The Synthesis of Annulated Azepin-3-one Derivatives from 1,3,4-Pentatrienyl Nitrones by a Heterocyclization−Rearrangement Sequence

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Dedicated to Professor Horst Prinzbach on the occasion of his 70th birthday

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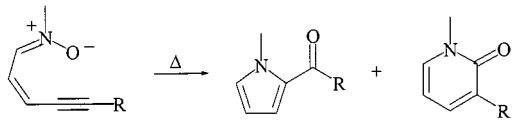
Treatment of various *o*-propargylaryl nitrones of type **6** with potassium hydroxide or sodium methoxide in methanol at room temperature provides 1,2-dihydro[*c*]benzazepin-3-ones **9**. The high product yields and the ease of the reactions under surprisingly mild conditions are particularly intriguing in view of the complex mechanistic pathway involved in the overall transformation. A mechanism based on a multistep rearrangement is proposed, involving conjugated allene nitrones of type **13** as precursors of a 1,7-dipolar cyclization process that is followed by further bond reorganizations, with cyclopropanones **16** as key intermediates. In agreement with the allene formation is the fact that the same transformation can be achieved with the triple bond isomers **12** and **37**, which contain terminal alkyl groups. The intermediacy of cyclopropanones **16** is supported by the competing formation of the isoindoles **20** as minor products. On treatment of dihydronaphtho-annulated nitrones **30** with base, formation of the azepinones **31** as the main products is also accompanied by that of the isomeric isoindoles **32**. Some selective C=O and C=C hydrogenation reactions, together with conversions into the thioketone **42** and the vinyl bromide **9p**, have been demonstrated with representative examples of **9**.

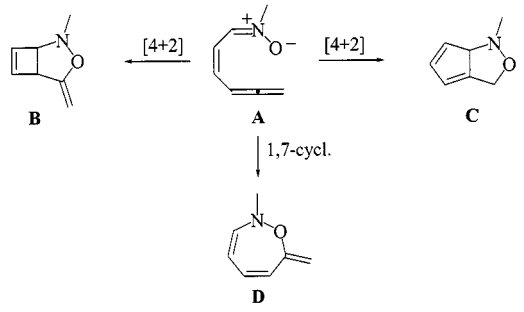
Introduction

Among the numerous heterocyclization methods, ring-forming processes of conjugated 1,3-dipoles are of particular importance for the construction of five-membered ring systems.[1] Over the past fifteen years, however, this methodology has successfully been extended to the synthesis of seven-membered heterocycles, using conjugated nitrile ylides, nitrile imines, diazo compounds, carbonyl ylides, azomethine ylides, azomethine imines, and nitrones.[2] Especially valuable applications have been achieved with dipoles of the latter type substituted by a butenynyl group.[3] The behaviour of such dipolar 8π-species differs from that of other systems, in which the primary ring products are unstable and undergo cleavage of the weak, newly created NO bond (a latent functionality or "Sollbruchstelle"),[4,5] followed by several rearrangement steps. These finally end up in the efficient formation of 2-acylpyrroles and/or α-pyridones, respectively (Scheme 1).[3,6]



Scheme 1

In the light of these results, the question arose of whether 1,3,4-pentatrienyl groups would similarly be suitable π-systems for 1,7-dipolar ring-closure reactions. Although the use of allene units in pericyclic reactions is amply documented in the forms of intermolecular [2+2],[7,8] Diels−Alder,[7,8,9] and 1,3-dipolar cycloaddition reactions,[10] there are still relatively few examples of their involvement in electrocyclizations.[11] Conjugated nitrones of type **A** may undergo three different cyclization processes: the two intramolecular [4+2] cycloaddition alternatives resulting in the formation of the bicyclic derivatives **B** and **C**, respectively, and the 1,7-ring-closure affording the *exo*-methyleneoxazepine **D** (Scheme 2). Here we report in detail the results obtained with various benzo-, furo-, and alkeno-annulated systems of type **A**.[12,13]



Scheme 2

Results and Discussion

For the construction of the cyclization precursors it is necessary to consider three functionalities: the nitrone, the

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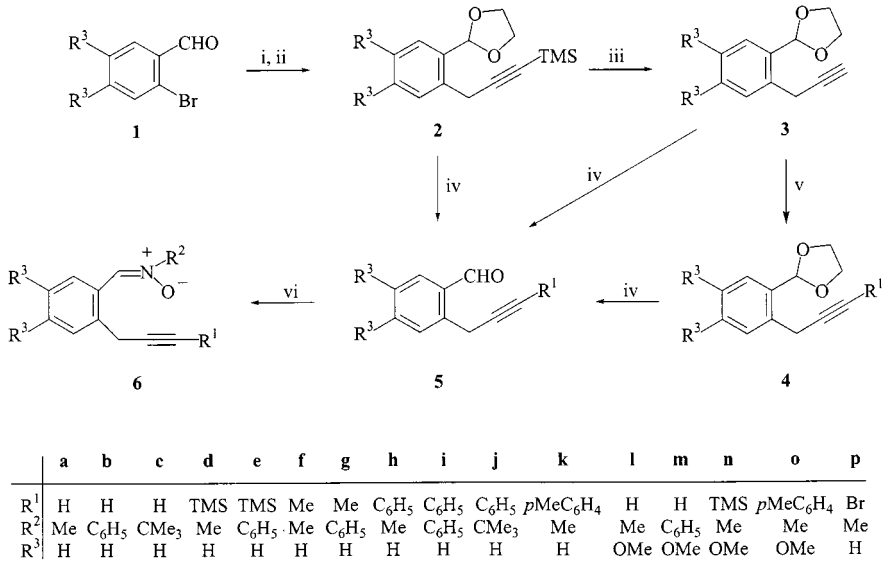
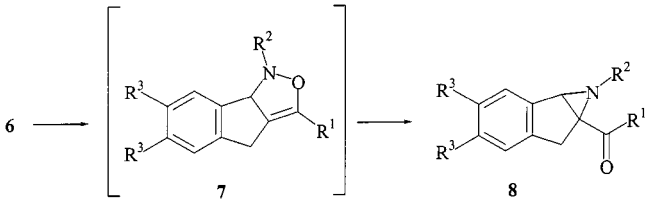


	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
R^1	H	H	H	TMS	TMS	Me	Me	C_6H_5	C_6H_5	C_6H_5	*p*MeC$_6$H$_4$	H	H	TMS	*p*MeC$_6$H$_4$	Br
R^2	Me	C_6H_5	CMe_3	Me	C_6H_5	Me	C_6H_5	Me	C_6H_5	CMe_3	Me	Me	C_6H_5	Me	Me	Me
R^3	H	H	H	H	H	H	H	H	H	H	H	OMe	OMe	OMe	OMe	H

Scheme 3. Reagents: (i) $HOCH_2CH_2OH$, PTSA; (ii) a) *n*BuLi, b) $MgBr_2$, c) $BrCH_2C{\equiv}CSiMe_3$; (iii) Bu_4NHSO_4, NH_4Cl, KF; (iv) PTSA, acetone/H_2O; (v) ArI, $PdCl_2(PPh_3)_2$, CuI, NEt_3 or a) *n*BuLi, b) CH_3I; (vi) $CH_3NHOH{\cdot}HCl$, NaOAc or PhNHOH, CH_2Cl_2

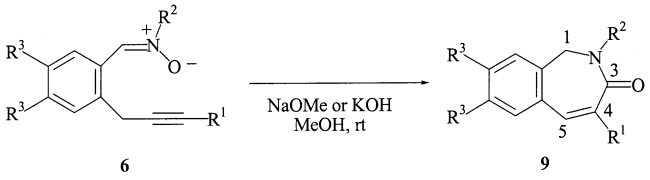
central (*Z*)-configured C=C bond and the allene moiety. Whereas an aldehyde group is most convenient for the dipole formation, and the required geometry of the double bond is given by its incorporation in a cyclic system, there are several procedures that might be appropriate for the generation of the allene part.[7,8,14] Relying on the relative high kinetic stability of the nitrone function and the need for only small equilibrium concentrations of the allene isomer, we decided to use the propargyl−allene isomerization in our investigations.[7,9c,15] The synthetic route to the benzo-annulated dipole systems **6a−o**, prepared as previously reported by us,[13] is shown in Scheme 3.

The nitrone compounds **6**, obtained from **1** in crystalline form with overall yields of 30−50%, were unambiguously characterized by their analytical data (see Exp. Sect.). In some cases minor by-products were detected in varying amounts (< 10%); these turned out to possess the epimino structure **8** (Scheme 4), formed by rearrangement of the isoxazolines **7**,[16] the direct intramolecular cycloadducts of **6**.



Scheme 4

With the correctly designed nitrones **6** in hand, the tautomerization of the propargyl moiety into the required allenes was studied next. To our great surprise it turned out that, on treatment with base even at ambient temperature, the reaction did not stop at the allene stage but continued directly to the final products. The experiments were typically carried out by stirring solutions of the nitrones **6a−o** in methanol in the presence of sodium methoxide or potassium hydroxide. In most cases total consumption of the starting material was reached after 0.5−5.0 h, although **6f** and **6g** required ca. 20 h for complete conversion. Careful aqueous workup followed by flash chromatography of the reaction mixtures in each case afforded a single monomeric product − namely **9** − mostly in good yield (see Scheme 5 and Table 1). As a result of partial hydrodesilylation during the reaction of **6d**, **6e**, and **6n**, additional quantities of **9a**, **9b**, and **9l** had to be added in those cases.



Scheme 5

Table 1. Yields of the benzazepinones **9a−o** from cycloisomerization of **6a−o**

	9[a]		**9**[a]
a	84[b]	**i**	40[b]
b	84[c]	**j**	77[b]
c	85[c]	**k**	64[c]
d	24[b][d]	**l**	77[b]
e	68[c][e]	**m**	93[c]
f	86[b][f]	**n**	25[c][g]
g	46[b] [f]	**o**	76[c]
h	75[c]		

[a] Reaction conditions: 0.2 M in MeOH, 0.5−1.0 equiv. of base, 0.5−5.0 h (**f**: 24 h; **g**: 20 h), room temperature. − [b] Base: NaOMe. − [c] Base: KOH. − [d] +29% of **9a**. − [e] + 26% of **9b**. − [f] Solvent: CH_2Cl_2. − [g] +43% of **9l**.

According to their elemental and MS analyses, the crystalline reaction products are isomers of the starting compounds. Their structural identification as 1,2-dihydro[*c*]-benzazepin-3-ones **9** was mainly based on spectroscopic information, especially from the ^1H and ^{13}C NMR data. As demonstrated in the case of **9a**, the strong IR absorption at 1650 cm^{-1} and the ^{13}C signal at δ = 166.3 indicate the presence of the lactam carbonyl group, while the ^1H NMR spectrum shows signals in the aromatic region (4 protons), the singlet of the *N*-methyl group (δ = 3.11), a singlet for the methylene protons at C-1 (δ = 4.24) and an AB pattern attributable to the olefinic hydrogen atoms at C-4 and C-5 (δ = 6.41 and 7.08, J = 12.2 Hz). The final proof of the simple, but mechanistically quite unexpected, benzazepinone structure was provided by crystallographic analysis of **9a** (Figure 1).[17]

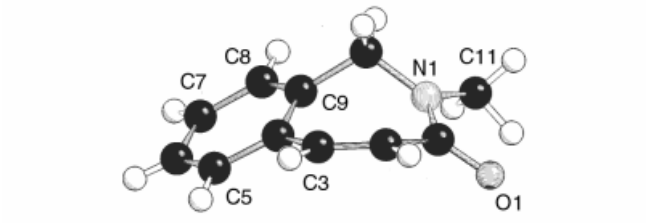


Figure 1. Crystal structure of the benzazepinone **9a** (SCHAKAL drawing, hydrogen atoms omitted; the numbering does not correspond with the correct nomenclature); selected bond lengths [Å] and torsion angels [°]: C1−O 1.234, C1−N 1.342, C1−C2 1.480, C2−C3 1.330, C3−C4 1.463, C4−C9 1.394, C9−C10 1.497, C10−N 1.462; C1−C2−C3−C4 −8.8, N−C1−C2−C3 41.2, C10−N−C1−C2 4.4, C9−C10−N−C1 −71.04, C4−C9−C10−N 67.21, C3−C4−C9−C10 −3.1, C9−C4−C3−C2 −30.7

The boat-shape geometry of the 7-membered ring aside, there are evidently no particular structural features concerning the bond lengths and angles. The nonplanarity of the system is also nicely reflected in the ^1H NMR spectrum of the *N*-*tert*-butyl derivative **9j**, in which the protons at C-1 appear as an AB system (δ = 4.24 and 4.53, J = 15.3 Hz), demonstrating the increasing influence of the bulky substituent on the ring-flipping process at ambient temperature. On the basis of dynamic NMR measurements, a coalescence temperature of 51 °C and a $\Delta G^{\ddagger}$ value of 15.6 kcal/mol (27 °C, $CDCl_3$) were determined for the ring-inversion process; the two relevant conformations of derivative **9a** are shown in Figure 2. In order to obtain a qualitative measure of the influence of the particular ring substituents, the coalescence temperatures of the derivatives **a**, **b**, **c**, and **h** were similarly determined. As can be seen in Table 2, groups at C-4 (R^1) and the N atom (R^2) both contribute to the decrease in the rate of the inversion process, although to a smaller extent for R^2.

From inspection of the structural differences associated with the transformation of the starting compounds into the final products, it is obvious that there is no simple connection between the nitrone and azepinone isomers. As far as the base-free behaviour of the nitrones **6** − namely the intramolecular cycloaddition to **7** and its subsequent rearrangement to **8** − is concerned, the originally anticipated tautomerization to the allenyl derivatives **13** is the most

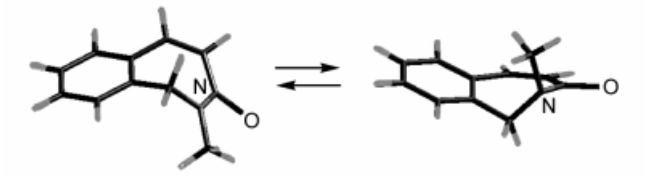
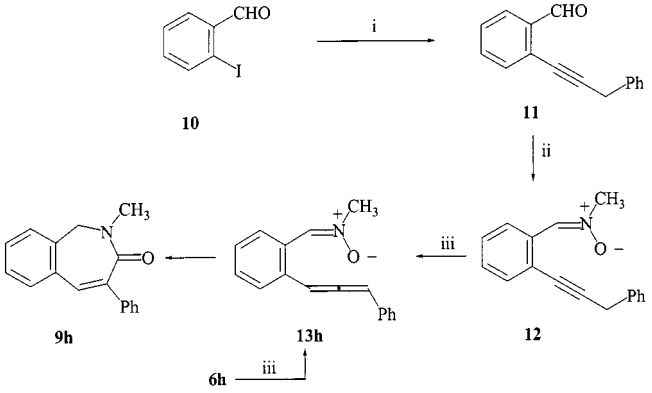


Figure 2. Minimum geometries of **9a** calculated with SPARTAN 1.5 (AM1 method)

Table 2. Coalescence temperatures for the ring-inversion of the dihydroazepinones **9a**, **9b**, **9c**, **9h**, and **9j**

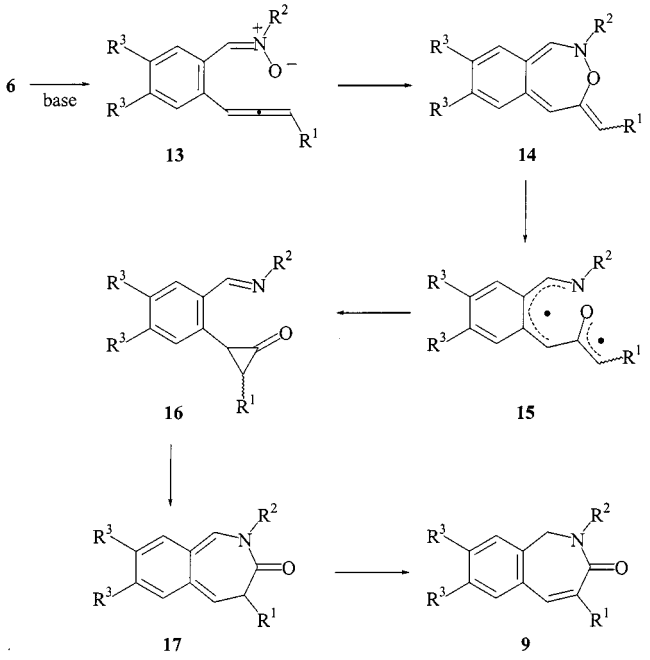
	R^1	R^2	T_c [°C]
9a	H	CH_3	−37
9b	H	C_6H_5	−25
9h	C_6H_5	CH_3	+10
9c	H	$C(CH_3)_3$	+34
9j	C_6H_5	$C(CH_3)_3$	+51

plausible initiating reaction (see Scheme 7). Further evidence for the intermediacy of an allene species was obtained by treatment of the conjugated *o*-alkynylaryl nitrone **12**, prepared from **10** as shown in Scheme 6, with base. Under the usual conditions, **12** was transformed into **9h** (81% yield after chromatography and crystallization), the already known reaction product of **6h** (see above); the same allene tautomer **13h** is undoubtedly involved in both cases.

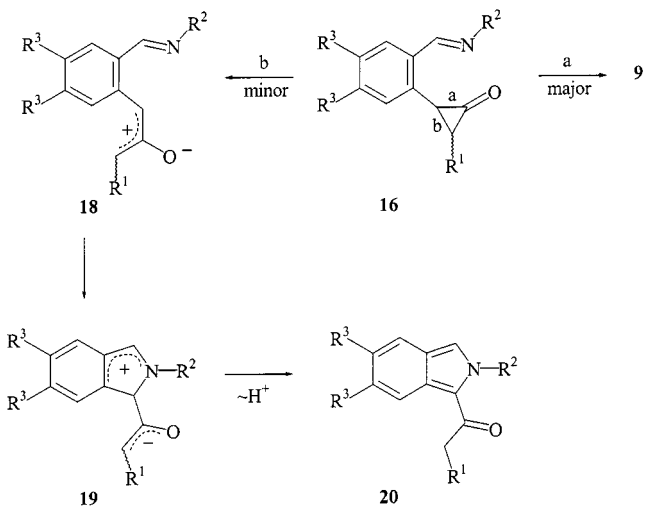


Scheme 6. Reagents: (i) $HC{\equiv}CCH_2Ph$, $PdCl_2(PPh_3)_2$, CuI, NEt_3, C_6H_6; (ii) $CH_3NHOH{\cdot}HCl$, NaOAc, CH_2Cl_2; (iii) NaOMe, MeOH

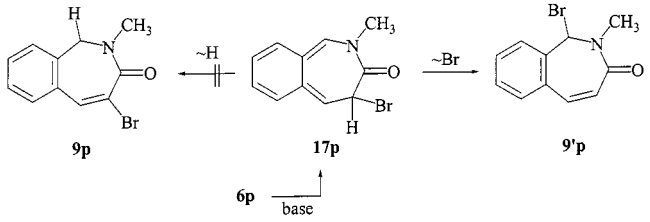
A particularly striking feature of the nitrone allene−benzazepinone transformation concerns the exchange of the terminal and central positions of the allene group of **13**, in which the terminal carbon atom connected to R^1 ends up at C-4, now flanked by both former allene carbon atoms. A possible but still tentative mechanism for this transformation is outlined in Scheme 7 and includes the following steps: (i) 8π-cyclization (**13** → **14**),[2,3,5,18] (ii) cleavage of the weak NO bond (**14** → **15**),[4] (iii) diradical combination (**15** → **16**), (iv) one- or two-step cyclization of the azadienylcyclopropanone **16** to **17**, and finally (v) a 1,5-H-shift affording the final products **9**.



Scheme 7



Scheme 8



Scheme 9

Although there is precedent for at least the first two steps of this sequence, and also the last one, the involvement of the cyclopropanone **16** is especially intriguing.[19] The formation of isoindoles **20** as minor side products in a few cases lends further support to the occurrence of intermediates **16** (Scheme 8). Because of the low concentrations and the chromatographic lability of **20**, evidence for the latter is based only on the ^{1}H NMR and IR spectra. The arylmethyl derivative **20o**, however, could be isolated in 12% yield and used for a more in-depth spectroscopic and MS/HRMS analysis. The presence of the carbonyl group is confirmed by the IR absorption at 1705 cm^{-1} and the ^{13}C singlet at δ = 186.1, while important ^{1}H resonances are observed at δ = 4.26 (s, 2-H) and 6.89 (s, 3′-H). Together with the other data, these values are in full agreement with the isoindole structure **20o** (R^1 = *p*-tolyl, R^2 = Me, R^3 = OMe).[20] Further confirmation for this structural assignment was obtained from investigations with some nitrone precursors that were not benzo-annulated (such as structures **32a** and **32b**, see below) and from comparison with structurally related compounds obtained by a different route.[6]

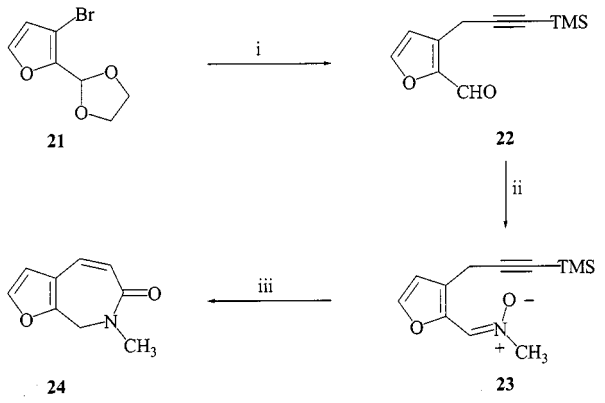
The formation of **20** from **16** can easily be explained by C−C (instead of C−CO) cleavage of the cyclopropanone ring, affording the oxyallyl derivative **18**, and subsequent nucleophilic ring-closure to give the bicyclic dipole **19**, followed by a proton shift (Scheme 8).

Concerning the concluding 1,5-H-shift producing **9a**−**o**, preliminary results with the terminal bromide **6p** are interesting because the final product **9′p** (Scheme 9) contains the Br substituent at C-1 and not at C-4; that is, 1,5-Br-migration (**17p** → **9′p**) is favoured over an H-shift (**17p** → **9p**).[21] Whereas a few examples have been reported for 1,5-Cl-migrations,[22] the involvement of Br, to the best of our knowledge, is otherwise still unknown.

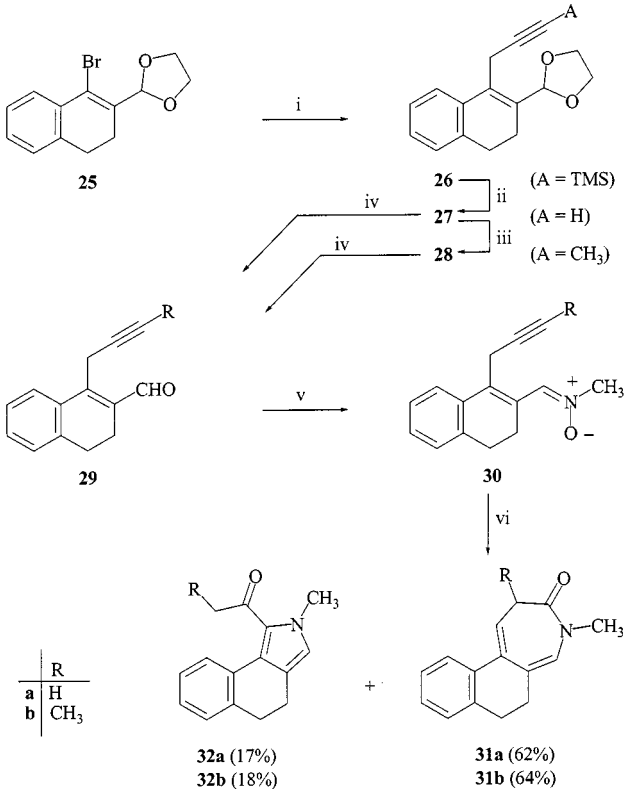
In order to evaluate the structural requirements for the transformation of type **6** → **9**, an example in which the annulated benzo ring was replaced by a furo ring was investigated. The synthesis of **23** as a representative compound of this type was accomplished from the protected 3-bromofurfural **21**, according to the route outlined in Scheme 10. Under basic conditions (NaOMe, MeOH, room temperature), a clean reaction again took place to afford the furoazepinone **24** in almost quantitative yield (91% after crystallization). The straightforward formation of **24** is of special importance because, to the best of our knowledge, only derivatives with the carbonyl group next to the furan ring have so far been described for this heterobicyclic system.

