δ = 3.76 (s, 3 H, NCH_3), 3.96 (s, 2 H, 6-H), 7.28–7.45 (m, 8 H, Ar-H), 7.60 (d, $^3J_{2,1}$ = 10.1 Hz, 1 H, 2-H), 7.70 (d, $^3J_{1,2}$ = 10.1 Hz, 1 H, 1-H), 7.75–7.81 (m, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 26.3 (C-6), 52.8 (NCH_3), 79.3 (C-4), 100.0 (C-5), 122.3 (C-Ar), 126.7 (C-Ar), 127.0 (C-Ar/-2), 127.9/128.6/128.8/129.2 (C-Ar/-2), 128.9 (C_q), 136.2 (C_q), 136.7 (C_q), 136.9 (C-1) ppm. MS (EI, 70 eV): *m/z* (%) = 275 (26) $[M]^+$, 202 (26), 184 (100) $[M - CH_2Ph]^+$, 115 (62), 91 (62) $[CH_2Ph]^+$, 77 (25) $[C_6H_5]^+$, 42 (41). $C_{19}H_{17}NO$ (275.35): calcd. C 82.88, H 6.22, N 5.09; found C 82.62, H 5.95, N 4.86.

Methyl{[(*Z*)-3-methylhex-2-en-4-yn-2-yl]methylene}amine *N*-Oxide (16): Treatment of **15**[24] (423 mg, 3.91 mmol, 1.5 h) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 1:2, ethyl acetate/methanol, 10:1), gave **16** (486 mg, 90%) as a colorless solid, m.p. 95–97 °C (diethyl ether). IR (CCl_4): $\tilde{\nu}$ = 2945, 2920, 1550, 1410, 1325, 1175, 1135, 1030 cm^{-1}. ^1H NMR (250 MHz): δ = 2.00 (s, 3 H, 6-H), 2.07 (s, 3 H, 3-CH_3), 3.73 (s, 3 H, NCH_3), 6.86 (d, $^3J_{2,1}$ = 9.8 Hz, 1 H, 2-H), 7.44 (d, $^3J_{1,2}$ = 9.8 Hz, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz): δ = 4.7 (C-6), 14.8 (3-CH_3), 52.4 (NCH_3), 78.5 (C-4), 96.3 (C-5), 124.3 (C-2), 128.2 (C-3), 136.2

(C-1) ppm. MS (EI, 70 eV): *m/z* (%) = 137 (45) $[M]^+$, 122 (100) $[M - CH_3]^+$, 77 (23), 53 (39), 51 (19), 42 (63). $C_8H_{11}NO$ (137.18): calcd. C 70.04, H 8.08, N 10.21; found C 69.99, H 8.17, N 10.12.

1-Methyl-3,5-diphenyl-1,3-dihydro-2*H*-azepin-2-one (17): Treatment of **14** (100 mg, 0.36 mmol, NaOMe, 30 min) according to the general procedure, and subsequent purification (cyclohexane/ethyl acetate, 10:1), gave **17** (94 mg, 94%) as a yellow solid, m.p. 74–76 °C (diethyl ether). IR (CCl_4): $\tilde{\nu}$ = 3060, 3035, 2925, 1680 (C=O), 1635, 1585, 1495, 1370, 1265, 1210, 1080 cm^{-1}. ^1H NMR (250 MHz): δ = 3.23 (s, 3 H, NCH_3), 3.80 (d, $^3J_{3,4}$ = 6.3 Hz, 1 H, 3-H), 5.99 (d, $^3J_{4,3}$ = 6.3 Hz, 1 H, 4-H), 6.17 (d, $^3J_{6,7}$ = 8.9 Hz, 1 H, 6-H), 6.50 (d, $^3J_{7,6}$ = 8.9 Hz, 1 H, 7-H), 7.28–7.43 (m, 10 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 36.3 (C-3), 52.7 (NCH_3), 115.3/124.9/127.3/127.9/132.6 (C-4/-6/-7/-Ar), 127.1 (C-Ar), 128.4 (C-Ar), 128.5 (C-Ar), 129.7 (C-Ar), 138.1 (C_q), 138.2 (C_q), 138.7 (C_q), 166.7 (C-2) ppm. MS (EI, 70 eV): *m/z* (%) = 275 (77) $[M]^+$, 274 (100), 219 (23), 196 (38), 170 (44), 128 (14), 115 (21). HRMS ($C_{19}H_{17}NO$): calcd. 275.1310; found 275.1310.

1-Methyl-3,5-diphenyl-1,7-dihydro-2*H*-azepin-2-one (19): A solution of **17** (62 mg, 0.23 mmol) in dry toluene (4 mL) was refluxed for 6 h and then concentrated in vacuo. Separation of the isomers by flash chromatography (cyclohexane/ethyl acetate, 5:1, 1:2) gave **17** (58 mg, 97%) and also **19** (2 mg, 3%) as a pale-yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3060, 3025, 2925, 2855, 1645 (C=O), 1495, 1445, 1395, 1205, 1075, 1005 cm^{-1}. ^1H NMR (250 MHz): δ = 3.17 (s, 3 H, NCH_3), 3.93 (d, $^3J_{7,6}$ = 6.9 Hz, 2 H, 7-H), 6.55 (t, $^3J_{6,7}$ = 6.9 Hz, 1 H, 6-H), 7.00 (s, 1 H, 4-H), 7.29–7.46 (m, 8 H, Ar-H), 7.63–7.68 (m, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz): δ = 34.9 (NCH_3), 47.3 (C-7), 125.5/128.2/128.3/130.1 (C-4/-6/-Ar), 126.8 (C-Ar), 128.1 (C-Ar), 128.4 (C-Ar), 128.7 (C-Ar), 129.6 (C_q), 138.8 (C_q), 142.7 (C_q), 167.3 (C-2) ppm. MS (EI, 70 eV): *m/z* (%) = 275 (100) $[M]^+$, 274 (70), 246 (50) $[M - NCH_3]^+$, 196 (49), 170 (64), 158 (60), 77 (35) $[C_6H_5]^+$, 42 (79). HRMS ($C_{19}H_{17}NO$): calcd. 275.1310; found 275.1307.

1,5-Dimethyl-1,3-dihydro-2*H*-azepin-2-one (18): A solution of **16** (70 mg, 0.51 mmol) in dry DMF (3 mL) under N_2 was treated with NaH (40 mg, 1.02 mmol, 60% suspension in mineral oil), stirred at room temperature for 45 min, and then at 60 °C for 22 h. After cooling an aqueous solution of NH_4Cl (1:1) and then water were added and the reaction mixture was extracted with dichloromethane (3 × 10 mL). The combined organic phases were washed with saturated NH_4Cl and brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (cyclohexane/ethyl acetate, 10:1) afforded **18** (20 mg, 28%) as a colorless oil. IR (CCl_4): $\tilde{\nu}$ = 3030, 2920, 1675 (C=O), 1600, 1425, 1370, 1290, 1270, 1205, 1160, 1075 cm^{-1}. ^1H NMR (250 MHz): δ = 1.85 (d, ^4J = 1.2 Hz, 3 H, 5-CH_3), 2.85 (d, $^3J_{3,4}$ = 7.0 Hz, 2 H, 3-H), 3.12 (s, 3 H, NCH_3), 5.38 (mt, $^3J_{4,3}$ = 7.0 Hz, 1 H, 4-H), 5.70 (d, $^3J_{6,7}$ = 9.0 Hz, 1 H, 6-H), 6.17 (d, $^3J_{7,6}$ = 9.0 Hz, 1 H, 7-H) ppm. ^{13}C NMR (100 MHz): δ = 20.7 (5-CH_3), 35.5 (C-3), 37.5 (NCH_3), 117.2/118.2 (C-6/-7), 130.6 (C-4), 135.3 (C-5), 167.4 (C-2) ppm. MS (EI, 70 eV): *m/z* (%) = 137 (100) $[M]^+$, 122 (16) $[M - CH_3]^+$, 108 (86) $[M - NCH_3]^+$, 94 (66). HRMS ($C_8H_{11}NO$): calcd. 137.0841; found 137.0841.

Photolysis of 17: A degassed (N_2) solution of **17** (90 mg, 0.33 mmol) in freshly distilled acetone (100 mL) was irradiated at 20 °C for 15 min with a high-pressure Hg lamp (Hanau TQ 150, 150 W) using a Solidex filter ($\lambda > 270$ nm). Concentration in vacuo and flash chromatography (cyclohexane/ethyl acetate, 3:1, 2:1) afforded, besides unreacted **17** (50 mg, 56%), *endo*-2-methyl-4,6-diphenyl-2-azabicyclo[3.2.0]hept-6-en-3-one (**20**) (13 mg, 14%) and *exo*-2-methyl-4,6-diphenyl-2-azabicyclo[3.2.0]hept-6-en-3-one (**21**) (12 mg, 13%). After irradiation in diethyl ether under comparable conditions (Solidex filter, 30 min), **17** (27 mg, 30%), **20** (27 mg, 30%), and **21** (27 mg, 30%) were isolated.

Compound 20: Colorless solid, m.p. 172–174 °C (diethyl ether). IR (CCl_4): $\tilde{\nu}$ = 3060, 3025, 2925, 1700 (C=O), 1490, 1450, 1395, 1220, 1175, 1095 cm^{-1}. ^1H NMR (400 MHz): δ = 3.06 (s, 3 H, NCH_3), 4.04 (d, $^3J_{4,5}$ = 10.7 Hz, 1 H, 4-H), 4.17 (dd, $^3J_{5,4}$ = 10.7, $^3J_{5,1}$ = 4.3 Hz, 1 H, 5-H), 4.39 (d, $^3J_{1,5}$ = 4.3 Hz, 1 H, 1-H), 6.76 (s, 1 H, 7-H), 6.77–6.80 (m, 2 H, Ar-H), 6.93–7.06 (m, 8 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 28.6 (NCH_3), 44.1 (C-5), 50.7 (C-1), 58.4 (C-4), 125.1 (C-Ar), 126.9 (C-Ar), 127.7 (C-Ar), 128.0 (C-Ar), 128.1 (C-Ar), 129.9 (C-Ar), 130.5 (C-7), 132.7 (C_q-Ar), 137.4 (C_q-Ar), 152.1 (C-6), 174.8 (C-3) ppm. MS (EI, 70 eV): *m/z* (%) = 275 (88) $[M]^+$, 274 (100), 204 (27), 202 (22), 196 (39), 170 (32), 144 (37). HRMS ($C_{19}H_{17}NO$): calcd. 275.1304; found 275.1310.

Compound 21: Amorphous solid. IR (CCl_4): $\tilde{\nu}$ = 3060, 3025, 2925, 1695 (C=O), 1490, 1450, 1420, 1390, 1295, 1095 cm^{-1}. ^1H NMR (400 MHz): δ = 3.01 (s, 3 H, NCH_3), 3.74 (br. s, 1 H, 4-H), 3.79 (ddd, $^3J_{5,1}$ = 4.1, $^3J_{5,4}$ = 2.7, $^4J_{5,7}$ = 0.6 Hz, 1 H, 5-H), 4.51 (dd, $^3J_{1,5}$ = 4.1, $^4J_{1,4}$ = 1.5 Hz, 1 H, 1-H), 6.71 (d, $^4J_{7,5}$ = 0.6 Hz, 1 H, 7-H), 7.26–7.30 (m, 3 H, Ar-H), 7.33–7.40 (m, 7 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 28.6 (NCH_3), 46.3 (C-5), 50.9 (C-4), 125.5 (C-Ar), 127.2 (C-Ar), 127.8 (C-Ar), 128.9 (C-Ar), 129.0 (C-Ar), 129.2 (C-Ar), 129.3 (C-7), 131.9 (C_q-Ar), 141.0 (C_q-Ar), 152.9 (C-6), 175.1 (C-3) ppm. MS (EI, 70 eV): *m/z* (%) = 275 (56) $[M]^+$, 274 (58), 196 (15), 173 (100), 170 (16), 144 (53). HRMS ($C_{19}H_{17}NO$): calcd. 275.1310; found 275.1310.

Photolysis of 10a (in Diethyl Ether): A degassed (N_2) solution of **10a** (30 mg, 0.13 mmol) in diethyl ether (100 mL) was irradiated at 20 °C for 1 h with a high-pressure Hg lamp (Hanau TQ 150, 150 W) using a quartz filter ($\lambda > 210$ nm). Concentration in vacuo and purification by flash chromatography (cyclohexane/ethyl acetate, 5:1) afforded 2-[(*E*)-2-phenylvinyl]cyclopent-1-ene-1-carbaldehyde (**22a**) (24 mg, 80%).[29]

Photolysis of 10b (in Diethyl Ether): A degassed (N_2) solution of **10b** (30 mg, 0.12 mmol) in diethyl ether (100 mL) was irradiated at 20 °C for 1 h with a high-pressure Hg lamp (Hanau TQ 150, 150 W) using a quartz filter ($\lambda > 210$ nm). Concentration in vacuo and purification (cyclohexane/ethyl acetate, 5:1) afforded 2-[(*E*)-2-phenylvinyl]cyclohex-1-ene-1-carbaldehyde (**22b**) (18 mg, 59%).[29]

Photolysis of 10b (in Acetone): A degassed (N_2) solution of **10b** (100 mg, 0.39 mmol) in freshly distilled acetone (100 mL) was irradiated at 20 °C for 2 h with a high-pressure Hg lamp (Hanau TQ 150, 150 W) using a Solidex filter ($\lambda > 270$ nm). Concentration in vacuo and purification (cyclohexane/ethyl acetate, 20:1, 10:1, 5:1) afforded, besides unreacted **10b** (6 mg, 6%), 2-methyl-1-phenyl-1,2,6,7,8,9-hexahydro-3*H*-2-benzazepin-3-one (**25b**) as a colorless amorphous solid (42 mg, 42%). IR (CCl_4): $\tilde{\nu}$ = 3025, 2935, 2855, 1635 (C=O), 1495, 1450, 1395, 1250, 1220 cm^{-1}. ^1H NMR (250 MHz): δ = 1.67–1.85 (m, 4 H, 7-H, 8-H), 2.14–2.23 (m, 2 H, 6-/9-H), 2.44–2.54 (m, 2 H, 6-/9-H), 3.36 (s, 3 H, NCH_3), 4.72 (s, 1 H, 1-H), 5.85 (d, $^3J_{4,5}$ = 12.2 Hz, 1 H, 4-H), 5.98 (d, $^3J_{5,4}$ = 12.2 Hz, 1 H, 5-H), 7.04–7.13 (m, 2 H, Ar-H), 7.19–7.25 (m, 3 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 22.3/22.6 (C-7/-8), 23.9/24.0 (C-6/-9), 39.2 (NCH_3), 67.0 (C-1), 125.4 (C-Ar), 126.8 (C-4/-5/-Ar), 127.1/137.5 (C-4/-5/-Ar), 128.1 (C-Ar), 132.2 (C_q), 138.7 (C_q), 140.1 (C_q), 167.4 (C-3) ppm. MS (EI, 70 eV): *m/z* (%) = 253 (100) $[M]^+$, 252 (63), 224 (67) $[M - NCH_3]^+$, 176 (23) $[M - C_6H_5]^+$, 148 (24), 77 (23) $[C_6H_5]^+$. HRMS ($C_{17}H_{19}NO$): calcd. 253.1567; found 253.1568.

