Synthetic Applications of Conjugated Nitrones, 5[◇]

A Novel Entry to the 13-Azasteroid System☆

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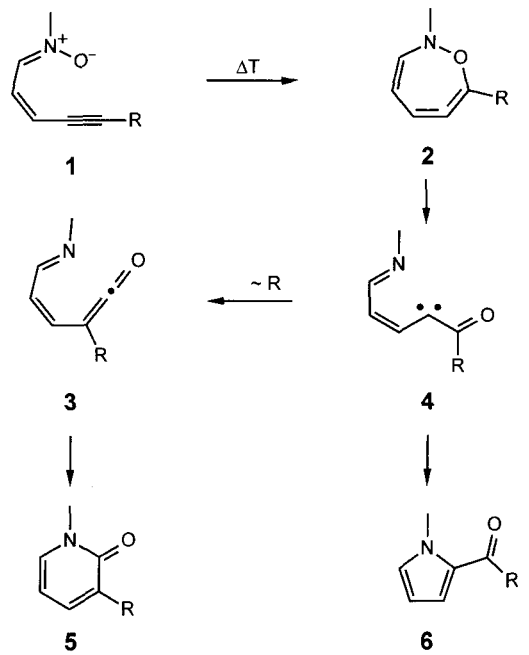
A synthetic approach to 13-azasteroid and C-nor-13-azasteroid derivatives (type **17/18**) as well as to the 4,13-diaza analogues **27/28** is described. For the construction of the tetracyclic compounds precursors with preformed rings A, B and D containing a conjugated nitrone system were used (**16/26**). These were prepared from the annulated cyclohexenones **10/20a, b** in six steps according to slightly modified standard procedures. The failure in obtaining the terminal silyl alkynes **15b** by Michael addition of the enolate of **14b** to nitrostyrene is explained on the basis of a strong Si–O complexation. After replacement of the trimethylsilyl substituent by the sterically more demanding triisopropylsilyl group the formation of **15c** was accomplished as expected. Upon thermally induced 1,7-cyclization of the nitrones **16/26** a multistep rearrangement of the primary cycloallenic intermediates takes place resulting in the formation of the corresponding 6,6,6,5- and 6,6,5,5-ring steroids (**17/27** and **18/28**) in 55–86% yield.

A frequently used concept for the development of compounds with altered biological activity is based on the replacement of one or more carbon atoms in the structure of known drugs by a heteroatom. This idea turned out to be very fruitful also for modified steroids, especially in the case of azasteroids, and has stimulated many research projects aimed at the synthesis of potentially bioactive and possibly less toxic new substances[5,6]. Numerous azasteroids are known and many of them possess useful pharmaceutical properties which might differ quite significantly from those of *all-C*-steroids[7]. The broad scope of pharmaceutical applications[6] includes antiinflammatory[8], contraceptive[9], antileukemic[10], antibacterial and antifungal activities[11] as well as the use as 5α-reductase inhibitor[12] and neuromuscular blocker[13]. Besides the so-called extranuclear azasteroids, which bear a nitrogen atom as part of an attached substituent (many of the naturally occurring azasteroids belong to this type), seventeen positionally different nuclear monoaza systems are possible. Whereas examples of basically every member of the latter series have been synthesized, the number of the respective compounds varies considerably: according to a literature search 2-, 3-, 4-, 6-, 8-, 11-, 15-, 16-, and 17-azasteroids are described much more often than the corresponding 1-, 5-, 7-, 9-, 10-, 12-, 13-, and 14-isomers. Consequently, methods for the preparation of the latter steroid analogues – either on the basis of a partial[6] or a total synthesis[5a,14] – are of particular interest.

We report on a novel access to 13-azasteroid derivatives[15,16] which is based on the 1,7-electrocyclization of conjugated enynyl nitrones as key step[1–4].

As indicated in Scheme 1 nitrones of type **1** are thermally transformed into α-pyridones **5** and 2-acylpyrroles **6**, respectively, according to a pathway which involves the allenic oxazepine **2** as primary intermediate[17].

Scheme 1



In the course of the reaction besides imino cyclopropenes and diradicals (which are not shown in the simplified Scheme 1) the azabutadienyl ketocarbene **4** is formed as a

[◇]For part 4 see ref.[1].

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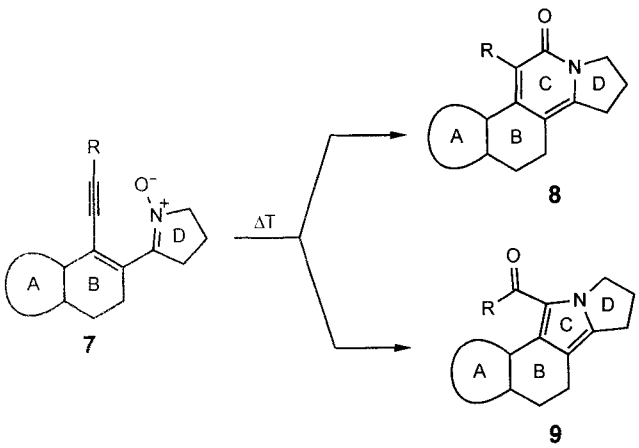
relay species which reacts either by direct 6-π cyclization to afford the pyrrole **6** or furnishes the α-pyridone **5** after a Wolff rearrangement to the ketene **3**. It is the special advantage of this method that the chemoselectivity depends on the migratory aptitude of the group R[18]; i.e. substituents like hydrogen or silyl[19,20] favor the formation of α-pyridones whereas phenyl or *t*-butyl groups rather tend to increase the amount of pyrroles. Hence, the product distribution can be influenced by the proper choice of R. Despite the complexity of the reaction mechanism the transformations normally take place with surprisingly high efficiency[1–4].

In our approach to the synthesis of 13-azasteroids we used precursors with preformed rings A, B and D (see structure **7**) which on 1,7-cyclization and subsequent reorganization should afford tetracyclic systems of type **8** and/or the 12-nor-steroid analogues **9**. With respect to the lactam moiety of **8** it is interesting to note that this functionality seems to be essential for the antitumor activity of some homo-azasteroid compounds having a 6,6,7,5-ring skeleton[6b].

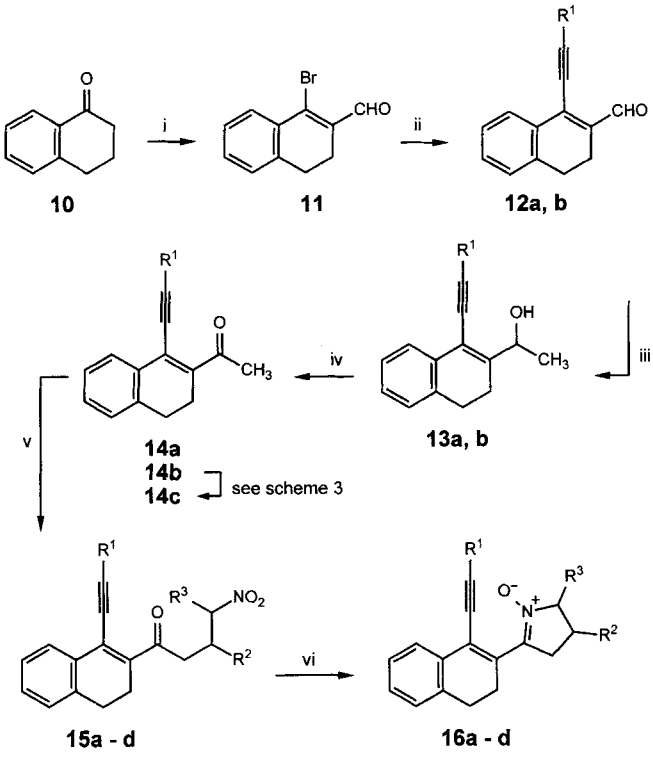


The required nitrones of type **7** were prepared according to the reaction sequence sketched in Scheme 2 for the synthesis of the benzo derivatives **16**[20].

The transformation of α-tetralone (**10**) into the bromo carbaldehyde **11** under Vilsmeier conditions is a known reaction[21]; however, it is recommendable to reduce the solvent to about 10–20% of the volume given in the literature. Subsequent alkynylation of **11** with phenyl- or trimethylsilylacetylene using the Sonogashira modification of the Heck coupling procedure[22] afforded compounds **12a, b** (ca. 90%)[23] which were treated with methyllithium to give **13a, b** (ca. 90%). Oxidation of the secondary alcohols with triethylamine/DMSO in the presence of the SO_3–pyridine complex[24] gave the ketones **14a, b** (the overall yield for the sequence **10** → **14** was 52–60%). In the next step deprotonation of **14** with lithium diisopropylamide (LDA) and Michael addition of the resulting enolate to a nitro alkene should lead to the γ-nitrobutanone system **15**, the precursor of the nitrone **16**. Surprisingly, whereas the reaction with β-nitrostyrene was successfully performed with **14a** resulting in a 60% yield of **15a**, the same treatment of the silyl derivative **14b** gave only 50% conversion with formation of less than 15% of compound **15b**. Similar results were obtained by modification of the reaction conditions (increase of the reaction time and temperature, addition of TMEDA as cosolvent) or replacement of LDA by other bases like sodium hydride or the metal-free phosphacene base *t*Bu-P4[25]. Our speculation that the enolate species might be stabilized, i.e. deactivated, by interaction with the silicon center at the alkyne terminus (see structure **14b-Li**) was supported by the observation that addition of DMPU as cosolvent gave **15b** in yields up to 40%[26]. This effect is probably due to the weakening of the intramolecular Si–O coordination by competitive interactions with the oxygen-containing cosolvent[27].

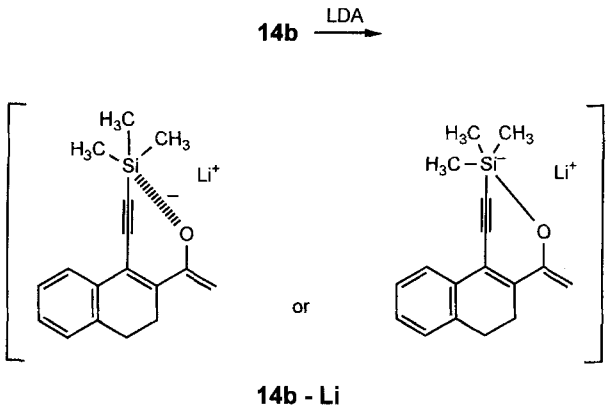
Another way to circumvent the considerable decrease of nucleophilicity of the enolate involved the reaction of the triisopropylsilylalkyne **14c** instead of the trimethyl derivative with the Michael acceptor. In this case the intramolecular Si–O interaction should be strongly reduced by steric shielding. For the synthesis of **14c** the trimethylsilyl derivative **14b** was transformed in a three-step "trans-silylation" procedure (see sequence **14b** → **14e** → **14f** → **14c**). To the

Scheme 2



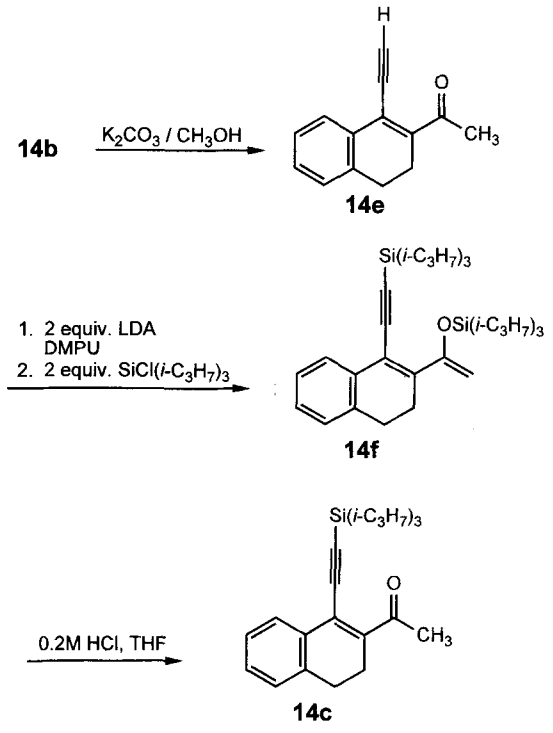
12 - 16	R¹	R²	R³
a	C_6H_5	C_6H_5	H
b	$Si(CH_3)_3$	C_6H_5	H
c	$Si(i\text{-}C_3H_7)_3$	C_6H_5	H
d	C_6H_5	H	CH_3

i: PBr_3, DMF. – ii: $R^1C{\equiv}CH$, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3. – iii: MeLi, THF, –78°C. – iv: SO_3–Py, DMSO, NEt_3. – v: LDA, THF, –78°C, then (*E*)-β-nitrostyrene (**15a–c**) or 2-nitropropene (**15d**). – vi: Fe, HCl, H_2O.



best of our knowledge the reaction of alkynyllithium with triisopropyl chloride (TIPS-Cl) has not been described so far[29]; instead, either alkynyllithium compounds and TIPS-triflate[30] or the corresponding Grignard compound and TIPS-Cl[31] were used for the preparation of such silyl derivatives. Our studies revealed that the introduction of the terminal TIPS group can be accomplished in excellent yield by sequential lithiation of **14e** and addition of TIPS-Cl, provided that DMPU is used as cosolvent. For selective monodeprotection of the disilyl derivative **14f** treatment with 0.2 N HCl was successfully employed affording **14c** in 75% yield.