As an additional type of pentenynyl nitrones, the dihydronaphtho derivatives **30a**/**30b** were studied next. The synthetic route followed the same approach as described for the preparation of **6a**−**o** (see Scheme 11): (a) Grignard coupling (**25** → **26**, 88%); (b) hydrodesilylation (**26** → **27**, 98%), (c) deprotonation−methylation−deprotection (**27** → **28** → **29b**, 79%, 84%), (d) deprotection (**27** → **29a**, 99%), (e) nitrone formation (**29a**,**b** → **30a**,**b**, both 62%).

To examine the chemical reactivity of the nitrone systems, methanolic solutions were treated with potassium hydroxide (**30a**) or sodium methoxide (**30b**) at ambient temperature. After workup, product analysis showed that the base-in-



Scheme 10. Reagents: (i) a) *n*BuLi, b) $MgBr_2$, c) $BrCH_2C{\equiv}CSiMe_3$, d) PTSA, acetone/H_2O; (ii) $CH_3NHOH{\cdot}HCl$, NaOAc, CH_2Cl_2; (iii) NaOAc, MeOH



Scheme 11. Reagents: (i) a) *n*BuLi, b) $MgBr_2$, c) $BrCH_2C{\equiv}CSiMe_3$; (ii) K_2CO_3, MeOH; (iii) a) *n*BuLi, b) CH_3I; (iv) PTSA, acetone/H_2O; (v) $CH_3NHOH{\cdot}HCl$, CH_2Cl_2; (vi) NaOMe or KOH, MeOH

duced reactions had both resulted in the formation of azepinone derivatives **31a** or **31b** as major products (62%, 64%); however, the isoindole-type by-products **32a** or **32b** could be isolated in much larger quantities (ca. 20% yield after purification) than in the case of the nitrones **6** (see above). Clear structural characterization could be achieved for both systems on the basis of their IR, $^1H/^{13}C$ NMR and MS/HRMS data.

Surprisingly, the arrangement of the C=C bonds in the dihydroazepinones **31a** and **31b** ("dienamine"-type) differs from that in the analogues **9a–o** ("dienone"-type). Obviously the concluding 1,5-H shift, favoured by the rearomatization process for **17** → **9** (see Scheme 7), does not take place for **31a** and **31b** – the fact that this structure contains a seemingly unfavourable bis(*exo*-methylene) arrangement notwithstanding.

In order to rule out any doubt in the structural assignment, a crystallographic analysis of **31a** was carried out (Figure 3).[17] Despite the difference in the arrangement of the C=C bonds, the geometries of the structures of **31a** and **9a** were quite similar. Again, there are no unusual bond lengths or angles, and the torsions in the heterocyclic components are comparable in both cases (i.e., −30.7° in **9a** and −35.2° in **31a**).

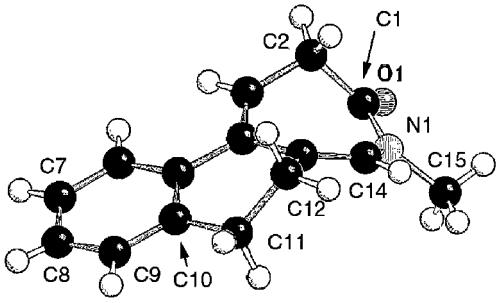
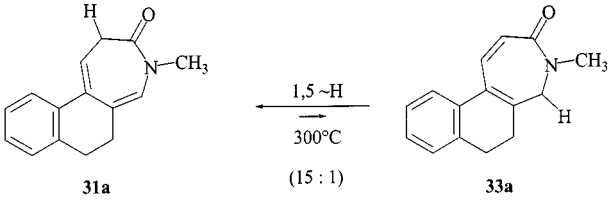


Figure 3. SCHAKAL plot of the crystal structure of the dihydronaphthazepinone **31a** (hydrogen atoms omitted; the numbering does not correspond with the correct nomenclature); selected bond lengths [Å] and torsion angels [°]: C1–O 1.228, C1–N 1.355, C2–C1 1.507, C2–C3 1.497, C3–C4 1.345, C4–C13 1.464, C13–C14 1.344, C14–N 1.406; N–C14–C13–C4 −4.1, C1–N–C14–C13 39.2, C2–C1–N–C14 5.5, C3–C2–C1–N −70.2, C4–C3–C2–C1 68.9, C13–C4–C3–C2 −1.4, C3–C4–C13–C14 −35.2

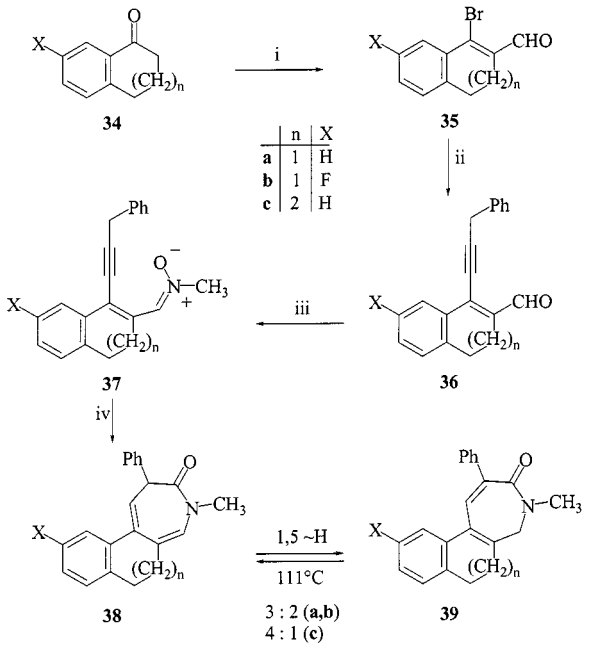
Separate experiments showed that **31a** is indeed the thermodynamically more stable bond isomer. Only when it was heated to ca. 300 °C could the formation of its isomer **33a** in very small amounts be detected by ^1H NMR spectroscopy (Scheme 12). The equilibrium concentration of **31a**/**33a** was determined as approximately 15:1. On the other hand, there was no evidence at all for the 1,5-H-migration process after **31b** had been heated under the same conditions.



Scheme 12

Introduction of a phenyl group at the 4-position of the tricyclic system should be expected to produce a change in the equilibrium in favour of the endocyclic tautomer. For the synthesis of appropriate precursors, the α-tetralones **34a** and **34b** (n = 1) and the benzosuberone **34c** (n = 2) were used as starting materials. Transformation into **37a**, **37b**, and **37c** was accomplished by a straightforward sequence of (i) Vilsmeier bromoformylation, (ii) Sonogashira coup-

ling, and (iii) nitrone formation (Scheme 13). In analogy to compound **12**, but in contrast to all the other nitrone system used in this work, **37a**, **37b**, and **37c** contain conjugated propargyl groups, which means that the reactive allene unit is formed by formal shift of an "outer" proton.

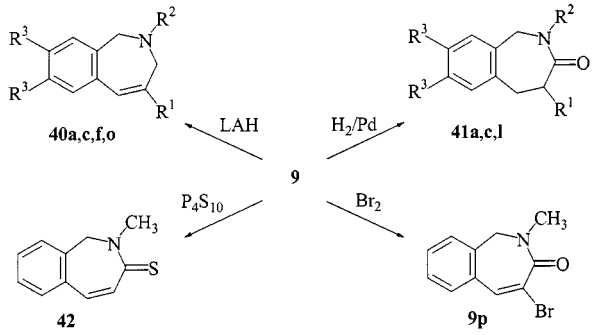


Scheme 13. Reagents: (i) PBr_3, DMF, $CHCl_3$; (ii) $HC{\equiv}CCH_2Ph$, $PdCl_2(PPh_3)_2$, CuI, K_2CO_3 and/or NEt_3, C_6H_6; (iii) $CH_3NHOH{\cdot}HCl$, NaOAc, CH_2Cl_2; (iv) NaOMe or KOH, MeOH

After treatment of **37a**, **37b**, and **37c** with base (NaOMe or KOH in MeOH) at 20 °C, single monomeric products were detected in each case. These were the *exo*-methylene-type annulated azepinones **38a** (78%), **38b** (90%), and **38c** (67%; all yields after chromatography and crystallization), respectively. On their being heated in boiling toluene, however, tautomerization into the endocyclic compounds **39** took place, reaching equilibrium ratios of 3:2 (**a**, **b**) and 4:1 (**c**), although still in favour of the former isomer **38**.

Reactivity of Some Dihydrobenzazepin-3-ones

The kinetic stability, both thermal and chemical, of the heterocycles is unusually high. For instance, no cleavage of the amide bond could be detected even under forced acidic or basic conditions. The chemical reactivity of the benzazepinone system was investigated with several representative examples. Reduction of either the C=C or the C=O groups of **9a** and **9c**, for instance, can be achieved chemoselectively, depending on the reducing agent. Whereas catalytic hydrogenation afforded the tetrahydrobenzazepinones **41**, treatment with lithium aluminium hydride resulted in the formation of the respective dihydroazepines **40** (Scheme 14). A further group transformation was effected by treatment of **9a** with P_4S_{10},[23] which afforded the thioketone **42**. Although the use of Lawesson's reagent has also been described for similar applications,[24] this was much less efficient in our example. In the case of the trimethylsilyl derivative **9d**, bromodesilylation was achieved by treatment with Br_2, producing the vinyl bromide **9p** (79%).[25]



Scheme 14

Conclusion

Despite the structural simplicity of the 1,2-dihydro[*c*]-benzazepin-3-one system **9**, which has been found as a substructure in several naturally occurring compounds,[26] no general synthetic procedures for it are available. Only a few syntheses have so far been described, these mostly having been elaborated for the preparation of further annulated compounds, which frequently possess biological activity.[27] The parent compound of **9** (**9a**, R^2 = H) has been synthesized in modest yield by irradiation of β-azidonaphthalene in methanol and subsequent hydrolysis of the iminoether.[28] The novel reaction principle described in this paper is a very useful and broadly applicable route to this class of compounds, and can easily be performed under extraordinarily mild conditions, with respect both to the base and to the reaction temperature; in many cases the reaction takes place even at 0 °C. The ease of the rearrangement and the high product yields are particularly surprising in view of the complexity of the overall reaction sequence. It should be mentioned that the transformation is quite general and not restricted to the preparation of annulated dihydroazepinones, being similarly applicable for monocyclic systems.[29]

Experimental Section

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

General Procedure for the Cleavage of 1,3-Dioxolanes: A 0.15 M solution of the dioxolane in a 1.2:1 mixture of acetone and water was treated with 5 mol % of PTSA and refluxed until completion of the reaction (TLC, 1−6 h). After this had cooled to room temp., satd. aqueous $NaHCO_3$ was added and the solution was extracted with diethyl ether. The combined organic phases were washed with

brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by flash chromatography (SiO_2).

General Procedure for the Preparation of *N*-Methyl-Substituted Nitrones: Sodium acetate (3 equiv.) was added to a 0.25 M suspension of *N*-methylhydroxylamine hydrochloride (1.3 equiv.) in dry CH_2Cl_2, followed after stirring for 15 min by the corresponding aldehyde (1 equiv.). The reaction mixture was stirred at room temp. until completion of the reaction (TLC), hydrolysed with water and extracted 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 (SiO_2).

General Procedure for the Preparation of *N*-Phenyl-Substituted Nitrones: A 0.2 M solution of the corresponding aldehyde in dry CH_2Cl_2 was treated with *N*-phenylhydroxylamine (1.1 equiv.) and stirred in the dark for 6−45 h. The mixture was treated with water and extracted 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 (SiO_2).

General Procedure for the Base-Catalysed Transformations of the Nitrones: A 0.2 M solution of the corresponding nitrone in dry methanol was treated with base (0.5 equiv.) and stirred at room temp. until completion of the reaction (TLC). The mixture was hydrolysed with water and extracted with CH_2Cl_2. The combined organic phases were washed with satd. aqueous NH_4Cl and with brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by flash chromatography (SiO_2).

{3-[2′-(1′′,3′′-Dioxolan-2′′-yl)-4′,5′-dimethoxyphenyl]prop-1-ynyl}-trimethylsilane (2n): A solution of *n*-butyllithium in *n*-hexane (2.4 M, 6.34 mL, 16.6 mmol) was added dropwise to a solution of 2-(2′-bromo-4′,5′-dimethoxyphenyl)-1,3-dioxolane[30] (4.00 g, 13.8 mmol) in dry THF (120 mL) at −78 °C under N_2. After this had stirred for 2 h at −78 °C, a solution of $MgBr_2$ in diethyl ether (10 mL), freshly prepared from Mg (480 mg, 19.8 mmol) and dibromoethane (2.86 g, 15.2 mmol),[31] was added slowly and the reaction mixture was allowed to warm to room temp. After 2 h, 1-bromo-3-(trimethylsilyl)prop-2-yne[32] (3.17 g, 16.6 mmol) was added and the solution was refluxed for 2 h. After cooling to room temp., the solution was treated with a 1:1 mixture of satd. NH_4Cl and water and extracted with diethyl ether (3 × 60 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (SiO_2; cyclohexane/ethyl acetate, 20:1, 10:1) afforded **2n** (2.85 g, 64%) as pale yellow oil, which crystallized from diethyl ether. − M.p. 60−62 °C (diethyl ether). − IR (CCl_4): $\tilde{\nu}$ = 2960, 2890, 2175 (C≡C), 1520, 1465, 1400, 1295, 1270, 1200, 1120, 1005 cm^{-1}. − ^1H NMR (250 MHz): δ = 0.19 (s, 9 H, $SiMe_3$), 3.57 (s, 2 H, 3-H), 3.70 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 3.89 (m_c, 4 H, 4′′-H, 5′′-H), 5.89 (s, 1 H, 2′-H), 7.08 (s, 1 H, Ar-H), 7.16 (s, 1 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 0.1 ($SiMe_3$), 22.6 (C-3), 55.8 (OCH_3), 56.0 (OCH_3), 87.6 (C-2), 101.6 (C-2′′), 104.5 (C-1), 109.7 (C-3′/6′), 112.3 (C-3′/6′), 126.7 (C-1′/2′), 127.5 (C-1′/2′), 147.5 (C-4′/5′), 149.4 (C-4′/5′). − MS (70 eV; EI): *m*/*z* (%) = 320 (16) [M^+], 261 (24), 247 (13) [$M - Si(CH_3)_3]^+$, 233 (26), 222 (26), 73 (100) [$Si(CH_3)_3^+$]. − $C_{17}H_{24}O_4Si$ (320.46): calcd. C 63.72, H 7.55; found C 63.41, H 7.51.

2-[4′,5′-Dimethoxy-2′-(prop-2′′-ynyl)phenyl]-1,3-dioxolane (3l): A solution of **2n** (14.4 g, 44.9 mmol) in CH_2Cl_2 (180 mL) was treated with Bu_4NHSO_4 (7.64 g, 22.5 mmol), KF (13.1 g, 22.5 mmol), and NH_4Cl (14.4 g, 270 mmol), and the resulting mixture was then stirred for 18 h at room temp. Water (80 mL) was added and the solution was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (SiO_2, cyclohexane/ethyl acetate 60:1) afforded **3l** (8.05 g, 72%) as pale yellow crystals. − M.p. 67−70 °C (diethyl ether). − IR (CCl_4): $\tilde{\nu}$ = 3315 (≡C−H), 2995, 2955, 2880, 2115 (C≡C), 1610, 1515, 1465, 1300, 1275, 1225, 1120, 1075, 1010 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.20 (t, $^4J_{3'',1''}$ = 2.7 Hz, 1 H, 3′′-H), 3.71 (d, $^4J_{1'',3''}$ = 2.7 Hz, 2 H, 1′′-H), 3.89 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.09 (m_c, 4 H, 4-H, 5-H), 5.92 (s, 1 H, 2-H), 7.09 (s, 1 H, Ar-H), 7.10 (s, 1 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 21.3 (C-1′′), 56.1 (OCH_3), 56.2 (OCH_3), 65.2 (C-4, C-5), 70.7 (C-3′′), 82.0 (C-2′′), 101.6 (C-2), 109.9 (C-3′/6′), 112.5 (C-3′/6′), 126.8 (C-1′/2′), 127.3 (C-1′/2′), 147.7 (C-4′/5′), 149−6 (C-4′/5′). − MS (70 eV; EI): *m*/*z* (%) = 248 (83) [M^+], 204 (100), 188 (62), 176 (68), 161 (60), 73 (74). − $C_{14}H_{16}O_4$ (248.28): calcd. C 67.52, H 6.50; found C 67.52, H 6.39.

2-[2′-(But-2′′-ynyl)phenyl]-1,3-dioxolane (4f): A solution of *n*-butyllithium in *n*-hexane (2.4 M, 9.8 mL, 23.5 mmol) was added dropwise at −78 °C under N_2 to a solution of **3a**[33] (4.00 g, 21.4 mmol) in 100 mL of dry THF. The mixture was stirred for 2 h and methyl iodide (3.33 g, 23.5 mmol) was added at −78 °C. The solution was allowed to warm to room temp. and stirred for a further 70 h. A 1:1 mixture of satd. NH_4Cl and water was added and the reaction mixture was extracted with diethyl ether (3 × 40 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (SiO_2; cyclohexane/ethyl acetate, 50:1) afforded **4f** (3.14 g, 73%) as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 2950, 2920, 2885, 1480, 1450, 1390, 1220, 1110, 1075 cm^{-1}. − ^1H NMR (250 MHz): δ = 1.85 (t, $^5J_{4'',1''}$ = 2.6 Hz, 3 H, 4′′-H), 3.71 (q, $^5J_{1'',4''}$ = 2.6 Hz, 2 H, 1′′-H), 4.08 (m_c, 4 H, 4-H, 5-H), 6.02 (s, 1 H, 2-H), 7.21−7.41 (m, 2 H, Ar-H), 7.55 (m_c, 2 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 3.6 (C-4′′), 22.1 (C-1′′), 65.2 (C-4, C-5), 76.4 (C-2′′/3′′), 78.3 (C-2′′/3′′), 101.9 (C-2), 126.1 (Ar-C), 126.6 (Ar-C), 129.1 (Ar-C), 129.3 (Ar-C), 134.8 (Ar-C_q), 136.1 (Ar-C_q). − MS (70 eV; EI): *m*/*z* (%) = 201 (12) [$M^+ - 1$], 187 (44), 141 (47), 129 (98), 105 (93). − HRMS ($C_{13}H_{14}O_2$) [$M^+ - 1$]: calcd. 201.0916; found 201.0917.

2-[2′-(3′′-Phenylprop-2′′-ynyl)phenyl]-1,3-dioxolane (4n): Freshly distilled iodobenzene (0.36 mL, 3.20 mmol), $PdCl_2(PPh_3)_2$ (94 mg, 0.13 mmol) and CuI (ca. 10 mg) were added to a solution of **3a**[33] (500 mg, 2.67 mmol) in dry and degassed (Ar) triethylamine (10 mL). After stirring under argon for 5 h at room temp., the mixture was filtered and the solution was concentrated in vacuo. The brown residue was purified by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 40:1) to afford **4n** (580 mg, 82%) as a yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 3065, 2950, 2885, 1595, 1490, 1455, 1390, 1220, 1115, 1075, 1030 cm^{-1}. − ^1H NMR (250 MHz): δ = 4.00 (s, 2 H, 1′′-H), 4.01−4.20 (m, 4 H, 4-H, 5-H), 6.10 (s, 1 H, 2-H), 7.22−7.50 (m, 7 H, Ar-H), 7.52−7.70 (m, 2 H, Ar-H). − ^{13}C NMR (125 MHz): δ = 22.8 (C-1′′), 65.3 (C-4, C-5), 83.2 (C-2′′/3′′), 87.3 (C-2′′/3′′), 102.1 (C-2), 123.4 (Ar-C_q), 126.4 (Ar-C), 126.8 (Ar-C), 127.9 (Ar-C), 128.3 (Ar-C), 129.2 (Ar-C), 129.5 (Ar-C), 131.7 (Ar-C), 134.9 (Ar-C_q), 134.9 (Ar-C_q). − MS (70 eV; EI): *m*/*z* (%) = 264 (12) [M^+], 203 (47), 192 (100) [$PhCH_2C{\equiv}CPh^+$], 105 (92). − HRMS ($C_{18}H_{16}O_2$): calcd. 264.1150; found 264.1151.

2-{2′-[3′′-(4′′′-Methylphenyl)prop-2′′-ynyl]phenyl}-1,3-dioxolane (4k): A solution of **3a**[33] (1.00 g, 5.34 mmol) and 4-iodotoluene (1.40 g, 6.41 mmol) in dry Et_3N (20 mL) was degassed (Ar) and treated with $PdCl_2(PPh_3)_2$ (187 mg, 0.27 mmol) and CuI (ca. 15 mg). After stirring under argon for 4 h at room temp., the reaction mixture was filtered and the solution was concentrated in vacuo. Purification of the brown residue by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 40:1) afforded **4k** (1.00 g, 67%) as

a yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 3030, 2950, 2885, 1510, 1455, 1395, 1220, 1115, 1075 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.34 (s, 3 H, Ar-CH_3), 3.99 (s, 2 H, 1′′-H), 4.10 (m_c, 4 H, 4-H, 5-H), 6.06 (s, 1 H, 2-H), 7.10 (m_c, 2 H, Ar-H), 7.27−7.41 (m, 4 H, Ar-H), 7.56 (m_c, 1 H, Ar-H), 7.64 (m_c, 1 H, Ar-H). − MS (70 eV; EI): *m*/*z* (%) = 278 (1) [M^+], 149 (36), 115 (90), 105 (68), 91 (46) [CH_2Ph^+], 77 (52). − HRMS ($C_{19}H_{18}O_2$): calcd. 278.1307; found 278.1308.