Photolysis of 10c (in Acetone): A degassed (N_2) solution of **10c** (50 mg, 0.19 mmol) in freshly distilled acetone (100 mL) was irradi-

ated at 20 °C for 1 h with a high-pressure Hg lamp (Hanau TQ 150, 150 W) using a Solidex filter ($\lambda > 270$ nm). Concentration in vacuo and purification (cyclohexane/ethyl acetate, 3:1) afforded a mixture of **25c/26c** (30 mg, 60%) as a colorless oil. Upon standing the mixture in solution the ratio of the isomers changed rapidly in favor of 2-methyl-1-phenyl-4,6,7,8,9,10-hexahydrocyclohepta[*c*]azepin-3(2*H*)-one (**26c**), which can be isolated in the pure form. IR (CCl_4): $\tilde{\nu}$ = 2930, 2855, 1665 (C=O), 1445, 1425, 1380, 1345, 1300, 1105, 1055 cm^{-1}. ^1H NMR (400 MHz): δ = 1.45–1.54 (m, 2 H, 8-H), 1.60–1.71 (m, 2 H, 7-/9-H), 1.72–1.86 (m, 2 H, 7-/9-H), 2.25–2.37 (m, 3 H, 6-/10-H), 2.44–2.52 (m, 1 H, 6-/10-H), 2.69 (s, 3 H, NCH_3), 2.77 (dd, ^2J = 12.2, $^3J_{4,5}$ = 7.7 Hz, 1 H, 4-H_a), 3.19 (dd, ^2J = 12.2, $^3J_{4,5}$ = 6.0 Hz, 1 H, 4-H_b), 5.66 (m_c, 1 H, 5-H), 7.22–7.28 (m, 2 H, Ar-H), 7.33 (m_c, 1 H, Ar-H), 7.38 (m_c, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 29.2/31.1/32.0/32.6/34.9 (C-6/-7/-8/-9/-10), 34.2 (NCH_3), 36.5 (C-4), 121.3 (C-Ar), 127.9 (C-Ar), 128.3 (C-Ar), 130.0 (C-5), 132.9 (C_q), 137.4 (C_q), 137.5 (C_q), 143.6 (C_q), 170.2 (C-3) ppm. MS (EI, 70 eV): *m/z* (%) = 267 (84) $[M]^+$, 266 (80), 252 (18) $[M - CH_3]^+$, 210 (20) $[M - CONCH_3]^+$, 118 (29), 77 (26) $[C_6H_5]^+$. HRMS ($C_{18}H_{21}NO$): calcd. 267.1623; found 267.1623.

Photolysis of 10d (in Acetone): A degassed (N_2) solution of **10d** (100 mg, 0.35 mmol) in freshly distilled acetone (100 mL) was irradiated at 20 °C for 30 min with a high-pressure Hg lamp (Hanau TQ 150, 150 W) using a Solidex filter ($\lambda > 270$ nm). Concentration in vacuo and purification (cyclohexane/ethyl acetate, 10:1, 3:1) afforded, besides unreacted **10d** (16 mg, 16%), 2-methyl-1-phenyl-1,2,6,7,8,9,10,11-octahydro-3*H*-cycloocta[*c*]azepin-3-one (**25d**) (62 mg, 62%) as a colorless solid, m.p. 111–113 °C (diethyl ether). IR (CCl_4): $\tilde{\nu}$ = 2930, 2850, 1650 (C=O), 1630 (C=C), 1590, 1470, 1445, 1395, 1250, 1010 cm^{-1}. ^1H NMR (250 MHz): δ = 1.21–1.92 (m, 8 H, 7-H, 8-H, 9-H, 10-H), 2.07–2.18 (m, 1 H, 6-/11-H), 2.24–2.38 (m, 1 H, 6-/11-H), 2.55–2.69 (m, 1 H, 6-/11-H), 2.73–2.87 (m, 1 H, 6-/11-H), 3.36 (s, 3 H, NCH_3), 4.92 (s, 1 H, 1-H), 5.90 (d, $^3J_{4,5}$ = 12.2 Hz, 1 H, 4-H), 6.03 (d, $^3J_{5,4}$ = 12.2 Hz, 1 H, 5-H), 7.08–7.14 (m, 2 H, Ar-H), 7.19–7.26 (m, 3 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 26.0/26.5/28.9/29.8 (C-7/-8/-9/-10), 32.5/35.3 (C-6/-11), 38.5 (NCH_3), 67.2 (C-1), 125.5 (C-Ar), 127.1 (C-Ar), 128.0 (C-Ar), 128.2/138.1 (C-4/-5), 135.4 (C_q), 138.6 (C_q), 142.5 (C_q), 167.3 (C-3) ppm. MS (EI, 70 eV): *m/z* (%) = 281 (100) $[M]^+$, 252 (70) $[M - NCH_3]^+$, 224 (35) $[M - CONCH_3]^+$, 210 (28), 118 (30), 77 (21) $[C_6H_5]^+$. HRMS ($C_{19}H_{23}NO$): calcd. 281.1780; found 281.1777.

1-[2′-(3′′-Phenylprop-1′′-ynyl)cyclopent-1′-en-1′-yl]prop-2-en-1-ol (29a): A solution of **8a** (2.00 g, 9.51 mmol) in dry THF (100 mL) under N_2 was treated at –78 °C with a 0.9 M solution of vinylmagnesium bromide (9.99 mmol, 11.1 mL) in THF. The reaction mixture was stirred for 100 min and then the solution was warmed to room temperature, hydrolyzed with saturated NH_4Cl (10 mL), diluted with water (100 mL) and then extracted with diethyl ether. The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (cyclohexane/ethyl acetate, 60:1, 40:1) afforded **29a** (1.57 g, 69%) as an orange oil. IR (CCl_4): $\tilde{\nu}$ = 3618 (OH, s), 3418 (OH, br.), 3083, 3065, 3028, 2958, 2925, 2851, 1549, 1251, 1216, 1112, 1067, 993, 919 cm^{-1}. ^1H NMR (250 MHz): δ = 1.88 (quint, ^3J = 7.5 Hz, 2 H, 4′-H), 1.98 (1 H, OH), 2.33–2.41 (m, 1 H, 3′-/5′-H), 2.48–2.55 (m, ^3J = 7.5 Hz, 3 H, 3′-H, 5′-H), 3.78 (s, 2 H, 3′′-H), 5.13 (td, $^3J_{3c,2}$ = 10.4, $^2J_{3c,3t}$ = 1.6 Hz, 1 H, 3_{cis}-H), 5.17 (td, $^3J_{1,2}$ = 5.8, J = 0.7 Hz, 1 H, 1-H), 5.29 (td, $^3J_{3t,2}$ = 17.2, $^2J_{3t,3c}$ = 1.6 Hz, 1 H, 3_{trans}-H), 5.91 (ddd, $^3J_{2,3t}$ = 17.2, $^3J_{2,3c}$ = 10.4, $^3J_{2,1}$ = 5.8 Hz, 1 H, 2-H), 7.22–7.25 (m, 1 H, Ar-H), 7.30–7.36 (m, 4 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 22.4 (C-4′), 26.1 (C-3′′), 31.3/37.2 (C-3′/-5′), 71.3 (C-1), 78.4 (≡C), 93.4 (≡C), 114.9 (C-3), 120.2 (C-2′), 126.7 (C-Ar), 127.9 (2 C-Ar), 128.6 (2 C-Ar), 136.8 (C_q-Ar), 138.1 (C-2), 149.6 (C_q-1′) ppm. MS (EI, 70 eV): *m/z* (%) = 239 (4) $[M + 1]^+$, 238 (22) $[M]^+$, 237 (24) $[M - 1]^+$, 223 (33), 221 (11) $[M - OH]^+$, 220 (9), 219 (13), 211 (7), 210 (23) $[M - C_2H_4]^+$, 209 (47), 207 (11), 205 (17), 196 (10) $[M - C_3H_6]^+$, 183 (18), 181 (31) $[C_{14}H_{13}]^+$, 167 (53), 165 (55), 161 (10) $[M - C_6H_5]^+$, 155 (37) $[C_{12}H_{11}]^+$, 147 (75) $[M - PhCH_2]^+$, 134 (53), 133 (26), 115 (60) $[C_9H_7]^+$, 91 (100) $[PhCH_2]^+$. HRMS ($C_{17}H_{18}O$): calcd. 238.1358; found 238.1358.

1-[2′-(3′′-Phenylprop-1′′-ynyl)cyclohex-1′-en-1′-yl]prop-2-en-1-ol (29b): A solution of **8b** (1.00 g, 4.46 mmol) in dry THF (50 mL) under N_2 was treated at –78 °C with a 0.9 M solution of vinylmagnesium bromide (4.68 mmol, 5.2 mL) in THF. The reaction mixture was stirred for 30 min and then the solution was warmed to room temperature, hydrolyzed with saturated NH_4Cl (10 mL), diluted with water (50 mL), and then extracted with diethyl ether. The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (cyclohexane/ethyl acetate, 50:1, 30:1) afforded **29b** (1.00 g, 90%) as an orange oil. IR (CCl_4): $\tilde{\nu}$ = 3620 (OH), 3482 (OH, br.), 3088, 3067, 3031, 2935, 2862, 2840, 2217, 1707, 1604, 1495, 1453, 1436, 1418, 1224 cm^{-1}. ^1H NMR (250 MHz): δ = 1.60 (m_c, 4 H, 4′-H, 5′-H), 1.82 (1 H, OH), 1.94–2.07 (m, 1 H, 3′-/6′-H), 2.21 (m_c, 3 H, 3′-H, 6′-H), 3.77 (s, 2 H, 3′′-H), 5.13 (ddd, $^3J_{3c,2}$ = 10.4, J = 1.8, J = 1.5 Hz, 1 H, 3_{cis}-H), 5.28 (ddd, $^3J_{3t,2}$ = 17.1, J = 1.8, J = 1.5 Hz, 1 H, 3_{trans}-H), 5.38 (br. d, $^3J_{1,2}$ = 4.9 Hz, 1 H, 1-H), 5.90 (ddd, $^3J_{2,3t}$ = 17.1, $^3J_{2,3c}$ = 10.4, $^3J_{2,1}$ = 4.9 Hz, 1 H, 2-H), 7.20–7.37 (m, 5 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 22.1/22.4/23.1 (C-4′/-5′/-6′), 25.9/30.6 (C-3′/-3′′), 74.2 (C-1), 81.9 (≡C), 91.4 (≡C), 114.4 (C-3), 117.0 (C_q-2′), 126.6 (C-Ar), 127.9 (2 C-Ar), 128.5 (2 C-Ar), 136.9 (C_q-Ar), 138.2 (C-2), 144.0 (C_q-1′) ppm. MS (EI, 70 eV): *m/z* (%) = 253 (2), 252 (13) $[M]^+$, 251 (7), 238 (2), 237 (14), 235 (7) $[M - OH]^+$, 234 (8), 225 (3) $[M - C_2H_3]^+$, 224 (5), 223 (15), 221 (12), 219 (8), 209 (7), 195 (6) $[M - C_3H_5O]^+$, 191 (13), 186 (10), 179 (14), 178 (15), 167 (16), 165 (24), 161 (68) $[M - C_7H_7]^+$, 155 (12) $[C_{12}H_{11}]^+$, 153 (12), 152 (15), 141 (21), 129 (15), 115 (40) $[C_9H_7]^+$, 105 (23), 91 (100) $[C_7H_7]^+$. HRMS ($C_{18}H_{20}O$): calcd. 252.1514; found 252.1512.

1-[2′-(3′′-Phenylprop-1′′-ynyl)phenyl]prop-2-en-1-ol (29c): A solution of **28**[7] (1.71 g, 7.77 mmol) in dry THF (90 mL) under N_2 was treated at –78 °C with a 0.9 M solution of vinylmagnesium bromide (8.16 mmol, 9.1 mL) in THF. The reaction mixture was stirred for 2 h, and then the solution was warmed to room temperature, hydrolyzed with saturated NH_4Cl (9 mL), diluted with water (90 mL), and then extracted with diethyl ether. The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (cyclohexane/ethyl acetate, 60:1) afforded **29c** (1.86 g, 86%) as a yellow-orange oil. IR (CCl_4): $\tilde{\nu}$ = 3619 (OH), 3472 (OH), 3067, 3030, 2891, 2228 (C≡C), 1956, 1850, 1707, 1640, 1602, 1555, 1495, 1453, 1419, 1336, 1294, 1187, 1129, 1021, 995 cm^{-1}. ^1H NMR (500 MHz): δ = 2.31 (1 H, OH), 3.85 (s, 2 H, 3′′-H), 5.13 (td, $^3J_{3c,2}$ = 10.5, $^2J_{3c,3t}$ = 1.5 Hz, 1 H, 3_{cis}-H), 5.28 (td, $^3J_{3t,2}$ = 17.2, $^2J_{3t,3c}$ = 1.5 Hz, 1 H, 3_{trans}-H), 5.65 (d, $^3J_{1,2}$ = 5.4 Hz, 1 H, 1-H), 6.04 (ddd, $^3J_{2,3t}$ = 17.2, $^3J_{2,3c}$ = 10.5, $^3J_{2,1}$ = 5.4 Hz, 1 H, 2-H), 7.21 (m_c, ^3J = 7.7, ^3J = 7.4 Hz, 1 H, Ar-H), 7.25 (m_c, ^3J = 7.4 Hz, 1 H, Ar-H), 7.28–7.35 (m, ^3J = 7.4 Hz, 3 H, Ar-H), 7.39 (m_c, 2 H, Ar-H), 7.44 (dd, ^3J = 7.7, J = 1.4 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 25.9 (C-3′′), 73.1 (C-1), 80.5 (≡C), 92.9 (≡C), 114.9 (C-3), 121.6 (C_q-Ar), 125.9 (C-Ar), 126.8 (C-Ar), 127.4 (C-Ar), 128.0 (C-Ar), 128.5 (C-Ar), 128.7 (C-Ar), 132.6 (C-Ar), 136.6 (C_q-Ar), 139.3 (C-2), 144.3 (C_q-Ar) ppm. MS (EI, 70 eV): *m/z* (%) = 248 (3) $[M]^+$, 231 (7) $[M - OH]^+$, 230 (19),

229 (29), 228 (12), 221 (2) [M – C_2H_3]$^+$, 219 (31), 215 (41), 203 (24), 191 (20) [M – C_3H_5O]$^+$, 189 (31), 171 (2) [M – Ph]$^+$, 165 (20), 157 (68) [M – C_7H_7]$^+$, 145 (8) [M – C_8H_7]$^+$, 144 (16), 141 (27), 129 (46), 128 (48), 103 (12) [C_8H_7]$^+$, 91 (100) [C_7H_7]$^+$. HRMS ($C_{18}H_{16}O$): calcd. 248.1201; found 248.1202.