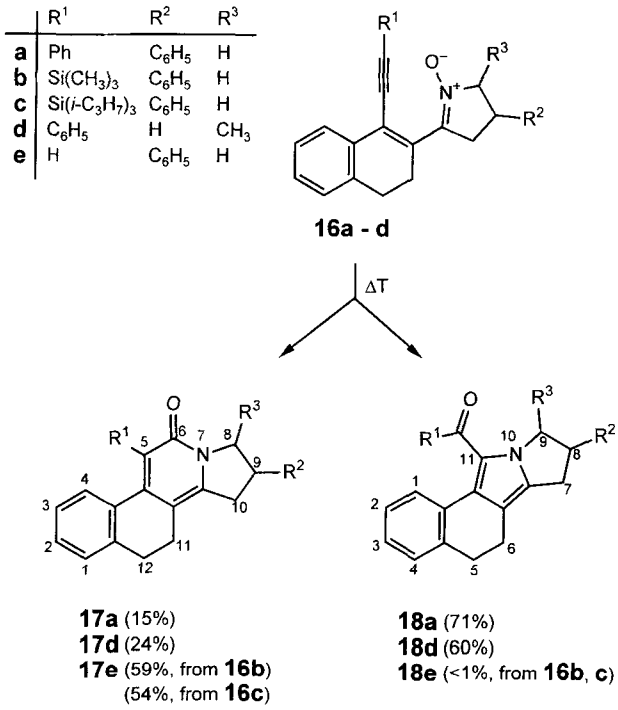
Scheme 3



According to the expectation the Michael reaction of **14c** with nitrostyrene under the conditions applied to the phenyl derivative **14a** gave basically the same results (59% of **15c**). This outcome supports the hypothesis suggesting a strong intramolecular complexation of Si and the enolate **14b-Li**.

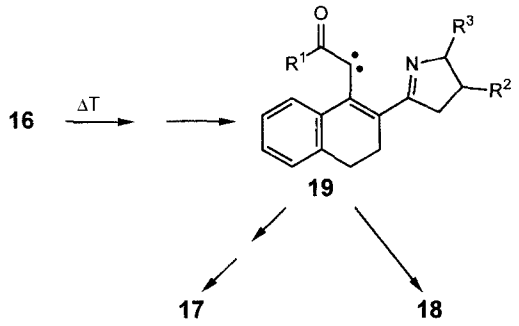
The success of the C,C-coupling reaction depends also on the nature of the Michael component: when 2-nitropropene is used in the reaction with **14a** the (non-optimized) yield of **15d** was only 34%[32].

The cyclization experiments with **16a–d** were performed by heating ca. 10^{-2} M solutions of **16** in benzene in a 100-ml autoclave apparatus. After a reaction time of 1.5 h (**16a**, **16d**), 3 h (**16b**), and 7 h (**16c**) at 200 °C, complete conversion of the starting materials was indicated by TLC analysis. Careful chromatographic work-up of the crude material allowed the separation of new products. In the case of the phenyl derivatives **16a/16d** two compounds were isolated in each case as yellow crystals in 15/24 and 71/60% yield, which turned out to be the 6,6,6,5- and 6,6,5,5-ring steroid analogues **17a/d** and **18a/d**, respectively. The detection and clean separation of the isomers was facilitated by the characteristic fluorescence and the low R_f value of the α-pyridone derivatives.



The structural proof of **17a/d** and **18a/d** is based on the elemental analysis and the MS, IR as well as NMR data. Despite the similarity of the ^{1}H-NMR spectra of the isomers there is one important difference, namely the low-field signal (δ = 7.78/7.78) of the two *o*-protons of the benzoyl group of **18a/d**. Further evidence for the structural assignment comes from the ^{13}C-NMR data. Besides other criteria the ^{13}C-chemical shift of the carbonyl groups is a clear indication of the difference of the two systems: whereas the carbonyl absorptions of **18a/d** at δ = 187/186 correspond quite well with the benzoyl functionality at the pyrrole ring, **17a/d** give rise to higher field absorptions at δ = 161/161 which are characteristic of the respective pyridone carbons[33].

In contrast to the results with **16a**, **d** thermal treatment of the silyl derivatives **16b**, **c** afforded almost exclusively the 6,6,6,5-steroids **17e** with only traces of the corresponding

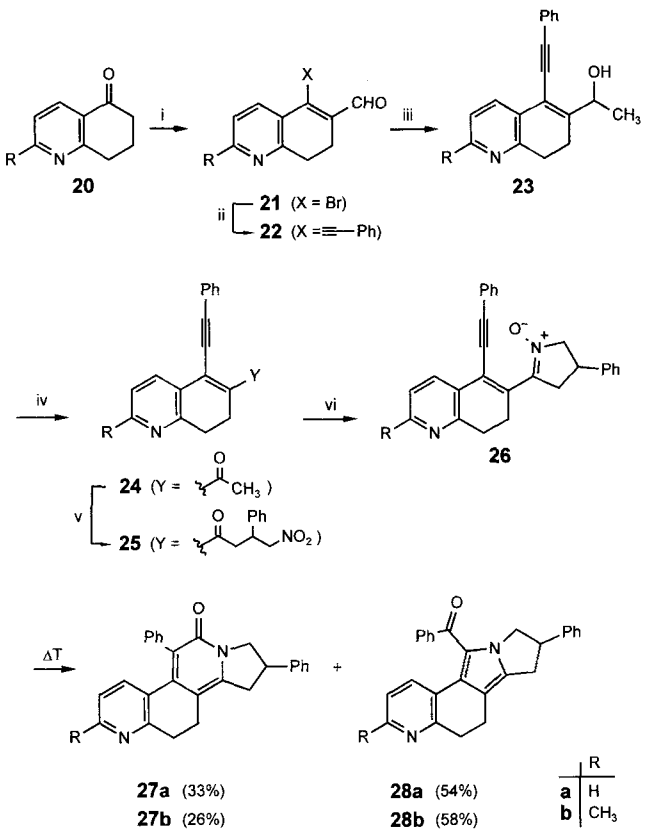


C-nor-analogue **18e**. Also, the isolated products do not contain a silyl substituent as would be the case for the expected compounds **17b** or **17c** (see below). The predominant formation of the pyridone isomer **17** is readily explained on the basis of the general mechanism sketched in Scheme 1. According to the suggested multistep transformation the vinyl ketocarbene **19** undergoes either direct cyclization to the pyrrole product **18** or initial Wolff migration of R^1 followed by an azahexatriene cyclization with formation of the α-pyridone moiety of **17**. As we have shown for other examples the migratory aptitude of silyl groups in such 1,2-shifts is equal or even superior to that of hydrogen[19,20,34,35], which is usually supposed to be the best migrating group[18]. Consequently, the route to the pyridone derivative is favored for R^1 = silyl. On the other hand, phenyl tends to be a poor migrating group; therefore, it is the pyrrole system **18** which is predominately formed by starting from **16a** or **16d**. As far as the protodesilylation step is concerned (see **16b, c** → **17e/18e**), we strongly favor the hypothesis – supported mainly by comparison with the results of related nitrones[19,20,34] – that the silyl exchange takes place after the Wolff rearrangement.

Despite the complex mechanism of the transformation **16** → **17/18** involving several reactive intermediates the intramolecular reactivity of the system is surprisingly high, resulting in excellent to reasonable overall yields in the **a, d** (ca. 85%) and **c, b** series (ca. 60%), respectively.

In order to broaden the scope of this synthetic approach preliminary investigations of the preparation of 4,13-diaza steroid analogues were carried out. The required starting material was provided according to the same methodology as used for the synthesis of the nitrones **16**. Thus, the tetrahydroquinolinones **20a, b**, available by known procedures[36,37], were first transformed into the bromo carbaldehydes **21** which subsequently provided the alkynyl derivatives **22** by application of the Sonogashira coupling conditions (ca. 60% for two steps). While the formation of the secondary alcohols **23** by reaction of **22** with methyllithium (see **12** → **13**) was not very effective, inverse addition of the less basic Grignard reagent methylmagnesium iodide resulted in much higher yields of **23a, b** (ca. 90%). The further reactions were executed as described for the preparation of **16a–d**, and gave the nitrones **26** as yellow crystalline compounds.

The thermal transformation of the nitrone precursors **26a, b** was again studied by heating 10^{-2} to 10^{-3} molar



i: PBr_3, DMF. – ii: PhC≡CH, $Pd(PPh_3)_2Cl_2$, CuI, NEt_3. – iii: MeMgI, EtO_2, reflux. – iv: SO_3–Py, DMSO, NEt_3. – v: LDA, THF, –78 °C, then (*E*)-β-nitrostyrene. – vi: Fe, HCl, H_2O.

benzene solutions at 200 °C. After complete conversion (1.5 h) flash-chromatographic separation of the reaction mixture revealed the formation of two main products in each case, namely the 4,13-diazasteroids **27a, b** and the corresponding C-nor-derivatives **28a, b** in about 30 and 55% yield, respectively, the yield of pure products amounting to 85%. The structural identification of the new products was based on the usual physical data (see Experimental), and especially on the ^{1}H- and ^{13}C-NMR data which expectedly resemble those of the corresponding monoaza derivatives **17/18**.

Owing to the relatively easy availability of the starting nitrones, the described preparation of several mono- and diazasteroid derivatives with a benzo or pyrido moiety as ring A represents a promising new and rather flexible synthetic alternative. Ongoing experiments include the modification of the ring systems as well as the substitution pattern, and special efforts are directed to the preparation of optically active products.

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Experimental

Melting points are uncorrected. – IR: Perkin-Elmer 257 Infracord. – ^{1}H NMR: Bruker WM 250 (250 MHz); ^{13}C NMR: Bruker WM 400 (100 MHz); $CDCl_3$ as solvent and TMS as internal standard; δ values marked by an asterisk might be exchanged. – MS: Finnigan MAT 44 S (70 eV) with Data system MAT SS 200. –

Elemental analyses: Perkin-Elmer Elemental Analyzer 240. – Products were isolated by flash chromatography on silica gel (Silica 32–36, ICN Biomedicals) or aluminium oxide (Alumina N, Biomedicals). – TLC: SiO_2 60 F-254, 0.2 mm (Merck); Al_2O_3 60 F-254, neutral type E, 0.2 mm (Merck). – Solution thermolyses were performed in 100-ml autoclaves, Carl Roth GmbH & Co., type 1.

3,4-Dihydro-1-(phenylethynyl)naphthalene-2-carbaldehyde (**12a**): To a stirred solution of 1-bromo-3,4-dihydronaphthalene-2-carbaldehyde (**11**)[21] (1.00 g, 4.2 mmol) and phenylethyne (0.62 g, 6.1 mmol) in 10 ml of dry triethylamine bis(triphenylphosphane)palladium(II) chloride (0.15 g, 0.2 mmol) and CuI (10 mg, 0.05 mmol) were added under argon. After stirring for 50 min at 50 °C the mixture was filtered through a small SiO_2 column. Flash chromatography of the residue (SiO_2, cyclohexane/ethyl acetate, 30:1) afforded 0.97 g (89%) of **12a** as a brown solid which was recrystallized from diethyl ether to afford yellow crystals, m.p. 86 °C. – IR (CCl_4): $\tilde{\nu}$ = 3070 cm^{-1}, 2950, 2840/2740 (CHO), 2210 (C≡C), 1670 (C=O), 1600 (C=C), 1370, 1250, 1180. – ^1H NMR: δ = 2.66* (t, $J_{3,4}$ = 8.0 Hz, 2H, 3-H), 2.87* (t, $J_{3,4}$ = 8.0 Hz, 2H, 4-H), 7.22 (m, 1H, Ar-H), 7.38 (m, 5H, Ar-H), 7.60 (m, 2H, Ar-H), 7.95 (m, 1H, Ar-H), 10.51 (s, 1H, CHO). – $C_{19}H_{14}O$ (258.3): calcd. C 88.34, H 5.46; found C 88.18, H 5.39.

3,4-Dihydro-1-[(trimethylsilyl)ethynyl]naphthalene-2-carbaldehyde (**12b**): A stirred suspension of 1-bromo-3,4-dihydronaphthalene-2-carbaldehyde (**11**)[21] (4.50 g, 19.0 mmol), (trimethylsilyl)-ethyne (2.80 g, 28.5 mmol), 40 ml of dry triethylamine, bis(triphenylphosphane)palladium(II) chloride (335 mg, 0.47 mmol), and CuI (36 mg, 0.19 mmol) was heated under argon in a closed tube (provided with a relief valve) at 35 °C for 1.5 h. After filtration through a small SiO_2 column the solvent was removed in vacuo. Flash chromatography of the residue (SiO_2, cyclohexane/ethyl acetate, 30:1) afforded 4.67 g (97%) of **12b** as a brown solid which was recrystallized from diethyl ether/pentane to give yellow crystals, m.p. 71 °C. – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 2960, 2840, 2730 (CHO), 2150 (C≡C), 1670 (C=O), 1600 (C=C), 1370, 1290, 1180. – ^1H NMR: δ = 0.32 [s, 9H, $Si(CH_3)_3$], 2.60* (t, $J_{3,4}$ = 8.0 Hz, 2H, 3-H), 2.82* (t, $J_{3,4}$ = 8.0 Hz, 2H, 4-H), 7.20 (m, 1H, Ar-H), 7.34 (m, 2H, Ar-H), 7.82 (m, 1H, Ar-H), 10.41 (s, 1H, CHO). – $C_{16}H_{18}OSi$ (254.4): calcd. C 75.54, H 7.13; found C 75.15, H 7.16.