2-{4′,5′-Dimethoxy-2′-[3′′-(4′′′-methylphenyl)prop-2′′-ynyl]phenyl}-1,3-dioxolane (4o): A solution of **3l** (2.59 g, 7.65 mmol) in benzene (20 mL) was treated with dry Et_3N and degassed (Ar). 4-Iodotoluene (2.00 g, 9.18 mmol), $PdCl_2(PPh_3)_2$ (268 mg, 0.38 mmol), and CuI (ca. 10 mg) were added, and the solution was stirred under Ar for 50 h at room temp. The reaction mixture was filtered and the solution was concentrated in vacuo. Purification of the brown residue by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 5:1, 2:1) afforded **4o** (1.62 g, 63%) as pale yellow crystals, m.p. 99−100 °C (diethyl ether). − IR (CCl_4): $\tilde{\nu}$ = 2955, 2880, 1510, 1465, 1400, 1275, 1205, 1180, 1120, 1070, 1010 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.34 (s, 3 H, CH_3), 3.90 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.11 (m_c, 4 H, 4-H, 5-H), 5.99 (s, 1 H, 2-H), 7.10 (m_c, 2 H, Ar-H), 7.12 (s, 1 H, 3′/6′-H), 7.16 (s, 1 H, 3′/6′-H), 7.33 (m_c, 2 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 21.5 (CH_3), 22.3 (C-1′′), 56.0 (OCH_3), 56.1 (OCH_3), 65.2 (C-4, C-5), 83.1 (C-2′′/3′′), 86.8 (C-2′′/3′′), 101.6 (C-2), 109.7 (Ar-C), 112.6 (Ar-C), 120.7 (Ar-C_q), 126.9 (Ar-C_q), 128.1 (Ar-C_q), 129.1 (Ar-C), 131.5 (Ar-C), 137.9 (Ar-C_q), 147.6 (Ar-C_q), 149.5 (Ar-C_q). − MS (70 eV; EI): *m*/*z* (%) = 338 (1) [M^+], 136 (71), 119 (64), 92 (20), 91 (100). − HRMS ($C_{21}H_{22}O_4$): calcd. 338.1518; found 338.1518.

2-(Prop-2′-ynyl)benzaldehyde (5a): Treatment of **3a**[33] (4.00 g, 21.4 mmol, 6 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 40:1), gave **5a** (2.87 g, 93%) as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 3315 (≡C−H), 2825, 2730, 2120 (C≡C), 1700 (C=O), 1600, 1575, 1490, 1450, 1325, 1295, 1195 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.27 (t, $^4J_{3',1'}$ = 2.7 Hz, 1 H, 3′-H), 4.10 (d, $^4J_{1',3'}$ = 2.7 Hz, 2 H, 1′-H), 7.49 (m_c, 1 H, Ar-H), 7.60 (m_c, 1 H, Ar-H), 7.65 (m_c, 1 H, Ar-H), 7.72 (m_c, 1 H, Ar-H), 10.21 (s, 1 H, CHO). − ^{13}C NMR (125 MHz): δ = 22.6 (C-1′), 71.8 (C-3′), 81.2 (C-2′), 127.4 (Ar-C), 129.9 (Ar-C), 133.2 (Ar-C_q), 133.9 (Ar-C), 134.0 (Ar-C), 137.0 (Ar-C_q), 192.8 (CHO). − MS (70 eV; EI): *m*/*z* (%) = 144 (39) [M^+], 128 (9), 116 (48), 115 (100) [M − CHO]$^+$. − HRMS ($C_{10}H_8O$): calcd. 144.0575; found 144.0576.

2-[3′-(Trimethylsilyl)prop-2′-ynyl]benzaldehyde (5d): Treatment of **2d**[33] (6.00 g, 23.0 mmol, 4 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 20:1), gave **5d** (4.75 g, 95%) as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 2960, 2735, 2180 (C≡C), 1700 (C=O), 1600, 1575, 1490, 1455, 1400, 1320, 1290, 1200, 1030 cm^{-1}. − ^1H NMR (250 MHz): δ = 0.17 [s, 9 H, $Si(CH_3)_3$], 4.09 (s, 2 H, 1′-H), 7.43 (m_c, 1 H, 4/5-H), 7.57 (m_c, 1 H, 4/5-H), 7.71 (m_c, 1 H, 3/6-H), 7.79 (m_c, 1 H, 3/6-H), 10.37 (s, 1 H, CHO). − ^{13}C NMR (100 MHz): δ = 0.1 [$Si(CH_3)_3$], 24.0 (C-1′), 88.6 (C-3′), 103.5 (C-2′), 127.3 (Ar-C), 129.9 (Ar-C), 133.3 (Ar-C_q), 133.4 (Ar-C), 134.1 (Ar-C), 138.5 (Ar-C_q), 192.7 (C=O). − MS (70 eV; EI): *m*/*z* (%) = 216 (42) [M^+], 201 (86), 186 (16), 141 (21), 73 (100) [$Si(CH_3)_3^+$]. − HRMS ($C_{13}H_{16}OSi$): calcd. 216.0970; found 216.0969.

2-(But-2′-ynyl)benzaldehyde (5f): Treatment of **4f** (2.00 g, 9.94 mmol, 2 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 50:1), gave **5f** (1.42 g, 91%) as a colourless oil that rapidly turned yellow. − IR (CCl_4): $\tilde{\nu}$ = 2920, 2855, 2735, 1700 (C=O), 1600, 1575, 1450, 1325, 1295, 1195 cm^{-1}. − ^1H NMR (250 MHz): δ = 1.89 (t, $^5J_{4',1'}$ = 2.6 Hz, 3 H, 4′-H), 4.00 (q, $^5J_{1',4'}$ = 2.6 Hz, 2 H, 1′-H), 7.44 (m_c, 1 H, Ar-H), 7.58 (m_c, 1 H, Ar-H), 7.69 (m_c 1 H, Ar-H), 7.81 (m_c, 1 H, Ar-H), 10.26 (s, 1 H, CHO). − ^{13}C NMR (100 MHz): δ = 3.6 (C-4′), 22.9 (C-1′), 76.1 (C-2′/3′), 79.3 (C-2′/3′), 127.2 (Ar-C), 130.0 (Ar-C), 132.9 (Ar-C), 133.3 (Ar-C_q), 134.0 (Ar-C), 139.8 (Ar-C_q), 192.7 (CHO). − MS (70 eV; EI): *m*/*z* (%) = 158 (100) [M^+], 129 (82) [M − CHO]$^+$, 128 (76), 115 (74). − HRMS ($C_{11}H_{10}O$): calcd. 158.0732; found 158.0731.

2-(3′-Phenylprop-2′-ynyl)benzaldehyde (5h): Treatment of **4h** (560 mg, 2.12 mmol, 4 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 40:1), gave **5h** (339 mg, 72%) as a dark yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 3060, 2815, 2730, 1700 (C=O), 1600, 1575, 1490, 1440, 1325, 1285, 1215, 1145, 1075 cm^{-1}. − ^1H NMR (250 MHz): δ = 4.20 (s, 2 H, 1′-H), 7.22−7.35 (m, 3 H, Ar-H), 7.40−7.51 (m, 3 H, Ar-H), 7.61 (m_c, 1 H, Ar-H), 7.82 (m_c, 2 H, Ar-H), 10.29 (s, 1 H, CHO). − ^{13}C NMR (125 MHz): δ = 23.6 (C-1′), 84.0 (C-2′/3′), 86.8 (C-2′/3′), 123.5 (Ar-C_q), 127.4 (Ar-C), 128.0 (Ar-C), 128.3 (Ar-C), 130.0 (Ar-C), 131.7 (Ar-C), 133.4 (Ar-C_q), 133.6 (Ar-C), 134.1 (Ar-C), 138.8 (Ar-C_q), 192.8 (CHO). − MS (70 eV; EI): *m*/*z* (%) = 220 (81) [M^+], 191 (100) [M − CHO]$^+$, 189 (67), 165 (59), 118 (69). − HRMS ($C_{16}H_{12}O$): calcd. 220.0889; found 220.0888.

2-[3′-(4′′-Methylphenyl)prop-2′-ynyl]benzaldehyde (5k): Treatment of **4k** (887 mg, 3.19 mmol, 2 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 40:1), gave **5k** (618 mg, 83%) as a yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 3025, 2920, 2825, 2735, 1700 (C=O), 1600, 1510, 1325, 1195 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.34 (s, 3 H, CH_3), 4.28 (s, 2 H, 1′-H), 7.11 (m_c, 2 H, Ar-H), 7.34 (m_c, 2 H, Ar-H), 7.46 (m_c, 1 H, Ar-H), 7.60 (m_c, 1 H, Ar-H), 7.82 (m_c, 2 H, Ar-H), 10.27 (s, 1 H, CHO). − ^{13}C NMR (100 MHz): δ = 21.5 (CH_3), 23.6 (C-1′), 84.1 (C-2′/3′), 86.0 (C-2′/3′), 120.4 (Ar-C_q), 127.3 (Ar-C), 129.1 (Ar-C), 130.0 (Ar-C), 131.6 (Ar-C), 133.4 (Ar-C_q), 133.5 (Ar-C), 134.1 (Ar-C), 138.1 (Ar-C_q), 139.0 (Ar-C_q), 192.7 (CHO). − MS (70 eV; EI): *m*/*z* (%) = 234 (83) [M^+], 219 (48), 205 (53) [M − CHO]$^+$, 191 (100), 118 (48). − HRMS ($C_{17}H_{14}O$): calcd. 234.1045; found 234.1044.

4,5-Dimethoxy-2-(prop-2′-ynyl)benzaldehyde (5l): Treatment of **4l** (2.00 g, 8.05 mmol, 6 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 30:1, 10:1), gave **5l** (1.34 g, 82%) as colourless crystals, m.p. 103−104 °C (diethyl ether). − IR (CCl_4): $\tilde{\nu}$ = 3310 (≡C−H), 3000, 2935, 2845, 2715, 2120 (C≡C), 1695 (C=O), 1600, 1570, 1520, 1465, 1280, 1230, 1180, 1110 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.28 (t, $^4J_{3',1'}$ = 2.7 Hz, 1 H, 3′-H), 3.94 (s, 3 H, OCH_3), 4.00 (s, 3 H, OCH_3), 4.03 (md, $^4J_{1',3'}$ = 2.7 Hz, 2 H, 1′-H), 7.16 (s, 1 H, Ar-H), 7.34 (s, 1 H, Ar-H), 10.16 (s, 1 H, CHO). − ^{13}C NMR (100 MHz): δ = 21.8 (C-1′), 56.2 (OCH_3), 71.8 (C-3′), 81.4 (C-2′), 112.4 (C-3/6), 113.8 (C-3/6), 126.2 (C-1/2), 133.1 (C-1/2), 148.1 (C-4/5), 153.8 (C-4/5), 190.2 (CHO). − MS (70 eV; EI): *m*/*z* (%) = 204 (100) [M^+], 189 (51), 161 (64), 133 (51), 118 (35), 105 (28). − HRMS ($C_{12}H_{12}O_3$): calcd. 204.0786; found 204.0786.

4,5-Dimethoxy-2-[3′-(trimethylsilyl)prop-2′-ynyl]benzaldehyde (5n): Treatment of **2n** (1.94 g, 6.06 mmol, 2 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 30:1. 10:1), gave **5n** (1.41 g, 84%) as colourless crystals, m.p. 88−90 °C (diethyl ether). − IR (CCl_4): $\tilde{\nu}$ = 3000, 2960, 2835, 2175 (C≡C), 1695 (C=O), 1600, 1570, 1520, 1465, 1350, 1280, 1230, 1175, 1100, 1000 cm^{-1}. − ^1H NMR (400 MHz): δ = 0.19 (s, 9 H, $SiMe_3$), 3.94 (s, 3 H, OCH_3), 3.99 (s, 3 H, OCH_3), 4.06 (s, 2 H, 1′-H), 7.22 (s, 1 H, Ar-H), 7.33 (s, 1 H, Ar-H), 10.16 (s, 1 H, CHO). − ^{13}C NMR

(100 MHz): δ = 0.1 ($SiMe_3$), 23.1 (C-1′), 56.1 (OCH_3), 56.2 (OCH_3), 88.7 (C-2′), 103.7 (C-3′), 112.3 (C-3/6), 113.5 (C-3/6), 126.2 (C-1/2), 133.5 (C-1/2), 148.0 (C-4/5), 153.7 (C-4/5), 190.2 (CHO). − MS (70 eV; EI): *m/z* (%) = 276 (32) $[M]^+$, 261 (23), 231 (25), 203 (10) $[M - Si(CH_3)_3]^+$, 73 (100) $[Si(CH_3)_3^+]$. − HRMS ($C_{15}H_{20}O_3Si$): calcd. 276.1182; found 276.1181.

4,5-Dimethoxy-2-[3′-(4′′-methylphenyl)prop-2′-ynyl]benzaldehyde (5o): Treatment of **4o** (784 mg, 2.32 mmol, 3 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 20:1), gave **5o** (559 mg, 82%) as colourless crystals, m.p. 92−93 °C (diethyl ether). − IR (CCl_4): ṽ = 3005, 2955, 2840, 2710, 1690 (C=O), 1600, 1570, 1515, 1465, 1280, 1230, 1175, 1105 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.34 (s, 3 H, CH_3), 3.95 (s, 3 H, OCH_3), 3.99 (s, 3 H, OCH_3), 4.22 (s, 2 H, 1′-H), 7.11 (m_c, 2 H, Ar-H), 7.21 (s, 1 H, 3/6-H), 7.22 (m_c, 2 H, Ar-H), 7.37 (s, 1 H, 3/6-H), 10.25 (s, 1 H, CHO). − ^{13}C NMR (100 MHz): δ = 21.5 (CH_3), 22.7 (C-1′), 56.2 (OCH_3), 84.1 (C-2′/3′), 86.2 (C-2′/3′), 112.5 (Ar-C), 113.2 (Ar-C), 120.3 (Ar-C), 126.4 (Ar-C), 129.1 (C-3/6), 131.5 (C-3/6), 134.2 (C-1/2), 138.2 C-1/2), 148.1 (C-4/5), 153.8 (C-4/5), 190.2 (CHO). − MS (70 eV; EI): *m/z* (%) = 294 (100) $[M^+]$, 279 (16), 194 (39), 178 (36), 165 (61). − $C_{19}H_{18}O_3$ (294.35): calcd. C 77.53, H 6.16; found C 77.52, H 6.06.

Methyl{[2′-(prop-2′′-ynyl)phenyl]methylene}amine *N*-Oxide (6a): Treatment of **5a** (2.31 g, 16.0 mmol, 2 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 3:1, 1:2), gave **6a** (2.40 g, 86%) as colourless crystals, m.p. 100−101 °C (diethyl ether, decomp.). − IR (CCl_4): ṽ = 3310 (≡C−H), 3065, 3020, 2049, 2115 (C≡C), 1580, 1560, 1425, 1190, 1175 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.25 (t, $^4J_{3'',1''}$ = 2.8 Hz, 1 H, 3′′-H), 3.62 (d, $^4J_{1'',3''}$ = 2.8 Hz, 2 H, 1′′-H), 3.92 (s, 3 H, NCH_3), 7.30−7.48 (m, 3 H, Ar-H), 7.68 (s, 1 H, 1-H), 9.02 (m_c, 1 H, 6′-H). − ^{13}C NMR (100 MHz): δ = 23.4 (C-1′′), 55.0 (NCH_3), 71.6 (C-3′′), 81.1 (C-2′′), 127.5 (Ar-C), 128.4 (Ar-C), 128.5 (Ar-C_q), 129.1 (Ar-C), 130.4 (Ar-C), 131.7 (C-1), 134.2 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 173 (23) $[M^+]$, 134 (27), 128 (100) $[M - NOCH_3]^+$, 115 (21), 77 (25). − HRMS ($C_{11}H_{11}NO$): calcd. 173.0841; found 173.0843.

***N*-{[2′-(Prop-2′′-ynyl)phenyl]methylene}aniline *N*-Oxide (6b):** Treatment of **5a** (300 mg, 2.08 mmol, 30 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 20:1, 10:1), gave **6b** (184 mg, 38%) as a colourless solid (50% of **5a** was recovered). − M.p. 122−123 °C (ethanol). − IR (CCl_4): ṽ = 3310 (≡C−H), 3065, 1700, 1595, 1540, 1485, 1415, 1200, 1105, 1070, 1025 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.26 (t, $^4J_{3'',1''}$ = 2.7 Hz, 1 H, 3′′-H), 3.69 (d, $^4J_{1'',3''}$ = 2.7 Hz, 2 H, 1′′-H), 7.41−7.44 (m, 3 H, Ar-H), 7.46 (m_c, 3 H, Ar-H), 7.77−7.83 (m, 2 H, Ar-H), 8.26 (s, 1 H, 1-H), 9.22−9.33 (m, 1 H, 6′-H). − ^{13}C NMR (100 MHz): δ = 23.7 (C-1′′), 71.7 (C-3′′), 81.3 (C-2′′), 121.9 (Ar-C), 127.7 (Ar-C), 128.6 (Ar-C), 128.7 (Ar-C_q), 129.3 (Ar-C), 130.1 (Ar-C), 130.9 (Ar-C), 131.4 (C-1), 135.0 (Ar-C_q), 149.6 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 235 (29) $[M^+]$, 218 (100), 206 (79), 115 (84), 77 (46). − $C_{16}H_{13}NO$ (235.28): calcd. C 81.68, H 5.57, N 5.95; found C 81.48, H 5.50, N 5.72.

***tert*-Butyl{[2′-(prop-2′′-ynyl)phenyl]methylene}amine *N*-Oxide (6c):** A suspension of *N*-*tert*-butylhydroxylamine hydrochloride (113 mg, 0.90 mmol) and sodium acetate (170 mg, 2.08 mmol) in dry CH_2Cl_2 (5 mL) was stirred for 15 min and then treated with **5a** (100 mg, 0.69 mmol). After this had stirred for 72 h at room temp., water (15 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Purification of the residue by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 5:1) afforded **6c** (141 mg, 95%) as colourless crystals, m.p. 36−37 °C (ethanol). − IR (CCl_4): ṽ = 3310 (≡C−H), 3065, 2975, 2935, 1555, 1470, 1430, 1360, 1195, 1135 cm^{-1}. − ^1H NMR (250 MHz): δ = 1.64 (s, 9 H, CH_3), 2.21 (t, $^4J_{3'',1''}$ = 2.7 Hz, 1 H, 3′′-H), 3.63 (d, $^4J_{1'',3''}$ = 2.7 Hz, 2 H, 1′′-H), 7.31−7.39 (m, 3 H, Ar-H), 7.94 (s, 1 H, 1-H), 9.01−9.07 (m, 1 H, 6′-H). − ^{13}C NMR (125 MHz): δ = 23.6 (C-1′′), 28.3 (CH_3), 71.2 (C-3′′), 71.5 (C_q), 81.3 (C-2′′), 126.6 (Ar-C_q), 127.5 (Ar-C), 128.4 (Ar-C), 129.1 (Ar-C), 129.9 (Ar-C), 134.6 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 215 (16) $[M^+]$, 159 (19), 142 (29), 128 (24), 57 (100) $[C(CH_3)_3^+]$. − HRMS ($C_{14}H_{17}NO$): calcd. 215.1310; found 215.1309.

Methyl{[2′-(3′′-trimethylsilylprop-2′′-ynyl)phenyl]methylene}amine *N*-Oxide (6d): Treatment of **5d** (1.20 g, 5.55 mmol, 5 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 3:1, 1:2), gave **6d** (904 mg, 66%) as a colourless solid, m.p. 67−68 °C (ethanol, decomp.). − IR (CCl_4): ṽ = 2935, 2855, 2175 (C≡C), 1715, 1580, 1560, 1450, 1420, 1250, 1190, 1015 cm^{-1}. − ^1H NMR (400 MHz): δ = 0.17 (s, 9 H, $SiMe_3$), 3.66 (s, 2 H, 1′′-H), 3.93 (s, 3 H, NCH_3), 7.32−7.51 (m, 3 H, Ar-H), 7.72 (s, 1 H, 1-H), 9.03 (m_c, 1 H, 6′-H). − ^{13}C NMR (100 MHz): δ = 0.0 ($SiMe_3$), 24.9 (C-1′′), 55.0 (NCH_3), 88.1 (C-3′′), 103.3 (C-2′′), 127.4 (Ar-C), 128.3 (Ar-C), 128.6 (Ar-C_q), 129.2 (Ar-C), 130.3 (Ar-C), 131.8 (C-1), 134.5 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 245 (10) $[M^+]$, 230 (36), 172 (19) $[M - Si(CH_3)_3]^+$, 144 (34), 73 (100) $[Si(CH_3)_3^+]$. − $C_{14}H_{19}NOSi$ (245.40): calcd. C 68.52, H 7.80, N 5.71; found C 68.49, H 7.82, N 5.64.

***N*-({2′-[3′′-(Trimethylsilyl)prop-2′′-ynyl]phenyl}methylene)aniline *N*-Oxide (6e):** Treatment of **5d** (1.00 g, 4.62 mmol, 6 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 10:1), gave **6e** (796 mg, 58%) as colourless crystals, m.p. 96−97 °C (diethyl ether, decomp.). − IR (CCl_4): ṽ = 3065, 2960, 2895, 2175 (C≡C), 1590, 1545, 1490, 1460, 1250, 1205, 1015 cm^{-1}. − ^1H NMR (250 MHz): δ = 0.15 (s, 9 H, $SiMe_3$), 3.73 (s, 2 H, 1′′-H), 7.35−7.56 (m, 6 H, Ar-H), 7.78−7.90 (m, 2 H, Ar-H), 8.38 (s, 1 H, 1-H), 9.38 (m_c, 1 H, 6′-H). − ^{13}C NMR (100 MHz): δ = 0.2 ($SiMe_3$), 25.2 (C-1′′), 88.1 (C-3′′), 103.5 (C-2′′), 121.9 (Ar-C), 127.7 (Ar-C), 128.6 (Ar-C), 128.9 (Ar-C_q), 129.2 (Ar-C), 129.6 (Ar-C), 130.9 (Ar-C), 131.5 (C-1), 135.4 (Ar-C_q), 149.7 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 307 (30) $[M^+]$, 306 (54), 218 (51), 77 (22), 73 (100) $[Si(CH_3)_3^+]$. − $C_{19}H_{21}NOSi$ (307.47): calcd. C 74.22, H 6.88, N 4.56; found C 74.19, H 6.98, N 4.66.

{[2′-(But-2′′-ynyl)phenyl]methylene}methylamine *N*-Oxide (6f): Treatment of **5f** (535 mg, 3.38 mmol, 2.5 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 1:2), gave **6f** (533 mg, 84%) as colourless crystals, m.p. 99−100 °C (ethanol). − IR (CCl_4): ṽ = 2945, 2920, 1715, 1560, 1420, 1260, 1190, 1175, 1070 cm^{-1}. − ^1H NMR (250 MHz): δ = 1.82 (t, $^5J_{4'',1''}$ = 2.6 Hz, 3 H, 4′′-H), 3.55 (q, $^5J_{1'',4''}$ = 2.6 Hz, 2 H, 1′′-H), 3.92 (s, 3 H, NCH_3), 7.30−7.42 (m, 3 H, Ar-H), 7.70 (s, 1 H, 1-H), 9.01−9.15 (m, 1 H, 6′-H). − ^{13}C NMR (100 MHz): δ = 3.9 (C-4′′), 23.7 (C-1′′), 55.0 (NCH_3), 76.0 (C-2′′/3′′), 79.1 (C-2′′/3′′), 127.2 (Ar-C), 128.3 (Ar-C), 128.4 (Ar-C_q), 129.1 (Ar-C), 130.3 (Ar-C), 131.9 (C-1), 135.8 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 187 (13) $[M^+]$, 186 (37), 172 (41), 144 (100), 115 (31). − $C_{12}H_{13}NO$ (187.24): calcd. C 76.98, H 7.00, N 7.48; found C 76.76, H 7.06, N 7.22.