1-[2′-(3′′-Phenylprop-1′′-ynyl)cyclopent-1′-en-1′-yl]prop-2-en-1-one (30a): *o*-Iodoxybenzoic acid (IBX, 2.03 g, 7.25 mmol) was added to a stirred solution of **29a** (1.33 g, 5.52 mmol) in dry DMSO (140 mL) under argon. The mixture was stirred for a further 1.5 h, and then the solution was cooled in an ice bath and treated with diethyl ether/water (150 mL, 1:2 mixture). After extraction with diethyl ether the organic phase was washed with saturated $NaHCO_3$ and brine, dried ($MgSO_4$), and then concentrated in vacuo. Flash chromatography (cyclohexane/ethyl acetate, 60:1) gave **30a** (1.21 g, 92%) as a yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3060, 3028, 2959, 2849, 2210 (C≡C), 1652 (C=O), 1455, 982 cm^{-1}. ^{1}H NMR (500 MHz): δ = 1.89 (quint, $^3J_{4',3'/5'}$ = 7.7 Hz, 2 H, 4′-H), 2.75 (m_c, $^3J_{3'/5',4'}$ = 7.7 Hz, 4 H, 3′-H, 5′-H), 3.86 (s, 2 H, 3′′-H), 5.56 (dd, $^3J_{3c,2}$ = 10.5, $^2J_{3c,3t}$ = 2.0 Hz, 1 H, 3_{cis}-H), 6.28 (dd, $^3J_{3t,2}$ = 16.9, $^2J_{3t,3c}$ = 2.0 Hz, 1 H, 3_{trans}-H), 7.26 (m_c, 1 H, Ar-H), 7.34 (m_c, 4 H, Ar-H), 7.45 (dd, $^3J_{2,3t}$ = 16.9, $^3J_{2,3c}$ = 10.5 Hz, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz): δ = 21.8 (C-4′), 26.5 (C-3′′), 33.4/40.9 (C-3′/-5′), 79.7 (≡C), 101.1 (≡C), 126.9 (C-3), 127.7 (C-Ar), 128.1 (C-Ar), 128.7 (C-Ar), 133.9 (C-2), 134.4 (C_q-2′), 135.9 (C_q-Ar), 146.5 (C_q-1′), 188.6 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 238 (2), 237 (16) [M + 1]$^+$, 236 (100) [M]$^+$, 221 (11), 207 (12), 193 (7), 179 (18), 178 (25), 166 (11), 165 (30), 152 (15), 115 (5), 91 (9) [$PhCH_2$]$^+$. HRMS ($C_{17}H_{16}O$): calcd. 236.1201; found 236.1193.

1-[2′-(3′′-Phenylprop-1′′-ynyl)cyclohex-1′-en-1′-yl]prop-2-en-1-one (30b): *o*-Iodoxybenzoic acid (IBX, 2.74 g, 9.78 mmol) was added to a stirred solution of **29b** (1.90 g, 7.52 mmol) in dry DMSO (180 mL) under argon. The mixture was stirred for a further 1.5 h, and then the solution was cooled in an ice bath and treated with diethyl ether/water (210 mL, 1:2 mixture). After extraction with diethyl ether the organic phase was washed with saturated $NaHCO_3$ and brine, dried ($MgSO_4$), and then concentrated. Flash chromatography (cyclohexane/ethyl acetate, 60:1) gave **30b** (1.69 g, 90%) as a yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3067, 3031, 2939, 2862, 2210 (C≡C), 1662 (C=O), 1601, 1495, 1453, 1433, 1401, 1359, 1275, 1230, 1197 cm^{-1}. ^{1}H NMR (250 MHz): δ = 1.66 (m_c, ^3J = 6.4, ^3J = 5.5 Hz, 4 H, 4′-H, 5′-H), 2.34 (m_c, ^3J = 6.4, ^3J = 4.9 Hz, 4 H, 3′-H, 6′-H), 3.73 (s, 2 H, 3′′-H), 5.62 (dd, $^3J_{3c,2}$ = 10.4, $^2J_{3c,3t}$ = 1.5 Hz, 1 H, 3_{cis}-H), 6.21 (dd, $^3J_{3t,2}$ = 17.1, $^2J_{3t,3c}$ = 1.5 Hz, 1 H, 3_{trans}-H), 6.93 (dd, $^3J_{2,3t}$ = 17.1, $^3J_{2,3c}$ = 10.4 Hz, 1 H, 2-H), 7.22–7.32 (m, 5 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 21.7/22.0 (C-4′/-5′), 26.1/26.2 (C-3′′/-3′/-6′), 31.9 (C-3′/-6′), 82.7 (≡C), 95.8 (≡C), 125.5 (C_q-2′), 126.7 (C-Ar), 128.1 (2 C-Ar), 128.2 (C-3), 128.6 (2 C-Ar), 135.6 (C-2), 136.3 (C_q-Ar), 143.0 (C_q-1′), 196.0 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 252 (3), 251 (19), 250 (100) [M]$^+$, 249 (62), 236 (15) [M – CH_2]$^+$, 235 (81), 223 (5) [M – C_2H_3]$^+$, 221 (22), 208 (10) [M – C_3H_6]$^+$, 207 (34), 195 (13) [$C_{15}H_{15}$]$^+$, 193 (18), 186 (26), 179 (45), 178 (35), 165 (39), 152 (22), 115 (35) [C_9H_7]$^+$, 103 (10) [C_8H_7]$^+$, 91 (31) [C_7H_7]$^+$. HRMS ($C_{18}H_{18}O$): calcd. 250.1358; found 250.1358.

1-[2′-(3′′-Phenylprop-1′′-ynyl)phenyl]prop-2-en-1-one (30c): *o*-Iodoxybenzoic acid (IBX, 2.36 g, 8.44 mmol) was added to a stirred solution of **29c** (1.60 g, 6.50 mmol) in dry DMSO (160 mL) under argon. The mixture was stirred for a further 1.5 h, and then the solution was cooled in an ice bath and treated with diethyl ether/water (180 mL, 1:2 mixture). After extraction with diethyl ether the organic phase was washed with saturated $NaHCO_3$ and brine, dried ($MgSO_4$), and then concentrated. Flash chromatography (cyclohexane/ethyl acetate, 60:1) afforded **30c** (1.32 g, 83%) as a yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3067, 3031, 2894, 2235 (C≡C), 1672 (C=O), 1606, 1442, 1400, 995, 961 cm^{-1}. ^{1}H NMR (500 MHz): δ = 3.82 (s, 2 H, 3′′-H), 5.83 (dd, $^3J_{3c,2}$ = 10.5, $^2J_{3c,3t}$ = 1.4 Hz, 1 H, 3_{cis}-H), 6.21 (dd, $^3J_{3t,2}$ = 17.4, $^2J_{3t,3c}$ = 1.4 Hz, 1 H, 3_{trans}-H), 6.95 (dd, $^3J_{2,3t}$ = 17.4, $^3J_{2,3c}$ = 10.5 Hz, 1 H, 2-H), 7.24 (m_c, 1 H, Ar-H), 7.33 (m_c, 2 H, Ar-H), 7.35–7.37 (m, 3 H, Ar-H), 7.41 (dd, ^3J = 7.5, J = 1.4 Hz, 1 H, Ar-H), 7.52 (m_c, ^3J = 7.5, J = 1.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 26.1 (C-3′′), 80.9 (≡C), 93.7 (≡C), 122.1 (C_q), 126.8 (C-Ar), 127.8 (C-Ar), 128.1 (C-Ar), 128.4 (C-Ar), 128.6 (C-Ar), 130.4 (C-3), 130.7 (C-Ar), 133.4 (C-Ar), 135.8 (C-2), 136.1 (C_q-Ar), 141.2 (C_q-Ar), 194.8 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 247 (18) [M + 1]$^+$, 246 (100) [M]$^+$, 245 (53), 231 (10), 219 (3) [M – C_2H_3]$^+$, 217 (22), 215 (28), 204 (64), 191 (9) [M – C_3H_7O]$^+$, 190 (12), 189 (42), 165 (15), 115 (14) [C_9H_7]$^+$. HRMS ($C_{18}H_{14}O$): calcd. 246.1045; found 246.1044.

4-Nitro-1-[2′-(3′′-phenylprop-1′′-ynyl)cyclopent-1′-en-1′-yl]pentan-1-one (31a): Compound **30a** (830 mg, 3.51 mmol) was added to a solution of nitroethane (5.04 mL, 70.24 mmol), dry diisopropylamine (1.62 mL, 11.90 mmol), and dry chloroform (80 mL) under argon. This solution was stirred for 66 h at room temperature and then a 1:1 mixture of saturated NH_4Cl and brine (80 mL) was added. The reaction mixture was extracted with chloroform, and the organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography of the residue (cyclohexane/ethyl acetate, 60:1) gave **31a** (663 mg, 60%) as a red-orange oil. IR (CCl_4): $\tilde{\nu}$ = 3028, 2941, 2210 (C≡C), 1654 (C=O), 1590 cm^{-1}. ^{1}H NMR (500 MHz): δ = 1.48 (d, $^3J_{5,4}$ = 6.8 Hz, 3 H, 5-H), 1.86 (quint, $^3J_{4',3'/5'}$ = 7.7 Hz, 2 H, 4′-H), 2.04–2.11 (m, $^3J_{3,2}$ = 4.6 Hz, 1 H, 3-H), 2.16 (m_c, $^3J_{3,2}$ = 7.2 Hz, 1 H, 3-H), 2.67 (m_c, $^3J_{3'/5',4'}$ = 7.7, $^4J_{3',5'}$ = 2.3 Hz, 2 H, 3′-/5′-H), 2.72 (m_c, $^3J_{3'/5',4'}$ = 7.7, $^4J_{3'/5'}$ = 2.3 Hz, 2 H, 3′-/5′-H), 2.99 (ddd, $^3J_{2,3}$ = 7.2, $^3J_{2,3}$ = 4.6 Hz, 2 H, 2-H), 3.86 (s, 2 H, 3′′-H), 4.54 (m_c, $^3J_{4,5}$ = 6.8 Hz, 1 H, 4-H), 7.25–7.29 (m, 1 H, Ar-H), 7.34–7.35 (m, 4 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 19.4 (C-5), 21.7 (C-4′), 26.4 (C-3′′), 29.2 (C-3), 32.9/37.1/40.8 (C-2/-3′/-5′), 79.6 (≡C), 83.0 (C-4), 102.2 (≡C), 127.0 (C-Ar), 128.1 (2 C-Ar), 128.8 (2 C-Ar), 134.8 (C_q-2′), 135.9 (C_q-Ar), 145.7 (C_q-1′), 196.4 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 311 (33) [M]$^+$, 310 (100) [M – 1]$^+$, 265 (30) [M – NO_2]$^+$, 264 (15), 263 (39), 249 (11), 239 (12), 237 (11), 236 (30), 235 (18), 225 (13), 223 (30) [M – $C_3H_6NO_2$]$^+$, 222 (85), 209 (53) [M – $C_4H_8NO_2$]$^+$, 197 (26) [M – C_9H_7]$^+$, 181 (33) [M – $C_5H_8NO_3$]$^+$, 166 (30), 165 (53), 152 (33). HRMS ($C_{19}H_{20}NO_3$ [M – 1]): calcd. 310.1443; found 310.1443.

4-Nitro-1-[2′-(3′′-phenylprop-1′′-ynyl)cyclohex-1′-en-1′-yl]pentan-1-one (31b): Compound **30b** (1.69 g, 6.75 mmol) was added to a solution of nitroethane (9.05 mL, 126.0 mmol), dry diisopropylamine (3.12 mL, 22.26 mmol), and dry chloroform (130 mL) under argon. This solution was stirred for 66 h at room temperature and then a 1:1 mixture of saturated NH_4Cl and brine (100 mL) was added. The reaction mixture was extracted with chloroform and the organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography of the residue (cyclohexane/ethyl acetate, 60:1, 40:1) gave **31b** (2.01 g, 91%) as a yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3066, 3028, 2939, 2862, 2210 (C≡C), 1659 (C=O), 1593, 1551, 1494, 1453, 1386, 1354, 1221, 1170 cm^{-1}. ^{1}H NMR (500 MHz): δ = 1.47 (d, $^3J_{5,4}$ = 6.6 Hz, 3 H, CH_3), 1.62 (m_c, 4 H, 4′-H, 5′-H), 2.04 (m_c, ^2J = 14.9, $^3J_{3,4}$ = 4.6 Hz, 1 H, 3-H), 2.13 (m_c, ^2J = 14.9, $^3J_{3,4}$ = 9.1, $^3J_{3,2}$ = 6.2 Hz, 1 H, 3-H), 2.29 (m_c, 2 H, 3′-/6′-H), 2.36 (m_c, 2 H, 3′-/6′-H), 2.96 (m_c, $^3J_{2,3}$ = 6.2 Hz, 2 H, 2-H), 3.80 (s, 2 H, 3′′-H), 4.50 (m_c, $^3J_{4,3}$ = 9.1, $^3J_{4,5}$ = 6.6, $^3J_{4,3}$ = 4.6 Hz, 1 H, 4-H), 7.25–7.27 (m, 1 H, Ar-H), 7.32–7.35 (m, 4 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 19.4 (C-5), 21.7/21.9 (C-4′/-5′/-6′), 25.7/33.0 (C-

3′/-6′), 26.2 (C-3′′), 29.4/37.9 (C-3/-2), 82.9 (C-4), 83.1 (≡C), 97.5 (≡C), 126.9 (C-Ar), 127.5 (C_q-2′/-Ar), 128.1 (2 C-Ar), 128.8 (2 C-Ar), 136.3 (C_q-2′/-Ar), 142.2 (C_q-1′), 201.8 (C=O) ppm. MS (EI, 70 eV): *m/z* (%) = 325 (9) $[M]^+$, 324 (28), 295 (32), 280 (14), 279 (62) $[M – NO]^+$, 278 (38), 277 (36), 263 (35), 251 (17) $[M – C_2H_4NO_2]^+$, 250 (57), 249 (30), 239 (29), 238 (23), 237 (100) $[M – C_3H_6NO_2]^+$, 236 (61), 235 (39), 234 (5) $[M – C_7H_7]^+$, 224 (14), 223 (60) $[C_{16}H_{15}O]^+$, 221 (20), 213 (46), 212 (36), 211 (76), 210 (6) $[C_{11}H_{16}NO_3]^+$, 209 (32), 195 (27) $[C_{15}H_{16}]^+$, 194 (16), 183 (20), 179 (36), 178 (34), 167 (37), 166 (24), 165 (57), 153 (33), 152 (40), 141 (38), 129 (22), 115 (55), 105 (18), 91 (86). HRMS ($C_{20}H_{22}NO_3$ [M – 1]): calcd. 324.1600; found 324.1604.