1-[3,4-Dihydro-1-(phenylethynyl)naphthalen-2-yl]ethanol (**13a**): To a stirred solution of **12a** (8.45 g, 32.7 mmol) in 400 ml of dry THF 24.5 ml (39.2 mmol) of a 1.6 M solution of methyllithium in diethyl ether was added dropwise at −78 °C under nitrogen. The mixture was stirred for an additional 30 min at −78 °C and then hydrolyzed at −30 °C with a satd. ammonium chloride solution. After warming up to room temp. the organic solution was separated, and the aqueous layer was extracted three times with 250-ml portions of dichloromethane. The combined organic phases were washed with a satd. sodium chloride solution and then dried with $MgSO_4$. Removal of the solvent in vacuo and flash chromatographic purification of the resulting residue (SiO_2, cyclohexane/ethyl acetate, 5:1) gave 8.43 g (94%) of **13a** as a yellow oil. – IR (CCl_4): $\tilde{\nu}$ = 3610 cm^{-1} (O–H), 3060, 2980, 2930, 1490, 1255, 1240, 1050. – ^1H NMR: δ = 1.41 (d, J = 7.0 Hz, 3H, CH_3), 1.93 [s (br.), 1H, OH], 2.42* (m, 1H, 3'-H), 2.60* (m, 1H, 3'-H), 2.83* (t, $J_{3',4'}$ = 8.0 Hz, 2H, 4'-H), 5.37 (q, $J_{CH,CH3}$ = 7.0 Hz, 1H, CH), 7.20 (m, 3H, Ar-H), 7.35 (m, 3H, Ar-H), 7.54 (m, 2H, Ar-H), 7.70 (m, 1H, Ar-H). – MS (EI), *m/z* (%): 274 (18) [M^+], 259 (50), 231 (100), 229 (33), 228 (32), 216 (32), 215 (55).

1-{3,4-Dihydro-1-[(trimethylsilyl)ethynyl]naphthalen-2-yl}-ethanol (**13b**): To a stirred solution of **12b** (4.00 g, 15.7 mmol) in 200 ml of dry THF 15.0 ml (24.0 mmol) of a 1.6 M solution of methyllithium in diethyl ether was added dropwise at −78 °C under nitrogen. The mixture was stirred for an additional 1 h at −78 °C and then hydrolyzed at −30 °C with a satd. ammonium chloride solution. After warming up to room temp. the organic solution was separated, and the aqueous layer was extracted three times with 200-ml portions of dichloromethane. The combined organic phases were washed with a satd. sodium chloride solution and then dried with $MgSO_4$. Removal of the solvent in vacuo and flash chromatographic purification of the resulting residue (SiO_2, cyclohexane/ethyl acetate 5:1) gave 3.66 g (86%) of **13b** as a pale yellow oil; from diethyl ether/pentane **13b** was obtained as colorless needles, m.p. 86 °C. – IR (CCl_4): $\tilde{\nu}$ = 3620 cm^{-1} (br., O–H), 3060, 2960, 2150 (C≡C), 1250, 1070. – ^1H NMR: δ = 0.28 [s, 9H, $Si(CH_3)_3$], 1.37 (d, J = 7.0 Hz, 3H, CH_3), 1.96 [s (br.), 1H, OH], 2.38* (m, 1H, 3'-H), 2.54* (m, 1H, 3'-H), 2.78* (t, $J_{3',4'}$ = 8.0 Hz, 2H, 4'-H), 5.25 (q, $J_{CH,CH3}$ = 7.0 Hz, 1H, CH), 7.16 (m, 3H, Ar-H), 7.59 (m, 1H, Ar-H). – $C_{17}H_{22}OSi$ (270.5): calcd. C 75.50, H 8.20; found C 75.15, H 8.28.

1-[3,4-Dihydro-1-(phenylethynyl)naphthalen-2-yl]ethanone (**14a**): To a vigorously stirred solution of **13a** (8.50 g, 31.0 mmol) and dry triethylamine (52.20 g, 0.516 mol) in 75 ml of dry DMSO a solution of the SO_3–pyridine complex (15.00 g, 94.2 mmol) in 75 ml of DMSO, was slowly added under argon the temperature being maintained at <29 °C. The mixture was stirred for an additional 45 min at room temp. before the reaction was quenched with 400 ml of ice/water. The mixture was extracted with diethyl ether (4 × 800 ml), and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2, cyclohexane/ethyl acetate, 50:1) of the residue afforded 6.90 g (82%) of **14a** as a yellow oil. – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 2940, 2200 (C≡C), 1660 (C=O), 1600 (C=C), 1365, 1260, 1200. – ^1H NMR: δ = 2.71 (m, 2H, CH_2), 2.81 (m, 5H, CH_2, CH_3), 7.21 (m, 1H, Ar-H), 7.32 (m, 2H, Ar-H), 7.42 (m, 3H, Ar-H), 7.59 (m, 2H, Ar-H), 7.96 (m, 1H, Ar-H). – MS (EI), *m/z* (%): 273 (9) [M^+ + 1], 272 (47), 229 (95), 228 (72),227 (41), 202 (36).

1-{3,4-Dihydro-1-[(trimethylsilyl)ethynyl]naphthalen-2-yl}-ethanone (**14b**): To a vigorously stirred solution of **13b** (7.85 g, 29.0 mmol) and dry triethylamine (39.90 g, 0.395 mol) in 70 ml of dry DMSO a solution of the SO_3–pyridine complex (13.86 g, 87.1 mmol) in 70 ml of DMSO was slowly added, the temperature being maintained at <29 °C. The mixture was stirred for an additional 1.5 h at room temp. before the reaction was quenched with 400 ml of ice/water. The mixture was extracted with diethyl ether (4 × 400 ml), and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2, cyclohexane/ethyl acetate 20:1) of the residue afforded 6.42 g (82%) of **14b** as a yellow oil. – IR (CCl_4). $\tilde{\nu}$ = 3060 cm^{-1}, 2960, 2140 (C≡C), 1660 (C=O), 1370, 1290, 1250. – ^1H NMR: δ = 0.30 [s, 9H, $Si(CH_3)_3$], 2.64 (m, 2H, CH_2), 2.77 (m, 5H, CH_2, CH_3), 7.16 (m, 1H, Ar-H), 7.29 (m, 2H, Ar-H), 7.82 (m, 1H, Ar-H). – MS (EI), *m/z* (%): 268 (21) [M^+], 267 (31), 253 (53), 195 (22), 194 (80), 193 (21), 179 (49).

1-{3,4-Dihydro-1-[(triisopropylsilyl)ethynyl]naphthalen-2-yl}-ethanone (**14c**). – a) *1-(3,4-Dihydro-1-ethynylnaphthalen-2-yl)ethanone* (**14e**): A solution of **14b** (0.91 g, 3.4 mmol) in 120 ml of dry methanol was treated with vigorous stirring with 50 mg of potassium carbonate. The mixture was stirred for 35 min at room temp., quenched with 50 ml of water, extracted with dichloromethane (4 × 70 ml), and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1) of the residue gave **14e** (0.62 g, 93%) as a pale yellow solid; after recrystallization from diethyl ether/pentane colorless crystals, m.p. 61 °C. – IR (CCl_4): $\tilde{\nu}$ = 3310

cm^{-1} (C≡C–H), 3060, 2940, 1660 (C=O), 1600 (C=C), 1360, 1300, 1280. – ^1H NMR: δ = 2.67 (m, 5H, CH_2, CH_3), 2.80 (m, 2H, CH_2), 3.71 (s, 1H, C≡CH), 7.18 (m, 1H, Ar-H), 7.30 (m, 2H, Ar-H), 7.85 (m, 1H, Ar-H). – MS (EI), *m/z* (%): 197 (15) [M^+ + 1], 196 (100), 195 (85), 181 (38), 153 (66), 152 (69). – $C_{14}H_{12}O$ (196.3): calcd. C 85.68, H 6.16; found C 85.44, H 6.17.

b) *1-{3,4-Dihydro-1-[(triisopropylsilyl)ethynyl]naphthalen-2-yl}-1-(triisopropylsilyl)oxyethene* (**14f**): A stirred solution of diisopropylamine (0.87 ml, 6.2 mmol) and *N,N'*-dimethylpropyleneurea (7.5 ml, 62.2 mmol) in 15 ml of dry THF was cooled under nitrogen to −78 °C and treated dropwise with a 2.5 M solution of *n*-butyllithium in *n*-hexane (2.5 ml, 6.2 mmol). After the mixture had been stirred for 1 h at −78 °C a solution of **14e** (0.55 g, 2.8 mmol) in 10 ml of THF was added. Stirring was continued for 1 h, then triisopropylsilyl chloride (1.5 ml, 7.0 mmol) was added by means of a syringe. The mixture was allowed to warm up to −30 °C, stirred for an additional 1.5 h, the reaction was quenched with a satd. ammonium chloride solution at −30 °C and the mixture extracted with dichloromethane (3 × 75 ml). The combined organic phases were dried ($MgSO_4$), concentrated in vacuo and the residue was filtrated through SiO_2. According to the ^1H-NMR analysis the oily residue (1.50 g) contained **14f** as the main component; it was treated to **14c** without further purification. – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 2950, 1610, 1460, 1300, 1290, 1010. – ^1H NMR: δ = 1.10 [m, 42H, Si(iC_3H_7)$_3$], 2.58* (t, $J_{3',4'}$ = 8.0 Hz, 2H, 3'-H), 2.79* (t, $J_{3',4'}$ = 8.0 Hz, 2H, 4'-H), 4.60 (d, $J_{2,2}$ = 1.2 Hz, 1H, 2-H), 5.01 (d, $J_{2,2}$ = 1.2 Hz, 1H, 2-H), 7.19 (m, 3H, Ar-H), 7.73 (m, 1H, Ar-H).

c) **14c**: The solution of **14f** (see above) in 40 ml of THF was treated with 40 ml of 0.2 M HCl and stirred for 5 d at room temp. After dilution with diethyl ether the mixture was extracted with diethyl ether (3 × 50 ml) and the combined organic phases were washed with a satd. sodium chloride solution, dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2, cyclohexane/ethyl acetate, 50:1) of the residue gave **14c** (0.74 g, 75%, referred to **14e**) as a pale yellow oil. – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 2950, 2140 (C≡C), 1660 (C=O), 1600, 1460, 1360, 1280. – ^1H NMR: δ = 1.18 [m, 21H, Si(iC_3H_7)$_3$], 2.65 (m, 2H, CH_2), 2.79 (m, 5H, CH_2, CH_3), 7.19 (m, 1H, Ar-H), 7.30 (m, 2H, Ar-H), 7.90 (m, 1H, Ar-H). – MS (EI), *m/z* (%): 352 (5) [M^+], 310 (41), 309 (100), 307 (15), 268 (27), 267 (100), 251 (12).

1-[3,4-Dihydro-1-(phenylethynyl)naphthalen-2-yl]-4-nitro-3-phenylbutan-1-one (**15a**): A stirred solution of diisopropylamine (2.53 g, 25.1 mmol) in 350 ml of dry THF under nitrogen was cooled to −78 °C and treated dropwise with a 2.5 M solution of *n*-butyllithium in *n*-hexane (10 ml, 25.1 mmol). After the mixture had been stirred for 1 h at −78 °C a solution of **14a** (6.00 g, 22.0 mmol) in 100 ml of THF was added. Stirring was continued for 1 h and, after the addition of a solution of (*E*)-β-nitrostyrene (4.10 g, 27.5 mmol) in 150 ml of THF, for further 2.5 h. The mixture was allowed to warm up to −30 °C, stirred for 15 h, the reaction was quenched with a satd. ammonium chloride solution at −30 °C and the mixture extracted with dichloromethane (3 × 75 ml) at room temp. The combined organic phases were dried ($MgSO_4$), concentrated in vacuo and the residue purified by flash chromatography (SiO_2, cyclohexane/dichloromethane, 3:1 and 2:1) to give **14a** (0.60 g, 10%), and **15a** (5.56 g, 60%, yellow solid); from diethyl ether/dichloromethane **15a** was obtained as colorless crystals, m.p. 145 °C. – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 3030, 2940, 2200 (C≡C), 1650 (C=O), 1600 (C=C), 1375, 1230. – ^1H NMR: δ = 2.60* (m, 2H, 3'-H), 2.77* (m, 2H, 4'-H), 3.67 (dd, $J_{2,2}$ = 17.5, $J_{2,3}$ = 8.5 Hz, 1H, 2-H), 3.83 (dd, $J_{2,2}$ = 17.5, $J_{2,3}$ = 6.5 Hz, 1H, 2-H), 4.22 (m, 1H, 3-H), 4.66 (dd, $J_{4,4}$ = 12.5, $J_{3,4}$ = 8.5 Hz, 1H, 4-H), 4.83 (dd, $J_{4,4}$ = 12.5, $J_{3,4}$ = 6.5 Hz, 1H, 4-H), 7.15–7.45 (m, 13H, Ar-H), 7.91 (m, 1H, Ar-H). – MS (EI), *m/z* (%): 421 (34) [M^+], 287 (31), 273 (31), 272 (68), 271 (46), 270 (32), 259 (37). – $C_{28}H_{23}NO_3$ (421.5): calcd. C 79.79, H 5.50, N 3.32; found C 79.58, H 5.48, N 3.28.