***N*-{[2′-(But-2′′-ynyl)phenyl]methylene}aniline *N*-Oxide (6g):** Treatment of **5f** (350 mg, 2.21 mmol, 28 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 40:1, 10:1), gave **6g** (390 mg, 71%) as a beige solid (15% of **5f** was recovered). − M.p. 99−100 °C (ethanol). − IR (CCl_4): ṽ = 3070, 2920, 2855, 1705, 1595, 1545, 1490, 1460, 1410, 1295, 1205, 1105, 1070, 1025

cm^{-1}. − ^1H NMR (250 MHz): δ = 1.84 (t, $^5J_{4'',1''}$ = 2.6 Hz, 3 H, 4''-H), 3.62 (q, $^5J_{1'',4''}$ = 2.6 Hz, 2 H, 1''-H), 7.38−7.58 (m, 6 H, Ar-H), 7.75−7.88 (m, 2 H, Ar-H), 8.32 (s, 1 H, 1-H), 9.30−9.41 (m, 1 H, 6'-H). − ^{13}C NMR (100 MHz): δ = 3.6 (C-4''), 24.1 (C-1''), 76.3 (C-2''/3''), 79.2 (C-2''/3''), 121.9 (Ar-C), 127.5 (Ar-C), 128.5 (Ar-C), 128.7 (Ar-C_q), 129.2 (Ar-C), 129.3 (Ar-C), 130.0 (Ar-C), 130.9 (Ar-C), 131.6 (C-1), 136.5 (Ar-C_q), 149.7 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 249 (11) $[M]^+$, 206 (23), 141 (22), 115 (27), 77 (64). − HRMS ($C_{17}H_{15}NO$): calcd. 249.1154: found 249.1152.

Methyl{[2'-(3''-phenylprop-2''-ynyl)phenyl]methylene}amine *N*-Oxide (6h): Treatment of **5h** (290 mg, 1.32 mmol, 4 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 1:2), gave **6h** (207 mg, 63%) as a beige solid, m.p. 110−112 °C (ethanol). − IR (CCl_4): ṽ = 3060, 3020, 2945, 1715, 1560, 1490, 1420, 1190, 1170 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.86 (s, 2 H, 1''-H), 3.94 (s, 3 H, NCH_3), 7.22−7.57 (m, 8 H, Ar-H), 7.79 (s, 1 H, 1-H), 9.00−9.11 (m, 1 H, 6'-H). − ^{13}C NMR (100 MHz): δ = 24.4 (C-1''), 55.1 (NCH_3), 83.7 (C-2''/3''), 86.6 (C-2''/3''), 123.3 (Ar-C_q), 128.2 (Ar-C), 128.3 (Ar-C), 128.4 (Ar-C), 128.6 (Ar-C_q), 129.3 (Ar-C), 130.4 (Ar-C), 131.6 (Ar-C), 131.8 (C-1), 134.9 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 249 (64) $[M^+]$, 220 (25), 132 (100), 105 (32), 77 (24). − HRMS ($C_{17}H_{15}NO$): calcd. 249.1152; found 249.1154.

***N*-{[2'-(3''-Phenylprop-2''-ynyl)phenyl]methylene}aniline *N*-Oxide (6i):** Treatment of **5h** (263 mg, 1.54 mmol, 8 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 30:1, 3:1), gave **6i** (796 mg, 55%) as a pale yellow, noncrystalline solid (19% of **5h** was recovered). − IR (CCl_4): ṽ = 3065, 3020, 2945, 1560, 1490, 1420, 1190, 1170 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.91 (s, 2 H, 1''-H), 7.25−7.50 (m, 11 H, Ar-H), 7.75−7.85 (m, 2 H, Ar-H), 8.41 (s, 1 H, 1-H), 9.35 (m_c, 1 H, 6'-H). − MS (170 eV; CI, isobutane): *m/z* (%) = 306 (2), 250 (100), 234 (4) $[M - C_6H_5]^+$, 221 (8), 205 (8), 105 (5).

***tert*-Butyl{[2'-(3''-phenylprop-2''-ynyl)phenyl]methylene}amine *N*-Oxide (6j):** A suspension of *N*-*tert*-butylhydroxylamine hydrochloride (60 mg, 0.45 mmol) and sodium acetate (90 mg, 1.10 mmol) in dry CH_2Cl_2 (5 mL) was stirred for 15 min and then treated with **5h** (81 mg, 0.37 mmol). After this had stirred for 24 h at room temp., water (15 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Purification of the residue by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 2:1) afforded **6j** (84 mg, 78%) as colourless crystals, m.p. 117−118 °C (ethanol). − IR (CCl_4): ṽ = 3065, 2975, 2930, 1555, 1490, 1470, 1360, 1195, 1135 cm^{-1}. − ^1H NMR (250 MHz): δ = 1.62 (s, 9 H, CH_3), 3.85 (s, 2 H, 1''-H), 7.24−7.31 (m, 3 H, Ar-H), 7.33−7.44 (m, 5 H, Ar-H), 8.04 (s, 1 H, 1-H), 9.07−9.16 (m, 1 H, 6'-H). − ^{13}C NMR (125 MHz): δ = 24.8 (C-1''), 28.4 (CH_3), 71.5 (C_q), 83.3 (C-2''/3''), 86.9 (C-2''/3''), 123.3 (Ar-C_q), 126.7 (C-1), 127.5 (Ar-C), 128.1 (Ar-C), 128.3 (Ar-C), 128.5 (Ar-C), 129.2 (Ar-C_q), 129.3 (Ar-C), 130.0 (Ar-C), 131.5 (Ar-C), 135.3 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 291 (3) $[M^+]$, 234 (41), 206 (54), 130 (43), 105 (49), 57 (100) $[C(CH_3)_3^+]$. − $C_{20}H_{21}NO$ (291.39): calcd. C 82.44, H 7.26, N 4.81; found C 82.50, H 7.12, N 4.65.

Methyl{[2'-(3''-phenylprop-2''-ynyl)phenyl]methylene}amine *N*-Oxide (6k): Treatment of **5k** (180 mg, 0.78 mmol, 4.5 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 3:1, 1:1), gave **6k** (258 mg, 70%) as colourless crystals, m.p. 110−112 °C (ethanol). − IR (CCl_4): ṽ = 3025, 2925, 2870, 1605, 1510, 1460, 1420, 1170, 1020 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.34 (s, 3 H, CH_3), 3.83 (s, 2 H, 1''-H), 3.93 (s, 3 H, NCH_3), 7.10 (m_c, 1 H, Ar-H), 7.29 (m_c, 1 H, Ar-H), 7.34−7.41 (m, 2 H, Ar-H), 7.43−7.49 (m, 2 H, Ar-H), 7.76 (s, 1 H, 1-H), 9.06 (m_c, 1 H, 6'-H). − ^{13}C NMR (100 MHz): δ = 21.5 (CH_3), 24.4 (C-1''), 55.0 (NCH_3), 83.7 (C-2''/3''), 85.8 (C-2''/3''), 120.2 (Ar-C_q), 127.4 (Ar-C), 128.4 (Ar-C), 128.6 (Ar-C_q), 129.2 (Ar-C), 130.4 (Ar-C), 131.5 (Ar-C), 131.9 (C-1), 135.0 (Ar-C_q), 138.2 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 263 (12) $[M^+]$, 235 (32), 144 (50), 119 (100), 91 (51). − $C_{18}H_{17}NO$ (263.34): calcd. C 81.90, H 6.06, N 5.62; found C 81.67, H 6.07, N 5.58.

Methyl{[4',5'-dimethoxy-2'-(prop-2''-ynyl)phenyl]methylene}amine *N*-Oxide (6l): Treatment of **5l** (500 mg, 2.45 mmol, 6 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 1:2; ethyl acetate), gave **6l** (434 mg, 76%) as colourless crystals, m.p. 118−120 °C (ethanol, decomp.). − IR (CCl_4): ṽ = 3310 (≡C−H), 2995, 2930, 2825, 1600, 1505, 1460, 1285, 1230, 1075, 1010 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.25 (t, $^4J_{3'',1''}$ = 2.7 Hz, 1 H, 3''-H), 3.59 (d, $^4J_{1'',3''}$ = 2.7 Hz, 2 H, 1''-H), 3.91 (s, 3 H, CH_3), 3.92 (s, 3 H, CH_3), 3.93 (s, 3 H, CH_3), 6.94 (s, 1 H, 3'-H), 7.58 (s, 1 H, 1-H), 9.01 (s, 1 H, 6'-H). − ^{13}C NMR (100 MHz): δ= 22.8 (C-1''), 54.8 (NCH_3), 55.9 (OCH_3), 56.0 (OCH_3), 71.6 (C-3''), 81.2 (C-2''), 111.3 (C-3'/6'), 112.2 (C-3'/6'), 121.2 (C-1'/2'), 127.9 (C-1'/2'), 131.5 (C-1), 147.4 (C-4'/5'), 150.2 (C-4'/5'). − MS (70 eV; EI): *m/z* (%) = 233 (54) $[M^+]$, 216 (78), 194 (70), 188 (100) $[M - NOCH_3]^+$, 185 (46). − $C_{13}H_{13}NO_3$ (233.27): calcd. C 66.94, H 6.48, N 6.00; found C 66.77, H 6.49, N 5.80.

***N*-{[4',5'-Dimethoxy-2'-(prop-2''-ynyl)phenyl]methylene}aniline *N*-Oxide (6m):** Treatment of **5l** (400 mg, 1.96 mmol, 45 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 10:1), gave **6m** (207 mg, 36%) as a beige solid (32% of **5l** was recovered). − M.p. 130−134 °C (ethanol, decomp.). − IR (CCl_4): 3310 (≡C−H), 3000, 2935, 2830, 1695, 1600, 1500, 1465, 1280, 1115, 1010 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.29 (t, $^4J_{3'',1''}$ = 2.8 Hz, 1 H, 3''-H), 3.65 (d, $^4J_{1'',3''}$ = 2.8 Hz, 2 H, 1''-H), 3.96 (s, 3 H, OCH_3), 3.99 (s, 3 H, OCH_3), 6.96 (s, 1 H, 3'-H), 7.45−7.54 (m, 3 H, Ar-H), 7.76−7.83 (m, 2 H, Ar-H), 8.19 (s, 1 H, 1-H), 9.29 (s, 1 H, 6'-H). − ^{13}C NMR (100 MHz): δ = 23.1 (C-1''), 56.0 (OCH_3), 56.1 (OCH_3), 71.2 (C-3''), 81.3 (C-2''), 111.5 (Ar-C), 112.5 (Ar-C), 121.5 (Ar-C_q), 121.8 (Ar-C), 129.2 (Ar-C_q), 129.8 (Ar-C), 131.2 (C-1), 147.5 (Ar-C_q), 149.5 (Ar-C_q), 150.7 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 295 (44) $[M^+]$, 278 (100), 256 (60), 188 (34), 77 (60). − HRMS ($C_{18}H_{17}NO_3$): calcd. 295.1208; found 295.1212.

({4',4'-Dimethoxy-2'-[3''-(trimethylsilyl)prop-2''-ynyl]phenyl}-methylene)methylamine *N*-Oxide (6n): Treatment of **5n** (350 mg, 1.27 mmol, 7 h) according to the general procedure, after purification (ethyl acetate), gave **6n** (271 mg, 70%) as pale yellow crystals, m.p. 122−124 °C (ethanol). − IR (CCl_4): ṽ = 3000, 2960, 2830, 2175 (C≡C), 1600, 1510, 1465, 1425, 1300, 1285, 1250, 1225, 1075 cm^{-1}. − ^1H NMR (250 MHz): δ = 0.17 (s, 9 H, $SiMe_3$), 3.45 (s, 3 H, NCH_3) 3.73 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 6.79 (s, 1 H, 3'-H), 7.44 (s, 1 H, 1-H), 8.85 (s, 1 H, 6'-H). − ^{13}C NMR (100 MHz): δ = 0.0 ($SiMe_3$), 24.2 (C-1''), 54.7 (NCH_3), 55.8 (OCH_3), 56.0 (OCH_3), 88.3 (C-2''), 103.4 (C-3''), 111.2 (C-3'/6'), 112.3 (C-3'/6'), 121.2 (C-1'/2'), 128.3 (C-1'/2'), 131.7 (C-1), 147.3 (C-4'/5'), 150.1 (C-4'/5'). − MS (70 eV; EI): *m/z* (%) = 305 (19) $[M^+]$, 290 (21), 262 (39), 204 (14), 73 (100) $[Si(CH_3)_3^+]$. − HRMS ($C_{16}H_{23}NO_3Si$): calcd. 305.1447; found 305.1447.

({4',5'-Dimethoxy-2'-[3''-(4'''-methylphenyl)but-2''-ynyl]phenyl}-methylene)methylamine *N*-Oxide (6o): Treatment of **5o** (474 mg, 1.61 mmol, 6 h) according to the general procedure, after purifica-

tion (ethyl acetate/methanol, 10:1), gave **6o** (485 mg, 87%) as colourless crystals, m.p. 141−143 °C (ethanol, decomp.). − IR (CCl_4): $\tilde{\nu}$ = 3000, 2935, 2830, 1600, 1510, 1465, 1285, 1230, 1175, 1075, 1010 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.34 (s, 3 H, CH_3), 3.79 (s, 2 H, 1′′-H), 3.90 (d, $^4J_{NCH3,1}$ = 0.6 Hz, 3 H, NCH_3), 3.93 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 6.99 (s, 1 H, 3′-H), 7.10 (m_c, 2 H, Ar-H), 7.28 (m_c, 2 H, Ar-H), 7.68 (m_c, 1 H, 1-H), 9.04 (s, 1 H, 6′-H). − ^{13}C NMR (100 MHz): δ = 21.4 (CH_3), 23.8 (C-1′′), 54.8 (NCH_3), 55.9 (OCH_3), 56.0 (OCH_3), 83.8 (C-2′′/3′′), 85.9 (C-2′′/3′′), 111.3 (Ar-C), 112.3 (Ar-C), 120.1 (Ar-C), 121.3 (Ar-C), 128.9 (C-1′/2′), 129.1 (C-3′/6′), 131.4 (C-3′/6′), 131.8 (C-1), 138.3 (C-1′/2′), 147.3 (C-4′/5′), 150.2 (C-4′/5′). − MS (70 eV; EI): *m*/*z* (%) = 323 (79) [M^+], 308 (19), 278 (24), 204 (72), 119 (100). − $C_{20}H_{21}NO_3$ (323.39): calcd. C 74.13, H 6.62, N 4.32; found C 74.28, H 6.55, N 4.33.

1,2-Dihydro-2-methyl-3*H*-2-benzazepin-3-one (9a): Treatment of **6a** (50 mg, 0.29 mmol; NaOMe, 30 min) according to the general procedure, after purification (cyclohexane/ethyl acetate, 1:1, 1:2), gave **9a** (42 mg, 84%) as colourless crystals, m.p. 132−133 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 3065, 3020, 2920, 1650 (C=O), 1615, 1475, 1430, 1400, 1345, 1220, 1105 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.11 (s, 3 H, NCH_3), 4.24 (s, 2 H, 1-H), 6.41 (d, $^3J_{4,5}$ = 12.2 Hz, 1 H, 4-H), 7.08 (d, $^3J_{5,4}$ = 12.2 Hz, 1 H, 5-H), 7.25−7.44 (m, 4 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 35.0 (NCH_3), 53.4 (C-1), 127.3 (C-4), 127.6 (Ar-C), 128.4 (Ar-C), 129.2 (Ar-C), 129.3 (Ar-C), 135.4 (Ar-C_q), 136.2 (Ar-C_q), 136.3 (C-5), 166.3 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 173 (100) [M^+], 144 (74) [$M - NCH_3]^+$, 132 (18), 115 (34). − $C_{11}H_{11}NO$ (173.21): calcd. C 76.28, H 6.40, N 8.09; found C 76.29, H 6.51, N 8.15.

1,2-Dihydro-2-phenyl-3*H*-2-benzazepin-3-one (9b): Treatment of **6b** (114 mg, 0.48 mmol; KOH, 2 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 10:1, 3:1), gave **9b** (97 mg, 84%) as colourless crystals, m.p. 109−110 °C (diethyl ether, decomp.). − IR (CCl_4): $\tilde{\nu}$ = 3065, 3030, 2905, 1650 (C=O), 1595, 1495, 1440, 1415, 1340, 1290, 1215, 1100 cm^{-1}. − ^1H NMR (250 MHz): δ = 4.66 (s, 2 H, 1-H), 6.55 (d, $^3J_{4,5}$ = 12.2 Hz, 1 H, 4-H), 7.20 (d, $^3J_{5,4}$ = 12.2 Hz, 1 H, 5-H), 7.21−7.50 (m, 9 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 54.8 (C-1), 126.4 (Ar-C/C-4), 126.9 (Ar-C/C-4), 127.5 (Ar-C/C-4), 127.7 (Ar-C/C-4), 128.6 (Ar-C/C-4), 129.2 (Ar-C/C-4), 129.4 (Ar-C/C-4), 129.5 (Ar-C/C-4), 135.5 (Ar-C_q), 136.7 (Ar-C_q), 136.8 (C-5), 143.1 (Ar-C_q), 165.8 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 235 (100) [M^+], 206 (88), 194 (90), 115 (35), 77 (16). − $C_{16}H_{13}NO$ (235.28): calcd. C 81.68, H 5.57, N 5.95; found C 81.70, H 5.62, N 5.87.

2-*tert*-Butyl-1,2-dihydro-3*H*-2-benzazepin-3-one (9c): Treatment of **6c** (100 mg, 0.46 mmol, KOH, 4 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 5:1), gave **9c** (85 mg, 85%) as a colourless solid, m.p. 146−147 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 3025, 2970, 1640 (C=O), 1410, 1365, 1340, 1195, 1100 cm^{-1}. − ^1H NMR (250 MHz): δ = 1.48 (s, 3 H, CH_3), 3.96−4.40 (m, 2 H, 1-H), 6.36 (d, $^3J_{4,5}$ = 12.1 Hz, 1 H, 4-H), 6.98 (d, $^3J_{5,4}$ = 12.1 Hz, 1 H, 5-H), 7.30−7.39 (m, 4 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 29.0 (CH_3), 47.2 (C-1), 58.1 (C_q), 126.8 (C-4), 128.1 (Ar-C), 129.0 (Ar-C), 129.4 (Ar-C), 130.3 (Ar-C), 135.0 (C-5), 135.8 (Ar-C_q), 138.7 (Ar-C_q), 167.6 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 215 (54) [M^+], 159 (100), 142 (43), 115 (46), 58 (13) [$C(CH_3)_3^+$]. − $C_{14}H_{17}NO$ (215.29): calcd. C 78.10, H 7.96, N 6.51; found C 78.14, H 7.83, N 6.31.

1,2-Dihydro-2-methyl-4-(trimethylsilyl)-3*H*-2-benzazepin-3-one (9d): Treatment of **6d** (150 mg, 0.61 mmol; NaOMe, 2 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 5:1), gave **9d** (36 mg, 24%) and **9a** (31 mg, 29%; see above), both as colourless solids. Compound **9d**: M.p. 104−106 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 2955, 1625 (C=O), 1425, 1395, 1335, 1245, 1120 cm^{-1}. − ^1H NMR (250 MHz): δ = 0.30 (s, 9 H, $SiMe_3$), 3.06 (s, 3 H, NCH_3), 4.12 (s, 2 H, 1-H), 7.20 (s, 1 H, 5-H), 7.21−7.40 (m, 4 H, Ar-H). − ^{13}C NMR (100 MHz): δ = −0.7 ($SiMe_3$), 34.5 (NCH_3), 53.1 (C-1), 126.9 (Ar-C), 128.3 (Ar-C), 128.7 (Ar-C), 129.0 (Ar-C), 136.7 (Ar-C_q/C-4), 137.0 (Ar-C_q/C-4), 141.5 (C-5), 144.0 (Ar-C_q), 169.2 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 245 (12) [M^+], 230 (100), 132 (13), 115 (28), 73 (11) [$Si(CH_3)_3^+$]. − $C_{14}H_{19}NOSi$ (245.40): calcd. C 68.52, H 7.80, N 5.71; found C 68.49, H 7.81, N 5.87.

1,2-Dihydro-2-phenyl-4-(trimethylsilyl)-3*H*-2-benzazepin-3-one (9e): Treatment of **6e** (110 mg, 0.36 mmol; KOH, 2 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 20:1, 3:1), gave **9e** (75 mg, 68%) and **9b** (22 mg, 26%; see above), both as colourless solids. Compound **9e**: M.p. 111−112 °C (ethanol). − ^1H NMR (250 MHz): δ = 0.34 (s, 9 H, $SiMe_3$), 4.55 (br. s, 2 H, 1-H), 7.16−7.46 (m, 10 H, 5-H, Ar-H). − ^{13}C NMR (100 MHz): δ = 0.0 ($SiMe_3$), 55.1 (C-1), 127.3 (Ar-C), 127.5 (Ar-C), 127.8 (Ar-C), 129.1 (Ar-C), 129.7 (Ar-C), 129.8 (Ar-C), 129.9 (Ar-C), 137.8 (Ar-C_q), 137.9 (C-4), 142.9 (C-5), 144.0 (Ar-C_q), 144.7 (Ar-C_q), 169.6 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 307 (16) [M^+], 292 (17), 194 (100), 115 (9), 77 (10). − $C_{19}H_{21}NOSi$ (307.47): calcd. C 74.22, H 6.88, N 4.56; found C 73.85, H 7.10, N 4.58.

1,2-Dihydro-2,4-dimethyl-3*H*-2-benzazepin-3-one (9f): Treatment of **6f** (145 mg, 0.77 mmol; 1 equiv. NaOMe, 24 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 2:1), gave **9f** (124 mg, 86%) as colourless crystals, m.p. 114−115 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 2950, 2925, 1645 (C=O), 1620, 1475, 1450, 1425, 1395, 1265, 1215, 1070, 1010 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.20 (d, $^4J_{CH3,5}$ = 1.5 Hz, 3 H, CH_3), 3.01 (s, 3 H, NCH_3), 4.10 (br. s, 2 H, 1-H), 6.89 (q, $^4J_{5,CH3}$ = 1.5 Hz, 1 H, 5-H), 7.12−7.31 (m, 4 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 21.7 (CH_3), 34.7 (NCH_3), 53.2 (C-1), 126.8 (Ar-C), 128.1 (Ar-C), 128.9 (Ar-C), 132.3 (C-5), 135.9 (C_q), 136.0 (C_q), 136.1 (C_q), 167.5 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 187 (100) [M^+], 172 (46), 158 (39), 144 (46), 132 (37), 115 (30). − $C_{12}H_{13}NO$ (187.24): calcd. C 76.98, H 7.00, N 7.48; found C 76.73, H 6.98, N 7.37.

1,2-Dihydro-4-methyl-2-phenyl-3*H*-2-benzazepin-3-one (9g): Treatment of **6g** (160 mg, 0.64 mmol; 1 equiv. NaOMe, 20 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 10:1), gave **9g** (100 mg, 62%) as colourless crystals, m.p. 128−130 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 3065, 3030, 2920, 1650 (C=O), 1620, 1595, 1500, 1440, 1335, 1215, 1090 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.34 (d, $^4J_{CH3,5}$ = 1.2 Hz, 3 H, CH_3), 4.57 (br. s, 2 H, 1-H), 7.06 (q, $^4J_{5,CH3}$ = 1.2 Hz, 1 H, 5-H), 7.15−7.44 (m, 9 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 21.9 (CH_3), 54.5 (C-1), 126.7 (Ar-C), 126.8 (Ar-C), 126.9 (Ar-C), 128.3 (Ar-C), 128.4 (Ar-C), 129.0 (Ar-C), 129.1 (Ar-C), 133.0 (C-5), 135.7 (C_q), 136.0 (C_q), 136.4 (C_q), 143.3 (C_q), 167.1 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 249 (77) [M^+], 220 (13), 194 (100), 128 (13), 77 (18). − HRMS ($C_{17}H_{15}NO$): calcd. 249.1154; found 249.1155.