4-Nitro-1-[2′-(3′′-phenylprop-1′′-ynyl)phenyl]pentan-1-one (31c): A solution of nitroethane (12.5 mL, 174.6 mmol), dry diisopropylamine (4.04 mL, 28.8 mmol), and dry chloroform (190 mL) under argon was treated with a solution of **30c** (2.15 g, 8.73 mmol) in chloroform (10 mL). This solution was stirred for 66 h at room temperature and then a 1:1 mixture of saturated NH_4Cl and brine (200 mL) was added. The reaction mixture was extracted with chloroform and the organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography of the residue (cyclohexane/ethyl acetate, 50:1, 30:1) gave **31c** (2.53 g, 90%) as a yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3364, 3066, 3032, 2987, 2939, 2894, 2232 (C≡C), 1695, 1684 (C=O), 1388, 1357 cm^{-1}. ^1H NMR (500 MHz): δ = 1.51 (d, $^3J_{5,4}$ = 6.6 Hz, 3 H, CH_3), 2.13–2.20 (m, ^2J = 14.8, $^3J_{3,2}$ = 7.3, $^3J_{3,4}$ = 4.6 Hz, 1 H, 3-H), 2.21–2.29 (m, ^2J = 14.8, $^3J_{3,4}$ = 9.1, $^3J_{3,2}$ = 6.2 Hz, 1 H, 3-H), 3.15 (ddd, $^3J_{2,3}$ = 7.3, $^3J_{2,3}$ = 6.2, $^4J_{2,4}$ = 2.2 Hz, 2 H, 2-H), 3.88 (s, 2 H, 3′′-H), 4.57 (m_c, $^3J_{4,3}$ = 9.1, $^3J_{4,5}$ = 6.6, $^3J_{4,3}$ = 4.6, $^4J_{4,2}$ = 2.2 Hz, 1 H, 4-H), 7.27 (t, ^3J = 7.2 Hz, 1 H, Ar-H), 7.35 (t, ^3J = 7.6 Hz, 3 H, Ar-H), 7.42 (m_c, ^3J = 7.6 Hz, 3 H, Ar-H), 7.54 (dd, ^3J = 7.7, J = 0.8 Hz, 1 H, Ar-H), 7.62 (dd, ^3J = 7.7, J = 1 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 19.5/26.1 (C-3′′/-5), 29.3/38.0 (C-2/-3), 81.3 (≡C), 82.8 (C- 4), 94.2 (≡C), 121.8 (C_q-Ar), 126.9 (C-Ar), 128.1 (C-Ar), 128.2 (C-Ar), 128.8 (C-Ar), 131.3 (C-Ar), 134.2 (C-Ar), 136.3 (C_q-Ar), 140.5 (C_q-Ar), 201.2 (C=O) ppm. MS (EI, 70 eV): *m/z* (%) = 321 (6) $[M]^+$, 320 (25), 275 (20) $[M – NO_2]^+$, 273 (15), 247 (5) $[M – C_2H_4NO_2]^+$, 246 (13), 245 (29), 244 (6) $[M – C_6H_5]^+$, 235 (27), 233 (26) $[M – C_3H_6NO_2]^+$, 232 (48), 231 (50), 219 (51) $[M – C_4H_8NO_2]^+$, 218 (26), 215 (30), 207 (50), 205 (15), 204 (20), 203 (32), 202 (33), 191 (41) $[C_{15}H_{11}]^+$, 190 (44), 189 (100), 165 (39), 115 (11) $[C_9H_7]^+$, 109 (20), 105 (11), 103 (7) $[C_8H_7]^+$, 91 (12) $[C_7H_7]^+$. HRMS ($C_{20}H_{18}NO_3$ [M – 1]): calcd. 320.1286; found 320.1282.

4-Nitro-1-[2′-(3′′-phenylprop-1′′-ynyl)phenyl]butan-1-one (32c): A solution of nitromethane (9.46 mL, 174.6 mmol), dry diisopropylamine (4.04 mL, 28.8 mmol), and dry chloroform (190 mL) under argon was treated with a solution of **30c** (2.15 g, 8.73 mmol) in chloroform (10 mL). This solution was stirred for 66 h at room temperature and then triethylamine (4 mL) was added and the solution stirred for a further 5 h. A 1:1 mixture of saturated NH_4Cl and brine (200 mL) was added and the reaction mixture was extracted with chloroform. The organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography of the residue (cyclohexane/ethyl acetate, 60:1, 50:1, 30:1) gave **32c** (1.57 g, 58%) as a yellow oil. IR (PTFE): $\tilde{\nu}$ = 3059, 3029, 2925, 2227 (C≡C), 1695, 1684 (C=O), 1555, 1495, 1455 cm^{-1}. ^1H NMR (500 MHz): δ = 2.32 (quint, $^3J_{3,2/4}$ = 6.8 Hz, 2 H, 3-H), 3.20 (t, $^3J_{2/4,3}$ = 6.8 Hz, 2 H, 2-/4-H), 3.97 (s, 2 H, 3′′-H), 4.35 (t, $^3J_{4/2,3}$ = 6.8 Hz, 2 H, 4-/2-H), 7.27 (m_c, 1 H, Ar-H), 7.34–7.41 (m, 5 H, Ar-H), 7.44 (dt, ^3J = 7.5, J = 1.4 Hz, 1 H, Ar-H), 7.54 (dd, ^3J = 7.7, J = 1.2 Hz, 1 H, Ar-H), 7.63 (dd, ^3J = 7.7, J = 1.2 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 21.8 (C-3), 26.2 (C-3′′), 38.3/74.7 (C-2/-4), 81.4 (≡C), 94.3 (≡C), 121.8 (C_q-Ar), 127.0 (C-Ar), 128.1 (C-Ar), 128.2 (C-Ar), 128.8 (C-Ar), 131.4 (C-Ar), 134.2 (C-Ar), 136.2 (C_q-Ar), 140.5 (C_q-Ar), 201.1 (C=O) ppm. MS (EI, 70 eV): *m/z* (%) = 307 (19) $[M]^+$, 306 (90), 261 (23) $[M – NO_2]^+$, 260 (28), 247 (11) $[M – CH_2NO_2]^+$, 235 (27), 233 (67) $[M – C_2H_4NO_2]^+$, 232 (91), 231 (45), 220 (33), 219 (91) $[M – C_3H_6NO_2]^+$, 218 (26), 216 (21) $[M – C_7H_7]^+$, 215 (35), 207 (63), 204 (35) $[M – C_8H_7]^+$, 203 (38), 202 (51), 192 (10) $[C_{10}H_{10}NO_3]^+$, 191 (48), 190 (58), 189 (100), 165 (47), 116 (6) $[C_4H_6NO_3]^+$, 115 (21) $[C_9H_7]^+$, 109 (33), 103 (9) $[C_8H_8]^+$, 91 (24) $[C_7H_7]^+$, 89 (20) $[C_3H_6NO_2]^+$. HRMS ($C_{19}H_{16}NO_3$ [M – 1]): calcd. 306.1130; found 306.1130.

4-Nitro-4-phenyl-1-[2′-(3′′-phenylprop-1′′-ynyl)phenyl]butan-1-one (33c): A solution of phenylnitromethane (1.14 g, 8.34 mmol), dry diisopropylamine (1.17 mL, 8.34 mmol), and dry chloroform (110 mL) under argon was treated with a solution of **30c** (1.58 g, 6.41 mmol) in chloroform (10 mL). This solution was stirred for 24 h at room temperature and then a 1:1 mixture of saturated NH_4Cl and brine (120 mL) was added. The reaction mixture was extracted with chloroform and the organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography of the residue (cyclohexane/ethyl acetate, 60:1, 40:1) gave **33c** as bright-yellow solid (2.19 g, 89%), m.p. 63–64 °C (ethanol). IR (CCl_4): $\tilde{\nu}$ = 3088, 3067, 3033, 2939, 2902, 2233 (C≡C), 1684 (C=O), 1593, 1360 cm^{-1}. ^1H NMR (400 MHz): δ = 2.49 (m_c, $^2J_{3,3}$ = 7.3, $^3J_{3,4}$ = 6.5 Hz, 1 H, 3-H), 2.77 (m_c, $^3J_{3,4}$ = 9.0, $^2J_{3,3}$ = 7.3, $^3J_{3,2}$ = 6.9 Hz, 1 H, 3-H), 3.13 (dd, $^3J_{2,3}$ = 6.9, J = 2.1 Hz, 2 H, 2-H), 3.82 (s, 2 H, 3′′-H), 5.51 (dd, $^3J_{4,3}$ = 9.0, $^3J_{4,3}$ = 6.5 Hz, 1 H, 4-H), 7.27 (m_c, J = 6.9 Hz, 1 H, Ar-H), 7.34–7.41 (m, 11 H, Ar-H), 7.52 (dd, ^3J = 7.7, J = 1.3 Hz, 1 H, Ar-H), 7.58 (dd, ^3J = 7.7, J = 1.3 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz): δ = 26.0 (C-3′′), 28.3 (C-3), 38.1 (C-2), 81.3 (≡C), 90.4 (C-4), 94.2 (≡C), 121.8 (C_q), 126.9 (C-Ar), 127.8 (C-Ar), 128.0 (C-Ar), 128.1 (C-Ar), 128.2 (C-Ar), 128.8 (C-Ar), 129.1 (C-Ar), 129.9 (C-Ar), 131.4 (C-Ar), 134.2 (C-Ar), 134.4 (C_q), 136.2 (C_q), 140.5 (C_q), 201.1 (C=O) ppm. MS (CI, isobutane, 150 eV): *m/z* (%) = 383 (1) $[M]^+$, 339 (11), 338 (29), 337 (100) $[M – NO_2]^+$, 319 (7), 247 (4) $[M – C_7H_7NO_2]^+$, 233 (9) $[M – C_8H_8NO_2]^+$, 232 (6), 219 (5) $[M – C_9H_{10}NO_2]^+$, 191 (3) $[C_{15}H_{11}]^+$, 189 (5), 115 (2) $[C_9H_7]^+$, 91 (7) $[C_7H_7]^+$. $C_{25}H_{21}NO_3$ (383.4): calcd. C 78.31, H 5.52, N 3.65; found C 78.10, H 5.58, N 3.57.

General Procedure for the Reductive Cyclization of the Nitro Compounds 31a–c, 32c, and 33c: A suspension of the nitro derivative and hydrogen-reduced iron powder[36] (5 equiv.) in ethanol, efficiently stirred with a magnet bar, was refluxed and then treated with 0.5 M HCl (0.5 mL per 1 mmol of nitro compound). Another portion of reduced iron powder (5 equiv.) was added, and the solution was refluxed for a further 2.5 h. The mixture was then filtered and the filter cake carefully washed with dichloromethane; the combined organic solutions were neutralized with saturated $NaHCO_3$ and then concentrated in vacuo. Purification was accomplished by flash chromatography (ethyl acetate, ethyl acetate/methanol, 50:1, 20:1).

2-Methyl-5-[2′-(3′′-phenylprop-1′′-ynyl)cyclopent-1′-en-1′-yl]-3,4-dihydro-2*H*-pyrrole *N*-Oxide (34a): According to the general procedure, treatment of **31a** (820 mg, 2.63 mmol) with a total of 1.47 g (26.3 mmol) of hydrogen-reduced iron powder and 0.5 M HCl (1.5 mL) in ethanol (3 mL) gave, after work up, **34a** (417 mg, 56%) as a brown oil. IR (CCl_4): $\tilde{\nu}$ = 3028, 2971, 2932, 1561, 1453, 1418, 1316, 1246, 1221, 1068, 1005, 976 cm^{-1}. ^1H NMR (500 MHz): δ = 1.43 (d, $^3J_{CH3,2}$ = 6.6 Hz, 3 H, CH_3), 1.65 (m_c, ^2J = 12.8, $^3J_{3,4}$ = 9.4, $^3J_{3,2}$ = 6.9 Hz, 1 H, 3-H), 1.89 (quint, $^3J_{4',3'/5'}$ = 7.7 Hz, 2 H, 4′-H), 2.25 (m_c, ^2J = 12.8, $^3J_{3,4}$ = 4.8 Hz, 1 H, 3-H), 2.54 (t, $^3J_{3'/5',4'}$ = 7.7 Hz, 2 H, 3′-/5′-H), 3.01 (m_c, ^2J = 16.6 Hz, 1 H, 4-H), 3.14 (m_c, ^2J = 16.6, $^3J_{4,3}$ = 9.4, $^3J_{4,3}$ = 4.8 Hz, 1 H, 4-H), 3.21

(m_c, $^3J_{3'/5',4'}$ = 7.7 Hz, 2 H, 3′-/5′-H), 3.79 (s, 2 H, 3′′-H), 4.02 (m, $^3J_{2,3}$ = 6.9, $^3J_{2,CH3}$ = 6.6 Hz, 1 H, 2-H), 7.23–7.27 (m, 1 H, Ar-H), 7.31–7.34 (m, 4 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 18.6 (CH_3), 23.2 (C-4′), 26.0/26.4 (C-3/-4/-3′′), 29.3/34.1/38.6 (C-3/-4/-3′/-5′), 68.9 (C-2), 80.6 (≡C), 97.7 (≡C), 126.8 (C-Ar), 127.9 (2 C-Ar), 128.4 (C_q-5/-Ar), 128.6 (2 C-Ar), 136.3/137.4 (C_q-1′/-2′), 140.6 (C_q-5/-Ar) ppm. MS (EI, 70 eV): *m*/*z* (%) = 280 (12) $[M + 1]^+$, 279 (54) $[M]^+$, 278 (28), 264 (5) $[M – CH_3]^+$, 262 (33), 260 (52), 250 (31), 236 (12), 220 (15), 202 (8) $[M – C_6H_5]^+$, 189 (16), 188 (100), 178 (13), 160 (42), 146 (33), 91 (24). HRMS ($C_{19}H_{21}NO$): calcd. 279.1623; found 279.1620.