1-{[3,4-Dihydro-1-(trimethylsilyl)ethynyl]naphthalen-2-yl}-4-nitro-3-phenylbutan-1-one (**15b**): A stirred solution of diisopropylamine (0.63 ml, 4.5 mmol) and *N,N'*-dimethylpropyleneurea (DMPU) (5.0 ml, 41.4 mmol) in 10 ml of dry THF was cooled under nitrogen to −78 °C and treated dropwise with a 2.5 M solution of *n*-butyllithium in *n*-hexane (1.8 ml, 4.5 mmol). After the mixture had been stirred for 1 h at −78 °C a solution of **14b** (1.01 g, 3.8 mmol) in 5 ml of THF was added. Stirring was continued for 45 min before addition of a solution of (*E*)-β-nitrostyrene (0.64 g, 4.3 mmol) in 150 ml of THF. After 5 min the mixture was hydrolyzed at −78 °C with a satd. ammonium chloride solution, warmed up to room temp. and extracted with diethyl ether (5 × 50 ml). Residual DMPU was removed by filtration of the cyclohexane solution (200 ml) through a SiO_2 column. The organic phases were dried ($MgSO_4$), concentrated in vacuo and the residue purified by flash chromatography (SiO_2, cyclohexane/dichloromethane, 3:1 and 2:1) to afford **14b** (200 mg, 20%), and **15b** (630 mg, 40%, yellow oil); from diethyl ether/pentane **15b** was obtained as pale yellow crystals, m.p. 80 °C. – IR (CCl_4): $\tilde{\nu}$ = 3070 cm^{-1}, 3040, 2960, 2140 (C≡C), 1660 (C=O), 1550, 1380, 1250. – ^1H NMR: δ = 0.24 (s, 9H, TMS), 2.50* (m, 2H, 3'-H), 2.70* (m, 2H, 4'-H), 3.61 (dd, $J_{2,2}$ = 17.5, $J_{2,3}$ = 8.5 Hz, 1H, 2-H), 3.78 (dd, $J_{2,2}$ = 17.5, $J_{2,3}$ = 6.5 Hz, 1H, 2-H), 4.19 (m, $J_{2,3}$ = $J_{3,4}$ = 6.5 Hz, 1H, 3-H), 4.66 (dd, $J_{4,4}$ = 12.5, $J_{3,4}$ = 8.5 Hz, 1H, 4-H), 4.79 (dd, $J_{4,4}$ = 12.5, $J_{3,4}$ = 6.5 Hz, 1H, 4-H), 7.15 (m, 1H, Ar-H), 7.30 (m, 7H, Ar-H), 7.79 (m, 1H, Ar-H). – $C_{25}H_{27}NO_3Si$ (417.6): calcd. C 71.91, H 6.52, N 3.35; found C 71.77, H 6.52, N 3.30.

1-{[3,4-Dihydro-1-(triisopropylsilyl)ethynyl]naphthalen-2-yl}-4-nitro-3-phenylbutan-1-one (**15c**): A stirred solution of diisopropylamine (0.23 ml, 1.6 mmol) in 7 ml of dry THF was cooled under nitrogen to −78 °C and treated dropwise with a 2.5 M solution of *n*-butyllithium in *n*-hexane (0.64 ml, 1.6 mmol). After the mixture had been stirred for 1 h at −78 °C a solution of **14c** (0.48 g, 1.4 mmol) in 3 ml of THF was added. Stirring was continued for 1 h before addition of a solution of (*E*)-β-nitrostyrene (0.24 g, 1.6 mmol) in 3 ml of THF. After stirring for 1.5 h the mixture was warmed up to −30 °C, hydrolyzed with a satd. ammonium chloride solution, warmed up to room temp. and extracted with dichloromethane (3 × 30 ml). The combined organic phases were dried ($MgSO_4$), concentrated in vacuo and the residue was purified by flash chromatography (SiO_2, cyclohexane/dichloromethane 3:1 and 2:1) to afford **15c** (0.40 g, 59%) as a yellow oil; from diethyl ether/pentane **15c** was obtained as pale yellow crystals, m.p. 53 °C. – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 2940, 2130 (C≡C), 1650 (C=O), 1550, 1460, 1380. – ^1H NMR: δ = 1.10 [m, 21H, Si(iC_3H_7)$_3$], 2.49 (m, 2H, CH_2), 2.69 (m, 2H, CH_2), 3.50 (dd, $J_{2,2}$ = 17.5, $J_{2,3}$ = 8.5 Hz, 1H, 2-H), 3.82 (dd, $J_{2,2}$ = 17.5, $J_{2,3}$ = 6.5 Hz, 1H, 2-H), 4.19 (m, $J_{2,3}$ = $J_{3,4}$ = 6.5 Hz, 1H, 3-H), 4.65 (dd, $J_{4,4}$ = 12.5, $J_{3,4}$ = 8.5 Hz, 1H, 4-H), 4.79 (dd, $J_{4,4}$ = 12.5, $J_{3,4}$ = 6.5 Hz, 1H, 4-H), 7.15 (m, 1H, Ar-H), 7.29 (m, 7H, Ar-H), 7.85 (m, 1H, Ar-H). – $C_{31}H_{39}NO_3Si$ (501.8): calcd. C 74.21, H 7.84, N 2.79; found C 73.97, H 7.81, N 2.80.

1-[3,4-Dihydro-1-(phenylethynyl)naphthalen-2-yl]-4-nitropentan-1-one (**15d**): A stirred solution of diisopropylamine (214 mg, 2.1 mmol) in 35 ml of dry THF was cooled under nitrogen to −78 °C and treated dropwise with a 2.3 M solution of *n*-butyllithium in *n*-

hexane (1.0 ml, 2.3 mmol). After the mixture had been stirred for 45 min at −78 °C a solution of **14a** (500 mg, 1.84 mmol) in 20 ml of THF was added. Stirring was continued for 1 h before addition of a solution of 2-nitropropene (201 mg, 2.3 mmol) in 15 ml of THF (T < −60 °C). After stirring for 4 h the mixture was warmed up to −40 °C, hydrolyzed with a satd. ammonium chloride solution, warmed up to room temp. and extracted with dichloromethane (3 × 30 ml). The combined organic phases were dried ($MgSO_4$), concentrated in vacuo and the residue was purified by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 20:1) to afford **15d** (224 mg, 34%) as yellow crystals, m.p. 63 °C (diethyl ether/pentane/trichloromethane). – IR (CCl_4): $\tilde{\nu}$ = 3063 cm^{-1}, 2936, 2890, 2834, 2198, 1667, 1452, 1362, 1314, 1227, 1186, 919. – ^1H NMR: δ = 1.57 (d, J = 6.7 Hz, 3H, CH_3), 2.17–2.43 (m, 2H, 3-H), 2.69 (m, J = 8.6 Hz, 2H, 3′-H), 2.82 (m, 2H, 4′-H), 3.31 (t, J = 7.2 Hz, 2H, 2-H), 4.71 (m, 1H, 4-H), 7.18–7.95 (m, 9H, Ar-H). – MS (EI), *m/z* (%): 359 (5) [M^+], 313 (42), 372 (37), 257 (100), 229 (58), 226 (36), 202 (14), 114 (12), 112 (13). – $C_{23}H_{21}NO_3$ (359.4): calcd. C 76.86, H 5.89, N 3.90; found C 76.84, H 5.94, N 3.89.

3,4-Dihydro-5-[3,4-dihydro-1-(phenylethynyl)naphthalen-2-yl]-3-phenyl-2H-pyrrole 1-Oxide (**16a**): A solution of **15a** (1.09 g, 2.6 mmol) in ethanol (20 ml), THF (1.5 ml) and water (8 ml) was treated with concd. HCl (0.25 ml) and hydrogen-reduced iron powder (1.56 g, 27.9 mmol), and the mixture was refluxed under argon for 45 min. After filtration the filter cake was treated with warm ethanol and dichloromethane, and the combined solutions were neutralized with a satd. sodium bicarbonate solution and then concentrated. The residue was carefully extracted several times with dichloromethane; the combined organic phases were dried ($MgSO_4$), concentrated in vacuo and purified by flash chromatography (SiO_2, dichloromethane/ethanol 150:1) to give **16a** (0.55 g, 55%) as a yellow solid; after recrystallization from diethyl ether/dichloromethane **16a** was obtained as yellow crystals, m.p. 135 °C. – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 3030, 2940, 1600, 1510, 1490, 1240, 690. – ^1H NMR: δ = 2.87* (m, 2H, 3′-H), 3.03* (m, 2H, 4′-H), 3.78 (m, 3H, 3-H, 4-H), 4.22 (m, 1H, 2-H), 4.47 (m, 1H, 2-H), 7.19 (m, 1H, Ar-H), 7.25–7.49 (m, 12H, Ar-H), 7.80 (m, 1H, Ar-H). – MS (EI), *m/z* (%): 389 (32) [M^+], 372 (35), 371 (100), 370 (30), 361 (18), 360 (23). – $C_{28}H_{23}NO$ (389.5): calcd. C 86.34, H 5.95, N 3.60; found C 86.22, H 5.96, N 3.63.

3,4-Dihydro-5-{3,4-dihydro-1-[(trimethylsilyl)ethynyl]naphthalen-2-yl}-3-phenyl-2H-pyrrole 1-Oxide (**16b**): A solution of **15b** (0.50 g, 1.2 mmol) in ethanol (8 ml), THF (0.7 ml) and water (3 ml) was treated with concd. HCl (0.07 ml) and hydrogen-reduced iron powder (0.65 g, 11.6 mmol), and the mixture was refluxed under argon for 1 h. After work-up as for **16a** (see above) flash chromatography (SiO_2, dichloromethane/ethanol, 120:1) gave **16b** (0.29 g, 62%) as a yellow oil, which precipitated from diethyl ether as yellow crystals, m.p. 100 °C. – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 3020, 2960, 2140 (C≡C), 1520, 1450, 1250. – ^1H NMR: δ = 0.20 [s, 9H, $Si(CH_3)_3$], 2.82* (m, 2H, 3′-H), 2.99* (m, 2H, 4′-H), 3.70 (m, 3H, 3-H, 4-H), 4.21 (m, 1H, 2-H), 4.40 (m, 1H, 2-H), 7.17 (m, 1H, Ar-H), 7.22–7.42 (m, 7H, Ar-H), 7.69 (m, 1H, Ar-H. – $C_{25}H_{27}NOSi$ (385.6): calcd. C 77.88, H 7.06, N 3.63; found C 77.83, H 7.03, N 3.56.

3,4-Dihydro-5-{3,4-dihydro-1-[(triisopropylsilyl)ethynyl]naphthalen-2-yl}-3-phenyl-2H-pyrrole 1-Oxide (**16c**): A solution of **15c** (0.32 g, 0.6 mmol) in ethanol (4.5 ml), THF (0.5 ml) and water (1.5 ml) was treated with concd. HCl (0.04 ml) and hydrogen-reduced iron powder (0.35 g, 6.2 mmol), and the mixture was refluxed under argon for 1.5 h. After work-up as for **16a** (see above) flash chromatography (SiO_2, dichloromethane/ethanol, 100:1) yielded **16c** (0.18 g, 60%) as a yellow oil. – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 3020, 2940, 2140 (C≡C), 1600, 1460, 1270, 1230. – ^1H NMR: δ = 1.09 [m, 21H, $Si(iC_3H_7)_3$], 2.83* (m, 2H, 3′-H), 3.03* (m, 2H, 4′-H), 3.55–3.85 (m, 3H, 3-H, 4-H), 4.32 (m, 2H, 2-H), 7.30 (m, 8H, Ar-H), 7.75 (m, 1H, Ar-H). – MS (EI), *m/z* (%): 469 (48) [M^+], 468 (70), 426 (20), 296 (23), 179 (20), 165 (23), 132 (19).

3,4-Dihydro-5-[3,4-dihydro-1-(phenylethynyl)naphthalen-2-yl]-2-methyl-2H-pyrrole 1-Oxide (**16d**): The mixture of **15d** (400 mg, 1.11 mmol) in ethanol (9.5 ml), THF (1.0 ml), water (3.5 ml), concd. HCl (0.04 ml) and hydrogen-reduced iron powder (0.670 g, 12.0 mmol) was refluxed under argon for 1.5 h. After work-up as described for **16a** (see above) flash chromatography (SiO_2, ethyl acetate/methanol, 10:1) yielded **16d** (220 mg, 61%) as colorless crystals, m.p. 75–76 °C (diethyl ether/pentane/trichloromethane). – IR (CCl_4): $\tilde{\nu}$ = 3067 cm^{-1}, 2977, 2938, 2836, 1502, 1489, 1444, 1351, 1330, 1236. – ^1H NMR: δ = 1.52 (d, J = 7 Hz, 3H, CH_3), 1.87 (m, 1H, 3-H), 2.45 (m, 1H, 3-H), 2.85* (m, 2H, 3′-H), 2.99* (m, 2H, 4′-H), 3.34 (m, 2H, 4-H), 4.13 (sext, J = 7 Hz, 1H, 2-H), 7.14–7.58 (m, 8H, Ar-H), 7.76–7.82 (m, 1H, Ar-H). – MS (EI), *m/z* (%): 327 (58) [M^+], 326 (100) [M^+ – H, 100], 310 (28), 268 (12), 250 (13), 226 (8), 200 (7), 104 (9), 77 (7).

General Procedure for the Thermolysis of the Nitrones: A 10^{-2} to 10^{-3} M solution of the nitrone in dry benzene (ca. 75 ml) was placed into a 100-ml autoclave, degassed with argon for 10 min, and then heated for the given periods. The progress of the reaction was monitored by TLC taking samples after cooling of the reaction vessel with ice/water. Before thermolysis was continued, the solution was again flushed with argon. After complete conversion the reaction mixture was concentrated in vacuo, the residue was analyzed by ^1H NMR and then purified as indicated.