1,2-Dihydro-2-methyl-4-phenyl-3*H*-2-benzazepin-3-one (9h): Treatment of **6h** (190 mg, 0.76 mmol; KOH, 4 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 2:1), gave **9h** (142 mg, 75%) as colourless crystals, m.p. 116 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 3060, 3020, 2920, 1645 (C=O), 1485, 1445, 1425, 1395, 1185, 1000 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.13 (s, 3 H, NCH_3), 4.29 (br. s, 2 H, 1-H), 7.29−7.46 (m, 8 H, 5-H, Ar-H), 7.64−7.68 (m, 2 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 34.4

(NCH_3), 53.2 (C-1), 126.9 (Ar-C), 128.0 (Ar-C), 128.2 (Ar-C), 128.4 (Ar-C), 128.6 (Ar-C), 129.6 (Ar-C), 131.7 (C-5), 135.9 (C_q), 136.1 (C_q), 139.1 (C_q), 139.7 (C_q), 166.6 (C-3). − MS (70 eV; EI): *m/z* (%) = 249 (77) [M^+], 220 (24) [M − NCH_3]$^+$, 192 (16), 144 (39), 132 (100). − $C_{17}H_{15}NO$ (249.31): calcd. C 81.90, H 6.06, N 5.62; found C 81.93, H 6.03, N 5.48.

1,2-Dihydro-2,4-diphenyl-3*H*-2-benzazepin-3-one (9i): Treatment of **6i** (100 mg, 0.32 mmol; NaOMe, 4 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 1:2), gave **9i** (40 mg, 40%) as a colourless solid, m.p. 154−156 °C (diethyl ether). − IR (CCl_4): $\tilde{\nu}$ = 3065, 3030, 1655 (C=O), 1595, 1495, 1440, 1405, 1330, 1190, 1105 cm^{-1}. − ^1H NMR (250 MHz): δ = 4.72 (br. s, 2 H, 1-H), 7.23−7.59 (m, 13 H, 5-H, Ar-H), 7.78 (m_c, 2 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 54.7 (C-1), 126.7 (Ar-C), 127.0 (Ar-C), 127.1 (Ar-C), 128.1 (Ar-C), 128.3 (Ar-C), 128.4 (Ar-C), 128.6 (Ar-C), 129.0 (Ar-C), 129.2 (Ar-C), 129.9 (Ar-C), 132.6 (C-5), 136.0 (C-4), 136.7 (Ar-C_q), 139.3 (Ar-C_q), 139.4 (Ar-C_q), 143.0 (Ar-C_q), 166.3 (C-3). − MS (70 eV; EI): *m/z* (%) = 311 (24) [M^+], 194 (100), 116 (5), 77 (8). − $C_{22}H_{17}NO$ (311.38): calcd. C 84.86, H 5.50, N 4.50; found C 84.78, H 5.54, N 4.44.

2-(*tert*-Butyl)-1,2-dihydro-4-phenyl-3*H*-2-benzazepin-3-one (9j): Treatment of **6j** (60 mg, 0.21 mmol; NaOMe, 8 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 10:1), gave **9j** (48 mg, 80%) as a colourless solid, m.p. 130−131 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 3065, 3025, 2975, 2925, 1640 (C=O), 1485, 1400, 1330, 1205, 1185, 1110 cm^{-1}. − ^1H NMR (250 MHz): δ = 1.50 (s, 9 H, CH_3), 4.24 (d, ^2J = 15.3 Hz, 1 H, 1-H_a), 4.53 (d, ^2J = 15.3 Hz, 1 H, 1-H_b), 7.20 (s, 1 H, 5-H), 7.26−7.45 (m, 7 H, Ar-H), 7.61 (m_c, 2 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 29.3 (CH_3), 47.3 (C-1), 58.4 (C_q), 126.5 (Ar-C), 127.7 (Ar-C), 128.0 (Ar-C), 128.2 (Ar-C), 128.3 (Ar-C), 128.4 (Ar-C), 129.6 (Ar-C), 130.2 (C-5), 136.2 (C_q), 138.3 (C_q), 140.0 (C_q), 141.8 (C_q), 167.5 (C-3). − MS (70 eV; EI): *m/z* (%) = 291 (47) [M^+], 235 (100), 234 (71), 191 (22), 118 (18). − HRMS ($C_{20}H_{21}NO$): calcd. 291.1623; found 291.1624.

1,2-Dihydro-2-methyl-4-(4′-methylphenyl)-3*H*-2-benzazepin-3-one (9k): Treatment of **6k** (92 mg, 0.35 mmol; KOH, 5 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 5:1), gave **9k** (59 mg 64%) as colourless crystals, m.p. 99−100 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 3025, 2965, 2925, 1645 (C=O), 1510, 1450, 1395, 1335, 1180, 1115, 1000 cm^{-1}. − ^1H NMR (500 MHz): δ = 2.37 (s, 3 H, CH_3), 3.13 (s, 3 H, NCH_3), 4.28 (br. s, 2 H, 1-H), 7.20 (m_c, 2 H, Ar-H), 7.28 (s, 1 H, 5-H), 7.29 (m_c, 1 H, Ar-H), 7.32 (m_c, 1 H, Ar-H), 7.37 (m_c, 1 H, Ar-H), 7.42 (m_c, 1 H, Ar-H), 7.56 (m_c, 1 H, Ar-H). − ^{13}C NMR (125 MHz): δ = 21.2 (CH_3), 34.3 (NCH_3), 53.8 (C-1), 126.8 (Ar-C), 128.0 (Ar-C), 128.3 (Ar-C), 128.5 (Ar-C), 129.1 (Ar-C), 129.5 (Ar-C), 130.8 (C-5), 135.9 (C_q), 136.0 (C_q), 136.1 (Ar-C_q), 137.9 (Ar-C_q), 139.6 (Ar-C_q), 166.7 (C-3). − MS (70 eV; EI): *m/z* (%) = 263 (44) [M^+], 234 (16) [M − NCH_3]$^+$, 189 (10), 144 (25), 132 (100). − HRMS ($C_{18}H_{17}NO$): calcd. 263.1310; found 263.1309.

1,2-Dihydro-7,8-dimethoxy-2-methyl-3*H*-benzazepin-3-one (9l): Treatment of **6l** (228 mg, 0.98 mmol; NaOMe, 1 h) according to the general procedure, after purification (ethyl acetate/methanol, 10:1), gave **9l** (176 mg, 77%) as colourless crystals, m.p. 124−126 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 3005, 2930, 2850, 1645 (C=O), 1600, 1520, 1460, 1380, 1265, 1195, 1110, 1010 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.10 (s, 3 H, NCH_3), 3.90 (s, 3 H, OCH_3), 3.94 (s, 3 H, OCH_3), 4.18 (s, 2 H, 1-H), 6.33 (d, $^3J_{4,5}$ = 12.2 Hz, 1 H, 4-H), 6.81 (s, 1 H, Ar-H), 6.86 (s, 1 H, Ar-H), 6.99 (d, $^3J_{5,4}$ = 12.2 Hz, 1 H, 5-H). − ^{13}C NMR (100 MHz): δ = 35.0 (NCH_3), 53.0 (C-1), 56.1 (OCH_3), 110.5 (Ar-C), 112.0 (Ar-C), 126.0 (C-4), 128.3 (C-5a/9a), 129.6 (C-5a/9a), 136.2 (C-5), 148.8 (C-7/8), 149.8 (C-7/8), 166.5 (C-3). − MS (70 eV; EI): *m/z* (%) = 233 (100) [M^+], 218 (17), 204 (37) [M − NCH_3]$^+$, 190 (18), 160 (10). − HRMS ($C_{13}H_{15}NO_3$): calcd. 233.1052; found 233.1052.

1,2-Dihydro-7,8-dimethoxy-2-phenyl-3*H*-benzazepin-3-one (9m): Treatment of **6m** (100 mg, 0.34 mmol; KOH, 2 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 1:2), gave **9m** (93 mg, 93%) as colourless crystals, m.p. 143−144 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 3005, 2930, 2840, 1640 (C=O), 1605, 1520, 1495, 1380, 1280, 1200, 1175, 1095 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.88 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.58 (s, 2 H, 1-H), 6.44 (d, $^3J_{4,5}$ = 12.2 Hz, 1 H, 4-H), 6.74 (s, 1 H, Ar-H), 6.91 (s, 1 H, Ar-H), 7.09 (d, $^3J_{5,4}$ = 12.2 Hz, 1 H, 5-H), 7.26 (m_c, 3 H, Ar-H), 7.38 (m_c, 2 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 54.5 (OCH_3), 56.1 (C-1), 110.5 (C-6/9), 112.2 (C-6/9), 125.9 (C-4), 126.4 (Ar-C), 126.9 (Ar-C) 128.4 (Ar-C_q), 129.2 (Ar-C), 130.0 (Ar-C_q), 136.9 (C-5), 143.1 (Ar-C_q), 149.0 (C-7/8), 150.0 (C-7/8), 166.1 (C-3). − MS (70 eV; EI): *m/z* (%) = 295 (71) [M^+], 266 (74), 149 (52), 77 (31), 69 (64), 57 (100). − HRMS ($C_{18}H_{17}NO_3$): calcd. 295.1208; found 295.1206.

1,2-Dihydro-7,8-dimethoxy-2-methyl-4-trimethylsilyl-3*H*-2-benzazepin-3-one (9n): Treatment of **6n** (91 mg, 0.30 mmol; KOH, 2 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 2:1, 1:2), gave **9n** (23 mg, 25%) and **9l** (30 mg, 43%; see above), both as colourless solids. Compound **9n**: M.p. 134−135 °C (diethyl ether). − IR (CCl_4): $\tilde{\nu}$ = 3005, 2950, 2900, 1620 (C=O), 1515, 1460, 1390, 1260, 1200, 1120 cm^{-1}. − ^1H NMR (250 MHz): δ = 0.29 (s, 9 H, $SiMe_3$), 3.06 (s, 3 H, NCH_3), 3.90 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 4.08 (s, 2 H, 1-H), 6.76 (s, 1 H, Ar-H), 6.86 (s, 1 H, Ar-H), 7.13 (s, 1 H, 5-H). − ^{13}C NMR (100 MHz): δ = −0.6 ($SiMe_3$), 34.6 (NCH_3), 52.8 (C-1), 56.2 (OCH_3), 110.1 (C-6/9), 111.9 (C-6/9), 130.0 (C_q), 130.1 (C_q), 141.4 (C-5), 142.0 (C_q), 148.1 (C-7/8), 149.5 (C-7/8), 169.4 (C-3). − MS (70 eV; EI): *m/z* (%) = 305 (15) [M^+], 290 (100), 274 (16), 221 (24), 73 (21) [$Si(CH_3)_3^+$]. − $C_{16}H_{23}NO_3Si$ (305.45): calcd. C 62.92, H 7.59, N 4.59; found C 62.85, H 7.40, N 4.55.

1,2-Dihydro-7,8-dimethoxy-2-methyl-4-(4′-methylphenyl)-3*H*-2-benzazepin-3-one (9o) and 1-(5′,6′-Dimethoxy-2′-methyl-2′*H*-isoindol-1′-yl)-2-(4′′-methylphenyl)ethan-1-one (20o): Treatment of **6o** (450 mg, 1.39 mmol; KOH, 5 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 5:1), gave **9o** (340 mg, 76%) and **20o** (54 mg, 12%). − **Compound 9o**: Colourless crystals, m.p. 181−182 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 3000, 2935, 2850, 1640 (C=O), 1600, 1515, 1465, 1395, 1275, 1200, 1125, 1015 cm^{-1}. − ^1H NMR (400 MHz): δ = 2.36 (s, 3 H, CH_3), 3.13 (s, 3 H, NCH_3), 3.90 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 4.22 (br. s, 2 H, 1-H), 6.80 (s, 1 H, 6/9-H), 6.92 (s, 1 H, 6/9-H), 7.19 (m_c, 2 H, Ar-H), 7.21 (s, 1 H, 5-H), 7.54 (m_c, 2 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 21.2 (CH_3), 34.5 (NCH_3), 53.0 (OCH_3), 56.2 (C-1), 110.1 (C-6/9), 112.3 (C-6/9), 127.9 (Ar-C), 128.9 (C_q), 129.1 (Ar-C), 129.4 (C_q), 130.9 (C-5), 136.4 (C_q), 137.6 (C_q), 138.2 (C_q), 148.9 (C-7/8), 149.3 (C-7/8), 166.9 (C-3). − MS (70 eV; EI): *m/z* (%) = 324 (22) [M^+], 323 (100), 308 (20), 204 (42), 149 (39). − $C_{20}H_{21}NO_3$ (323.39): calcd. C 74.28, H 6.55, N 4.33; found C 74.30, H 6.33, N 4.13. − **Compound 20o**: Pale yellow, non-crystalline solid. − IR (CCl_4): $\tilde{\nu}$ = 3005, 2935, 1705 (C=O), 1500, 1425, 1375, 1305, 1220, 1120, 1050 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.32 (s, 3 H, CH_3), 3.89 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 4.16 (s, 3 H, NCH_3), 4.26 (s, 2 H, 2-H), 6.89 (s, 1 H, 3′-H), 7.09−7.23 (m, 6 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 21.0 (CH_3), 40.0 (NCH_3), 46.5 (C-2), 55.7 (OCH_3), 55.8 (OCH_3), 99.1 (C-4′/7′), 99.4 (C-4′/7′), 119.0

(C_q), 121.2 (C_q), 124.7 (Ar-C), 129.3 (Ar-C), 132.3 (C_q), 136.1 (C_q), 147.5 (C-5′/6′), 150.8 (C-5′/6′), 186.1 (C-1). − MS (70 eV; EI): *m/z* (%) = 323 (4) [M^+], 221 (100), 206 (30), 177 (27), 121 (28), 105 (17). − HRMS ($C_{20}H_{21}NO_3$): calcd. 323.2222; found 323.2223.

2-(3′-Phenylprop-1′-ynyl)benzaldehyde (11): A degassed (Ar) solution of 2-iodobenzaldehyde[34] (619 mg, 2.67 mmol) in benzene (10 mL) was treated with $PdCl_2(PPh_3)_2$ (94 mg, 0.13 mmol), CuI (ca. 5 mg), 3-phenylprop-1-yne[35] (403 mg, 3.47 mmol) and dry Et_3N (102 mg, 2.93 mmol). After this had been stirred in a sealed tube for 2 h under Ar at room temp., dry Et_3N (0.5 mL) was added and the brown suspension was then heated for 4 h at ca. 40 °C. The mixture was filtered and the solution was concentrated in vacuo. Purification by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 60:1) gave **11** (426 mg, 73%) as a pale red oil. − IR (CCl_4): $\tilde{\nu}$ = 3065, 3030, 2840, 2745, 2230 (C≡C), 1700 (C=O), 1595, 1495, 1455, 1385, 1270, 1190 cm^{-1}. − ^1H NMR (400 MHz): δ = 3.91 (s, 2 H, 3′-H), 7.28 (m_c, 1 H, Ar-H), 7.33−7.38 (m, 2 H, Ar-H), 7.39−7.43 (m, 3 H, Ar-H), 7.50−7.58 (m, 2 H, Ar-H), 7.90 (m_c, 1 H, Ar-H), 10.56 (s, 1 H, CHO). − ^{13}C NMR (100 MHz): δ = 26.1 (C-3′), 78.4 (C-1′), 95.3 (C-2′), 127.0 (Ar-C), 127.2 (Ar-C), 127.4 (Ar-C_q), 128.0 (Ar-C), 128.3 (Ar-C), 128.8 (Ar-C), 133.5 (Ar-C), 133.8 (Ar-C), 136.1 (Ar-C_q), 136.2 (Ar-C_q), 192.0 (CHO). − MS (70 eV; EI): *m/z* (%) = 220 (73) [M^+], 219 (100), 192 (20), 191 (80), 165 (28), 115 (10). − HRMS ($C_{16}H_{12}O$): calcd. 220.0888; found 220.0880.

Methyl{[2′(3′′-phenylprop-1′′-ynyl)phenyl]methylene}amine *N*-Oxide (12): Treatment of **11** (180 mg, 0.78 mmol, 6 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 3:1), gave **12** (165 mg, 85%) as a reddish brown oil. − IR (CCl_4): $\tilde{\nu}$ = 3065, 3030, 2950, 1575, 1495, 1455, 1420, 1290, 1175 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.82 (s, 3 H, NCH_3), 3.89 (s, 2 H, 3′′-H), 7.24−7.45 (m, 7 H, Ar-H), 7.47−7.52 (m, 1 H, Ar-H), 7.93 (s, 1 H, 1-H) 9.22 (m_c, 1 H, 6′-H). − ^{13}C NMR (125 MHz): δ = 26.1 (C-3′′), 54.9 (NCH_3), 80.2 (C-1′′), 94.2 (C-2′′), 122.7 (Ar-C), 126.9 (Ar-C_q), 127.5 (Ar-C), 128.0 (Ar-C), 128.4 (Ar-C), 128.8 (Ar-C), 129.8 (Ar-C), 131.3 (Ar-C_q), 132.2 (Ar-C), 133.4 (C-1), 136.5 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 249 (21) [M^+], 232 (43), 158 (100) [M − CH_2Ph]$^+$, 130 (90), 103 (23). − HRMS ($C_{17}H_{15}NO$): calcd. 249.1154; found 249.1152.

2-[2′-(3′′-Bromoprop-2′′-ynyl)phenyl]-1,3-dioxolane (4p): A solution of **2d** (2.00 g, 7.68 mmol) in acetone (50 mL) was treated with silver nitrate (91 mg, 0.54 mmol) and NBS[36] (1.64 g, 9.22 mmol) and stirred at room temp. in the dark for 24 h. The reaction mixture was then cooled to 0 °C, diluted with cold water (30 mL) and extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (SiO_2; cyclohexane/ethyl acetate, 40:1) afforded **4p** (1.66 g, 81%) as a yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 2950, 2885, 1720, 1455, 1395, 1265, 1220, 1115, 1080, 1045 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.79 (s, 2 H, 1′′-H), 4.09 (m_c, 4 H, 4-H, 5-H), 5.97 (s, 1 H, 2-H), 7.30 (m_c, 1 H, Ar-H), 7.36 (m_c, 1 H, Ar-H), 7.49−7.57 (m, 2 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 23.0 (C-1′′), 40.8 (C-3′′), 65.2 (C-4, C-5), 77.7 (C-2′′), 102.1 (C-2), 126.5 (Ar-C), 127.0 (Ar-C), 129.2 (Ar-C), 129.5 (Ar-C), 134.5 (Ar-C_q), 134.8 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 267 (5) [M^+ − 1, for ^{81}Br], 265 (5) [M^+ − 1, for ^{79}Br], 187 (55) [M − Br]$^+$, 115 (100), 73 (50). − HRMS [M^+, for ^{79}Br] ($C_{12}H_{11}BrO_2$): calcd. 264.9864; found 264.9865.

2-(3′-Bromoprop-2′-ynyl)benzaldehyde (5p): Treatment of **4p** (200 mg, 0.75 mmol, 4 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 50:1), gave **5p** (133 mg, 80%) as a colourless oil, which rapidly turned yellow. − IR (CCl_4): $\tilde{\nu}$ = 2825, 2735, 1700 (C=O), 1600, 1575, 1490, 1450, 1400, 1320, 1295, 1195 cm^{-1}. − ^1H NMR (250 MHz): δ = 4.10 (s, 2 H, 1′-H), 7.48 (m_c, 1 H, Ar-H), 7.63 (m_c, 2 H, Ar-H), 7.81 (m_c, 1 H, Ar-H), 10.18 (s, 1 H, CHO). − ^{13}C NMR (125 MHz): δ = 23.9 (C-1′), 41.8 (C-3′), 77.2 (C-2′), 127.6 (Ar-C), 130.0 (Ar-C), 133.2 (Ar-C_q), 134.0 (Ar-C), 134.1 (Ar-C), 137.7 (Ar-C_q), 192.8 (CHO). − MS (70 eV; EI): *m/z* (%) = 225 (15) [M^+ + 1, for ^{81}Br], 223 (17) [M^+ + 1, for ^{79}Br], 149 (100), 143 (16) [M − Br]$^+$, 115 (58). − HRMS [M^+, for ^{79}Br] ($C_{10}H_7BrO$): calcd. 221.9680; found 221.9680.

{[2′-(3′′-Bromoprop-2′′-ynyl)phenyl]methylene}methylamine *N*-Oxide (6p): Treatment of **5p** (388 mg, 4.64 mmol, 4.5 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 2:1, 1:2), gave **6p** (297 mg, 33%) as a pale yellow solid, which rapidly turned brown. − M.p. 87−90 °C (decomp.). − IR (PTFE): $\tilde{\nu}$ = 3025, 2935, 1700, 1595, 1580, 1415, 1300, 1160 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.64 (s, 2 H, 1′′-H), 3.94 (s, 3 H, NCH_3), 7.35−7.39 (m, 3 H, Ar-H), 7.63 (s, 1 H, 1-H), 8.92−9.01 (m, 1 H, 6′-H). − MS (170 eV; CI, isobutane): *m/z* (%) = 254 (8) [M^+ + 1, for ^{81}Br], 252 (3) [M^+ + 1, for ^{79}Br], 238 (3), 236 (3), 225 (99), 223 (100), 145 (53).

1-Bromo-2-methyl-1,2-dihydro-3*H*-2-benzazepin-3-one (9′p): Treatment of **6p** (66 mg, 0.26 mmol, base, 30 min) according to the general procedure, after purification (cyclohexane/ethyl acetate, 1:1), afforded **9′p** (20 mg, 30%) as a pale brown oil. − IR (CCl_4): $\tilde{\nu}$ = 2995, 2940, 1645 (C=O), 1615, 1445, 1395, 1330, 1250, 1225, 1080, 1000 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.47 (br. s, 3 H, NCH_3), 5.30 (s, 1 H, 1-H), 6.41 (d, $^3J_{5,4}$ = 12.2 Hz, 1 H, 4-H), 7.02 (d, $^3J_{4,5}$ = 12.2 Hz, 1 H, 5-H), 7.33−7.51 (m, 4 H, Ar-H). − MS (70 eV; EI): *m/z* (%) = 188 (45), 173 (69), 172 (100) [M − Br]$^+$, 144 (74), 103 (47).

3-[3′-(Trimethylsilyl)prop-2′-ynyl]furan-2-carbaldehyde (22): A solution of *n*-butyllithium in *n*-hexane (2.4 M, 4.18 mL, 10.0 mmol) was added dropwise at −78 °C under N_2 to a solution of **21**[37] (2.00 g, 9.13 mmol) in dry THF (50 mL). After this had stirred for 1 h at −78 °C, a solution of $MgBr_2$ in diethyl ether (5 mL), freshly prepared from Mg (292 mg, 12.0 mmol) and dibromoethane (1.88 g, 10.0 mmol), was added slowly. After 2 h, 1-bromo-3-(trimethylsilyl-)prop-2-yne[32] (2.09 g, 10.1 mmol) was added, and the reaction mixture was allowed to warm to room temp. and stirred for 1 h. The solution was treated with a 1:1 mixture of satd. NH_4Cl and water and extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (SiO_2; cyclohexane/ethyl acetate, 30:1) afforded 1.31 g (58%) of a mixture containing the 3-propargyl derivatives, together with small amounts of the 5-isomer. Without separation of the regioisomers, liberation of the aldehyde function according to the general procedure, after purification (cyclohexane/ethyl acetate, 40:1), gave **22** (766 mg, 71%) as a yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 2960, 2815, 2180 (C≡C), 1685 (C=O), 1585, 1475, 1370, 1305, 1250, 1205 cm^{-1}. − ^1H NMR (250 MHz): δ = 0.16 (s, 9 H, $SiMe_3$), 3.82 (s, 2 H, 1′-H), 6.68 (md, $^3J_{4,5}$ = 1.2 Hz, 1 H, 4-H), 7.58 (d, $^3J_{5,4}$ = 1.2 Hz, 1 H, 5-H), 9.82 (s, 1 H, CHO). − ^{13}C NMR (100 MHz): δ = 0.0 ($SiMe_3$), 16.9 (C-1′), 87.0 (C-3′), 102.0 (C-2′), 114.6 (C-4), 131.9 (C-3), 147.1 (C-5), 148.0 (C-2), 178.9 (CHO). − MS (70 eV; EI): *m/z* (%) = 206 (12) [M^+], 191 (100), 163 (9), 133 (7), 73 (30) [$Si(CH_3)_3^+$]. − HRMS ($C_{11}H_{14}O_2Si$): calcd. 206.0763; found 206.0763.