2-Methyl-5-[2′-(3′′-phenylprop-1′′-ynyl)cyclohex-1′-en-1′-yl]-3,4-dihydro-2*H*-pyrrole *N*-Oxide (34b): According to the general procedure, treatment of **31b** (400 mg, 1.23 mmol) with a total of 686 mg (12.3 mmol) of hydrogen-reduced iron powder and 0.5 M HCl (0.6 mL) in ethanol (2 mL) gave, after work up, **34b** (144 mg, 40%) as an orange oil. IR (PTFE): $\tilde{\nu}$ = 3419, 3085, 3061, 3028, 2656, 2216 (C≡C), 1337, 1030 cm^{-1}. ^{1}H NMR (500 MHz): δ = 1.39 (d, $^3J_{CH3,2}$ = 6.6 Hz, 3 H, CH_3), 1.58 (m_c, $^2J_{3,3}$ = 12.8, $^3J_{3,4}$ = 9.1, $^3J_{3,2}$ = 6.5, $^3J_{3,4}$ = 6.3 Hz, 1 H, 3-H), 1.66 (m_c, 4 H, 4′-H, 5′-H), 2.19 (m_c, $^2J_{3,3}$ = 12.8, $^3J_{3,4}$ = 9.0, $^3J_{3,2}$ = 8.4, $^3J_{3,4}$ = 5.0 Hz, 1 H, 3-H), 2.28 (m_c, 2 H, 3′-/6′-H), 2.40–2.44 (m, 1 H, 3′-/6′-H), 2.52–2.56 (m, 1 H, 3′-/6′-H), 2.84 (dddd, $^2J_{4,4}$ = 17.7, $^3J_{4,3}$ = 9.0, $^3J_{4,3}$ = 6.3, $^4J_{4,2}$ = 1.7 Hz, 1 H, 4-H), 2.93 (dddd, $^2J_{4,4}$ = 17.7, $^3J_{4,3}$ = 9.1, $^3J_{4,3}$ = 5.0, $^4J_{4,2}$ = 2.1 Hz, 1 H, 4-H), 4.06 (m_c, $^3J_{2,3}$ = 8.4, $^3J_{2,3}$ = 6.5, $^3J_{2,CH3}$ = 6.6, $^4J_{2,4}$ = 2.1, $^4J_{2,4}$ = 1.7 Hz, 1 H, 2-H), 7.21–7.25 (m, 1 H, Ar-H), 7.29–7.32 (m, 4 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 18.6 (CH_3), 21.6/21.9/25.1/26.1/26.2/29.9/31.1 (C-3/-3′/-3′′/-4/-4′/-5′/-6′), 68.9 (C-2), 82.7 (≡C), 93.3 (≡C), 123.7 (C_q-2′), 126.7 (C-Ar), 128.0 (2 C-Ar), 128.6 (2 C-Ar), 134.3 (C_q-1′), 136.7 (C_q-Ar), 174.7 (C_q-5) ppm. MS (EI, 60 eV): *m*/*z* (%) = 293 (46) $[M]^+$, 276 (13) $[M – O]^+$, 237 (3) $[C_{16}H_{15}NO]^+$, 203 (24), 202 (100) $[M – C_7H_7]^+$, 192 (19), 186 (11) $[C_{13}H_{17}N – 1]^+$, 178 (9) $[C_{11}H_{16}NO]^+$, 174 (70), 164 (17) $[C_{11}H_{17}N – 1]^+$, 160 (16), 131 (20), 115 (8) $[C_9H_7]^+$, 105 (10), 91 (35). HRMS ($C_{20}H_{23}NO$): calcd. 293.1779; found 293.1779.

2-Methyl-5-[2′-(3′′-phenylprop-1′′-ynyl)phenyl]-3,4-dihydro-2*H*-pyrrole *N*-Oxide (34c): According to the general procedure, treatment of **31c** (321 mg, 1.0 mmol) with a total of 558 mg (10.0 mmol) of hydrogen-reduced iron powder and 0.5 M HCl (0.5 mL) in ethanol (2 mL) gave, after work up, **34c** (215 mg, 74%) as a red-brown oil. IR (PTFE): $\tilde{\nu}$ = 3416, 3059, 3028, 2971, 2929, 2227 (C≡C) cm^{-1}. ^{1}H NMR (500 MHz): δ = 1.49 (d, $^3J_{CH3,2}$ = 6.6 Hz, 3 H, CH_3), 1.67 (m_c, 1 H, 3-/4-H), 2.26 (m_c, 1 H, 3-/4-H), 3.06–3.12 (m, 1 H, 3-/4-H), 3.14–3.21 (m, 1 H, 3-/4-H), 3.83 (s, 2 H, 3′′-H), 4.19 (m_c, $^3J_{2,CH3}$ = 6.6 Hz, 1 H, 2-H), 7.26 (tt, 1 H, Ar-H), 7.29–7.38 (m, 6 H, Ar-H), 7.51 (dd, 1 H, Ar-H), 8.15 (dd, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 18.6 (CH_3), 25.9/26.1 (C-3′′/-3/-4), 30.7 (C-3/-4), 69.6 (C-2), 81.6 (≡C), 92.9 (≡C), 126.9 (C-Ar), 127.9 (C-Ar), 128.1 (2 C-Ar), 128.7 (2 C-Ar), 128.9 (C-Ar), 129.3 (C-Ar), 131.9 (C_q-2′), 133.5 (C-Ar), 136.4 (C_q-Ar/-1′), 141.8 (C_q-Ar/-1′), 174.2 (C_q-5) ppm. MS (EI, 70 eV): *m*/*z* (%) = 289 (9) $[M]^+$, 288 (25), 273 (15) $[M – O]^+$, 272 (66), 261 (19) $[M – C_2H_4]^+$, 260 (100), 247 (21), 233 (3) $[M – C_4H_8]^+$, 230 (17), 219 (16), 215 (18), 202 (15), 198 (98) $[M – C_7H_7]^+$, 186 (36) $[M – C_8H_7]^+$, 168 (23), 156 (64), 153 (21), 129 (23), 128 (56), 115 (20) $[C_9H_7]^+$, 103 (14) $[C_8H_7]^+$, 91 (14) $[C_7H_7]^+$. HRMS ($C_{20}H_{18}NO$ [M – 1]): calcd. 288.1388; found 288.1396.

5-[2′-(3′′-Phenylprop-1′′-ynyl)phenyl]-3,4-dihydro-2*H*-pyrrole *N*-Oxide (35c): According to the general procedure, treatment of **32c** (307 mg, 1.0 mmol) with a total of 558 mg (10.0 mmol) of hydrogen-reduced iron powder and 0.5 M HCl (0.5 mL) in ethanol (2 mL) gave, after work up, **35c** (100 mg, 36%) as a red-brown oil. IR (CCl_4): $\tilde{\nu}$ = 3416, 3066, 3028, 2956, 2878, 2232 (C≡C), 1375, 1225 cm^{-1}. ^{1}H NMR (500 MHz): δ = 2.04 (m_c, $^3J_{3,2/4}$ = 7.9 Hz, 2 H, 3-H), 3.22 (m_c, $^4J_{2,4}$ = 2.0 Hz, 2 H, 2-/4-H), 3.84 (s, 2 H, 3′′-H), 4.14 (m_c, $^3J_{2/4,3}$ = 7.9, $^4J_{2,4}$ = 2.0 Hz, 2 H, 2-/4-H), 7.27 (m_c, 1 H, Ar-H), 7.31–7.40 (m, 6 H, Ar-H), 7.52 (dd, ^3J = 7.7, J = 1.3 Hz, 1 H, Ar-H), 8.11 (dd, ^3J = 7.9, J = 1.3 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 17.6/33.0/63.5 (C-2/-3/-4), 26.1 (C-3′′), 81.4 (≡C), 93.1 (≡C), 122.5 (C_q-Ar), 126.9 (C-Ar), 127.9 (C-Ar), 128.1 (C-Ar), 128.7 (C-Ar), 128.8 (C-Ar), 129.5 (C-Ar), 131.4 (C_q-Ar), 133.5 (C-Ar), 136.3 (C_q-Ar), 143.6 (C-5) ppm. MS (EI, 70 eV): *m*/*z* (%) = 275 (9) $[M]^+$, 274 (22), 259 (19) $[M – O]^+$, 258 (63), 247 (15) $[M – C_2H_4]^+$, 246 (66), 233 (17) $[M – C_3H_6]^+$, 215 (13), 198 (6) $[M – C_6H_5]^+$, 191 (4) $[C_{15}H_{11}]^+$, 189 (14), 184 (100) $[M – C_7H_7]^+$, 172 (38) $[M – C_8H_7]^+$, 157 (18), 156 (81), 129 (56), 128 (52), 116 (22), 115 (26) $[C_9H_7]^+$, 103 (20) $[C_8H_7]^+$, 91 (17). HRMS ($C_{19}H_{16}NO$ [M – 1]): calcd. 274.1231; found 274.1230.

2-Phenyl-5-[2′-(3′′-phenylprop-1′′-ynyl)phenyl]-3,4-dihydro-2*H*-pyrrole *N*-Oxide (36c): According to the general procedure, treatment of **33c** (1.00 g, 2.61 mmol) with a total of 1.46 g (26.1 mmol) of hydrogen-reduced iron powder and 0.5 M HCl (1.2 mL) in ethanol (5 mL) gave, after flash chromatography (cyclohexane/ethyl acetate, 5:1, 1:2), **36c** (738 mg, 80%) as a green-brown oil. IR (PTFE): $\tilde{\nu}$ = 3405, 3059, 3029, 2950, 2227 (C≡C), 1956, 1373, 1029 cm^{-1}. ^{1}H NMR (500 MHz): δ = 2.08 (m_c, $^2J_{3,3}$ = 13.1, $^3J_{3,4}$ = 8.9, $^3J_{3,2}$ = 5.4, $^3J_{3,4}$ = 4.9 Hz, 1 H, 3-H), 2.54 (m_c, $^2J_{3,3}$ = 13.1, $^3J_{3,4}$ = 9.2, $^3J_{3,2}$ = 9.2, $^3J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 3.26 (dddd, $^2J_{4,4}$ = 17.9, $^3J_{4,3}$ = 9.2, $^3J_{4,3}$ = 4.9, $^4J_{4,2}$ = 1.2 Hz, 1 H, 4-H), 3.38 (dddd, $^2J_{4,4}$ = 17.9, $^3J_{4,3}$ = 9.1, $^3J_{4,3}$ = 8.9, $^4J_{4,2}$ = 2.0 Hz, 1 H, 4-H), 3.83 (s, 2 H, 3′′-H), 5.19 (m_c, $^3J_{2,3}$ = 9.2, $^3J_{2,3}$ = 5.4, $^4J_{2,4}$ = 2.0, $^4J_{2,4}$ = 1.2 Hz, 1 H, 2-H), 7.25 (m_c, 1 H, Ar-H), 7.30–7.39 (m, 11 H, Ar-H), 7.55 (dd, J = 7.9, J = 1.4 Hz, 1 H, Ar-H), 8.31 (dd, J = 7.9, J = 1.4 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 26.1 (C-3′′), 27.2 (C-3), 31.2 (C-4), 77.9 (C-2), 81.9 (≡C), 93.1 (≡C), 122.6 (C_q-5), 126.8 (C-Ar), 127.1 (2 C-Ar), 127.9 (C-Ar), 128.1 (C-Ar), 128.3 (C-Ar), 128.7 (C-Ar), 128.8 (2 C-Ar), 128.9 (C-Ar), 129.3 (C-Ar), 131.7 (C-2′), 133.6 (C-Ar), 136.2 (C_q-Ar), 138.6 (C-1′), 141.9 (C_q-Ar) ppm. MS (EI, 70 eV): *m*/*z* (%) = 351 (18) $[M]^+$, 350 (21) $[M – 1]^+$, 335 (17) $[M – O]^+$, 334 (54), 333 (25), 322 (35), 261 (21), 260 (100) $[M – PhCH_2]^+$, 244 (42), 232 (34), 231 (22), 230 (33), 219 (28), 218 (27), 217 (22), 215 (38), 202 (34), 191 (15) $[C_{15}H_{11}]^+$, 189 (31), 156 (66), 128 (78), 117 (22), 115 (32) $[C_9H_7]^+$, 91 (70) $[PhCH_2]^+$. HRMS ($C_{25}H_{20}NO$ [M – 1]): calcd. 350.1545; found 350.1545.

General Procedure for the Base-Catalyzed Transformations of the Nitrones 34a–c, 35c, and 36c: Solutions of the nitrones in the respective solvents were treated with a base, and in some cases tetra-*n*-butylammonium iodide (TBAI), at the given temperature. Work up of the reaction mixtures was accomplished by addition of water, extraction with diethyl ether, washing of the organic phases with saturated aqueous NH_4Cl and brine, drying ($MgSO_4$), concentration in vacuo, and flash chromatography of the residue followed by crystallization (if possible).

***cis*- and *trans*-3-Methyl-6-phenyl-2,3,6,8,9,10-hexahydrocyclopenta[*c*]pyrrolo[1,2-*a*]azepin-5(1*H*)-one (37 and 38):** A stirred mixture of **34a** (280 mg, 1.00 mmol) and TBAI (37 mg, 10 mol%) in dry toluene (5 mL) was treated with KOH (56 mg, 1.00 mmol). After refluxing the resulting suspension for 1 h and work up, flash chromatography (cyclohexane/ethyl acetate, 100:1, 60:1, 40:1) of the crude material afforded an approximate 1.7:1 mixture of **37** and **38** (238 mg, 85%). Colorless crystals of **37** (68 mg), m.p. 173–175 °C, were obtained from ethanol.

Compound 37:[37] IR (CCl_4): $\tilde{\nu}$ = 3064, 3023, 2967, 2925, 2873, 2847, 1667 (C=O), 1456, 1394, 1328, 1263, 1098, 1067 cm^{-1}. ^1H NMR (500 MHz): δ = 1.19 (d, $^3J_{CH3,3}$ = 6.5 Hz, 3 H, CH_3), 1.66 (m_c, ^2J = 12.6, $^3J_{2,1}$ = 8.9, $^3J_{2,3}$ = 1.9 Hz, 1 H, 2-H), 1.80 (m_c, ^3J = 8.5 Hz, 1 H, 9-H), 1.92 (m_c, 1 H, 9-H), 2.07 (m_c, ^2J = 12.6, $^3J_{2,3}$ = 8.0 Hz, 1 H, 2-H), 2.44–2.52 (m, J = 8.5 Hz, 4 H, 8-H, 10-H), 2.75 (m_c, $^3J_{1,2}$ = 8.9 Hz, 2 H, 1-H), 3.48 (m_c, $^3J_{6,7}$ = 5.2 Hz, 1 H, 6-H), 4.58 (m_c, $^3J_{3,2}$ = 8.0, $^3J_{3,CH3}$ = 6.5, $^3J_{3,2}$ = 1.9 Hz, 1 H, 3-H), 5.28 (d, $^3J_{7,6}$ = 5.2 Hz, 1 H, 7-H), 7.26–7.31 (m, 3 H, Ar-H), 7.34–7.32 (m, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 19.8 (CH_3), 24.4 (C-9), 28.3 (C-2), 29.2 (C-1), 30.8/32.1 (C-8/-10), 53.1 (C-6), 57.2 (C-3), 114.1 (C-7), 122.0 (C_q), 126.9 (C-Ar), 128.3 (2 C-Ar), 129.6 (2 C-Ar), 133.1 (C_q), 139.3 (C_q), 143.9 (C_q), 163.4 (C=O) ppm. MS (EI, 70 eV): *m/z* (%) = 280 (20) $[M + 1]^+$, 279 (100) $[M]^+$, 278 (73), 264 (9) $[M - CH_3]^+$, 262 (11), 251 (16) $[M - C_2H_4]^+$, 250 (12), 237 (8) $[M - C_3H_6]^+$, 236 (15), 202 (9) $[M - C_6H_5]^+$, 200 (10) $[C_{13}H_{14}NO]^+$, 174 (31), 91 (16), 77 (11). $C_{19}H_{21}NO$ (279.2): calcd. C 81.68, H 7.58, N 5.01; found C 81.36, H 7.40, N 4.87.