Thermolysis of **16a**: According to the general procedure a solution of **16a** (230 mg, 0.59 mmol) in 60 ml of dry benzene was heated at 200 °C for 1.5 h. The ^1H-NMR analysis of the crude material indicated two main products, 9,10,11,12-tetrahydro-5,9-diphenyl-8*H*-benzo[*f*]pyrrolo[2,1-*a*]isoquinolin-6-one (**17a**) and 11-benzoyl-5,6,8,9-tetrahydro-8-phenyl-7*H*-benzo[*e*]pyrrolo[2,1-*a*]isoindole (**18a**), in a 2:9 ratio. Purification by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1) afforded **17a** (34 mg, 15%) and **18a** (163 mg, 71%) as brown and yellow solids, respectively. – **17a**: M.p. 217 °C (dark yellow crystals from diethyl ether/trichloromethane). – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 2940, 1650 (C=O), 1600 (C=C), 1540, 1520, 905. – ^1H NMR: δ = 2.58* (m, 2H, 11-H), 2.85* (t; $J_{11,12}$ = 6.5 Hz, 2H, 12-H), 3.24 (dd, $J_{10,10}$ = 16.5 Hz, $J_{9,10}$ = 8.5 Hz, 1H, 10-H), 3.59 (dd, $J_{10,10}$ = 16.5 Hz, $J_{9,10}$ = 8.5 Hz, 1H, 10-H), 3.82 (quint, $J_{8,9}$ = $J_{9,10}$ = 8.5 Hz, 1H, 9-H), 4.21 (dd, $J_{8,8}$ = 13.0 Hz, $J_{8,9}$ = 8.5 Hz, 1H, 8-H), 4.73 (dd, $J_{8,8}$ = 13.0 Hz, $J_{8,9}$ = 8.5 Hz, 1H, 8-H), 6.83 (m, 2H, Ar-H), 7.11 (m, 1H, Ar-H), 7.20 (m, 1H, Ar-H), 7.32 (m, 10H, Ar-H). – ^{13}C NMR: δ = 25.0* (C-11), 30.1* (C-12), 38.5* (C-10), 40.6 (C-9), 55.6 (C-8), 112.5/125.6/126.4/127.0/127.1/127.4/127.7/128.3/128.5/129.0/130.9/131.1/132.4/137.3/140.5/141.0/142.9/144.3 (Ar-C and C=C), 161.3 (C=O). – MS (EI), *m/z* (%): 390 (20) [M^+], 389 (77), 388 (100), 256 (9), 230 (13), 228 (21). – $C_{28}H_{23}NO$ (389.5): calcd. C 86.34, H 5.95, N 3.60; found C 86.19, H 5.87, N 3.56.

18a: M.p. 151 °C (yellow crystals from diethyl ether). – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 2930, 1615 (C=O), 1600 (C=C), 1450, 1400, 1215. – ^1H NMR: δ = 2.58* (m, 2H, 6-H), 2.87* (t, $J_{5,6}$ = 7.5 Hz, 2H, 5-H), 2.95 (dd, $J_{7,7'}$ = 15.9, $J_{7,8}$ = 8.0 Hz, 1H, 7-H), 3.32 (dd, $J_{7,7'}$ = 15.9 Hz, $J_{7',8}$ = 8.0 Hz, 1H, 7′-H), 4.11 (quint, $J_{7,8}$ = $J_{8,9}$ = 8.0 Hz, 1H, 8-H), 4.27 (dd, $J_{9,9'}$ = 12.0 Hz, $J_{8,9}$ = 8.0 Hz, 1H, 9-H), 4.71 (dd, $J_{9,9'}$ = 12.0 Hz, $J_{8,9}$ = 8.0 Hz, 1H, 9′-H), 6.66 (m,

2H, Ar-H), 6.93 (m, 1H, Ar-H), 7.09–7.44 (m, 9H, Ar-H), 7.78 (m, 2H, Ar-H). – ^{13}C NMR: δ = 20.6* (C-6), 31.0* (C-5), 32.1* (C-7), 46.7 (C-8), 55.0 (C-9), 115.1/125.6/125.8/127.0/127.1/127.8/128.2/128.6/128.9/129.2/130.0/131.4/131.6/131.9/137.1/138.3/139.5/142.3 (Ar-C and pyrrole-C), 186.7 (C=O). – MS (EI), *m/z* (%): 390 (30) [M$^+$], 389 (100), 388 (12), 285 (13), 284 (13), 257 (37), 256 (25). – $C_{28}H_{23}NO$ (389.5): calcd. C 86.34, H 5.95, N 3.60; found C 86.31, H 5.96, N 3.64.

Thermolysis of **16b**: According to the general procedure a solution of **16b** (240 mg, 0.62 mmol) in 70 ml of dry benzene was heated at 200°C for 3 h. The ^{1}H-NMR analysis of the crude material indicated one main product, 9,10,11,12-tetrahydro-9-phenyl-8*H*-benzo[*f*]pyrrolo[2,1-*a*]isoquinolin-6-one (**17e**), and a very minor component, 5,6,8,9-tetrahydro-8-phenyl-7*H*-benzo[*e*]pyrrolo[2,1-*a*]isoindole-11-carbaldehyde (**18e**). Purification by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1, then ethyl acetate) afforded **17e** (115 mg, 59%) and **18e** (ca. 1 mg, <1%). – **17e**: M.p. 180°C (yellow crystals from dichloromethane/diethyl ether). – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 3030, 2940, 1670 (C=O), 1600 (C=C), 1580, 1530, 1380, 1260. – ^{1}H NMR: δ = 2.62* (m, 2H, 11-H), 2.88* (t, $J_{11,12}$ = 6.5 Hz, 2H, 12-H), 3.19 (dd; $J_{10,10'}$ = 16.5 Hz, $J_{9,10}$ = 8.5 Hz, 1H, 10-H), 3.53 (dd, $J_{10',10}$ = 16.5 Hz, $J_{9,10'}$ = 8.5 Hz, 1H, 10'-H), 3.80 (quint, $J_{8,9}$ = $J_{9,10}$ = 8.5 Hz, 1H, 9-H), 4.19 (dd, $J_{8,8'}$ = 13.0 Hz, $J_{8,9}$ = 8.5 Hz, 1H, 8-H), 4.70 (dd, $J_{8',8}$ = 13.0, $J_{8',9}$ = 8.5 Hz, 1H, 8'-H), 6.90 (s, 1H, 5-H), 7.30 (m, 8H, Ar-H), 7.75 (m, 1H, Ar-H). – ^{13}C NMR: δ = 23.5* (C-11), 29.0* (C-12), 38.0* (C-10), 40.6 (C-9), 54.7 (C-8), 110.5/111.3/125.2/126.8/127.3/127.31/128.5/129.0/129.7/131.9/138.5/140.9/144.7/147.1 (Ar-C and C=C), 161.8 (CO). – MS (EI), *m/z* (%): 314 (24) [M$^+$ + 1], 313 (100), 312 (30), 236 (13), 181 (11), 180 (12). – $C_{22}H_{19}NO$ (313.4): calcd. C 84.31, H 6.11, N 4.47; found C 84.11, H 6.05, N 4.60.

18e: IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 3020, 2920, 1640 (C=O), 1600, 1460, 1420, 1390. – ^{1}H NMR: δ = 2.61 (m, 2H, 6-H), 2.91 (m, 3H, 5a/b-H, 7a-H), 3.30 (dd, $J_{7,7}$ = 15.9, $J_{7,8}$ = 8.0 Hz, 1H, 7b-H), 4.12 (quint, $J_{7,8}$ = $J_{8,9}$ = 8.0 Hz, 1H, 8-H), 4.33 (dd, $J_{9,9}$ = 12.0, $J_{8,9}$ = 8.0 Hz, 1H, 9-H), 4.87 (dd, $J_{9,9}$ = 12.0, $J_{8,9}$ = 8.0 Hz, 1H, 9-H), 7.15–7.40 (m, 8H, Ar-H), 7.63 (m, 1H, Ar-H), 10.00 (s, 1H, CHO). – MS (EI), *m/z* (%): 314 (25) [M$^+$ + 1], 313 (100), 312 (13), 284 (14), 222 (22), 209 (28). – $C_{22}H_{19}NO$: calcd. 313.1467, found 313.1470 (MS).

Thermolysis of **16c**: According to the general procedure a solution of **16c** (120 mg, 0.26 mmol) in 35 ml of dry benzene was heated at 200°C for 7 h. The ^{1}H-NMR analysis of the crude material indicated one main product (**17e**). Purification by flash chromatography (SiO_2, ethyl acetate) afforded **17e** (43 mg, 54%); for physical data see above.

Thermolysis of **16d**: According to the general procedure a solution of **16d** (35 mg, 0.11 mmol) in 10 ml of dry benzene was heated at 200°C for 1.5 h. The ^{1}H-NMR analysis of the crude material indicated two main products, 9,10,11,12-tetrahydro-8-methyl-5-phenyl-8*H*-benzo[*f*]pyrrolo[2,1-*a*]isoquinolin-6-one (**17d**) and 11-benzoyl-5,6,8,9-tetrahydro-9-methyl-7*H*-benzo[*e*]pyrrolo[2,1-*a*]isoindole (**18d**). Purification by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 3:1, ethyl acetate/methanol, 20:1) afforded **17d** (8.5 mg, 24%) and **18d** (21 mg, 60%). – **17d**: Oil. – IR (CCl_4): $\tilde{\nu}$ = 3062 cm^{-1}, 3029, 2978, 2944, 2909, 2823, 1647, 1605, 1442, 1367, 1342, 1267, 1110, 928. – ^{1}H NMR: δ = 1.49 (d, *J* = 7 Hz, 3H, CH_3), 1.94 (m, 1H, 9-H), 2.38 (m, 1H, 9-H), 2.68 (t, *J* = 7 Hz, 2H, 11-H), 2.84 (t, *J* = 7 Hz, 2H, 12-H), 3.13 (m, 2H, 10-H), 4.95 (m, 1H, 8-H), 6.82 (m, 2H, Ar-H), 7.10–7.36 (m, 7H, Ar-H). – ^{13}C NMR: δ = 18.6 (CH_3), 25.0 (C-11), 28.8 (C-10), 29.0 (C-9), 29.9 (C-8), 30.2 (C-12), 111.6/125.5/126.4/127.0/127.6/128.3/130.9/131.3/132.7/137.6/140.5/143.2/143.7 (Ar-C and C=C), 161.0 (CO). – MS (EI), *m/z* (%): 327 (100) [M$^+$], 255 (5), 241 (5), 215 (7), 164 (7), 142 (5), 133 (5), 127 (5), 120 (5). – $C_{23}H_{21}NO$: calcd. 327.162, found 327.162 (MS).

18d: M.p. 116°C (diethyl ether/pentane). – IR (CCl_4): $\tilde{\nu}$ = 3062 cm^{-1}, 2986, 2918, 2820, 1616, 1505, 1454, 1396, 1292, 1216, 1027, 919. – ^{1}H NMR: δ = 1.30 (d, *J* = 7 Hz, 3H, CH_3), 2.75 (m, 1H, 8-H), 2.43–2.97 (m, 7H, 5-H/6-H/7-H/8-H), 4.98 (m_c, 1H, 9-H), 6.60 (m, 2H, Ar-H), 6.90 (m, 1H, Ar-H), 7.10–7.43 (m, 4H, Ar-H), 7.78 (m, 2H, Ar-H). – ^{13}C NMR: δ = 20.6* (CH_3), 21.3* (C-6), 22.0* (C-7), 30.9 (C-5), 34.5 (C-8), 55.6 (C-9), 114.4/121.8/125.5/125.53/127.8/128.2/128.6/130.0/131.6/131.8/132.2/137.0/138.5/139.2 (Ar-C and C=C), 186.7 (CO). – MS (EI), *m/z* (%): 327 (100) [M$^+$], 312 (18), 286 (17), 250 (13), 222 (27), 180 (15), 153 (11), 152 (11), 105 (42), 77 (54). – $C_{23}H_{21}NO$: calcd. 327.162, found 327.162 (MS).

5-Bromo-7,8-dihydroquinoline-6-carbaldehyde (**21a**): To a solution of DMF (5.71 g, 78.1 mmol) in 27 ml of dry trichloromethane, phosphorus tribromide (6.2 ml, 65 mmol) was added at 0°C under nitrogen. After the mixture had been stirred for 1 h at room temp., a solution of 5,6,7,8-tetrahydroquinolin-5-one (**20a**)[36] (3.83 g, 26.0 mmol) in dry trichloromethane (10 ml) was added. The mixture was refluxed for 2 h, hydrolyzed at 0°C with a satd. sodium bicarbonate solution, neutralized and then extracted with dichloromethane (3 × 150 ml). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography of the residue afforded **21a** (4.17 g, 67%) as yellow crystals, m.p. 98°C (diethyl ether/pentane). – IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1}, 2852, 1662, 1590, 1555, 1445, 1249, 1162, 947, 802. – ^{1}H NMR: δ = 2.75 (t, *J* = 8.1 Hz, 2H, 7-H), 3.07 (t, *J* = 8.1 Hz, 2H, 8-H), 7.30 (m, 1H, Py-H), 8.49 (m, 1H, Py-H), 8.49 (m, 1H, Py-H), 10.25 (s, 1H, CHO). – ^{13}C NMR: δ = 22.4 (7'-C), 29.8 (8'-C), 122.5/129.0/135.0/135.7/136.4 (Py-C), 150.9/158.8 (C=C), 192.5 (CHO). – MS (EI), *m/z* (%): 239 (56) [M$^+$ (^{81}Br)], 237 (58) [M$^+$ (^{79}Br)], 210 (27), 208 (27), 158 (46), 130 (100), 129 (87), 102 (27), 77 (21). – $C_{10}H_8NOBr$ (238.1): calcd. C 50.45, H 3.33, N 5.88; found C 50.22, H 3.34, N 5.76.