Methyl({3′-[3′′-(trimethylsilyl)prop-2′′-ynyl]furan-2′-yl}-methylene)amine *N*-Oxide (23): Treatment of **22** (285 mg, 1.38 mmol, 4 h) according to the general procedure, after purifica-

tion (cyclohexane/ethyl acetate, 1:1, 1:2), gave **23** (259 mg, 80%) as colourless crystals, m.p. 69−71 °C (decomp.). − IR (CCl_4): $\tilde{\nu}$ = 2960, 2895, 2175 (C≡C), 1715, 1600, 1490, 1415, 1250, 1205, 1050, 1010 cm^{-1}. − ^1H NMR (250 MHz): δ = 0.14 (s, 9 H, $SiMe_3$), 3.74 (s, 2 H, 1′′-H), 3.83 (s, 3 H, NCH_3), 6.82 (d, $^3J_{4',5'}$ = 1.8 Hz, 1 H, 4′-H), 7.44 (s, 1 H, 1-H), 7.49 (d, $^3J_{5',4'}$ = 1.8 Hz, 1 H, 5′-H). − ^{13}C NMR (100 MHz): δ = 0.1 ($SiMe_3$), 17.1 (C-1′′), 53.5 (NCH_3), 86.0 (C-3′′), 103.5 (C-2′′), 113.9 (C-4′), 124.7 (C-3′), 125.9 (C-1), 141.7 (C-2′), 143.9 (C-5′). − MS (70 eV; EI): *m/z* (%) = 235 (20) [M^+], 220 (61), 190 (19), 134 (60), 73 (100) [$Si(CH_3)_3^+$]. − HRMS ($C_{12}H_{17}NO_2Si$): calcd. 235.1029; found 235.1030.

7-Methyl-7,8-dihydrofuro[2,3-*c*]azepin-6-one (24): Treatment of **23** (322 mg, 1.37 mmol; NaOMe, 4 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 2:1), gave **24** (204 mg, 91%) as colourless crystals, m.p. 73−75 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 2930, 2890, 1645 (C=O), 1615, 1570, 1390, 1255, 1205, 1130, 1085 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.05 (s, 3 H, NCH_3), 6.24 (d, $^3J_{4,5}$ = 11.9 Hz, 1 H, 4-H), 6.40 (d, $^3J_{6,7}$ = 2.1 Hz, 1 H, 6-H), 6.74 (d, $^3J_{5,4}$ = 11.9 Hz, 1 H, 5-H), 7.30 (d, $^3J_{7,6}$ = 2.1 Hz, 1 H, 7-H). − ^{13}C NMR (100 MHz): δ = 35.7 (NCH_3), 44.3 (C-8), 108.9 (C-3), 119.0 (C-3a), 124.7 (C-4/5), 127.4 (C-4/5), 141.1 (C-2), 149.4 (C-82), 166.5 (C-6). − MS (70 eV; EI): *m/z* (%) = 163 (100) [M^+], 135 (47), 134 (88) [$M - NCH_3]^+$, 107 (26), 106 (26). − HRMS ($C_9H_9NO_2$): calcd. 163.0633; found 163.0638.

2-(1′-Bromo-3′,4′-dihydronaphthalen-2′-yl)-1,3-dioxolane (25): A solution of 1-bromo-3,4-dihydronaphthalene-2-carbaldehyde[38] (21.7 g, 91.4 mmol) in benzene (300 mL) was treated with ethylene glycol (14.2 g, 0.23 mol) and PTSA (870 mg, 4.57 mmol) and heated to reflux in a Dean−Stark apparatus for 3 h. After cooling to room temp., the mixture was washed with satd. aqueous $NaHCO_3$ and with brine. The organic phase was concentrated in vacuo and the residue was purified by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 30:1), affording **25** (24.6 g, 96%) as colourless solid, m.p. 56 °C (diethyl ether). − IR (CCl_4): $\tilde{\nu}$ = 2950, 2885, 1625 (C=C), 1480, 1380, 1250, 1180, 1090 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.43 (t, $^3J_{3',4'}$ = 7.9 Hz, 2 H, 3′-H), 2.83 (t, $^3J_{4',3'}$ = 7.9 Hz, 2 H, 4′-H), 4.04 (m_c, 4 H, 4-H, 5-H), 5.99 (s, 1 H, 2-H), 7.08−7.13 (m, 1 H, Ar-H), 7.23 (m_c, 2 H, Ar-H), 7.65−7.70 (m, 1 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 23.6 (C-3′/4′), 27.9 (C-3′/4′), 65.7 (C-4, C-5), 104.3 (C-2), 126.7 (Ar-C), 127.1 (Ar-C), 127.6 (Ar-C), 128.8 (Ar-C), 131.4 (C_q), 133.6 (C_q), 135.2 (C_q), 137.2 (C_q). − MS (70 eV; EI): *m/z* (%) = 282 (24) [M^+, for ^{81}Br], 280 (23) [M^+, for ^{79}Br], 201 (45) [$M - Br]^+$, 129 (100). − $C_{13}H_{13}BrO_2$ (281.15): calcd. C 55.54, H 4.66; found C 55.72, H 4.67.

{3-[2′-(1′′,3′′-Dioxolan-2′′-yl)-3′,4′-dihydronaphthalen-1′-yl]prop-1-ynyl}trimethylsilane (26): A solution of *n*-butyllithium in *n*-hexane (2.4 M, 6.50 mL, 15.7 mmol) was added dropwise at −78 °C under N_2 to a solution of **25** (4.00 g, 14.3 mmol) in dry THF (100 mL). After this had stirred for 2 h at −78 °C, a solution of $MgBr_2$ in diethyl ether (15 mL), freshly prepared from Mg (540 mg, 22.2 mmol) and dibromoethane (3.20 mg, 17.1 mmol), was added slowly and the reaction mixture was allowed to warm to room temp. After 2 h, 1-bromo-3-(trimethylsilyl)prop-2-yne[32] (3.26 g, 17.1 mmol) was added and the solution was refluxed for 2 h. After cooling to room temp., the solution was treated with a 1:1 mixture of satd. NH_4Cl and water and extracted with diethyl ether (3 × 60 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (SiO_2; cyclohexane/ethyl acetate, 40:1) afforded **26** (3.90 g, 88%) as a colourless solid. − M.p. 98 °C (diethyl ether). − IR (CCl_4): $\tilde{\nu}$ = 2960, 2890, 2175 (C≡C), 1490, 1450, 1385, 1250, 1185, 1090, 1000 cm^{-1}. − ^1H NMR (400 MHz): δ = 0.10 (s, 9 H, $SiMe_3$), 2.32 (t, $^3J_{3',4'}$ = 7.9 Hz, 2 H, 3′-H), 2.74 (t, $^3J_{4',3'}$ = 7.9 Hz, 2 H, 4′-H), 3.50 (s, 2 H, 3-H), 4.02 (m_c, 4 H, 4′′-H, 5′′-H), 5.83 (s, 1 H, 2′′-H), 7.11−7.25 (m, 3 H, Ar-H), 7.56 (m_c, 1 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 0.1 [$Si(CH_3)_3$], 18.4 (C-3), 19.3 (C-3′/4′), 21.5 (C-3′/4′), 65.5 (C-4′′, C-5′′), 85.7 (C-1), 101.2 (C-2′′), 104.3 (C-2), 124.2 (Ar-C), 126.4 (Ar-C), 127.3 (Ar-C), 127.5 (Ar-C), 131.8 (C_q), 133.3 (C_q), 134.8 (C_q), 137.0 (C_q). − MS (70 eV; EI): *m/z* (%) = 312 (13) [M^+], 239 (43) [$M - Si(CH_3)_3]^+$, 201 (68), 129 (85), 73 (100) [$Si(CH_3)_3^+$]. − $C_{19}H_{24}O_2Si$ (312.48): calcd. C 73.03, H 7.74; found C 73.17, H 7.76.

2-[3′,4′-Dihydro-1′-(prop-2′′-ynyl)naphthalen-2′-yl]-1,3-dioxolane (27): A solution of **26** (8.31 g, 26.6 mmol) in dry methanol (150 mL) was treated with K_2CO_3 (3.68 g, 26.6 mmol) and stirred at room temp. for 6 h. After ca. 100 mL of the solvent had been distilled off, water (100 mL) was added and the mixture was extracted with diethyl ether (3 × 50 mL). The combined organic phases were washed with satd. aqueous NH_4Cl and with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (SiO_2; cyclohexane/ethyl acetate, 30:1) afforded **27** (6.24 g, 98%) as colourless crystals, m.p. 60 °C (diethyl ether). − IR (CCl_4): $\tilde{\nu}$ = 3315 (≡C−H), 2945, 2890, 2830, 2115 (C≡C), 1445, 1385, 1235, 1185, 1095, 1005 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.04 (t, $^4J_{3'',1''}$ = 2.7 Hz, 1 H, 3′′-H), 2.33 (t, $^3J_{3',4'}$ = 7.8 Hz, 2 H, 3′-H), 2.76 (t, $^3J_{4',3'}$ = 7.8 Hz, 2 H, 4′-H), 3.49 (d, $^4J_{1'',3''}$ = 2.7 Hz, 2 H, 1′′-H), 4.04 (m_c, 4 H, 4-H, 5-H), 5.84 (s, 1 H, 2-H), 7.11−7.29 (m, 3 H, Ar-H), 7.53 (m_c, 1 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 17.6 (C-1′′), 21.2 (C-3′/4′), 28.2 (C-3′/4′), 65.5 (C-4, C-5), 69.3 (C-3′′), 81.9 (C-1′′), 101.1 (C-2), 123.9 (Ar-C), 126.5 (Ar-C), 127.4 (Ar-C), 127.6 (Ar-C), 131.6 (C_q), 133.5 (C_q), 134.4 (C_q), 136.9 (C_q). − MS (70 eV; EI): *m/z* (%) = 240 (76) [M^+], 201 (97), 167 (100), 129 (99). − $C_{16}H_{16}O_2$ (240.30): calcd. C 79.97, H 6.71; found C 79.81, H 6.71.

2-[1′-(But-2′′-ynyl)-3′,4′-dihydronaphthalene-2′-yl]-1,3-dioxolane (28): A solution of *n*-butyllithium in *n*-hexane (2.4 M, 7.0 mL, 16.8 mmol) was added at −78 °C under N_2 to a solution of **27** (3.66 g, 14.2 mmol) in dry THF (75 mL). The mixture was stirred for 2 h and a solution of methyl iodide (2.38 g, 16.8 mmol) in dry THF (5 mL) was added at −78 °C. The mixture was allowed to warm to room temp. and stirred for a further 3 h. A 1:1 mixture of satd. NH_4Cl and water was added and the reaction mixture was extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (SiO_2; cyclohexane/ethyl acetate, 30:1) afforded **28** (3.07 g, 79%) as a yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 2945, 2885, 2830, 1490, 1450, 1385, 1185, 1090, 1005 cm^{-1}. − ^1H NMR (250 MHz): δ = 1.74 (t, $^5J_{4'',1''}$ = 2.6 Hz, 3 H, 4′′-H), 2.31 (t, $^3J_{3',4'}$ = 7.9 Hz, 2 H, 3′-H), 2.75 (t, $^3J_{4',3'}$ = 7.9 Hz, 2 H, 4′-H), 3.40 (m_c, 2 H, 1′′-H), 4.03 (m_c, 4 H, 4-H, 5-H), 5.84 (s, 1 H, 2-H), 7.10−7.28 (m, 3 H, Ar-H), 7.55 (m_c, 1 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 3.8 (C-4′′), 17.9 (C-3′/4′), 21.4 (C-3′/4′), 28.3 (C-1′′), 65.6 (C-3, C-4), 69.3 (C-2′′/3′′), 76.6 (C-2′′/3′′), 101.2 (C-2), 124.1 (Ar-C), 126.4 (Ar-C), 127.3 (Ar-C), 127.4 (Ar-C), 132.6 (C_q), 132.7 (C_q), 134.8 (Cq), 137.0 (C_q). − MS (70 eV; EI): *m/z* (%) = 254 (12) [M^+], 182 (59), 167 (90), 129 (100), 73 (69). − HRMS ($C_{17}H_{18}O_2$): calcd. 254.1307; found 254.1305.

3,4-Dihydro-1-(prop-2′-ynyl)naphthalene-2-carbaldehyde (29a): Treatment of **27** (1.78 g, 7.35 mmol, 1 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 40:1), gave **29a** (1.44 g, 99%) as a yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 3310 (≡C−H), 2945, 2895, 2835, 2750, 2120 (C≡C), 1665 (C=O), 1615, 1440, 1365, 1300, 1240, 1155 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.13 (t, $^4J_{3',1'}$ = 2.7 Hz, 1 H, 3′-H), 2.54 (m_c, 2 H, 3-H), 2.77 (m_c, 2 H, 4-H), 3.87 (d, $^4J_{1',3'}$ = 2.7 Hz, 2 H, 1′-H), 7.19−7.28 (m, 1 H, Ar-

H), 7.32 (m_c, 2 H, Ar-H), 7.67−7.75 (m, 1 H, Ar-H), 10.37 (s, 1 H, CHO). − ^{13}C NMR (100 MHz): δ = 16.8 (C-1′), 20.5 (C-3/4), 27.5 (C-3/4), 70.2 (C-3′), 80.8 (C-2′), 125.4 (Ar-C), 127.0 (Ar-C), 128.1 (Ar-C), 130.3 (Ar-C), 133.6 (C_q), 134.4 (C_q), 139.0 (C_q), 146.0 (C_q), 190.2 (CHO). − MS (70 eV; EI): *m*/*z* (%) = 195 (100) [M^+], 177 (38), 167 (55), 152 (52), 128 (34). − HRMS ($C_{14}H_{12}O$): calcd. 196.0888; found 196.0886.

1-(But-2′-ynyl)-3,4-dihydronaphthalene-2-carbaldehyde (29b): Treatment of **28** (1.01 g, 3.95 mmol, 5 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 40:1), gave **29b** (679 mg, 84%) as pale yellow crystals, m.p. 63−64 °C (diethyl ether). − IR (CCl_4): ṽ = 2920, 2860, 1665 (C=O), 1610, 1565, 1450, 1365, 1295, 1180 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 1.76 (t, $^5J_{4',1'}$ = 2.6 Hz, 3 H, 4′-H), 2.48−2.58 (m, 2 H, 3/4-H), 2.71−2.80 (m, 2 H, 3/4-H), 3.79 (q, $^5J_{1',4'}$ = 2.6 Hz, 2 H, 1′-H), 7.18−7.25 (m, 2 H, Ar-H) 7.32 (m_c, 1 H, Ar-H), 7.74 (m_c, 1 H, Ar-H), 10.37 (s, 1 H, CHO). − ^{13}C NMR (100 MHz): δ = 3.7 (C-4′), 17.1 (C-1′), 20.3 (C-3/4), 27.5 (C-3/4), 75.7 (C-2′′/3′′), 78.1 (C-2′′′/3′′′), 125.6 (Ar-C), 126.9 (Ar-C), 128.0 (Ar-C), 130.2 (Ar-C), 134.0 (C_q), 139.0 (C_q), 147.5 (C_q), 190.6 (CHO). − MS (70 eV; EI): *m*/*z* (%) = 210 (43) [M^+], 209 (76), 195 (100), 181 (20), 165 (63). − $C_{15}H_{14}O$ (210.27): calcd. C 85.68, H 6.71; found C 85.47, H 6.81.

Methyl{[3′,4′-dihydro-1′-(prop-2′′-ynyl)naphthalen-2′-yl]-methylene}amine *N*-Oxide (30a): Treatment of **29a** (1.54 g, 7.85 mmol, 7 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 1:2), gave **30a** (1.10 g, 62%) as beige crystals, m.p. 108−109 °C (ethanol, decomp.). − IR (CCl_4): ṽ = 3310 (≡C−H), 3020, 2945, 2890, 2830, 1545, 1420, 1250, 1195, 1160, 1125 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.06 (t, $^4J_{3'',1''}$= 2.7 Hz, 1 H, 3′′-H), 2.75 (m_c, 2 H, 3′-H), 2.93 (m_c, 2 H, 4′-H), 3.43 (d, $^4J_{1'',3''}$= 2.7 Hz, 2 H, 1′′-H), 3.83 (s, 3 H, NCH_3), 7.13−7.29 (m, 3 H, Ar-H), 7.43 (s, 1 H, 1-H), 7.46−7.51 (m, 1 H, 8′-H). − ^{13}C NMR (100 MHz): δ = 18.9 (C-1′′), 20.5 (C-3′/4′), 28.1 (C-3′/4′), 54.4 (NCH_3), 69.8 (C-3′′), 81.1 (C-2′′), 124.1 (Ar-C), 126.6 (Ar-C), 127.5 (Ar-C), 128.2 (Ar-C), 129.2 (C_q), 133.9 (C_q), 134.0 (C_q), 134.3 (C-1), 137.7 (C_q). − MS (70 eV; EI): *m*/*z* (%) = 225 (39) [M^+], 196 (86), 182 (100), 167 (37), 152 (19), 115 (19). − HRMS ($C_{15}H_{15}NO$): calcd. 225.1154; found 225.1153.

{[1′-(But-2′′-ynyl)-3′,4′-dihydronaphthalen-2′-yl]-methylene}methylamine *N*-Oxide (30b): Treatment of **29b** (200 mg, 0.95 mmol, 6 h) according to the general procedure, after purification (ethyl acetate/methanol, 10:1), gave **30b** (142 mg, 62%) as beige crystals, m.p. 136−137 °C (acetone, decomp.). − IR (CCl_4): ṽ = 3025, 2940, 2890, 2830, 1670, 1545, 1415, 1175, 1155 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 1.75 (t, $^5J_{4'',1''}$= 2.6 Hz, 3 H, 4′′-H), 2.69−2.79 (m, 2 H, 3′/4′-H), 2.90−3.00 (m, 2 H, 3′/4′-H), 3.35 (q, $^5J_{1'',4''}$= 2.6 Hz, 2 H, 1′′-H), 3.82 (s, 3 H, NCH_3), 7.12−7.28 (m, 3 H, Ar-H), 7.44 (s, 1 H, 1-H), 7.48−7.53 (m, 1 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 3.7 (C-4′′), 19.2 (C-1′′), 23.3 (C-3′/4′), 28.2 (C-3′/4′), 54.3 (NCH_3), 75.8 (C-2′′/3′′), 77.1 (C-2′′/3′′), 124.3 (Ar-C), 126.6 (Ar-C), 127.4 (Ar-C), 128.1 (Ar-C), 128.7 (C_q), 134.3 (C_q), 134.5 (C-1), 135.3 (C_q), 137.8 (C_q). − MS (70 eV; EI): *m*/*z* (%) = 239 (36) [M^+], 196 (100), 186 (96), 167 (41), 165 (51). − $C_{16}H_{17}NO$ (239.32): calcd. C 80.20, H 7.16, N 5.85; found C 80.05, H 7.31, N 5.93.

4-Methyl-2,4,6,7-tetrahydro-3*H*-naphtho[2,1-*c*]azepin-3-one (31a) and 1-(2′-Methyl-4′,5′-dihydro-2′*H*-benzo[*e*]isoindol-1′-yl)ethan-1-one (32a): Treatment of **30a** (100 mg, 0.44 mmol; KOH, 1.5 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 2:1), gave **31a** (62 mg, 62%) and **32a** (17 mg, 17%). − **Compound 31a:** Colourless solid, m.p. 145−146 °C (ethanol). − IR (CCl_4): ṽ = 3015, 2930, 2855, 1675 (C=O), 1590, 1480, 1375, 1305, 1275, 1200, 1060 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.55 (mt, $^3J_{6,7}$ = 6.4 Hz, 2 H, 6-H), 2.93 (t, $^3J_{7,6}$ = 6.4 Hz, 2 H, 7-H), 3.06 (d, $^3J_{2,1}$ = 7.3 Hz, 2 H, 2-H), 3.11 (s, 3 H, NCH_3), 6.19 (t, $^3J_{1,2}$ = 7.3 Hz, 1 H, 1-H), 7.08−7.23 (m, 3 H, Ar-H), 7.60−7.69 (m, 1 H, Ar-H). − ^{13}C NMR (125 MHz): δ = 29.7 (C-6/7), 31.6 (C-6/7), 35.3 (NCH_3), 37.3 (C-2), 115.3 (Ar-C), 123.0 (C-1), 126.0 (C_q), 126.6 (Ar-C), 127.2 (Ar-C), 127.6 (Ar-C), 129.0 (C-5), 132.7 (C_q), 135.3 (C_q), 136.3 (C_q), 167.1 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 225 (60) [M^+], 196 (100) [$M - NCH_3]^+$, 167 (12), 152 (12), 128 (14). − $C_{15}H_{15}NO$ (225.29): calcd. C 79.97, H 6.71, N 6.22; found C 79.90, H 6.72, N 6.22. − **Compound 32a**: Pale yellow oil. − IR (CCl_4): ṽ = 3020, 2935, 2835, 1650 (C=O), 1515, 1435, 1400, 1375, 1305, 1195 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.50−2.61 (m, 2 H, 4′/5′-H), 2.52 (s, 3 H, 2-H), 2.78−2.88 (m, 2 H, 4′/5′-H), 3.80 (s, 3 H, NCH_3), 6.59 (s, 1 H, 3′-H), 7.13−7.34 (m, 4 H, Ar-H). − ^{13}C NMR (125 MHz): δ = 20.7 (C-4′/5′), 30.1 (C-2/4′/5′), 31.0 (C-2/4′/5′), 37.2 (NCH_3), 121.8 (C_q), 124.4 (Ar-C), 126.3 (Ar-C), 127.6 (C_q), 127.8 (Ar-C), 127.9 (C_q), 128.3 (Ar-C), 131.3 (C_q), 137.8 (C-3′), 192.3 (C-1). − MS (70 eV; EI): *m*/*z* (%) = 225 (93) [M^+], 210 (100), 182 (20) [$M - COCH_3]^+$, 141 (24). − HRMS ($C_{15}H_{15}NO$): calcd. 225.1154; found 225.1155.