Selected ^1H NMR Spectroscopic Data for 38: ^1H NMR (250 MHz, taken from the mixture with **37**): δ = 1.22 (d, ^3J = 6.4 Hz, 3 H, CH_3), 1.55–1.6 (2 H), 2.4–2.55 (4 H), 2.6–2.65 (2 H), 2.85–2.9 (dd, ^3J = 4.9, J = 1.6 Hz, 2 H), 3.63–3.68 (m, ^3J = 4.9 Hz, 1 H, 6-H), 4.52–4.64 (1 H, 3-H), 5.55 (s, 1 H, 7-H), ca. 7.2 (3 H, Ar-H), 7.2–7.25 (2 H, Ar-H) ppm.

***cis*- and *trans*-3-Methyl-6-phenyl-1,2,3,6,8,9,10,11-octahydro-5*H*-pyrrolo[2,1-*a*][2]benzazepin-5-one (39 and 40):** A stirred mixture of **34b** (120 mg, 0.41 mmol) and TBAI (15 mg, 10 mol%) in dry toluene (3 mL) was treated with KOH (23 mg, 0.41 mmol). After refluxing the resulting suspension for 1 h and work up, flash chromatography (cyclohexane/ethyl acetate, 10:1) of the crude material afforded an approximate 2.5:1 mixture of **39** and **40** (67 mg, 56%). Colorless crystals of **39** (31 mg), m.p. 177–179 °C, were obtained from ethanol.

Compound 39: IR (PTFE): $\tilde{\nu}$ = 3060, 3023, 2962, 2923, 2855, 2088, 1653 (C=O), 1558, 1456, 1394, 1336, 1215, 1154 cm^{-1}. ^1H NMR (500 MHz): δ = 1.19 (d, $^3J_{CH3,3}$ = 6.5 Hz, 3 H, CH_3), 1.58 (m_c, $^2J_{2,2}$ = 12.5, $^3J_{2,3}$ = 3.4 Hz, 3 H, 2-H, 8-/9-/10-/11-H), 1.85 (m_c, 2 H, 8-/9-/10-/11-H), 2.07 (m_c, $^2J_{2,2}$ = 12.5, $^3J_{2,1}$ = 10.2, $^3J_{2,1}$ = 7.8 Hz, 1 H, 2-H), 2.18–2.29 (m, ^2J = 14.3, J = 12.3 Hz, 2 H, 8-/9-/10-/11-H), 2.38 (m_c, ^2J = 14.3, J = 3.9 Hz, 1 H, 8-/9-/10-/11-H), 2.52 (m_c, J = 3.9 Hz, 1 H, 8-/9-/10-/11-H), 2.67 (m_c, ^2J = 16.2, $^3J_{1,2}$ = 10.2 Hz, 1 H, 1-H), 2.87 (m_c, ^2J = 16.2, $^3J_{1,2}$ = 10.2 Hz, 1 H, 1-H), 3.45 (dd, $^3J_{6,7}$ = 6.0 Hz, 1 H, 6-H), 4.56 (m_c, $^3J_{3,CH3}$ = 6.5, $^3J_{3,2}$ = 3.4 Hz, 1 H, 3-H), 5.30 (dd, $^3J_{7,6}$ = 6.0 Hz, 1 H, 7-H), 7.26–7.38 (m, 5 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 20.6 (CH_3), 25.6/25.8/29.4/32.7 (C-8/-9/-10/-11), 28.3 (C-1), 28.4 (C-2), 51.8 (C-6), 55.7 (C-3), 119.8 (C_q-11a), 120.9 (C-7), 126.9 (C-Ar), 128.3 (2 C-Ar), 129.8 (2 C-Ar), 134.1/137.8/138.9 (C_q-7a/-11a/-Ar), 166.7 (C=O) ppm. MS (EI, 70 eV): *m/z* (%) = 294 (20) $[M + 1]^+$, 293 (100) $[M]^+$, 292 (94), 278 (13) $[M - CH_3]^+$, 264 (12), 216 (14) $[M - C_6H_5]^+$, 202 (23), 188 (16), 115 (9), 91 (17). $C_{20}H_{23}NO$ (293.2): calcd. C 81.87, H 7.90, N 4.77; found C 81.71, H 7.97, N 4.67.

Selected ^1H NMR Spectroscopic Data of 40: ^1H NMR (500 MHz, taken from the mixture with **39**): δ = 1.25 (d, ^3J = 6.3 Hz, 3 H, CH_3), 1.5–1.6 (2 H), 1.6–1.7 (2 H), ca. 1.9–2.0 (2 H), 2.0–2.15 (2 H), 2.3–2.4 (2 H), 2.4–2.45 (1 H), 2.45–2.5 (1 H), 4.30 (s, 1 H, 6-H), 4.5–4.55 (1 H, 3-H), 5.54 (d, ^3J = 8.0 Hz, 1 H, 7-H), ca. 7.2 (3 H, Ar-H), 7.2–7.25 (2 H, Ar-H) ppm.

1-(3′-Methyl-2′,3′,6′,7′,8′,9′-hexahydro-1′*H*-pyrrolo[2′,1′-*a*]isoindol-5′-yl)-2-phenylethanone (41): A mixture of **34b** (74 mg, 0.25 mmol) in dry methanol (3 mL) and NaOMe (14 mg, 0.25 mmol) was stirred for 5 h at room temperature. After work up, flash chromatography (cyclohexane/ethyl acetate, 50:1) of the crude material afforded **41** (12 mg, 16%) and a 1.3:1 mixture of **39** and **40** (33 mg, 44%).

Compound 41: IR (CCl_4): $\tilde{\nu}$ = 3031, 2934, 2857, 1619 (C=O), 1550, 1462, 1444, 1404, 1279, 1245, 1049, 879 cm^{-1}. ^1H NMR (500 MHz): δ = 1.25 (d, $^3J_{CH3,3'}$ = 6.5 Hz, 3 H, CH_3), 1.72 (2 H)/1.80 (2 H)/2.08 (1 H)/2.44 (2 H)/2.54–2.62 (1 H)/2.65 (1 H)/2.76 (1 H)/2.90 (2 H) (1′-/2′-/6′-/7′-/8′-/9′-H), 3.98 (s, 2 H, 2-H), 5.00 (m_c, $^3J_{3',CH3}$ = 6.5 Hz, 1 H, 3′-H), 7.20–7.24 (m, 5 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 21.1/21.7/22.9/23.8 (C-6′/-7′/-8′/-9′), 21.8/25.8 (C-1′/CH_3), 34.3/46.7/56.4 (C-2′/-3′/-2), 113.4/141.4 (C-5′a/-9′a), 126.5 (C-Ar), 128.5 (2 C-Ar), 129.6 (2 C-Ar), 130.9/132.8/135.9 (C-5′/-5′a/-9′b/-Ar), 132.8 (C-5′/-9′b/-Ar), 135.9 (C_q-5′/-9′b/-Ar), 141.4 (C_q-5′a/-9′a), 185.8 (C=O) ppm. MS (EI, 70 eV): *m/z* (%) = 293 (11) $[M]^+$, 203 (13), 202 (100) $[M - C_7H_7]^+$, 189 (8), 174 (15) $[C_{12}H_{16}N]^+$, 149 (8), 117 (6), 91 (20), 79 (7). HRMS ($C_{20}H_{23}NO$): calcd. 293.1780; found 293.1779.

***cis*- and *trans*-3-Methyl-6-phenyl-1,2,3,11b-tetrahydro-5*H*-pyrrolo[2,1-*a*][2]benzazepin-5-one (42 and 43):** A mixture of **34c** (385 mg, 1.33 mmol) and TBAI (49 mg, 10 mol%) in dry toluene (8 mL) was stirred for 5 min, treated with KOH (23 mg, 0.41 mmol) and then refluxed for 1 h. After work up, flash chromatography (cyclohexane/ethyl acetate, 30:1, 20:1, 10:1) of the crude material afforded an approximate 1.45:1 mixture of **42** and **43** (312 mg, 81%), from which, after repeated chromatography and crystallization (ethanol), fractions of pure **42** (50 mg) and **43** (109 mg) were isolated.

Compound 42: Colorless crystals, m.p. 103–104 °C (ethanol). ^1H NMR (500 MHz): δ = 1.19 (d, $^3J_{CH3,3}$ = 6.2 Hz, 3 H, CH_3), 1.89 (m_c, 1 H, 1-/2-H), 2.32 (m_c, 2 H, 1-/2-H), 2.72–2.77 (m, 1 H, 1-/2-H), 4.27 (m_c, J = 6.3 Hz, 1 H, 3-H), 4.69 (dd, J = 7.9, J = 7.3 Hz, 1 H, 11b-H), 7.33 (s, 1 H, 7-H), 7.35 (m_c, 1 H, Ar-H), 7.36–7.41 (m, 5 H, Ar-H), 7.45 (d, J = 7.3 Hz, 1 H, Ar-H), 7.66 (dd, J = 7.3, J = 1.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 20.7 (CH_3), 25.9/32.6 (C-1/-2), 55.3/57.9 (C-3/-11b), 122.0 (C-Ar), 127.5 (C-Ar), 127.8 (C-Ar), 128.1 (2 C-Ar), 128.8 (2 C-Ar), 128.9 (C-Ar), 130.4 (C-Ar), 134.2 (C-Ar), 135.9/139.6/140.2 (C_q-6/-7a/-11a/-Ar), 184.6 (C=O) ppm. $C_{20}H_{19}NO$ (289.2): calcd. C 83.01, H 6.62, N 4.84; found C 82.23, H 6.71, N 4.71 (crystals contain traces of water).

Compound 43:[37] Colorless crystals, m.p. 108–110 °C (ethanol). IR (CCl_4): $\tilde{\nu}$ = 3064, 3023, 2967, 2925, 1636 (C=O), 1419 cm^{-1}. ^1H NMR (500 MHz): δ = 1.40 (d, $^3J_{CH3,3}$ = 6.3 Hz, 3 H, CH_3), 1.77 (dd, $^2J_{2\alpha,2\beta}$ = 12.3, $^3J_{2\alpha,1\alpha}$ = 6.2 Hz, 1 H, 2α-H), 2.34 (m_c, $^3J_{2\beta,1\alpha}$ = 14.0, $^2J_{2\beta,2\alpha}$ = 12.3, $^3J_{2\beta,3}$ = 8.1, $^3J_{2\beta,1\beta}$ = 6.0 Hz, 1 H, 2β-H), 2.49 (m_c, $^3J_{1\alpha,2\beta}$ = 14.0, $^2J_{1\alpha,1\beta}$ = 13.5, $^3J_{1\alpha,11b}$ = 7.7, $^3J_{1\alpha,2\alpha}$ = 6.2 Hz, 1 H, 1α-H), 2.65 (dd, $^2J_{1\beta,1\alpha}$ = 13.5, $^3J_{1\beta,2\beta}$ = 6.0 Hz, 1 H, 1β-H), 4.36 (m_c, $^3J_{3,2\beta}$ = 8.1, $^3J_{3,CH3}$ = 6.3 Hz, 1 H, 3-H), 4.77 (d, $^3J_{11b,1\alpha}$ = 7.7 Hz, 1 H, 11b-H), 7.27 (s, 1 H, 7-H), 7.30–7.36 (m, 4 H, Ar-H), 7.39 (m_c, 3 H, Ar-H), 7.69 (m_c, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 19.4 (CH_3), 25.5/31.1 (C-1/-2), 54.0/57.7 (C-3/-11b), 122.6/127.6/128.0/128.2/128.4/128.6/130.0/131.3 (C-7/-Ar), 136.2/138.3/139.0/140.8 (C-6/-7a/-11a/-Ar), 164.4 (C=O) ppm. MS (EI, 60 eV): *m/z* (%) = 304 (5) $[M + H_2O]^+$, 289 (9) $[M]^+$, 274 (2) $[M - CH_3]^+$, 214 (16), 213 (100), 183 (40), 181 (17), 105 (8). $C_{20}H_{19}NO$ (289.4): calcd. C 83.01, H 6.62, N 4.84; found C 82.37, H 6.69, N 4.69 (crystals contain water).

1-(3′-Methyl-2′,3′-dihydro-1′*H*-pyrrolo[2′,1′-*a*]isoindol-5′-yl)-2-phenylethanone (44): A mixture of **34c** (90 mg, 0.315 mmol) in dry methanol (1 mL) and MeONa (17 mg, 0.31 mmol) was stirred for 4 h at room temperature. After work up, flash chromatography (cyclohexane/ethyl acetate, 40:1, 30:1, 20:1) of the crude material afforded **44** (13 mg, 14%) and a 3:2 mixture of **42** and **43** (29 mg,

26%). After a reaction time of 90 h, 16 mg (18%) of **44** and 73 mg (66%) of **42/43** (ca. 3:2 mixture) were isolated. ^{1}H NMR spectroscopic data for **44** (250 MHz): δ = 1.41 (d, $^3J_{CH3,3'}$ = 6.4 Hz, 3 H, CH_3), 2.31 (dddd, ^2J = 12.5, $^3J_{2',3'}$ = 7.3, $^3J_{2',1'}$ = 2.1, J = 0.9 Hz, 1 H, 2′-H), 2.79 (m_c, ^2J = 12.5, $^3J_{2',1'}$ = 10.4 Hz, 1 H, 2′-H), 3.07–3.23 (m, $^3J_{1',2'}$ = 10.4, $^3J_{1',2'}$ = 2.1 Hz, 2 H, 1′-H), 4.34 (d, J = 2.1 Hz, 2 H, 2-H), 5.44 (m_c, $^3J_{3',2'}$ = 7.3, $^3J_{3',CH3}$ = 6.4 Hz, 1 H, 3′-H), 7.11 (m_c, ^3J = 8.2 Hz, 1 H, 7′-/8′-H), 7.26 (dd, ^3J = 8.9 Hz, 1 H, 7′-/8′-H), 7.30–7.36 (m, 5 H, Ar-H), 7.62 (td, ^3J = 8.2, J = 1.2 Hz, 1 H, 6′-/9′-H), 7.95 (d, ^3J = 8.9 Hz, 1 H, 6′-/9′-H) ppm.