5-Bromo-7,8-dihydro-2-methylquinoline-6-carbaldehyde (**21b**): To a solution of DMF (13.5 ml, 175.1 mmol) in 60 ml of dry trichloromethane phosphorus tribromide (13.3 ml, 141.5 mmol) was added at 0°C under nitrogen. After the mixture had been stirred for 1 h at room temp., a solution of 5,6,7,8-tetrahydro-2-methylquinolin-5-one (**20b**)[37] (7.50 g, 46.5 mmol) in dry trichloromethane (10 ml) was added. The mixture was refluxed for 2 h, hydrolyzed at room temp. with a satd. sodium bicarbonate solution and extracted with dichloromethane (3 × 200 ml). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Recrystallization of the residue from cyclohexane/ethyl acetate afforded **21b** (9.36 g, 82%) as yellow crystals, m.p. 98°C. – IR (CCl_4): $\tilde{\nu}$ = 3055 cm^{-1}, 2960, 2895, 2855, 1675, 1585, 1422, 1233, 1154, 1031, 950, 850. – ^{1}H NMR: δ = 2.59 (s, 3H, CH_3), 2.73 (t, *J* = 8.2 Hz, 2H, 7-H), 3.02 (t, *J* = 8.2 Hz, 2H, 8-H), 7.15 (d, *J* = 7.9 Hz, 1H, Py-H), 8.00 (d, *J* = 7.9 Hz, 1H, Py-H), 10.23 (s, 1H, CHO). – ^{13}C NMR: δ = 22.35 (7'-C), 24.5 (Py-CH_3), 29.9 (8'-C), 122.0/126.3/134.0/136.0/137.0 (Py-C), 158.2/160.7 (C=C), 192.6 (CHO). – MS (EI), *m/z* (%): 253 (30) [M$^+$ (^{81}Br)], 251 (30) [M$^+$ (^{79}Br)], 224 (20), 222 (20), 172 (26), 145 (11), 144 (100), 143 (79), 142 (17), 128 (14), 115 (23), 102 (10), 77 (12). – $C_{11}H_{10}NOBr$ (252.1): calcd. C 52.41, H 4.00, N 5.52; found C 52.27, H 3.97, N 5.54.

7,8-Dihydro-5-(phenylethynyl)quinoline-6-carbaldehyde (**22a**): To a stirred suspension of **21a** (4.16 g, 17.47 mmol) and phenylethyne (2.50 g, 24.46 mmol) in 80 ml of dry triethylamine, bis(triphenyl-

phosphane)palladium(II) chloride (300 mg, 0.43 mmol) and CuI (ca. 20 mg) were added under argon. After stirring for 2 h at 50 °C the mixture was filtered through a small SiO_2 column by using 10 ml of ethyl acetate as final eluent. Concentration in vacuo and subsequent flash chromatography of the residue (SiO_2, ethyl acetate) afforded **22a** (3.40 g, 75%) as yellow crystals, m.p. 73 °C (diethyl ether/pentane). – IR (CCl_4): $\tilde{\nu}$ = 3055 cm^{-1}, 2960, 2890, 2840, 2205, 1683, 1591, 1444, 1361, 1245, 1166. – ^1H NMR: δ = 2.80 (t, *J* = 8.2 Hz, 2H, 7-H), 3.08 (t, *J* = 8.2 Hz, 2-H, 8-H), 7.27–7.64 (m, 6H, Ar-H, Py-H), 8.16 (m, 1H, Py-H), 8.53 (m, 1H, Py-H), 10.51 (s, 1H, CHO). – ^{13}C NMR: δ = 20.1 (C-7), 29.5 (8-C), 79.3 (C≡C), 82.0 (C≡C), 101.9/121.8/122.3/128.8/129.8/131.9/134.15/134.16/140.6 (Ar-C and Py-C), 150.52 (C=C), 158.1 (C=C), 191.8 (C=O). MS (EI): *m/z* (%): 259 (86) [M^+], 230 (100), 216 (11), 202 (34), 182 (14), 154 (31), 115 (19), 102 (23), 88 (16), 77 (15).

7,8-Dihydro-2-methyl-5-(phenylethynyl)quinoline-6-carbaldehyde (**22b**): To a stirred suspension of **21b** (9.30 g, 36.9 mmol) and phenylethyne (5.28 g, 51.7 mmol) in 170 ml of dry triethylamine, bis(triphenylphosphane)palladium(II) chloride (500 mg, 0.71 mmol) and CuI (ca. 10 mg) were added under argon. After stirring for 4 h at 50 °C the mixture was filtered through a small SiO_2 column by using 150 ml of ethyl acetate as final eluent. Concentration in vacuo afforded a brown solid, which crystallized from cyclohexane/ethyl acetate (10:1); **22b** (6.40 g, 63%) was obtained as yellow crystals, m.p. 129 °C. – IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 3010, 2945, 2840, 2210, 1656, 1581, 1548, 1359, 1240, 1160, 760. – ^1H NMR: δ = 2.60 (s, 3H, Py-CH_3), 2.78 (t, *J* = 8.5 Hz, 2H, 7-H), 3.04 (t, *J* = 8.5 Hz, 2H, 8-H), 7.14 (d, *J* = 7.6 Hz, 1H, Py-H), 7.38–7.63 (m, 5H, Ar-H), 8.03 (d, *J* = 7.6 Hz, 1H, Py-H), 10.49 (s, 1H, CHO). – ^{13}C NMR: δ = 20.1* (7′-C), 24.6 (Py-CH_3), 29.6* (8′-C), 82.2 (C≡C), 101.7 (C≡C), 121.79, 121.84, 125.1, 128.7, 129.7, 131.9, 134.45, 134.52, 139.7 (Ar-C and Py-C), 157.6 (C=C), 160.0 (C=C), 191.7 (CHO). – MS (EI), *m/z* (%): 273 (91) [M^+], 258 (8), 244 (100), 230 (30), 202 (26), 196 (10), 168 (16), 143 (6), 101 (10), 77 (5). – $C_{19}H_{15}NO$ (273.3): calcd. C 83.49, H 5.53, N 5.12; found C 83.38, H 5.61, N 5.19.

1-[7,8-Dihydro-5-(phenylethynyl)quinolin-6-yl]ethanol (**23a**): To a stirred solution of **22a** (3.00 g, 11.6 mmol) in 100 ml of dry diethyl ether, a solution of methylmagnesium iodide (0.24 g, 14.5 mmol) in 15 ml of diethyl ether was added dropwise under nitrogen. The yellow mixture was refluxed for 2 h, then hydrolyzed with 10 ml of water, neutralized with satd. ammonium chloride and extracted with diethyl ether (3 × 100 ml). The combined organic phases were dried ($MgSO_4$), concentrated in vacuo and the residue was purified by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 1:1) to give **23a** (3.02 g, 95%) as yellow crystals, m.p. 73 °C (diethyl ether/pentane). – IR (CCl_4): $\tilde{\nu}$ = 3620 cm^{-1}, 3060, 2978, 2835, 2201, 1492, 1445, 1232, 1171, 1058, 884. – ^1H NMR: δ = 1.43 (d, *J* = 6.3 Hz, 3H, CH_3), 1.70 (s, 1H, OH), 2.68* (t, 2H, 7′-H), 3.05* (t, *J* = 8.2 Hz, 2H, 8′-H), 5.35 (q, *J* = 6.3 Hz, 1H, 1-H), 7.15–7.57 (m, 6H, Ar-H, Py-H), 7.91 (m, 1H, Py-H), 8.36 (m, 1H, Py-H). – ^{13}C NMR: δ = 21.1* (7′-H), 21.8* (CH_3), 30.1* (C-8′), 68.9 (COH), 83.7 (C≡C), 96.8 (C≡C), 114.6/122.0/123.0/128.5/128.6/128.8/131.5/132.4/147.4 (Ar-C and Py-C), 151.8 (C=C), 155.8 (C=C). – MS (EI), *m/z* (%): 275 (20) [M^+], 260 (56), 232 (100), 217 (25), 202 (20), 154 (24), 130 (13), 127 (10), 115 (20), 102 (11), 77 (17).

1-[7,8-Dihydro-2-methyl-5-(phenylethynyl)quinolin-6-yl]ethanol (**23b**): To a stirred solution of **22b** (5.20 g, 19.0 mmol) in 150 ml of dry diethyl ether a solution of methylmagnesium iodide (0.58 g, 23.9 mmol) in 20 ml of diethyl ether was added dropwise under nitrogen. The yellow mixture was refluxed for 2 h, then hydrolyzed with 10 ml of water at room temp., neutralized with a satd. ammonium chloride solution and extracted with diethyl ether (3 × 200 ml). The combined organic phases were dried ($MgSO_4$), concentrated in vacuo and the residue was purified by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 1:1) to give **23b** (4.80 g, 87%) as yellow crystals, m.p. 130 °C (diethyl ether/pentane). – IR (KBr): $\tilde{\nu}$ = 3646 cm^{-1}, 3052, 2966, 2879, 1609, 1584, 1524, 1487, 1458, 1280, 1230, 1159, 1052, 829. – ^1H NMR: δ = 1.40 (d, *J* = 6.4 Hz, 3H, CH_3), 2.53 (s, 3H, Py-CH_3), 2.65 (m, 2H, 7′-H), 2.69 (s, 1H, OH), 2.99 (t, *J* = 8.3 Hz, 2H, 8′-H), 5.33 (q, *J* = 6.4 Hz, 1H, CH), 7.02 (d, *J* = 7.9 Hz, 1H, Py-H), 7.32–7.53 (m, 5H, Ar-H), 7.77 (d, *J* = 7.9 Hz, 1H, Py-H). – ^{13}C NMR: δ = 21.1* (7′-C), 21.9* ($COCH_3$), 24.2* (Py-CH_3), 30.3* (8′-C), 68.2 (COH), 84.0 (C≡C), 96.6 (C≡C), 114.8/121.4/123.1/125.9/128.5/128.6/131.5/132.9/150.4 (Ar-C and Py-C), 155.2/156.4 (C=C). – MS (EI), *m/z* (%): 289 (25) [M^+], 274 (68), 246 (100), 231 (15), 202 (16), 168 (14), 144 (9), 115 (12), 77 (10). – $C_{20}H_{19}NO$ (289.4): calcd. C 83.01, H 6.62, N 4.84; found C 82.90, H 6.56, N 4.43.

1-[7,8-Dihydro-5-(phenylethynyl)quinolin-6-yl]ethanone (**24a**): To a stirred solution of **23a** (2.88 g, 10.4 mmol) and dry triethylamine (17.5 g, 173.0 mmol) in 25 ml of dry DMSO a solution of the SO_3–pyridine complex (4.98 g, 31.3 mmol) in 25 ml of DMSO was slowly added under argon, the temperature being maintained at < 29 °C. The mixture was stirred for an additional 2 h at room temp. before the reaction was quenched with 150 ml of ice/water. The mixture was extracted with diethyl ether (3 × 150 ml), and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1) of the residue afforded **24a** (2.33 g, 82%) as yellow crystals, m.p. 86 °C (cyclohexane/pentane). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 2950, 2830, 2195, 1648, 1439, 1363, 1259, 1186, 758, 690. – ^1H NMR: δ = 2.82 (s, 3H, CH_3), 2.88* (t, *J* = 8.2 Hz, 2H, 7′-H), 3.04* (t, *J* = 8.2 Hz, 2H, 8′-H), 7.26–7.75 (m, 6H, Ar-H, Py-H), 8.28 (m, 1H, Py-H), 8.48 (m, 1H, Py-H). – ^{13}C NMR: δ = 24.3* (C-7′), 30.0* (CH_3), 30.7* (C-8′), 85.9 (C≡C), 101.8 (C≡C), 122.2/122.3/124.5/128.5/128.7/129.5/131.6/134.4/143.1 (Ar-C and Py-C), 149.5/157.3 (C=C), 199.9 (C=O). – MS (EI), *m/z* (%): 273 (93) [M^+], 258 (26), 230 (100), 227 (14), 202 (49), 176 (8), 150 (7), 114 (12), 101 (11), 77 (12).

