Model Reactions for the Synthesis of Azacorannulenes and Related Heteroaromatic Compounds[‡]

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Dedicated to Professor Manfred Christl on the occasion of his 60th birthday

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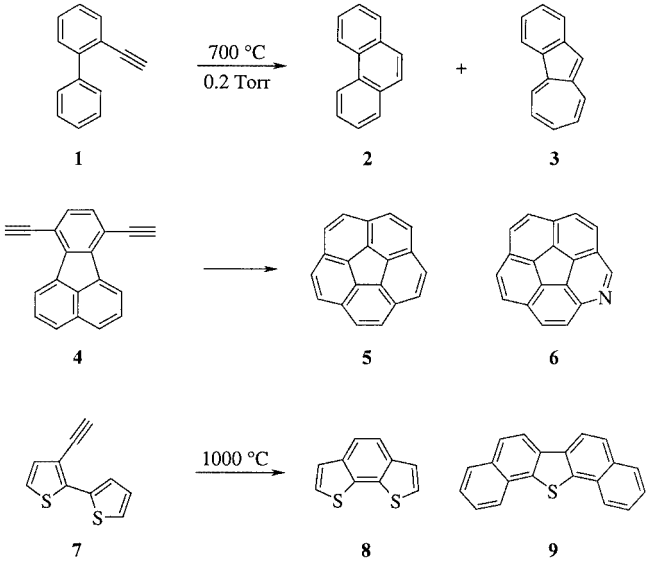
4-(2-Ethynylphenyl)pyridine (**10**), 3-(2-ethynylphenyl)pyridine (**11**), 2-(2-trimethylsilylethynylphenyl)pyridine (**26**), and 3-ethynyl-2-phenylpyridine (**13**) were prepared from readily available pyridine precursors by standard coupling reactions. Pyrolysis of **10** at 810 °C/0.5 Torr provided benzo[*f*]isoquinoline (**45**) and the benzopentalene dimer **47**. Pyrolysis of **11** (820 °C/0.5 Torr) afforded benzo[*f*]quinoline (**50**), benzo[*h*]isoquinoline (**52**), and a mixture of isomers of **47**. Pyrolysis of **13** (820 °C/0.3 Torr) provided benzo[*h*]quinoline (**56**) and the novel azulene derivative azuleno[1,2-*b*]pyridine (**58**). When **26** was desilylated by treatment with TBAF in THF/water, the unusual "dimerization" product **37** was produced; its structure was confirmed by X-ray structural analysis. The mechanisms of these transformations are discussed.

Introduction

In the early 1970s, Brown and co-workers, investigating the high-temperature behavior of arylalkynes under flash vacuum conditions, discovered that one of the simplest of their derivatives, 2-ethynylbiphenyl (**1**), isomerized to phenanthrene (**2**) and 1,2-benzazulene (**3**, total yield: 99%, product ratio 2.6:1) when heated to 700 °C at 0.2 Torr (Scheme 1).[2]

This process developed into one of the key reactions for the synthesis of bowl-shaped aromatics and other novel polycondensed aromatic hydrocarbons,[3−8] but only after the enormous growth in fullerene chemistry that set in after C_{60} became available in multigram quantities by the Krätschmer−Huffman route,[9] and when it was realized that long-known hydrocarbons such as corannulene (**5**) could be regarded as partial structures of C_{60} and its higher benzologues. In fact, the best current method for preparing **5**, developed by Scott and co-workers,[10] exploits a Brown-type isomerization involving the diethynyl derivative **4**



Scheme 1. Condensed aromatics and heteroaromatics by pyrolysis of alkynes

(7,10-diethynylfluoranthene), which cycloisomerizes to corannulene at 1000 °C under flash vacuum conditions. Although the ethynyl function is already present in the substrate to be pyrolyzed in many of these thermal isomerizations, derivatives with "latent triple bonds" such as halovinyl substituents or with protected acetylenes (trimethylsilylethynyl) have also been thermocyclized suc-