6-Phenyl-1,2,3,11b-tetrahydro-5*H*-pyrrolo[2,1-*a*][2]benzazepin-5-one (45): A solution of **35c** (100 mg, 0.36 mmol) and TBAI (13 mg, 10 mol%) in dry toluene (2 mL) was stirred for 5 min, treated with KOH (20 mg, 0.36 mmol), and then refluxed for 0.5 h. After work up, flash chromatography (cyclohexane/ethyl acetate, 10:1, 5:1, 3:1) of the crude material afforded **45** (75 mg, 75%) as an amorphous solid; colorless crystals were obtained from ethanol, m.p. 132–133 °C. IR (CCl_4): $\tilde{\nu}$ = 3064, 3023, 2976, 2950, 2930, 2878, 1636 (C=O), 1429, 1345 cm^{-1}. ^{1}H NMR (400 MHz): δ = 2.13 (m_c, 2 H, 1-/2-/3-H), 2.35 (m_c, 1 H, 1-/2-/3-H), 2.75 (m_c, 1 H, 1-/2-/3-H), 3.59 (m_c, 1 H, 1-/2-/3-H), 3.74 (m_c, 1 H, 1-/2-/3-H), 4.73 (d, ^3J = 7.1 Hz, 1 H, 11b-H), 7.32 (m_c, 2 H, Ar-H, 7-H), 7.34–7.44 (m, 6 H, Ar-H), 7.69 (m_c, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz): δ = 23.6/27.7/46.6/57.1 (C-1/-2/-3/-11b), 122.4/127.6/128.0/128.3/128.5/130.4/133.2 (C-Ar), 136.1/138.5/139.2/140.1 (C_q-6/-7a/-11a/-Ar), 164.6 (C=O) ppm. MS (EI, 70 eV): m/z (%) = 275 (54) $[M]^+$, 274 (23), 247 (6) $[M - C_2H_4]^+$, 246 (23), 218 (16), 198 (5) $[M - C_6H_5]^+$, 189 (9), 170 (19), 158 (100) $[C_{10}H_8NO]^+$, 108 (11). $C_{19}H_{17}NO$ (275.3): calcd. C 82.88, H 6.22, N 5.09; found C 82.31, H 6.3, N 4.92 (crystals contain traces of water).

1-(2′,3′-Dihydro-1′*H*-pyrrolo[2′,1′-*a*]isoindol-5′-yl)-2-phenylethanone (46): A mixture of **35c** (100 mg, 0.36 mmol) in dry methanol (2 mL) and MeONa (19 mg, 0.36 mmol) was stirred for 24 h at room temperature. After work up, flash chromatography (cyclohexane/ethyl acetate, 10:1, 5:1, 3:1) of the crude material afforded, besides **45** (65 mg, 65%), **46** (6 mg, 6%). ^{1}H NMR (250 MHz): δ = 2.65 (m_c, ^3J = 8.2, ^3J = 7.3 Hz, 2 H, 2′-H), 3.18 (t, ^3J = 7.3 Hz, 2 H, 1′-/3′-H), 4.33 (s, 2 H, 2-H), 4.71 (t, ^3J = 8.2 Hz, 2 H, 3′-/1′-H), 7.12 (m_c, ^3J = 8.2, ^3J = 6.7, J = 0.9 Hz, 1 H, 7′-/8′-H), 7.31–7.38 (m, ^3J = 6.7 Hz, 6 H, 7′-/8′-H, Ar-H), 7.63 (td, ^3J = 8.2, J = 0.9 Hz, 1 H, 6′-/9′-H), 7.96 (td, ^3J = 8.5, J = 0.9 Hz, 1 H, 6′-/9′-H) ppm.

3,6-Diphenyl-1,2,3,11b-tetrahydro-5*H*-pyrrolo[2,1-*a*][2]benzazepin-5-one (47 and 48): A solution of **36c** (466 mg, 1.33 mmol) and TBAI (49 mg, 10 mol%) in dry toluene (10 mL) was stirred for 5 min, treated with KOH (74 mg, 1.33 mmol), and then refluxed for 0.5 h. After work up, flash chromatography (cyclohexane/ethyl acetate, 50:1, 30:1, 10:1) of the crude material afforded an approximate 0.77:1 mixture of **47** (24%) and **48** (31%) (total yield 260 mg, 55%). Only the minor component, **47** (see Results and Discussion section), was isolated in the pure form. Treatment of a methanolic solution of **36c** with MeONa at room temperature for 4 h gave a similar result: After work up and purification an approximate 0.73:1 mixture of **47** (22%) and **48** (30%) was obtained.

Compound 47: Colorless crystals, m.p. 164 °C (ethanol). IR (PTFE): $\tilde{\nu}$ = 3054, 3027, 2977, 2945, 2888, 1949, 1621, 1491, 1414, 1335, 1265, 1249 cm^{-1}. ^{1}H NMR (500 MHz): δ = 2.16 (m_c, $^2J_{2\alpha,2\beta}$ = 12.5, $^3J_{2\alpha,3}$ = 7.5, $^3J_{2\alpha,1\beta}$ = 3.7 Hz, 1 H, 2α-H), 2.44 (m_c, $^2J_{1\alpha,1\beta}$ = 13.2, $^3J_{1\alpha,11b}$ = 7.7, $^3J_{1\alpha,2\beta}$ = 4.2 Hz, 1 H, 1α-H), 2.56 (m_c, $^2J_{2\beta,2\alpha}$ = 12.5, $^3J_{2\beta,3}$ = 7.5, $^3J_{2\beta,1\beta}$ = 7.1, $^3J_{2\beta,1\alpha}$ = 4.2 Hz, 1 H, 2β-H), 2.78 (m_c, $^2J_{1\beta,1\alpha}$ = 13.2, $^3J_{1\beta,2\beta}$ = 7.1, $^3J_{1\beta,2\alpha}$ = 3.7, $^3J_{1\beta,11b}$ = 3.2 Hz, 1 H, 1β-H), 4.90 (dd, $^3J_{11b,1\alpha}$ = 7.7, $^3J_{11b,1\beta}$ = 3.2 Hz, 1 H, 11b-H), 5.21 (t, $^3J_{3,2}$ = 7.5 Hz, 1 H, 3-H), 6.80 (dd, 2 H, Ar-H), 7.08 (m_c, 3 H, Ar-H), 7.30 (m_c, 1 H, Ar-H), 7.35 (m_c, 2 H, Ar-H), 7.39 (s, 1 H, 7-H), 7.41–7.46 (m, 3 H, Ar-H), 7.53 (m_c, 1 H, Ar-H), 7.66 (dd, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 26.6 (C-1), 35.0 (C-2), 58.4 (C-11b), 63.9 (C-3), 122.7 (C-Ar), 125.9 (2 C-Ar), 126.6 (C-Ar), 127.8 (C-Ar), 127.9 (C-Ar), 128.1 (2 C-Ar), 128.4 (2 C-Ar), 128.9 (2 C-Ar), 129.2 (C-7/-Ar), 130.9 (C-7/-Ar), 134.9 (C-7/-Ar), 136.1 (C_q), 139.1 (C_q), 139.5 (C_q), 139.8 (C_q), 142.4 (C_q), 164.7 (C=O) ppm. MS (EI, 70 eV): m/z (%) = 352 (18) $[M + 1]^+$, 351 (64) $[M]^+$, 335 (6) $[M - O]^+$, 334 (21), 274 (2) $[M - C_6H_5]^+$, 246 (18), 234 (35) $[C_{16}H_{12}NO]^+$, 233 (5) $[M - C_9H_{10}]^+$, 232 (11), 221 (2) $[C_{16}H_{15}N]^+$, 220 (13), 206 (5) $[C_{15}H_{10}O]^+$, 204 (13), 202 (11), 191 (10), 119 (100), 115 (15), 104 (12), 91 (17), 77 (11). $C_{25}H_{21}NO$ (351.4): calcd. C 85.44, H 6.02, N 3.99; found C 85.14, H 6.13, N 3.98.

^{1}H NMR Spectroscopic Data of 48: ^{1}H NMR (250 MHz, taken from the mixture with **47**): δ = 1.97 (m_c, 1 H, 1-/2-H), 2.48–2.69 (m, J = 7.9 Hz, 3 H, 1-H, 2-H), 5.06 (d, J = 7.3 Hz, 1 H, 11b-H), 5.37 (d, J = 7.9 Hz, 1 H, 3-H), 7.26–7.28 (m, 1 H, Ar-H), 7.30 (br. s, 2 H, Ar-H), 7.32–7.34 (m, 2 H, Ar-H), 7.35–7.37 (m, 2 H, Ar-H), 7.40 (m_c, 5 H, Ar-H), 7.44 (m_c, 1 H, Ar-H), 7.62–7.67 (m, 2 H, Ar-H) ppm.

5-Chloro-1-[2′-(3′′-phenylprop-1′′-ynyl)phenyl]pentan-1-ol (49): A solution of 4-chlorobutylmagnesium bromide, freshly prepared from 1-bromo-4-chlorobutane (1.26 mL, 11.0 mmol) and magnesium turnings (267 mg, 11.0 mmol) in THF (12 mL), was added to a stirred solution of **28** (2.02 g, 9.17 mmol) in dry THF (12 mL) at –40 °C under N_2. This mixture was stirred at –40 °C for a further 3 h, and then warmed to room temperature, treated with saturated NH_4Cl, and extracted with diethyl ether. The combined organic phases were washed with water, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (cyclohexane/ethyl acetate, 50:1, 40:1) afforded **49** (1.07 g, 37%) as a yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3067, 3028, 2939, 1698, 1650, 1453, 1252, 1068, 906 cm^{-1}. ^{1}H NMR (500 MHz): δ = 1.41–1.49 (m, J = 4.9 Hz, 1 H, 2-H), 1.56–1.62 (m, J = 7.9 Hz, 1 H, 2-H), 1.75 (m_c, J = 6.8 Hz, 4 H, 3-H, 4-H), 3.47 (t, J = 6.8 Hz, 2 H, 5-H), 3.87 (s, 2 H, 3′′-H), 5.13 (dd, J = 7.9, J = 4.9 Hz, 1 H, 1-H), 7.21 (dt, J = 7.5, J = 1.4 Hz, 1 H, Ar-H), 7.26 (m_c, 1 H, Ar-H), 7.31 (dd, J = 7.5, J = 1.4 Hz, 1 H, Ar-H), 7.55 (m_c, 2 H, Ar-H), 7.39 (d, J = 0.8 Hz, 1 H, Ar-H), 7.42 (m, 2 H, Ar-H), 7.47 (m_c, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 23.3 (C-3), 26.0 (C-3′′), 32.4/37.3 (C-2/-4), 44.9 (C-5), 72.1 (C-1), 80.3 (≡C), 92.9 (≡C), 120.9 (C-2′), 125.2/127.1/128.4/132.4 (C-3′/-4′/-5′/-6′), 126.8 (C-Ar), 127.9 (2 C-Ar), 128.7 (2 C-Ar), 136.6 (C_q-Ar), 146.4 (C-1′) ppm. MS (EI, 70 eV): m/z (%) = 312 (14) $[M]^+$, 235 (3) $[M - C_3H_6Cl]^+$, 222 (31), 221 (100) $[M - C_4H_8Cl]^+$, 204 (9), 203 (14), 193 (10), 191 (6) $[C_{15}H_{11}]^+$, 178 (16), 115 (21) $[C_9H_7]^+$, 105 (8), 91 (53). HRMS ($C_{20}H_{21}ClO$): calcd. 312.1281; found 312.1282.

5-Chloro-1-[2′-(3′′-phenylprop-1′-ynyl)phenyl]pentan-1-one (50): IBX (1.08 g, 3.86 mmol) was added to a stirred solution of **49** (0.93 g, 2.97 mmol) in dry DMSO (75 mL) under argon. The mixture was stirred for a further 4.5 h and then the solution was cooled in an ice bath and treated with diethyl ether/water (100 mL, 1:2 mixture). After extraction with diethyl ether, the organic phase was washed with saturated $NaHCO_3$ and brine, dried ($MgSO_4$), and then concentrated. Flash chromatography (cyclohexane/ethyl acetate, 60:1) of the residue gave **50** (769 mg, 83%) as a yellow oil. IR (CCl_4): $\tilde{\nu}$ = 3060, 3028, 2952, 2230 (C≡C), 1684 (C=O), 1539, 1494, 1453, 1252, 1221, 1072, 1004, 926 cm^{-1}. ^{1}H NMR (500 MHz): δ = 1.70–1.76 (m, $^3J_{3,2}$ = 6.9 Hz, 2 H, 3-H), 1.77–1.83 (m, $^3J_{4,5}$ = 6.5 Hz, 2 H, 4-H), 3.06 (t, $^3J_{2,3}$ = 6.9 Hz, 2 H, 2-H), 3.47 (t, $^3J_{5,4}$

= 6.5 Hz, 2 H, 5-H), 3.87 (s, 2 H, 3′′-H), 7.26 (m_c, J = 7.9 Hz, 1 H, Ar-H), 7.35 (m_c, J = 7.7 Hz, 3 H, Ar-H), 7.39–7.42 (m, J = 7.5 Hz, 3 H, Ar-H), 7.53 (dd, J = 7.7, J = 1.4 Hz, 1 H, Ar-H), 7.58 (d, J = 7.9 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 21.7 (C-3), 26.2 (C-3′′), 32.1 (C-4), 41.2 (C-2), 44.8 (C-5), 81.4 (≡C), 93.5 (≡C), 121.5 (C_q-1), 126.9 (C-Ar), 127.9/128.0/130.9/134.0 (C-3′/-4′/-5′/-6′), 128.1 (2 C-Ar), 128.8 (2 C-Ar), 136.3 (C_q-Ar), 141.5 (C_q-1′), 203.3 (C=O) ppm. MS (EI, 70 eV): *m/z* (%) = 311 (34) [M + 1]$^+$, 310 (48) [M]$^+$, 309 (91), 275 (7) [M – Cl]$^+$, 234 (20), 233 (100) [M – C_3H_6Cl]$^+$, 232 (14), 219 (42) [$C_{16}H_{11}O$]$^+$, 215 (26), 205 (17), 202 (20), 201 (14), 191 (40), 189 (80), 165 (40), 95 (13). HRMS ($C_{20}H_{19}ClO$): calcd. 310.1124; found 310.1125.