1-[7,8-Dihydro-2-methyl-5-(phenylethynyl)quinolin-6-yl]ethanone (**24b**): To a stirred solution of **23b** (930 mg, 3.2 mmol) and dry triethylamine (8.0 g, 57.4 mmol) in 8.4 ml of dry DMSO a solution of the SO_3–pyridine complex (1.80 g, 11.3 mmol) in 8.4 ml of DMSO was slowly added under argon, the temperature being maintained at < 29 °C. The mixture was stirred for an additional 2 h at room temp. before the reaction was hydrolyzed with 40 ml of ice/water. The mixture was extracted with diethyl ether (4 × 100 ml), and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography (SiO_2, cyclohexane/ethyl acetate, 10:1) of the residue afforded **24b** (821 mg, 89%) as yellow crystals, m.p. 101 °C (diethyl ether/pentane). – IR (KBr): $\tilde{\nu}$ = 3072 cm^{-1}, 3052, 2992, 2914, 2202, 1655, 1578, 1362, 1251, 1186, 1029, 762, 691. – ^1H NMR: δ = 2.58 (s, 3H, Py-CH_3), 2.79 (s, 3H, $COCH_3$), 2.84* (t, *J* = 8.2 Hz, 2H, 7′-H), 3.00* (t, *J* = 8.2 Hz, 2H, 8′-H), 7.12 (d, *J* = 7.9 Hz, 1H, Py-H), 7.37–7.60 (m, 5-H, Ar-H), 8.03 (d, *J* = 7.9 Hz, 1H, Py-H). – ^{13}C NMR: δ = 24.3* (C-7′), 24.4* (Py-CH_3), 30.1* ($COCH_3$), 30.7* (C-8′), 86.1 (C≡C), 101.7 (C≡C), 121.6/122.4/124.8/125.8/128.7/129.4/131.5/134.8/142.0 (Ar-C and Py-C), 156.7/158.7 (C=C), 199.7 (C=O). – MS (EI), *m/z* (%): 287 (100) [M^+], 286 (96), 272 (31), 244 (64), 202 (22), 176 (3), 144 (3), 101 (4), 77 (6). – $C_{20}H_{17}NO$ (287.4): calcd. C 83.60, H 5.96, N 4.87; found C 83.10, H 5.92, N 4.81.

1-[7,8-Dihydro-5-(phenylethynyl)quinolin-6-yl]-4-nitro-3-phenylbutan-1-one (**25a**): To a stirred solution of dry diisopropylamine (288 mg, 2.84 mmol) in 40 ml of dry THF, a 2.3 M solution of *n*-butyllithium in *n*-hexane (1.24 ml, 2.37 mmol) was added dropwise at −78 °C under nitrogen. After the mixture had been stirred for 1 h at −78 °C, a solution of **24a** (650 mg, 2.37 mmol) in 20 ml of THF was added slowly (T < −60 °C). Stirring at −78 °C was continued for 1 h and, after the addition of a solution of (*E*)-β-nitrostyrene (424 mg, 2.84 mmol) in 15 ml of THF (T < −60 °C), for a further 4 h. The mixture was allowed to warm up to −50 °C, treated with a satd. ammonium chloride solution at room temp., diluted with 10 ml of water, neutralized with a satd. sodium bicarbonate solution and extracted with dichloromethane (3 × 50 ml). The combined organic phases were dried ($MgSO_4$), concentrated in vacuo and the residue was purified by flash chromatography (SiO_2, dichloromethane/ethyl acetate, 40:1) to give **25a** (313 mg, 31%) as yellow crystals, m.p. 139 °C (diethyl ether/pentane). − IR (KBr): $\tilde{\nu}$ = 3054 cm^{-1}, 3028, 2952, 2898, 2189, 1635, 1582, 1553, 1455, 1383, 1222, 1135, 817, 760. − ^1H NMR: δ = 2.73* (t, *J* = 8.4 Hz, 2H, 7′-H), 2.98* (t, *J* = 8.4 Hz, 2H, 8′-H), 3.70 (dd, *J* = 18, *J* = 9 Hz, 1H, 2-H), 3.82 (dd, *J* = 18, *J* = 9 Hz, 1H, 2-H), 4.21 (quin, *J* = 9 Hz, 1H, 3-H), 4.70 (dd, *J* = 11, *J* = 7 Hz, 1H, 4-H), 4.83 (dd, *J* = 11, *J* = 7 Hz, 1H, 4-H), 7.23−7.48 (m, 11H, Ar-H, Py-H), 8.13 (m, 1H, Py-H), 8.48 (m, 1H, Py-H). − ^{13}C NMR: δ = 24.2* (C-7′), 29.9* (C-8′), 40.0 (C-3), 45.8 (C-2), 79.7 (C-4), 85.7 (C≡C), 102.4 (C≡C), 121.8/122.2/127.6/127.9/128.8/129.1/129.8/131.6/134.4/139.4/142.3/149.7 (Ar-C and Py-C), 152.5/157.2 (C=C), 199.1 (C=O). − MS (EI), *m/z* (%): 422 (11) [M^+], 376 (5), 273 (39), 258 (100), 242 (13), 232 (41), 228 (44), 202 (50), 117 (21), 115 (20), 105 (34), 91 (22), 77 (25).

1-[7,8-Dihydro-2-methyl-5-(phenylethynyl)quinolin-6-yl]-4-nitro-3-phenylbutan-1-one (**25b**): To a stirred solution of dry diisopropylamine (203 mg, 2.01 mmol) in 30 ml of dry THF, a 2.3 M solution of *n*-butyllithium in *n*-hexane (1.0 ml, 1.91 mmol) was added dropwise at −78 °C under nitrogen. After the mixture had been stirred for 30 min at −78 °C a solution of **24b** (500 mg, 1.74 mmol) in 20 ml of THF was added slowly (T < −60 °C). Stirring at −78 °C was continued for 1 h and, after the addition of a solution of (*E*)-β-nitrostyrene (325 mg, 2.18 mmol) in 15 ml of THF (T < −60 °C), for further 4 h. The mixture was allowed to warm up to −40 °C, treated with a satd. ammonium chloride solution (20 ml) at room temp., diluted with 10 ml of water, neutralized with a satd. sodium bicarbonate solution and extracted with dichloromethane (3 × 50 ml). The combined organic phases were dried ($MgSO_4$), concentrated in vacuo and the residue was purified by flash chromatography (SiO_2, dichloromethane/ethyl acetate, 20:1) to give **25b** (310 mg, 41%) as yellow crystals, m.p. 133 °C (diethyl ether/pentane/trichloromethane). − IR (CCl_4): $\tilde{\nu}$ = 3064 cm^{-1}, 3030, 2960, 2920, 2890, 2834, 2198, 1655, 1580, 1375, 1228, 1165, 1028, 698, 688. − ^1H NMR: δ = 2.57 (s, 3H, Py-CH_3), 2.73* (t, *J* = 8.0 Hz, 2H, 7′-H), 2.93* (t, *J* = 8.0 Hz, 2H, 8′-H), 3.67 (dd, *J* = 18, *J* = 9 Hz, 1H, 2-H), 3.80 (dd, *J* = 18, *J* = 9 Hz, 1H, 2-H), 4.12 (quin, *J* = 9 Hz, 1H, 3-H), 4.66 (dd, *J* = 14, *J* = 9 Hz, 1H, 4-H), 4.81 (dd, *J* = 14, *J* = 9 Hz, 1H, 4-H), 7.12 (d, *J* = 7.9 Hz, 1H, Py-H), 7.22−7.42 (m, 10H, Ar-H), 8.00 (d, *J* = 7.9 Hz, 1H, Py-H). − ^{13}C NMR: δ = 24.3* (C-7′), 24.5 (Py-CH_3), 30.0* (C-8′), 40.0 (C-3), 45.8 (C-2), 79.7 (C-4), 86.0 (C≡C), 102.3 (C≡C), 121.87121.9/125.0/125.6/127.6/127.9/128.8/129.1/129.7/131.6/134.9/139.5/141.3 (Ar-C and Py-C), 156.8/159.1 (C=C), 198.9 (C=O). − MS (EI), *m/z* (%): 436 (44) [M^+], 390 (10), 376 (11), 302 (29), 272 (100), 244 (57), 202 (26), 117 (17), 115 (13), 105 (36), 91 (18), 77 (22). − $C_{28}H_{24}N_2O_3$ (436.5): calcd. C 77.05, H 5.54, N 6.42; found C 76.83, H 5.50, N 6.31.

3,4-Dihydro-5-[7,8-dihydro-5-(phenylethynyl)quinolin-6-yl]-3-phenyl-2H-pyrrole 1-Oxide (**26a**): A solution of **25a** (150 mg, 0.35 mmol) in ethanol (3 ml), THF (1 ml) and water (1 ml) was treated with one drop of concd. HCl and hydrogen-reduced iron powder (195 mg, 3.5 mmol), and the mixture was refluxed under argon for 60 min. After filtration the filter cake was treated with warm ethanol (20 ml) and dichloromethane (10 ml). The combined solutions were neutralized with a satd. sodium bicarbonate solution and then concentrated. The residue was diluted with 10 ml of water followed by extraction with dichloromethane (4 × 10 ml); the combined organic solutions were dried ($MgSO_4$), concentrated in vacuo and the residue was purified by flash chromatography (SiO_2, dichloromethane/methanol, 40:1) to give **26a** (55 mg, 40%) as yellow crystals, m.p. 156 °C (diethyl ether/pentane). − IR (CCl_4): $\tilde{\nu}$ = 3062 cm^{-1}, 3025, 2950, 2200, 1488, 1443, 1395, 1326, 1239, 1187, 908. − ^1H NMR: δ = 3.04−3.25 (m, 4H, 7′-H, 8′-H), 3.74 (m, 3H, 3-H, 4-H), 4.24 (m_c, 1H, 2-H), 4.98 (m_c, 1H, 2-H), 7.20−7.44 (m, 11H, Ar-H, Py-H), 8.01 (dd, *J* = 7 Hz, 1H, Py-H), 8.44 (m, 1H, Py-H). − MS (EI), *m/z* (%): 390 (100) [M^+], 372 (34), 295 (9), 290 (12), 285 (12), 258 (25), 105 (30), 91 (11), 77 (25).

3,4-Dihydro-5-[7,8-dihydro-2-methyl-5-(phenylethynyl)quinolin-6-yl]-3-phenyl-2H-pyrrole 1-Oxide (**26b**): A solution of **25b** (300 mg, 0.69 mmol) in ethanol (5.5 ml), THF (0.5 ml) and water (2.2 ml) was treated with one drop of concd. HCl and hydrogen-reduced iron powder (420 mg, 7.5 mmol), and the mixture was refluxed under argon for 90 min. After filtration the filter cake was treated with warm ethanol (40 ml) and dichloromethane (20 ml). The combined solutions were neutralized with a satd. sodium bicarbonate solution and then concentrated. The residue was diluted with 20 ml of water followed by extraction with dichloromethane (3 × 30 ml). The combined organic solutions were dried ($MgSO_4$), concentrated in vacuo and the residue was purified by flash chromatography (SiO_2, dichloromethane/methanol, 40:1) to give **26b** (102 mg, 37%) as yellow crystals, m.p. 147 °C (diethyl ether/pentane/trichloromethane). − IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1}, 3024, 2948, 2920, 2192, 1589, 1513, 1448, 1235, 836, 758, 691. − ^1H NMR: δ = 2.56 (s, 3H, Py-CH_3), 3.10 (m, 4H, 7′-H/8′-H), 3.75 (m, 3H, 3-H/4-H), 4.22 (m, 1H, 2-H), 4.44 (m, 1H, CH_2), 7.07 (d, *J* = 7.9 Hz, 1H, Py-H), 7.26−7.41 (m, 10H, Ar-H), 7.88 (d, *J* = 7.9 Hz, 1H, Py-H). − MS (EI), *m/z* (%): 404 (54) [M^+], 299 (6), 272 (13), 193 (15), 105 (18).

Thermolysis of **26a**: According to the general procedure (see above) a solution of **26a** (70 mg, 0.18 mmol) in 30 ml of dry benzene was heated at 200 °C for 1.5 h. The ^1H-NMR analysis of the crude material indicated two main products, the bis-annulated α-pyridone **27a** and pyrrole **28a**. Purification by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 3:1, and cyclohexane/methanol, 20:1) afforded first **28a** (38 mg, 54%) and then **27a** (23 mg, 33%). − **27a**: Oil. − IR (CCl_4): $\tilde{\nu}$ = 3065 cm^{-1}, 3032, 1651, 1608, 1446, 1435, 1207, 1114. − ^1H NMR: δ = 2.70 (t, *J* = 6 Hz, 2H, 11-H), 3.09 (t, *J* = 6 Hz, 2H, 12-H), 3.27 (dd, *J* = 17, *J* = 10 Hz, 1H, 10-H), 3.62 (dd, *J* = 17, *J* = 10 Hz, 1H, 10-H), 3.84 (quin, *J* = 11 Hz, 1H, 9-H), 4.22 (dd, *J* = 13, *J* = 9 Hz, 1H, 8-H), 4.65 (dd, *J* = 17, *J* = 9 Hz, 1H, 8-H), 6.77 (m, 1H, 3-H), 7.03 (m, 1H, 4-H), 7.04−7.46 (m, 10H, Ar-H), 8.30 (m, 1H, 2-H). − MS (EI), *m/z* (%): 390 (92) [M^+], 389 (100), 318 (9), 257 (7), 214 (10), 156 (7), 105 (10), 91 (10), 77 (7). − $C_{27}H_{22}N_2O$: calcd. 390.173, found 390.174 (MS).