2,4-Dimethyl-2,4,6,7-tetrahydro-3*H*-naphtho[2,1-*c*]azepin-3-one (31b) and 1-(2-Methyl-4,5-dihydro-2*H*-benzo[*c*]isoindol-1-yl)propan-1-one (32b): Treatment of **30b** (86 mg, 0.36 mmol, 1 equiv. NaOMe, 5 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 3:1), gave **31b** (55 mg, 64%) and **32b** (15 mg, 18%). − **Compound 31b**: Pale yellow solid, m.p. 195−198 °C (ethanol). − IR (CCl_4): ṽ = 2975, 2935, 1675 (C=O), 1585, 1450, 1380, 1265, 1235, 1110, 1075 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 1.52 (d, $^3J_{CH3,2}$ = 6.6 Hz, 3 H, 2-CH_3), 2.42−2.54 (m, 1 H, 2-H), 2.56−2.72 (m, 2 H, 6-H), 2.93 (m_c, 2 H, 7-H), 3.13 (s, 3 H, NCH_3), 5.87 (d, $^3J_{1,2}$ = 5.8 Hz, 1 H, 1-H), 6.18 (d, ^4J = 1.5 Hz, 1 H, 5-H), 7.06−7.23 (m, 3 H, Ar-H), 7.60−7.68 (m, 1 H, Ar-H). − ^{13}C NMR (125 MHz): δ = 15.0 (2-CH_3), 29.5 (C-6/7), 31.6 (C-6/7), 35.6 (C-2), 39.6 (NCH_3), 122.9 (Ar-C/C-1), 123.1 (Ar-C/C-1), 126.2 (C_q), 126.6 (Ar-C/C-5), 126.7 (Ar-C/C-5), 127.5 (Ar-C/C-5), 129.0 (Ar-C/C-5), 132.7 (C_q), 133.6 (C_q), 136.3 (C_q), 169.1 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 239 (61) [M^+], 238 (100), 224 (16), 196 (97), 182 (15). − HRMS ($C_{16}H_{17}NO$): calcd. 239.1310; found 239.1306. − **Compound 32b**: Pale yellow oil. − IR (CCl_4): ṽ = 3065, 2935, 2835, 1650 (C=O), 1515, 1435, 1375, 1305, 1185, 1145 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 1.19 (t, $^3J_{3,2}$ = 7.5 Hz, 3 H, 3-H), 2.85 (q, $^3J_{2,3}$ = 7.5 Hz, 2 H, 2-H), 3.75 (s, 3 H, NCH_3), 6.58 (s, 1 H, 3′-H), 7.14−7.21 (m, 4 H, Ar-H). − MS (70 eV; EI): *m*/*z* (%) = 239 (26) [M^+], 210 (68), 182 (100), 167 (41). − HRMS ($C_{16}H_{17}NO$): calcd. 239.1310; found 239.1311.

1-Bromo-7-fluoro-3,4-dihydronaphthalene-2-carbaldehyde (35b): PBr_3 (1.01 g, 3.72 mmol) was added at 0 °C to a solution of DMF (268 mg, 3.66 mmol) in dry $CHCl_3$ (5 mL). After this had stirred for 1.5 h, a solution of **34b**[39] (200 mg, 1.22 mmol) in dry $CHCl_3$ (5 mL) was added. The reaction mixture was allowed to warm to room temp. (1 h) and was then heated to 50 °C for 1.5 h. After cooling to room temp., the solution was poured into a cold 1:1 mixture of satd. $NaHCO_3$ and water, neutralized with solid $NaHCO_3$, and extracted with chloroform (4 × 10 mL). The combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2; cyclohexane/ethyl acetate, 40:1) gave **35b** (183 mg, 59%) as a yellow solid. − M.p. 55−56 °C (diethyl ether). − IR (CCl_4): ṽ = 2945, 2900, 2860, 1670 (C=O), 1565, 1485, 1435, 1350, 1270, 1240, 1180, 1145, 1100 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.62 (m_c, 2 H, 3-H), 2.81 (m_c,

2 H, 4-H), 7.05 (m_c, 1 H, Ar-H), 7.18 (m_c, 1 H, Ar-H), 7.62 (m_c, 1 H, Ar-H), 10.24 (s, 1 H, CHO). − ^{13}C NMR (125 MHz): δ = 23.1 (C-3/4), 26.4 (C-3/4), 115.7 (d, $^2J_{6,F}$ = 24.8 Hz, C-6/8), 117.8 (d, $^2J_{8,F}$ = 21.5 Hz, C-6/8), 129.0 (d, $^3J_{5,F}$ = 7.9 Hz, C-5), 134.5 (d, $^4J_{4a,F}$ = 3.0 Hz, C-4a), 134.9 (d, $^3J_{8a,F}$ = 8.2 Hz, C-8a), 135.4 (C-2), 137.3 (d, $^4J_{1,F}$ = 2.4 Hz, C-1), 161.8 (d, $^1J_{7,F}$ = 244.6 Hz, C-7), 193.0 (CHO). − MS (70 eV; EI): *m*/*z* (%) = 256 (27) [M^+, for ^{81}Br], 254 (27) [M^+, for ^{79}Br], 175 (15) [$M - Br]^+$, 147 (74), 146 (100), 144 (100). − $C_{11}H_8BrFO$ (255.08): calcd. C 51.79, H 3.16; found C 51.60, H 3.13.

9-Bromo-6,7-dihydro-5*H*-benzo[*a*]cycloheptene-8-carbaldehyde (35c): PBr_3 (4.22 g, 15.6 mmol) was added at 0 °C to a solution of DMF (1.37 g, 18.7 mmol) in dry $CHCl_3$ (10 mL). After this had stirred for 1.5 h, a solution of **34c** (1.00 g, 6.24 mmol) in dry $CHCl_3$ (5 mL) was added. The reaction mixture was allowed to warm to room temp. (1 h) and then refluxed for 3 h. After cooling to room temp., the solution was poured into a cold 1:1 mixture of satd. $NaHCO_3$ and water, neutralized with solid $NaHCO_3$ and extracted with chloroform (4 × 10 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. Flash chromatography (SiO_2; cyclohexane/ethyl acetate, 20:1) gave **35c** (587 mg, 37%) as a colourless oil. − IR (CCl_4): ṽ = 2940, 2860, 1675 (C=O), 1600, 1580, 1565, 1445, 1250, 1150, 1020 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.06−2.27 (m, 4 H, 6-H, 7-H), 2.60 (t, $^3J_{5,6}$ = 6.9 Hz, 2 H, 5-H), 7.23 (m_c, 1 H, Ar-H), 7.36 (m_c, 2 H, Ar-H), 7.67 (m_c, 1 H, Ar-H), 10.21 (s, 1 H, CHO). − ^{13}C NMR (125 MHz): δ = 23.7 (C-6), 32.0 (C-5/7), 33.5 (C-5/7), 126.8 (Ar-C), 128.9 (Ar-C), 129.8 (Ar-C), 130.6 (Ar-C), 138.6 (C_q), 139.3 (C_q), 139.4 (C_q), 140.5 (C_q), 192.7 (CHO). − MS (70 eV; EI): *m*/*z* (%) = 252 (35) [M^+, for ^{81}Br], 250 (35) [M^+, for ^{79}Br], 171 (82), 142 (85), 128 (89), 115 (91). − HRMS ($C_{12}H_{11}BrO$) [M^+, for ^{79}Br]: calcd: 249.9993; found 249.9994.

3,4-Dihydro-1-(3′-phenylprop-1′-ynyl)naphthalene-2-carbaldehyde (36a): A degassed (Ar) solution of **35a** (2.00 g, 8.44 mmol) in benzene (80 mL) was treated with $PdCl_2(PPh_3)_2$ (296 mg, 0.42 mmol), CuI (ca. 10 mg) and 3-phenylprop-1-yne[35] (1.08 g, 9.28 mmol). After 15 min, K_3CO_3 (2.33 g, 16.9 mmol) was added, the mixture was stirred for 8 h at room temp., dry Et_3N (2 mL) was added, and stirring was continued for a further 21 h. The reaction mixture was filtered and the solution was concentrated in vacuo. Purification of the brown residue by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 60:1) afforded **36a** (1.25 g, 54%) as pale yellow crystals, m.p. 110 °C (diethyl ether). − IR (CCl_4): ṽ = 3030, 2945, 2895, 2220 (C≡C), 1665 (C=O), 1600, 1495, 1455, 1365, 1305, 1190 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.59 (t, $^3J_{3,4}$ = 8.0 Hz, 2 H, 3-H), 2.82 (t, $^3J_{4,3}$ = 8.0 Hz, 2 H, 4-H), 3.97 (s, 2 H, 3′-H), 7.16−7.27 (m, 1 H, Ar-H), 7.24−7.44 (m, 7 H, Ar-H), 7.82−7.87 (m, 1 H, Ar-H), 10.40 (s, 1 H, CHO). − ^{13}C NMR (100 MHz): δ = 19.8 (C-3/4), 26.2 (C-3/4/3′), 26.8 (C-3/4/3′), 76.4 (C-1′), 100.2 (C-2′), 126.9 (Ar-C), 127.0 (Ar-C), 127.3 (Ar-C), 127.9 (Ar-C), 130.6 (Ar-C), 132.6 (C_q), 135.8 (C_q), 136.4 (C_q), 137.7 (C_q), 140.3 (C_q), 192.5 (CHO). − MS (70 eV; EI): *m*/*z* (%) = 272 (100) [M^+], 243 (32), 165 (40), 91 (40). − $C_{20}H_{16}O$ (272.34): calcd. C 88.20, H 5.92; found C 88.30, H 5.81.

7-Fluoro-3,4-dihydro-1-(3′-phenylprop-1′-ynyl)naphthalene-2-carbaldehyde (36b): A degassed (Ar) solution of **35b** (500 mg, 1.96 mmol) in benzene (20 mL) was treated with $PdCl_2(PPh_3)_2$ (70 mg, 0.10 mmol), CuI (ca. 5 mg), and 3-phenylprop-1-yne[35] (250 mg, 2.16 mmol) and stirred in a sealed tube for 15 min K_2CO_3 (524 mg, 3.92 mmol) was added and the suspension was stirred under argon at ca. 50 °C for 3 h. After addition of 0.5 mL of Et_3N, stirring was continued at room temp. for 4 h. The brown mixture was filtered and the solution was concentrated in vacuo. Purification by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 100:1) gave **36b** (416 mg, 75%) as a yellow viscous oil. − IR (CCl_4): ṽ = 3035, 2945, 2840, 2215 (C≡C), 1670 (C=O), 1565, 1495, 1365, 1305, 1265, 1195 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.52−2.63 (m, 2 H, 3-H), 2.71−2.83 (m, 2 H, 4-H), 3.97 (s, 2 H, 3′-H), 7.01 (m_c, 1 H, Ar-H), 7.10−7.19 (m, 1 H, Ar-H), 7.23−7.43 (m, 5 H, Ar-H), 7.53 (m_c, 1 H, Ar-H), 10.39 (s, 1 H, CHO). − ^{13}C NMR (100 MHz): δ = 20.1 (C-3/4), 26.1 (C-3/4), 26.2 (C-3′), 76.0 (C-2′), 100.7 (C-1′), 114.1 (d, ^2J = 23.3 Hz, C-6/8), 117.1 (d, ^2J = 21.8 Hz, C-6/8), 127.2 (Ar-C), 128.0 (Ar-C), 128.9 (Ar-C), 129.1 (d, $^3J_{5,F}$ = 7.3 Hz, C-5), 132.2 (d, $^4J_{4a,F}$ = 2.9 Hz, C-4a), 134.4 (d, $^3J_{8a,F}$ = 7.3 Hz, C-8a), 135.3 (C_q), 135.7 (C_q), 141.1 (C_q), 161.8 (d, $^1J_{7,F}$ = 244.1 Hz, C-7), 192.4 (CHO). − MS (70 eV; EI): *m*/*z* (%) = 290 (68) [M^+], 261 (23), 183 (54), 91 (100), 77 (21). − HRMS ($C_{20}H_{15}FO$): calcd. 290.1107; found 290.1107.

6,7-Dihydro-9-(3′-phenylprop-1′-ynyl)-5*H*-benzo[*a*]cycloheptene-8-carbaldehyde (36c): A degassed (Ar) solution of **35c** (1.19 g, 4.74 mmol) in benzene (20 mL) was treated with $PdCl_2(PPh_3)_2$ (330 mg, 0.47 mmol), CuI (ca. 10 mg) and 3-phenylprop-1-yne[35] (660 mg, 5.69 mmol) and stirred in a sealed tube for 15 min. After addition of dry Et_3N (527 mg, 5.21 mmol), the suspension was stirred under argon at room temp. for 2 h and then maintained at 40 °C for 2 h. The dark red mixture was filtered and the solution was concentrated in vacuo. Purification by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 60:1) gave **36c** (868 mg, 76%) as a yellow, viscous oil. − IR (CCl_4): ṽ = 3065, 3030, 2940, 2860, 2215 (C≡C), 1675 (C=O), 1600, 1560, 1450, 1360, 1270, 1180, 1020 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.10−2.27 (m, 4 H, 6-H, 7-H), 2.58 (t, $^3J_{5,6}$ = 6.9 Hz, 2 H, 5-H), 3.90 (s, 2 H, 3′-H), 7.22−7.37 (m, 8 H, Ar-H), 7.60−7.68 (m, 1 H, Ar-H), 10.44 (s, 1 H, CHO). − ^{13}C NMR (100 MHz): δ = 21.4 (C-6), 26.3 (C-5/7), 32.0 (C-5/7), 34.2 (C-3′), 79.3 (C-1′), 99.2 (C-2′), 126.5 (Ar-C), 127.0 (Ar-C), 128.0 (Ar-C), 128.6 (Ar-C), 128.8 (Ar-C), 129.3 (Ar-C), 129.6 (Ar-C), 135.9 (C_q), 138.6 (C_q), 140.9 (C_q), 141.0 (C_q), 145.0 (C_q), 192.3 (CHO). − MS (70 eV; EI): *m*/*z* (%) = 286 (26) [M^+], 195 (100), 165 (35), 91 (32). − HRMS ($C_{21}H_{18}O$): calcd. 286.1358; found 286.1357.

Methyl{[3′,4′-dihydro-1′-(3′′-phenylprop-1′′-ynyl)naphthalen-2′-yl]-methylene}amine *N*-Oxide (37a): Treatment of **36a** (500 mg, 1.84 mmol, 6 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 1:2), gave **37a** (523 mg, 94%) as a yellow oil. − IR (CCl_4): ṽ = 3065, 3030, 2945, 2890, 1545, 1450, 1420, 1195, 1175, 1145 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.78 (t, $^3J_{3',4'}$ = 7.9 Hz, 2 H, 3′/4′-H), 3.22 (t, $^3J_{3',4'}$ = 7.9 Hz, 2 H, 3′/4′-H), 3.73 (s, 3 H, NCH_3), 3.95 (s, 2 H, 3′′-H), 7.10−7.16 (m, 1 H, Ar-H), 7.22 (m_c, 2 H, Ar-H), 7.27−7.45 (m, 5 H, Ar-H), 7.66 (m_c, 1 H, Ar-H), 7.74 (s, 1 H, 1-H). − ^{13}C NMR (125 MHz): δ = 22.9 (C-3′/4′), 26.3 (C-3′/4′/3′′), 27.4 (C-3′/4′/3′′), 54.6 (NCH_3), 78.7 (C-1′′), 99.0 (C-2′′), 123.8 (C_q), 126.5 (Ar-C), 126.6 (Ar-C), 127.0 (Ar-C), 127.2 (Ar-C), 128.0 (Ar-C), 128.6 (Ar-C), 128.7 (Ar-C), 128.8 (C_q), 133.1 (C_q), 136.4 (C_q), 136.5 (C_q), 136.6 (C-1). − MS (70 eV; EI): *m*/*z* (%) = 301 (18) [M^+], 210 (100), 141 (21), 115 (11), 91 (7). − HRMS ($C_{21}H_{19}NO$): calcd. 301.1467; found 301.1467.

{[7′-Fluoro-3′,4′-dihydro-1′-(3′′-phenylprop-1′′-ynyl)naphthalen-2′-yl]methylene}methylamine *N*-Oxide (37b): Treatment of **36b** (280 mg, 0.96 mmol, 9 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 1:2), gave 233 mg of **37b** (76%) as a yellow oil. − IR (CCl_4): ṽ = 3025, 2945, 2890, 2830, 1545, 1485, 1420, 1260, 1200, 1170, 1135, 1000 cm^{-1}. − ^{1}H NMR (400 MHz): δ = 2.73 (t, $^3J_{3',4'}$ = 7.9 Hz, 2 H, 3′-H), 3.20 (t, $^3J_{4',3'}$ = 7.9 Hz, 2 H, 4′-H), 3.73 (s, 3 H, NCH_3), 3.95 (s, 2 H, 3′′-H), 6.90

(m_c, 1 H, Ar-H), 7.07 (m_c, 1 H, Ar-H), 7.28 (m_c, 1 H, Ar-H), 7.33−743 (m, 5 H, Ar-H), 7.71 (s, 1 H, 1-H). − ^{13}C NMR (100 MHz): δ = 23.1 (C-3′/4′), 26.3 (C-3′/4′), 26.6 (C-3′′), 54.7 (NCH_3), 78.3 (C-2′′), 99.4 (C-1′′), 111.8 (d, ^2J = 23.3 Hz, C-6′/8′), 113.7 (d, ^2J = 20.3 Hz, C-6′/8′), 127.0 (Ar-C), 128.0 (Ar-C), 128.1 (d, $^3J_{5',F}$ = 7.3 Hz, C-5′), 128.8 (Ar-C), 130.6 (d, $^4J_{4'a,F}$ = 4.4 Hz, C-4′a), 133.5 (d, $^3J_{8'a,F}$ = 7.7 Hz, C-8′a), 134.9 (C-1), 135.1 (C_q), 136.1 (C_q), 160.4 (d, $^1J_{7',F}$ = 242.7 Hz, C-7′). − MS (70 eV; EI): *m*/*z* (%) = 319 (33) [M$^+$], 302 (38), 228 (100) [M − CH_2Ph]$^+$, 183 (23), 91 (47). − HRMS ($C_{21}H_{18}FNO$): calcd. 319.1372; found 319.1372.

{[8′,9′-Dihydro-5′-(3′′-phenylprop-1′′-ynyl)-7′*H*-benzo[*a*]cyclohept-5′-en-6′-yl]methylene}methylamine *N*-Oxide (37c): Treatment of **36c** (1.16 g, 4.05 mmol, 6 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 3:1, 1:1), gave **37c** (911 mg, 72%) as a viscous, yellow oil. − IR (CCl_4): ṽ = 3060, 3025, 2945, 2860, 1550, 1495, 1450, 1205, 1170, 1150, 1135 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.14 (m, 2 H, 6′-H), 2.58 (m_c, 4 H, 5′-H, 7′-H), 3.75 (s, 3 H, NCH_3), 3.87 (s, 2 H, 3′′-H), 7.18−7.41 (m, 8 H, Ar-H), 7.53−7.60 (m, 1 H, Ar-H), 7.79 (s, 1 H, 1-H). − ^{13}C NMR (125 MHz): δ = 25.3 (C-6′), 26.3 (C-5′/7′), 32.0 (C-5′/7′), 34.9 (C-3′′), 54.4 (NCH_3), 81.3 (C-3′′′), 97.2 (C-2′′′), 126.1 (Ar-C), 126.9 (Ar-C), 127.9 (Ar-C), 128.3 (Ar-C), 128.5 (Ar-C), 128.7 (Ar-C), 128.9 (Ar-C), 129.7 (Ar-C_q), 136.6 (Ar-C_q), 136.8 (C-1), 138.5 (C_q), 139.5 (C_q), 141.2 (C_q). − MS (70 eV; EI): *m*/*z* (%) = 315 (31) [M$^+$], 244 (100) [M − CH_2Ph]$^+$, 196 (17), 115 (16), 91 (31). − HRMS ($C_{22}H_{21}NO$): calcd. 315.1623; found 315.1620.

2,4,6,7-Tetrahydro-4-methyl-2-phenyl-3*H*-naphtho[2,1-*c*]azepin-3-one (38a): Treatment of **37a** (100 mg, 0.33 mmol; NaOMe, 3 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 1:1), gave **38a** (78 mg, 78%) as colourless crystals, m.p. 180−181 °C (ethanol). − IR (CCl_4): ṽ = 3065, 3030, 2940, 1680 (C=O), 1455, 1375, 1305, 1260, 1105 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.46−2.74 (m, 2 H, 6-H), 2.91−3.06 (m, 2 H, 7-H), 3.18 (s, 3 H, NCH_3), 2.89 (d, $^3J_{2,1}$ = 6.4 Hz, 1 H, 2-H), 6.26 (s, 1 H, 5-H), 6.32 (d, $^3J_{1,2}$ = 6.4 Hz, 1 H, 1-H), 7.09−7.21 (m, 3 H, Ar-H), 7.28−7.39 (m, 1 H, Ar-H), 7.41 (m_c, 4 H, Ar-H), 7.62−7.70 (m, 1 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 29.6 (C-6/7), 31.7 (C-6/7), 36.0 (NCH_3), 52.2 (C-2), 121.7 (C-1), 123.1 (Ar-C), 126.2 (C_q), 126.7 (Ar-C), 127.1 (Ar-C/C-5), 127.2 (Ar-C/C-5), 127.7 (Ar-C/C-5), 128.4 (Ar-C), 129.0 (Ar-C), 129.6 (Ar-C/C-5), 132.6 (C_q), 134.2 (C_q), 136.5 (C_q). 138.4 (C_q), 166.7 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 301 (100) [M$^+$], 286 (16), 272 (12) [M − NCH_3]$^+$, 244 (11), 224 (22), 196 (43). − $C_{21}H_{19}NO$ (301.38): calcd. C 83.69, H 6.35, N 4.65; found C 83.51, H 6.44, N 4.50.

10-Fluoro-2,4,6,7-tetrahydro-4-methyl-2-phenyl-3*H*-naphtho[2,1-*c*]-azepin-3-one (38b): Treatment of **37a** (52 mg, 0.16 mmol; NaOMe, 2 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 20:1), gave **38a** (47 mg, 90%) as yellow crystals, m.p. 143−145 °C (ethanol). − IR (CCl_4): ṽ = 3025, 2935, 1680 (C=O), 1575, 1490, 1450, 1375, 1305, 1265, 1185, 1100 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.46−2.72 (m, 2 H, 6-H), 2.88−2.97 (m, 2 H, 7-H), 3.19 (s, 3 H, NCH_3), 3.87 (d, $^3J_{2,1}$ = 6.3 Hz, 1 H, 2-H), 6.25 (d, $^3J_{1,2}$ = 6.3 Hz, 1 H, 1-H), 6.29 (s, 1 H, 5-H), 6.86 (m_c, 1 H, Ar-H), 7.08 (m_c, 1 H, Ar-H), 7.28−7.44 (m, 7 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 29.6 (C-6/7), 30.9 (C-6/7), 36.1 (NCH_3), 52.2 (C-2), 108.2 (d, ^2J = 23.3 Hz, C-9/11), 113.4 (d, ^2J = 20.4 Hz, C-9/11), 121.3 (C-1), 124.1 (C_q), 126.0 (Ar-C), 126.1 (C-1), 127.1 (Ar-C), 128.2 (Ar-C), 129.1 (d, $^3J_{8,F}$ = 7.3 Hz, C-8), 130.8 (d, $^4J_{7a,F}$ = 2.9 Hz, C-7a), 132.2 (C_q), 133.1 (d, $^3J_{11a,F}$ = 7.3 Hz, C-11a), 136.7 (C_q), 160.5 (d, $^1J_{10,F}$ = 242.7 Hz, C-10), 165.3 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 319 (100) [M$^+$], 304 (12), 290 (22), 262 (12), 242 (18). − HRMS ($C_{21}H_{18}FNO$): calcd. 319.1372; found 319.1372.