6-[2′-(3′′-Phenylprop-1′′-ynyl)phenyl]-2,3,4,5-tetrahydropyridine *N*-Oxide (51): A mixture of **50** (300 mg, 0.97 mmol), hydroxylamine hydrochloride (134 mg, 1.93 mmol), and potassium carbonate (133 mg, 0.97 mmol) in ethanol/water (6 mL, 1:1 mixture) was refluxed for 4 h. This solution was cooled to room temperature, brine (10 mL) was added, and the solution was extracted with ethyl acetate. The combined organic phases were washed with saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography (ethyl acetate/methanol, 50:1, 10:1) afforded **51** (119 mg, 42%) as an orange oil. IR (CCl_4): $\tilde{\nu}$ = 3060, 3028, 2952, 2862, 1252, 1068, 1004, 976 cm^{-1}. ^{1}H NMR (500 MHz): δ = 1.66 (m_c, J = 6.2, J = 5.7 Hz, 2 H, 3-/4-H), 1.86 (m_c, J = 6.2, J = 5.7 Hz, 2 H, 3-/4-H), 2.66 (tt, J = 6.3, J = 1.9 Hz, 2 H, 5-H), 3.81 (s, 2 H, 3′′-H), 3.86 (tt, J = 6.3, J = 1.9 Hz, 2 H, 2-H), 7.25 (m_c, 1 H, Ar-H), 7.30–7.35 (m, 5 H, Ar-H), 7.38 (m_c, 2 H, Ar-H), 7.52 (m_c, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 18.8/23.2 (C-3/-4), 26.0 (C-3′′), 30.6 (C-5), 58.9 (C-2), 80.4 (≡C), 91.6 (≡C), 121.8 (C_q-2′), 126.8 (C-Ar), 127.7/128.2/128.6/132.7 (C-3′/-4′/-5′/-6′), 128.1 (2 C-Ar), 128.7 (2 C-Ar), 136.8/137.9 (C_q-Ar/-1′), 145.2 (C_q-6) ppm. MS (EI, 70 eV): *m/z* (%) = 289 (6) [M]$^+$, 273 (13) [M – O]$^+$, 272 (26), 260 (56), 244 (16), 230 (14), 202 (17), 199 (17), 198 (100) [M – C_7H_7]$^+$, 189 (22), 186 (45), 170 (44), 168 (31), 158 (20), 153 (40), 143 (23), 128 (41), 115 (37), 103 (21), 91 (16). HRMS ($C_{20}H_{19}NO$): calcd. 289.1467; found 289.1469.

7-Phenyl-1,3,4,12b-tetrahydropyrido[2,1-*a*][2]benzazepin-6(2*H*)-one (52): KOH (18 mg, 0.33 mmol) was added to a stirred mixture of **51** (95 mg, 0.33 mmol) and TBAI (12 mg, 10 mol%) in dry toluene (3 mL). After refluxing the suspension for 1 h, work up was accomplished by addition of water (10 mL) and extraction with diethyl ether. The combined organic fractions were washed with saturated NH_4Cl and brine, dried ($MgSO_4$), and concentrated. Flash chromatography (cyclohexane/ethyl acetate, 40:1, 20:1, 5:1) of the crude material afforded **52** (50 mg, 52%); colorless crystals, m.p. 155–157 °C, were obtained from ethanol. IR (CCl_4): $\tilde{\nu}$ = 3068, 3023, 2943, 2861, 1634, 1416, 1255, 1232, 1002, 977 cm^{-1}. ^{1}H NMR (500 MHz): δ = 1.65 (m_c, J = 13.2, J = 3.7 Hz, 1 H, 2-/3-/4-H), 1.86 (m_c, J = 13.4 Hz, 1 H, 2-/3-/4-H), 1.93–2.03 (m, 2 H, 2-/3-/4-H), 2.12 (m_c, ^2J = 14.5, $^3J_{1,12b}$ = 6.9 Hz, 1 H, 1-H), 2.47 (m_c, ^2J = 14.5 Hz, 1 H, 1-H), 2.64 (m_c, J = 13.5, J = 3.7 Hz, 1 H, 2-/3-/4-H), 4.46 (m_c, J = 13.8 Hz, 1 H, 2-/3-/4-H), 4.75 (dd, $^3J_{12b,1}$ = 6.9, J = 2.6 Hz, 1 H, 12b-H), 7.27 (br. s, 1 H, 8-H), 7.32–7.45 (m, J = 9.5, J = 6.8 Hz, 6 H, Ar-H), 7.52 (d, J = 6.8 Hz, 1 H, Ar-H), 7.72 (m_c, J = 9.5 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (125 MHz): δ = 21.1/24.1/25.4 (C-1/-2/-3), 38.1/52.3 (C-4/-12b), 124.4 (C-Ar), 127.6/128.1/128.2/130.1 (C-9/-10/-11/-12), 128.4 (2 C-Ar), 130.6 (C-8), 136.2 (C_q), 138.4 (C_q), 139.5 (C_q), 139.7 (C_q), 167.0 (C=O) ppm. MS (EI, 70 eV): *m/z* (%) = 290 (20) [M + 1]$^+$, 289 (100) [M]$^+$, 288 (24), 261 (39) [M – C_2H_4]$^+$, 260 (33), 233 (5) [M – C_4H_8]$^+$, 212 (7) [M – C_6H_5]$^+$, 204 (27), 191 (13), 184 (72), 178 (11) [$C_{10}H_{10}$]$^+$, 172 (65), 159 (2) [$C_{11}H_{13}N$]$^+$, 115 (12), 109 (11), 77 (6). $C_{20}H_{19}NO$ (289.4): calcd. C 83.01, H 6.62, N 4.84; found C 82.85, H 6.56, N 4.78.

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[1] J. O. Hawthorne, E. L. Mihelic, U.S. Patent 3668232, **1972** [*Chem. Abstr.* **1972**, *77*, 101199s]; J. O. Hawthorne, E. L. Mihelic, U.S. Patent 3551414, **1970** [*Chem. Abstr.* **1971**, *74*, 125484v].

[2] A. A. Pessolano, B. E. Witzel, R. L. Clark, T.-Y. Shen, P. Graham, Ger. Offen. 2239024, **1973** [*Chem. Abstr.* **1973**, *78*, 136115j].

[3] a) P. Josee Voorstad, J. M. Chapman, G. H. Cocolas, S. D. Wyrick, I. H. Hall, *J. Med. Chem.* **1985**, *28*, 9–12; b) J. M. Chapman, S. D. Wyrick, P. Josee Voorstad, J. H. Maguire, G. H. Cocolas, I. H. Hall, *J. Pharm. Sci.* **1984**, *73*, 1482–1484.

[4] W. H. Miller, D. P. Alberts, P. K. Bhatnagar, W. E. Bondinell, J. F. Callahan, R. R. Calvo, R. D. Cousins, K. F. Erhard, D. A. Heerding, R. M. Keenan, C. Kwon, P. J. Manley, K. A. Newlander, S. T. Ross, J. M. Samanen, I. N. Uzinskas, J. W. Venslavsky, C. C.-K. Yuan, R. C. Haltiwanger, M. Gowen, S.-M. Hwang, I. E. James, M. W. Lark, D. J. Rieman, G. B. Stroup, L. M. Azzarano, K. L. Salyers, B. R. Smith, K. W. Ward, K. O. Johanson, W. F. Huffman, *J. Med. Chem.* **2000**, *43*, 22–26 and references cited therein.

[5] a) Y. Horiguchi, T. Saitoh, T. Kashiwagi, L. Katura, M. Itagaki, J. Toda, T. Sano, *Heterocycles* **2002**, *57*, 1063–1077; b) R. Ferraccioli, D. Carenzi, M. Catellani, *Synlett* **2002**, 1860–1864; c) A. Kamimura, Y. Taguchi, Y. Omata, M. Hagihara, *J. Org. Chem.* **2003**, *68*, 4996–4998; d) A. Kamimura, Y. Taguchi, *Tetrahedron Lett.* **2004**, *45*, 2335–2337 and references cited therein.

[6] K. Knobloch, W. Eberbach, *Org. Lett.* **2000**, *2*, 1117–1120.

[7] K. Knobloch, M. Keller, W. Eberbach, *Eur. J. Org. Chem.* **2001**, 3313–3332.

[8] For reviews, see: a) D. J. Pasto, *Tetrahedron* **1984**, *40*, 2805–2827; b) H. F. Schuster, G. M. Coppola, *Allenes in Organic Synthesis*, Wiley, New York, **1984**.

[9] a) H. Hopf in *The Chemistry of Allenes* (Ed.: S. R. Landor), Academic Press, New York, **1982**, vol. 2, pp. 525–562; b) P. H. Beusker, J. W. Scheeren in *The chemistry of dienes and polyenes* (Ed.: Z. Rappoport), John Wiley & Sons, New York, **2000**, vol. 2, pp. 331–337.

[10] For selected examples, see: a) R. W. M. Aben, S. Braverman, H. W. Scheeren, *Eur. J. Org. Chem.* **2003**, 894–897; b) B. Alcaide, P. Almendros, C. Aragoncillo, *Org. Lett.* **2003**, *5*, 3795–3798; c) A. Padwa, H. Lipka, S. H. Watterson, S. S. Murphree, *J. Org. Chem.* **2003**, *68*, 6238–6250.

[11] W. Carruthers, *Cycloaddition Reactions in Organic Synthesis*, Pergamon Press, Oxford, **1990**.

[12] For selected examples, see: a) U. Koop, G. Handke, N. Krause, *Liebigs Ann.* **1996**, 1487–1499; b) M. E. Jung, N. Nishimura, *J. Am. Chem. Soc.* **1999**, *121*, 3529–3530; c) K. L. McCaleb, R. L. Halcomb, *Org. Lett.* **2000**, *2*, 2631–2634; d) D. Regás, M. M. Afonso, J. A. Palenzuela, *Synthesis* **2004**, 757–760.

[13] For a review, see: G. Broggini, G. Zecchi, *Gazz. Chim. Ital.* **1996**, *126*, 479–488.

[14] For selected examples, see: a) T. Wirth, S. Blechert, *Synlett* **1994**, 717–718; b) A. Padwa, M. Meske, Z. Ni, *Tetrahedron* **1995**, *51*, 89–106; c) D. G. J. Young, D. Zeng, *Heterocycles* **2004**, *62*, 121–125.

[15] a) S.-K. Kang, T.-G. Baik, A. N. Kulak, Y.-H. Ha, Y. Lim, J. Park, *J. Am. Chem. Soc.* **2000**, *122*, 11529–11530; b) A. S. K. Hashmi, *Angew. Chem.* **2000**, *112*, 3737–3740, *Angew. Chem. Int. Ed.* **2000**, *39*, 3590–3593; c) J. Löfstedt, J. Franzén, J.-E. Bäckvall, *J. Org. Chem.* **2001**, *66*, 8015–8025; d) H. Ohno, K. Miyamura, Y. Takeoka, T. Tanaka, *Angew. Chem.* **2003**, *115*, 2751–2754, *Angew. Chem. Int. Ed.* **2003**, *42*, 2647–2650.

[16] a) T. Shibata, S. Kadowski, M. Hirase, K. Takagi, *Synlett* **2003**, 573–575; b) K. M. Brummond, H. Wan, J. L. Kent, *J. Org. Chem.* **1998**, *63*, 6535–6545.
[17] M. Ahmed, T. Arnauld, A. G. M. Barrett, D. C. Braddock, K. Flack, P. A. Procopiou, *Org. Lett.* **2000**, *2*, 551–553.
[18] K. Knobloch, Ph. D. Dissertation, University of Freiburg, **2000**.
[19] a) H. A. Lloyd, *Tetrahedron Lett.* **1965**, *6*, 1761–1767; b) G. L. Webster, *Systematic Botany* **1992**, *17*, 311–323.
[20] a) Z. Arnold, A. Holy, *Collect. Czech Chem. Commun.* **1961**, 3059–3073; b) T. L. Gilchrist, P. D. Kemmitt, A. L. Germain, *Tetrahedron* **1995**, *51*, 9119–9126.
[21] H. D. Beckhaus, S. Verevkin, manuscript in preparation.
[22] D. Prim, A. Fuss, G. Kirsch, A. M. S. Silva, *J. Chem. Soc., Perkin Trans. 2* **1999**, 1175–1180.
[23] The bromo formylation procedure gave an approximately 10:1 (*E*)/(*Z*) mixture of **12**, which could not be separated by chromatography. However, subsequent reaction of this mixture afforded the nitrone **16** with no detectable amounts of the corresponding (*E*) isomer.
[24] a) W. Eberbach, J. Roser, *Tetrahedron Lett.* **1987**, *28*, 2689–2692; b) U. Koop, G. Handke, N. Krause, *Liebigs Ann. Org. Bioorg. Chem.* **1996**, *10*, 1487–1500.
[25] H.-U. Reißig, *Nachr. Chem. Tech. Lab.* **1986**, *34*, 237–240.
[26] a) L. A. Paquette, *Tetrahedron Lett.* **1963**, *4*, 2027–2031; b) L. A. Paquette, *J. Am. Chem. Soc.* **1964**, *86*, 500–503; c) O. L. Chapman, E. D. Hoganson, *J. Am. Chem. Soc.* **1964**, *86*, 498–500; d) L. A. Paquette, *J. Am. Chem. Soc.* **1964**, *86*, 4092–4095.
[27] J. A. Pawlik, C. A. Seymour, *Tetrahedron Lett.* **1977**, *18*, 2555–2558.
[28] a) W. G. Dauben, R. L. Cargill, *Tetrahedron* **1961**, *12*, 186–189; b) G. Büchi, E. M. Burgess, *J. Am. Chem. Soc.* **1960**, *82*, 4333–4337.
[29] a) P. Schiess, R. Seeger, C. Suter, *Helv. Chim. Acta* **1970**, *53*, 1713–1722; b) I. R. Robertson, J. T. Sharp, *Tetrahedron* **1984**, *40*, 3095–3112.
[30] H. E. Zimmerman, W. Eberbach, *J. Am. Chem. Soc.* **1973**, *95*, 3970–3976.
[31] H. E. Zimmerman, H. G. Dürr, R. S. Givens, R. G. Lewis, *J. Am. Chem. Soc.* **1967**, *89*, 1863–1874.
[32] a) N. Hoshi, H. Hagiwara, H. Uda, *Chem. Lett.* **1979**, 1291–1294; b) N. Hoshi, H. Hagiwara, H. Uda, *Chem. Lett.* **1979**, 1295–1298; c) H. Ushiyama, H. Hagiwara, K. Sato, H. Uda, *Chem. Lett.* **1977**, 925–928.
[33] J. Koch, Ph. D. Dissertation, University of Freiburg, **2004**.
[34] Access by photochemical transformation of an oxaziridine precursor to a derivative of a benzo-annulated pyrrolidinoazepin-3-one with a saturated C-6–C-7 bond and a methyl group at the C-11b position has been described: G. P. Johnson, B. A. Marples, *Tetrahedron Lett.* **1985**, *26*, 4115–4118.
[35] E. Lopez-Calle, J. Höfler, W. Eberbach, *Liebigs Ann.* **1996**, 1855–1866.
[36] D. St. C. Black, R. J. Strauch, *Aust. J. Chem.* **1988**, *41*, 183–193.
[37] CCDC-262102 (for **37**), CCDC-262103 (for **43**), and CCDC-262104 (for **47**) 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.
[38] W. M. Bright, H. A. Lloyd, J. V. Silverton, *J. Org. Chem.* **1976**, *41*, 2454–2458.
[39] The relatively low yield of **49** (37%) is partly due to the formation of two side-products, namely the primary alcohol of **28** (ca. 20%, isolated as a mixture with **49**), obtained by a Grignard reduction process, and a higher molecular compound (ca. 15%, not isolated), which probably comes from the reaction of **28** with the 1,4-bis-Grignard reagent of butane.
[40] H. A. Brandman, R. T. Conley, *J. Org. Chem.* **1973**, *38*, 2236–2238.

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