28a: M.p. 121 °C (diethyl ether/pentane). − IR (CCl_4): $\tilde{\nu}$ = 3064 cm^{-1}, 3028, 2960, 2928, 2900, 1615, 1460, 1399, 1317, 1237, 1077, 912. − ^1H NMR: δ = 2.73 (t, *J* = 8 Hz, 2H, 6-H), 2.99 (dd, *J* = 18 Hz, *J* = 9 Hz, 1H, 7-H), 3.12 (t, *J* = 8 Hz, 2H, 5-H), 3.36 (dd, *J* = 18, *J* = 9 Hz, 1H, 7-H), 4.12 (quin, *J* = 9 Hz, 1H, 8-H), 4.28

(dd, J = 11, J = 9 Hz, 1H, 9-H), 4.70 (dd, J = 11, J = 9 Hz, 1H, 9-H), 6.63 (m, 1H, 2-H), 6.93 (m, 1H, 1-H), 7.24–7.59 (m, 8H, Ar-H), 7.77 (m, 2H, Ar-H), 8.16 (m, 1H, 3-H). – MS (EI), *m/z* (%): 390 (100) [M^+], 285 (11), 258 (32), 195 (5), 156 (6), 105 (28), 77 (28). – $C_{27}H_{22}N_2O$: calcd. 390.173, found 390.174 (MS).

Thermolysis of **26b**: According to the general procedure (see above) a solution of **26b** (27 mg, 0.07 mmol) in 30 ml of dry benzene was heated at 200°C for 1.5 h. The ^{1}H-NMR analysis of the crude material indicated two main products, the bis-annulated α-pyridone **27b** and pyrrole **28b**. Purification by flash chromatography (SiO_2, cyclohexane/ethyl acetate, 3:1, and cyclohexane/methanol, 20:1) afforded first **28b** (16 mg, 58%) and then **27b** (7 mg, 26%). – **27b**: Yellow oil. – IR (CCl_4): $\tilde{\nu}$ = 3080 cm^{-1}, 3022, 2922, 2865, 1660, 1615, 1460, 1398, 1298, 1225, 1125, 1039, 918. – ^{1}H NMR: δ = 2.49 (s, 3H, Py-CH_3), 2.70 (t, J = 7 Hz, 2H, 11-H), 3.06 (t, J = 7 Hz, 2H, 12-H), 3.27 (dd, J = 17, J = 9 Hz, 1H, 10-H), 3.60 (dd, J = 17, J = 9 Hz, 1H, 10-H), 3.83 (quin., J = 9 Hz, 1H, 9-H), 4.20 (dd, J = 12, J = 9 Hz, 1H, 8-H), 4.72 (dd, J = 12, J = 9 Hz, 1H, 8-H), 6.63* (d, J = 8 Hz, 1H, 3-H), 6.75* (d, J = 8 Hz, 1H, 4-H), 7.18–7.43 (m, 10H, Ar-H). – MS (EI), *m/z* (%): 404 (91) [M^+], 403 (M^+ – H, 100), 389 (8), 271 (5), 200 (12), 105 (6), 77 (5). – $C_{28}H_{24}N_2O$: calcd. 404.189, found 404.189 (MS).

28b: M.p. 99°C (diethyl ether/pentane). – IR (CCl_4): $\tilde{\nu}$ = 3061 cm^{-1}, 3024, 2991, 2832, 1615, 1479, 1448, 1400, 1316, 1218, 1175, 924. – ^{1}H NMR: δ = 2.42 (s, 3H, Py-CH_3), 2.70 (t, J = 7 Hz, 2H, 6-H), 2.96 (dd, J = 18, J = 9 Hz, 1H, 7-H), 3.09 (t, J = 7 Hz, 2H, 5-H), 3.32 (dd, J = 18, J = 9 Hz, 1H, 7-H), 4.10 (quin, J = 9 Hz, 1H, 8-H), 4.12 (dd, J = 11, J = 9 Hz, 1H, 9-H), 4.66 (dd, J = 11, J = 9 Hz, 1H, 9-H), 6.50* (d, J = 7 Hz, 1H, 2-H), 6.83* (dd, J = 7 Hz, 1H, 1-H), 7.25–7.46 (m, 8H, Ar-H), 7.74 (m, 2H, Ar-H). – ^{13}C NMR: δ = 20.1 (C-6), 24.2 (Py-CH_3), 32.1 (C-5), 33.5 (C-7), 46.8 (C-8), 55.2 (C-9), 114.5/120.5/123.1/124.2/127.0/127.2/128.5/128.9/129.8/130.1/132.1/135.1/138.5/139.3/142.1/154.7/156.8 (Ar-C and C=C), 186.4 (C=O). – MS (EI), *m/z* (%) = 404 (100) [M^+], 313 (15), 300 (20), 299 (22), 272 (59), 271 (42), 257 (13), 195 (10), 168 (11), 105 (67), 91 (18), 77 (81). – $C_{28}H_{24}N_2O$: calcd. 404.189, found 404.190 (MS).

☆ Dedicated to Professor *Horst Prinzbach* on the occasion of his 65th birthday.

[1] Part 4: J. Bussenius, N. Laber, T. Müller, W. Eberbach, *Chem. Ber.* **1994**, *127*, 247–259.

[2] Part 3: W. Eberbach, N. Laber, *Tetrahedron Lett.* **1992**, *33*, 61–64.

[3] Part 2: W. Eberbach, W. Maier, *Tetrahedron Lett.* **1989**, *30*, 5591–5594.

[4] Part 1: W. Eberbach, J. Roser, *Tetrahedron Lett.* **1987**, *28*, 2689–2692.

[5] [5a] H. O. Huisman, *Angew. Chem.* **1971**, *83*, 511–520; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 450–459. – [5b] H. O. Huisman, W. N. Speckamp, *Int. Rev. Sci.: Org. Chem. Ser. 2* **1976**, *8*, 207. – [5c] L. F. Tietze, U. Beifuß, M. Lökös, M. Rischer, A. Göhrt, G. M. Sheldrick, *Angew. Chem.* **1990**, *102*, 545–547; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 527–529; and references therein.

[6] [6a] J. W. Morzycki, *Polish J. Chem.* **1995**, *69*, 321–340. – [6b] P. Catsoulacos, D. Catsoulacos, *J. Heterocycl. Chem.* **1993**, *30*, 1–10; and references therein.

[7] P. Catsoulacos, D. Catsoulacos, *Anticancer Res.* **1993**, *13*, 1203; G. H. Rasmusson, G. F. Reynolds, N. G. Steinberg, E. Walton, G. F. Patel, T. Liang, M. A. Cascieri, A. H. Cheung, J. R. Brooks, C. Berman, *J. Med. Chem.* **1986**, *29*, 2298–2315; A. Vermeulen, V. A. Giagulli, P. De Schepper, A. Buntinx, E. Stoner, *Prostate* **1989**, *14*, 45.

[8] R. G. Strachan, N. G. Steinberg, M. Tischler, R. Hirschmann, *J. Med. Chem.* **1964**, *7*, 355.

[9] I. Dwivedy, A. K. Singh, M. M. Singh, S. Ray, *Steroids* **1993**, *58*, 69–73.

[10] H. Singh, V. Kumar, D. Paul, *Indian J. Chem.*, Sect. B, **1984**, *23B*, 1181.

[11] R. W. Chesnut, N. N. Durham, R. A. Brown, E. A. Mawdsley, J. D. Berlin, *Steroids* **1976**, *27*, 525–541.

[12] S. V. Frye, C. D. Haffner, P. R. Maloney, R. A. Mook, Jr., G. F. Dorsey, Jr., R. N. Hiner, C. M. Cribbs, T. N. Wheeler, J. A. Ray, R. C. Andrews, K. W. Batchelor, H. N. Bramson, J. D. Stuart, S. L. Schweiker, J. van Arnold, S. Croom, D. M. Bickett, M. L. Moss, G. Tian, R. J. Unwalla, F. W. Lee, T. K. Tippin, M. K. James, M. K. Grizzle, J. E. Long, S. V. Schuster, *J. Med. Chem.* **1994**, *37*, 2352–2360; H. Kurata, K. Ishibashi, S. Saito, T. Hamada, H. Horikoshi, Y. Furukawa, K. Kojima, *Chem. Pharm. Bull.* **1996**, *44*, 115–121.

[13] J. Abraham, D. P. Indian, H. Singh, G. K. Patnerik, R. C. Srimal, *Indian J. Chem. Sect. B*, **1992**, *31*, 566.

[14] F. A. Lakhvich, L. G. Lis, A. A. Akhrem, *Russ. Chem. Rev.* **1984**, *53*, 582–605.

[15] For some examples of 13-azasteroids, see: H. O. Huisman, W. N. Speckamp, *U. S. Patent* 3.597.436, **1969** [*Chem. Abstr.* **1971**, *75*, 141054f]; B. B. Aleksandrov, V. S. Shklyaev, Y. V. Shklyaev, *Khim. Geterotsikl. Soedin.* **1991**, *6*, 854–855 [*Chem. Abstr.* **1992**, *116*, 21305g]; S. V. Kessar, P. Jit, K. P. Mundra, A. K. Lumb, *J. Chem. Soc. (C)* **1971**, 266–269; A. J. Birch, G. S. R. Subba Rao, *J. Chem. Soc.* **1965**, 3007–3008; S. V. Kessar, M. Singh, A. Kumar, *Tetrahedron Lett.* **1965**, 3245–3247; W. R. Schleigh, A. Catala, F. D. Popp, *J. Heterocycl. Chem.* **1965**, *2*, 379–384.

[16] The numbering of the tetracyclic systems corresponds with the gonane system; it is not consistent with the nomenclature used in the experimental part.

[17] For analogous 8π cyclizations of conjugated carbonyl ylides, resulting in the formation of 2-vinyl furans as final products, see: ref.[1], and references therein.

[18] H. Meier, K.-P. Zeller, *Angew. Chem.* **1975**, *87*, 52–63; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 32; J. March, *Advanced Organic Chemistry*, 1083–1085, Wiley, New York, **1992**.

[19] E. Lopez-Calle, W. Eberbach, results to be published.

[20] E. Lopez-Calle, part of the Dissertation, University of Freiburg, **1995**.

[21] T. L. Gilchrist, R. J. Summersell, *J. Chem. Soc., Perkin Trans. 1*, **1988**, 2595–2601.

[22] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467–4470; K. Sonogashira, *Comprehensive Organic Synthesis*, B. M. Trost, I. Fleming, Eds., vol. 3, p. 521, Pergamon Press, New York, **1991**; K. C. Nicolaou, E. J. Sorensen, *Classics in Total Synthesis*, p. 582, VCH, Weinheim, **1996**.

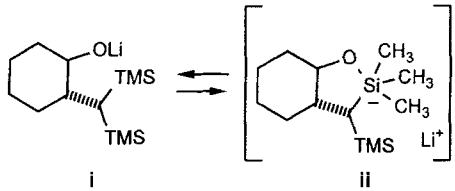
[23] The reaction can also be performed, however in slightly lower yields, by using the chloro analogue of **11**: T. Müller, Dissertation, University of Freiburg, **1993**.

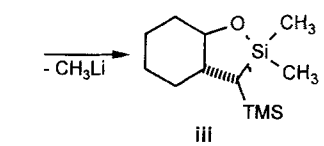
[24] J. R. Parikh, W. von E. Doering, *J. Am. Chem. Soc.* **1967**, *89*, 5505–5507; Y. Hamada, M. Shibata, T. Sugiura, S. Kato, T. Shioiri, *J. Org. Chem.* **1987**, *52*, 1252–1255.

[25] R. Schwesinger, *Nachr. Chem. Techn. Lab.* **1990**, *38*, 1214–1226.

[26] According to semiempirical calculations (program Sybyl 6.1/MOPAC) the distance between the phenyl ring at the alkyne terminus and the silyl group in **16a/b**, respectively, is approximately the same (ca. 2.3 Å); i.e. the different reactivity of the phenyl and the trimethyl silyl derivatives does not depend on purely steric reasons.

[27] A nice example for the strength of silicon interactions with an anionic oxygen center (see **ii**) has been observed by Rücker during studies with the compound **i** in which case subsequent elimination of methyl lithium occurs with formation of the cyclic siloxy derivative **iii**[28].





[28] C. Rücker, *Tetrahedron Lett.* **1984**, *25*, 4349–4352.
[29] C. Rücker, *Chem. Rev.* **1995**, *95*, 1009–1064.
[30] E. J. Corey, C. Rücker, *Tetrahedron Lett.* **1982**, *23*, 719–722; Y. Rubin, S. S. Lin, C. B. Knobler, J. Anthony, A. M. Boldi, F. Diederich, *J. Am. Chem. Soc.* **1991**, *113*, 6943–6949.
[31] T. K. Jones, S. E. Denmark, *Helv. Chim. Acta* **1983**, *66*, 2397–2411.
[32] J. Höfler, part of the Diplomarbeit, University of Freiburg, **1995**.
[33] H. O. Kalinowski, S. Berger, S. Braun, *^{13}C-NMR Spektroskopie*, p. 337, Thieme, Stuttgart, **1984**.
[34] W. Maier, part of the Diplomarbeit, University of Freiburg, **1988**.
[35] For related 1,2-Si shifts, see: T. J. Barton, G. C. Paul, *J. Am. Chem. Soc.* **1987**, *109*, 5292–5293; M. S. Baird, C. M. Dale, J. R. Al Dulayymi, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 1373–1374; X. Creary, Y.-X. Wang, *Tetrahedron Lett.* **1989**, *30*, 2493–2496; T. J. Barton, J. Lin, S. Ijadi-Maghsoodi, M. D. Power, X. Zhang, Z. Ma, H. Shimizu, M. S. Gordon, *J. Am. Chem. Soc.* **1995**, *117*, 11695–11703.
[36] **20a**: K. Berg-Nielsen, L. Skattebol, *Acta Chem. Scand., Ser. B* **1978**, *32*, 553–556.
[37] **20b**: E. Reimann, R. Reitz, *Liebigs Ann. Chem.* **1976**, 610–616.
[96150]