4,6,7,8-Tetrahydro-4-methyl-2-phenylbenzo[3,4]cyclohepta[1,2-*c*]-azepin-3(2*H*)-one (38c): Treatment of **37c** (213 mg, 0.68 mmol; KOH, 5 h) according to the general procedure, after purification (cyclohexane/ethyl acetate, 10:1), gave **38c** (135 mg, 63%) as colourless crystals, m.p. 168−169 °C (ethanol). − IR (CCl_4): ṽ = 3065, 3030, 2940, 2855, 1675 (C=O), 1450, 1375, 1295, 1265, 1155, 1085 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 1.87−2.18 (m, 3 H, 7/8-H), 2.28−2.43 (m, 1 H, 7/8-H), 2.51−2.64 (m, 1 H, 6-H_a), 2.78−2.93 (m, 1 H, 6-H_b), 3.24 (s, 3 H, NCH_3), 3.36 (d, $^3J_{2,1}$ = 6.3 Hz, 1 H, 2-H), 5.94 (d, $^3J_{1,2}$ = 6.3 Hz, 1 H, 1-H), 6.25 (s, 1 H, 5-H), 7.11 (m_c, 1 H, Ar-H), 7.21 (m_c, 2 H, Ar-H), 7.29−7.44 (m, 6 H, Ar-H). − ^{13}C NMR (125 MHz): δ = 29.3 (C-7), 31.0 (C-6/8), 31.6 (C-6/8), 36.2 (NCH_3), 52.6 (C-2), 125.1 (C-1), 126.8 (Ar-C), 127.2 (Ar-C), 127.6 (Ar-C), 128.4 (Ar-C), 128.5 (Ar-C), 128.6 (C_q), 128.7 (Ar-C), 129.1 (Ar-C), 129.7 (C-5), 137.3 (C_q), 138.4 (C_q), 139.0 (C_q), 141.6 (C_q), 166.1 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 315 (78) [M$^+$], 314 (100), 286 (11) [M − NCH_3]$^+$, 258 (15) [M − $CONCH_3$]$^+$, 236 (44), 210 (21). − $C_{22}H_{21}NO$ (315.41): calcd. C 83.78, H 6.71, N 4.44; found C 83.57, H 6.63, N 4.34.

4,5,6,7-Tetrahydro-4-methyl-2-phenyl-3*H*-naphtho[2,1-*c*]azepin-3-one (39a): A solution of **38a** (120 mg, 0.40 mmol) in toluene (35 mL) was refluxed for 2 h. After concentration in vacuo, separation by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 5:1, 3:1) afforded **39a** (47 mg, 39%), together with **38a** (72 mg, 60%). − M.p. 179−180 °C (ethanol). − IR (CCl_4): ṽ = 3060, 3025, 2935, 2885, 1645 (C=O), 1490, 1440, 1395, 1225, 1005 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.60−2.70 (m, 2 H, 6-H), 2.87 (t, $^3J_{7,6}$ = 7.9 Hz, 2 H, 7-H), 3.13 (s, 3 H, NCH_3), 3.96 (br. s, 2 H, 5-H), 7.13−7.44 (m, 8 H, Ar-H, 1-H), 7.65−7.72 (m, 2 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 28.2 (C-6/7), 29.5 (C-6/7), 35.3 (NCH_3), 53.6 (C-5), 124.4 (Ar-C), 127.0 (Ar-C), 127.6 (Ar-C), 127.7 (Ar-C), 128.0 (Ar-C), 128.1 (Ar-C), 128.4 (Ar-C), 129.1 (C-1), 132.9 (C_q), 133.8 (C_q), 135.2 (C_q), 138.6 (C_q), 138.9 (C_q), 141.3 (C_q), 167.5 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 301 (100) [M$^+$], 272 (31) [M − NCH_3]$^+$, 244 (28) [M − $CONCH_3$]$^+$, 224 (12), 184 (34). − $C_{21}H_{19}NO$ (301.38): calcd. C 83.69, H 6.35, N 4.65; found C 83.48, H 6.17, N 4.48.

10-Fluoro-4,5,6,7-tetrahydro-4-methyl-2-phenyl-3*H*-naphtho[2,1-*c*]-azepin-3-one (39b): A solution of **38b** (50 mg, 0.16 mmol) in toluene (15 mL) was refluxed for 2 h. After concentration in vacuo, separation by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 3:1) afforded **39b** (11 mg, 22%), together with **38b** (17 mg, 34%). − M.p. 168−170 °C (ethanol). − IR (CCl_4): ṽ = 3025, 2930, 2890, 1645 (C=O), 1495, 1440, 1395, 1265, 1225, 1165, 1005 cm^{-1}. − ^{1}H NMR (250 MHz): δ = 2.63 (t, $^3J_{6,7}$ = 7.8 Hz, 2 H, 6-H), 2.83 (t, $^3J_{7,6}$ = 7.8 Hz, 2 H, 7-H), 3.14 (s, 3 H, NCH_3), 3.97 (br. s, 2 H, 5-H), 6.89 (m_c, 1 H, Ar-H), 7.00 (m_c, 1 H, Ar-H), 7.07 (s, 1 H, 1-H), 7.12 (m_c, 1 H, Ar-H), 7.29−7.45 (m, 3 H, Ar-H), 7.65−7.71 (m, 2 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 27.4 (C-6/7), 29.7 (C-6/7), 35.3 (C-5), 53.5 (NCH_3), 111.4 (d, ^2J = 23.0 Hz, C-9/11), 113.9 (d, ^2J = 21.2 Hz, C-9/11), 128.1 (Ar-C), 128.2 (Ar-C), 128.3 (Ar-C), 128.5 (Ar-C), 128.8 (d, $^3J_{8,F}$ = 7.9 Hz, C-8), 130.6 (d, ^4J = 3.3 Hz, C-7a/11b), 132.3 (d, ^4J = 2.1 Hz, C-7a/11b), 135.5 (d, $^3J_{11a,F}$ = 7.6 Hz, C-11a), 138.7 (C_q), 139.8 (C_q), 141.8 (C_q), 162.0 (d, $^1J_{10,F}$ = 243.7 Hz, C-10), 167.3 (C-3). − MS (70 eV; EI): *m*/*z* (%) = 319 (100) [M$^+$], 290 (24) [M − NCH_3]$^+$, 262 (22) [M − $CONCH_3$]$^+$, 242 (15), 214 (35). − HRMS ($C_{21}H_{18}FNO$): calcd. 319.1372; found 319.1372.

5,6,7,8-Tetrahydro-4-methyl-2-phenylbenzo[3,4]cyclohepta[1,2-*c*]-azepin-3(2*H*)-one (39c): A solution of **38c** (244 mg, 0.77 mmol) in

toluene (50 mL) was refluxed for 2 h. After concentration in vacuo, separation by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 10:1, 3:1) afforded **39c** (48 mg, 20%), together with **38c** (194 mg, 80%). − M.p. 135−138 °C (diethyl ether). − IR (CCl_4): $\tilde{\nu}$ = 3060, 3020, 2930, 2855, 1640 (C=O), 1450, 1425, 1395, 1095 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.17−2.28 (m, 4 H, 6-H. 7-H), 2.52−2.61 (m, 2 H, 8-H), 3.19 (s, 3 H, NCH_3), 4.00 (br. s, 2 H, 5-H), 6.94 (s, 1 H, 1-H), 7.17−7.40 (m, 7 H, Ar-H), 7.57−7.64 (m, 2 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 32.0 (C-6/7/8), 32.1 (C-6/7/8), 34.5 (C-6/7/8), 34.9 (NCH_3), 54.6 (C-5), 126.5 (Ar-C), 127.7 (Ar-C), 127.9 (Ar-C), 128.1 (Ar-C), 128.3 (Ar-C), 128.4 (Ar-C), 128.5 (C_q), 129.0 (Ar-C), 132.6 (C-1), 137.2 (C_q), 139.1 (C_q), 140.4 (C_q), 140.5 (C_q), 140.6 (C_q), 167.1 (C-3). − MS (70 eV; EI): *m/z* (%) = 315 (100) [M^+], 287 (16) [$M - NCH_3]^+$, 258 (14) [$M - CONCH_3]^+$, 236 (36). − HRMS ($C_{22}H_{21}NO$): calcd. 315.1623; found 315.1621.

4-Bromo-1,2-dihydro-2-methyl-3*H*-2-benzazepin-3-one (9p): A solution of bromine in CCl_4 (0.5 M, 0.86 mL, 0.43 mmol) was added at 0 °C to a solution of **9d** (106 mg, 0.43 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was allowed to warm to room temp. and stirred for 24 h. The resulting pale yellow solution was treated with satd. aqueous NaS_2O_3 (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2; cyclohexane/ethyl acetate, 2:1) gave **9p** (86 mg, 79%) as colourless crystals, m.p. 150 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 2925, 1655 (C=O), 1555, 1445, 1395, 1265, 1205, 1115, 1000 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.13 (br. s, 3 H, NCH_3), 4.25 (s, 2 H, 1-H), 7.28−7.43 (m, 4 H, Ar-H), 7.66 (s, 1 H, 5-H). − ^{13}C NMR (100 MHz): δ = 35.7 (NCH_3), 53.3 (C-1), 121.6 (C_q), 127.3 (Ar-C), 128.8 (Ar-C), 129.1 (Ar-C), 129.6 (Ar-C), 134.7 (C_q), 135.7 (C_q), 138.2 (C-5), 162.4 (C-3). − MS (70 eV; EI): *m/z* (%) = 253 (19) [M^+, for $^{81}Br]^+$, 251 (19) [M^+, for ^{79}Br], 172 (100) [$M - Br]^+$, 143 (32), 115 (72). − $C_{11}H_{10}BrNO$ (252.11): calcd. C 52.41, H 4.00, N 5.56; found C 52.37, H 3.85, N 5.49.

2,3-Dihydro-2-methyl-1*H*-2-benzazepine (40a): A solution of **9a** (50 mg, 1.83 mmol) in dry diethyl ether (10 mL) was treated with LAH (44 mg, 1.15 mmol) and stirred for 4 h at room temp. The reaction mixture was poured into a 1:1 mixture of satd. NH_4Cl and water and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2; ethyl acetate) afforded **40a** (36 mg, 78%) as a colourless oil. − IR (CCl_4): $\tilde{\nu}$ = 3015, 2900, 2870, 2795, 1490, 1445, 1360, 1270, 1185, 1125, 1105, 1045 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.41 (s, 3 H, NCH_3), 3.54 (dd, $^3J_{3,4}$ = 3.8 Hz, $^4J_{3,5}$ = 2.1 Hz, 2 H, 3-H), 3.82 (s, 2 H, 1-H), 5.77 (td, $^3J_{4,5}$ = 12.2 Hz, $^3J_{4,3}$ = 3.8 Hz, 1 H, 4-H), 6.45 (td, $^3J_{5,4}$ = 12.2 Hz, $^4J_{5,3}$ = 2.1 Hz, 1 H, 5-H), 7.06−7.25 (m, 4 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 43.2 (NCH_3), 60.1 (C-1/3), 61.4 (C-1/3), 127.1 (Ar-C/C-4/5), 127.2 (Ar-C/C-4/5), 128.9 (Ar-C/C-4/5), 129.7 (Ar-C/C-4/5), 130.5 (Ar-C/C-4/5), 130.7 (Ar-C/C-4/5), 136.2 (Ar-C_q), 138.2 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 159 (39) [M^+], 158 (100) [$M^+ - 1$], 144 (36), 115 (44). − HRMS ($C_{11}H_{13}N$): calcd. 159.1048; found 159.1048.

2-(*tert*-Butyl)-2,3-dihydro-1*H*-2-benzazepine (40c): A solution of **9c** (70 mg, 0.33 mmol) in dry diethyl ether (10 mL) was treated with LAH (50 mg, 1.32 mmol) and stirred for 3 h at room temp. The reaction mixture was poured into a 1:1 mixture of satd. NH_4Cl and water and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2; ethyl acetate) afforded **40c** (60 mg, 92%) as a colourless oil. − IR (CCl_4): $\tilde{\nu}$ = 3015, 2970, 2820, 1490, 1465, 1450, 1390, 1360, 1265, 1200, 1105, 1060 cm^{-1}. − ^1H NMR (250 MHz): δ = 1.17 (s, 9 H, CH_3), 3.64 (s, 2 H, 1-H), 3.64 (m_c, 2 H, 3-H), 5.84 (td, $^3J_{4,5}$ = 12.2 Hz, $^3J_{4,3}$ = 4.0 Hz, 1 H, 4-H), 6.46 (td, $^3J_{5,4}$ = 12.2 Hz, $^4J_{5,3}$ = 2.1 Hz, 1 H, 5-H), 7.06−7.13 (m, 3 H, Ar-H), 7.14−7.20 (m, 1 H Ar-H). − ^{13}C NMR (100 MHz): δ = 26.7 (CH_3), 53.9 (C_q), 54.4 (C-1, C-3), 126.8 (Ar-C/C-4/5), 126.9 (Ar-C/C-4/5), 127.3 (Ar-C/C-4/5), 128.3 (Ar-C_q), 130.2 (Ar-C/C-4/5), 132.3 (Ar-C/C-4/5), 136.5 (Ar-C_q). − MS (70 eV; EI): *m/z* (%) = 201 (15) [M^+], 186 (100), 144 (32) [$M - C(CH_3)_3]^+$, 130 (11) [$M - NC(CH_3)_3]^+$. − HRMS ($C_{14}H_{19}N$): calcd. 201.1517; found 201.1517.

2,3-Dihydro-2,4-dimethyl-1*H*-2-benzazepine (40f): A solution of **9f** (85 mg, 5.34 mmol) in dry diethyl ether (8 mL) was treated with LAH (70 mg, 1.83 mmol) and stirred for 2 h at room temp. The reaction mixture was poured into a 1:1 mixture of satd. NH_4Cl and water and extracted with CH_2Cl_2 (3 × 10 mL) The combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2; ethyl acetate) afforded **40f** (74 mg, 95%) as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 3015, 2930, 1715, 1490, 1440, 1365, 1140, 1050 cm^{-1}. − ^1H NMR (250 MHz): δ = 1.80 (d, $^4J_{CH3,5}$ = 1.3 Hz, 3 H, CH_3), 2.32 (s, 3 H, NCH_3), 3.35 (s, 2 H, 1/3-H), 3.72 (s, 2 H, 1/3-H), 6.24 (q, $^4J_{5,CH3}$ = 1.3 Hz, 1 H, 5-H) 6.95−7.21 (m, 4 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 24.4 (CH_3), 43.2 (NCH_3), 60.9 (C-1/3), 63.7 (C-1/3), 126.3 (C-5/Ar-C), 126.5 (C-5/Ar-C), 127.2 (C-5/Ar-C), 128.8 (C-5/Ar-C), 130.0 (C-5/Ar-C), 136.5 (C_q), 137.5 (C_q), 138.7 (C_q). − MS (70 eV; EI): *m/z* (%) = 173 (77) [M^+], 158 (100), 144 (73), 128 (65), 115 (65). − HRMS ($C_{12}H_{15}N$): calcd. 173.1204; found 173.1204.

2,3-Dihydro-7,8-dimethoxy-2-methyl-4-(4′-methylphenyl)-1*H*-2-benzazepine (40o): A solution of **9o** (70 mg, 0.23 mmol) in dry diethyl ether (8 mL) was treated with LAH (33 mg, 0.87 mmol) and stirred for 5 h at room temp. The reaction mixture was poured into a 1:1 mixture of satd. NH_4Cl and water and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2; ethyl acetate/methanol, 10:1) afforded **40o** (43 mg, 65%) as a pale yellow oil. − IR (CCl_4): $\tilde{\nu}$ = 2930, 2835, 1710, 1510, 1340, 1265, 1235, 1125 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.38 (s, 3 H, 4′-CH_3), 2.55 (s, 3 H, NCH_3), 3.72 (s, 2 H, 1/3-H), 3.84 (s, 2 H, 1/3-H), 3.89 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3), 6.80 (s, 1 H, 6/9-H), 6.86 (s, 1 H, 6/9-H), 6.98 (s, 1 H, 5-H), 7.19 (md, $^3J_{o\text{-}Ar\text{-}H}$ = 8.0 Hz, 2 H, Ar-H), 7.41 (md, $^3J_{o\text{-}Ar\text{-}H}$ = 8.0 Hz, Ar-H). − ^{13}C NMR (125 MHz): δ = 22.4 (4′-CH_3), 41.5 (NCH_3), 56.0 (OCH_3), 56.3 (C-1/3), 57.7 (C-1/3), 112.7 (C-6/9), 113.0 (C-6/9), 126.0 (Ar-C), 127.7 (C_q), 129.4 (Ar-C), 130.0 (C.5), 130.7 (C_q), 137.3 (C_q), 137.6 (C_q), 138.6 (C_q), 148.3 (C-7/8), 148.5 (C-7/8). − MS (70 eV; EI): *m/z* (%) = 309 (62) [M^+], 218 (20), 204 (100), 91 (27). − HRMS ($C_{20}H_{23}NO_2$): calcd. 309.1729; found 309.1723.

1,2,4,5-Tetrahydro-2-methyl-3*H*-2-benzazepin-3-one (41a): A solution of **9a** (50 mg, 0.29 mmol) in methanol (20 mL) was treated with 10% Pd/C (10 mg) and hydrogen (12 bar) for 4 h at room temp. The reaction mixture was filtered (Kieselguhr) and concentrated in vacuo. Purification by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 3:1) gave **41a** (48 mg, 95%) as colourless crystals, m.p. 86−87 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 3020, 2945, 2905, 1665 (C=O), 1445, 1395, 1355, 1210, 1100, 1025 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.92 (t, $^3J_{4,5}$ = 6.8 Hz, 2 H, 4/5-H), 3.05 (s, 3 H, NCH_3), 3.17 (t, $^3J_{4,5}$ = 6.8 Hz, 2 H, 4/5-H), 4.49 (s, 2 H, 1-H), 7.04−7.18 (m, 3 H, Ar-H), 7.20−7.26 (m, 1 H, Ar-H). − ^{13}C NMR (125 MHz): δ = 28.8 (C-4/5), 33.6 (C-4/5), 35.2 (NCH_3), 54.5 (C-1), 126.0 (Ar-C), 128.2 (Ar-C), 128.8 (Ar-C), 130.5 (Ar-C), 134.3

($Ar\text{-}C_q$), 137.7 ($Ar\text{-}C_q$), 173.6 (C-3). − MS (70 eV; EI): *m/z* (%) = 175 (36) [M^+], 146 (17) [$M - NCH_3]^+$, 118 (46) [$M - CONCH_3]^+$, 117 (100). − $C_{11}H_{13}NO$ (175.23): calcd. C 75.40, H 7.48, N 7.89; found C 75.27, H 7.20, N 8.04.

2-*tert*-Butyl-1,2,4,5-tetrahydro-3*H*-2-benzazepin-3-one (41c): A solution of **9c** (100 mg, 0.46 mmol) in methanol (20 mL) was treated with 10% Pd/C (20 mg) and hydrogen (12 bar) for 4 h at room temp. The reaction mixture was filtered (Kieselguhr) and concentrated in vacuo. Purification by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 1:2) gave **41c** (97 mg, 96%) as colourless crystals, m.p. 90−91 °C (ethanol). − IR (CCl_4): $\tilde{\nu}$ = 3020, 2975, 2915, 1660 (C=O), 1440, 1400, 1350, 1340, 1195, 1100 cm^{-1}. − ^1H NMR (250 MHz): δ = 1.42 (s, 9 H, CH_3), 2.90−2.99 (m, 2 H, 4/5-H), 3.12−3.22 (m, 2 H, 4/5-H), 4.55 (s, 2 H, 1-H), 7.00−7.06 (m, 1 H, Ar-H), 7.07−7.15 (m, 2 H, Ar-H), 7.17−7.25 (m, 1 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 29.1 (CH_3), 29.2 (C-4/5), 36.5 (C-4/5), 48.4 (C-1), 57.6 (C_q), 125.9 (Ar-C), 127.7 (Ar-C), 128.2 (Ar-C), 130.6 (Ar-C), 136.0 ($Ar\text{-}C_q$), 137.6 ($Ar\text{-}C_q$), 175.2 (C-3). − MS (70 eV; EI): *m/z* (%) = 217 (44) [M^+], 160 (27) [$M - C(CH_3)_3]^+$, 118 (20) [$M - CONC(CH_3)_3]^+$, 117 (100), 57 (20) [$C(CH_3)_3^+$]. − HRMS: ($C_{14}H_{19}NO$): calcd. 217.1467; found 217.1466.

1,2,4,5-Tetrahydro-7,8-dimethoxy-2-methyl-3*H*-2-benzazepin-3-one (41l): A solution of **9l** (38 mg, 0.16 mmol) in methanol (15 mL) was treated with 10% Pd/C (10 mg) and hydrogen (10 bar) for 4 h at room temp. The reaction mixture was filtered (through kieselguhr) and concentrated in vacuo. Purification by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 1:2) gave **41l** (35 mg, 92%) as a colourless oil. − IR (CCl_4): $\tilde{\nu}$ = 2935, 2905, 2850, 1665 (C=O), 1520, 1465, 1395, 1345, 1260, 1205, 1110, 1010 cm^{-1}. − ^1H NMR (250 MHz): δ = 2.87−2.96 (m, 2 H, 4/5-H), 3.03−3.15 (m, 2 H, 4/5-H), 3.06 (s, 3 H, NCH_3), 3.85 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 4.43 (s, 2 H, 1-H), 6.58 (s, 1 H, Ar-H), 6.64 (s, 1 H, Ar-H). − ^{13}C NMR (100 MHz): δ = 28.5 (C-4/5), 33.5 (C-4/5), 35.3 (NCH_3), 54.1 (C-1), 56.0 (OCH_3), 56.1 (OCH_3), 112.3 (Ar-C), 113.5 (Ar-C), 126.3 (C-5a/9a), 129.8 (C-5a/9a), 146.7 (C-7/8), 148.7 (C-7/8), 173.9 (C-3). − MS (70 eV; EI): *m/z* (%) = 235 (100) [M^+], 220 (25), 178 (26), 162 (21). − HRMS ($C_{13}H_{17}NO_3$): calcd. 235.1208; found 235.1208.

1,2-Dihydro-2-methyl-3*H*-2-benzazepine-3-thione (42): A suspension of P_4S_{10} (156 mg, 0.35 mmol) and sodium carbonate (37 mg, 0.35 mmol) in THF (5 mL) was stirred for 30 min at room temp., treated with **9a** (50 mg, 0.29 mmol) and heated to reflux for 13 h. The yellow reaction mixture was concentrated in vacuo and the crude material was purified by flash chromatography (SiO_2; cyclohexane/ethyl acetate, 2:1, 1:2) to afford **42** (36 mg, 65%) as yellow crystals, together with **9a** (17 mg, 34%). − M.p. 146−147 °C (diethyl ether). − IR (CCl_4): $\tilde{\nu}$ = 3070, 3025, 2920, 1495, 1395, 1345, 1295, 1280, 1235, 1100 cm^{-1}. − ^1H NMR (250 MHz): δ = 3.58 (s, 3 H, NCH_3), 4.50 (s, 2 H, 1-H), 6.84 (d, $^3J_{4,5}$ = 11.9 Hz, 1 H, 4-H), 7.08 (d, $^3J_{5,4}$ = 11.9 Hz, 1 H, 5-H), 7.28−7.34 (m, 1 H, Ar-H), 7.38−7.46 (m, 3 H, Ar-H). − ^{13}C NMR (125 MHz): δ = 43.4 (NCH_3), 58.3 (C-1), 127.3 (C-4), 128.9 (Ar-C), 129.1 (Ar-C), 129.8 (Ar-C), 133.8 ($Ar\text{-}C_q$), 134.6 (C-5), 135.6 ($Ar\text{-}C_q$), 190.3 (C-3). − MS (70 eV; EI): *m/z* (%) = 189 (100) [M^+], 156 (27), 128 (43), 116 (13). − HRMS ($C_{11}H_{11}NS$): calcd. 189.0612; found 189.0609.

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