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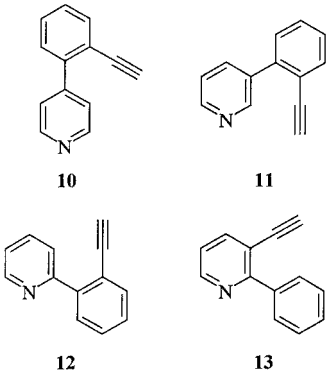
cessfully.[5,8] As far as the mechanisms of these ring closures are concerned, at least three alternatives are currently under discussion. Since the above arylacetylenes all formally contain a 1,3-hexadien-5-yne subunit, they could in principle rearrange by an electrocyclic process, initially yielding an isobenzene intermediate.[11−14] This in turn could subsequently stabilize itself by hydrogen-shift processes to yield the novel benzene nucleus. Alternatively, the terminal alkynes could undergo an acetylene/vinylidene isomerization to provide a carbene intermediate that would furnish the new six-membered ring by C−H insertion. Examples illustrating both types of mechanisms are discussed in detail below. Whereas these two possibilities would be most likely to take place at lower temperatures (ca. 200 °C in a static system, ca. 600 °C in a flow system), it has been postulated that at temperatures above 900 °C (flow system) the ring closure should be initiated by the addition of hydrogen atoms to the unsaturated (sub)systems involving the triple bond.[14]

In this paper we describe the high-temperature isomerization of various acetylenic pyridine derivatives, heteroaromatics that, we hope, will pave the way to aza variants of corannulene, such as **6** and related bowl-shaped heteroaromatics. Provided that these compounds also possess curved structures, questions such as their resolution into enantiomers, the heights of the racemization barriers, and their possible uses as concave reagents[15] would become important. It has been demonstrated by Otsubo and co-workers[16] that heteroorganic variants of the Brown cyclization can indeed be accomplished. These workers, inter alia, thermocyclized the ethynylthiophene **7** to **8**; analogously, 3,4-diethynyl-2,5-diphenylthiophene underwent double cyclization to **9**.

Selection and Syntheses of Ethynylpyridines for Pyrolysis

If the analogy to Brown's biphenyl derivatives is to be kept to as closely as possible, the three ethynylpyridines **10**−**12** immediately come to mind (Scheme 2).

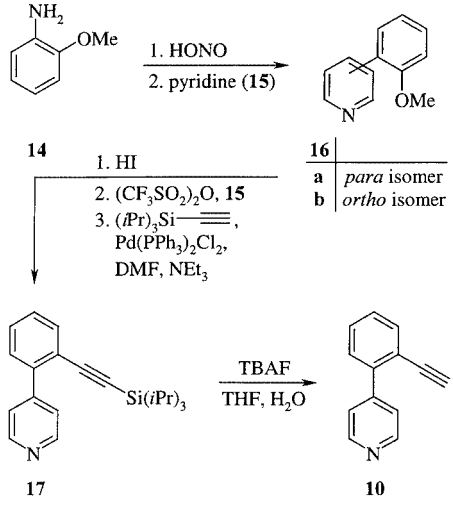


Scheme 2. A selection of (ethynylphenyl)pyridine derivatives

Formally, these three isomers are derived from 2-ethynylbiphenyl by replacement of the *para*- (**10**), the *meta*- (**11**), and the *ortho*-CH group (**12**), respectively, of the unfunctionalized benzene ring of **1** by an isovalent nitrogen atom. Obviously, the ethynylated ring of **1** offers four possibilities for such an exchange. For an exploratory study, however, we considered it sufficient to investigate one representative example of this series of isomers, and selected 3-ethynyl-2-phenylpyridine (**13**).

a) 4-(2-Ethynylphenyl)pyridine (10)

For the preparation of **10**, the commercially available *ortho*-anisidine (**14**, 2-methoxyaniline) was chosen as the starting material. In the first step it was converted into 4-(2-methoxyphenyl)pyridine by means of a Gomberg−Bachmann reaction involving diazotization of **14** and coupling of the resulting diazonium salt with pyridine (**15**). Although this reaction provided all three (*o*-methoxyphenyl)pyridine isomers, and **16a** was produced in only 7% yield, we still decided to use this route because of the low price of **14** and the ease of separation of **16a**, which could readily be obtained from the product mixture in gram amounts. Fortunately, the next three steps − ether cleavage of **16a** with HI, treatment of the resulting phenol with triflic anhydride in pyridine, and Sonogashira coupling of the obtained triflate with (triisopropylsilyl)acetylene in the presence of $Pd(PPh_3)_2Cl_2$ in DMF/triethylamine solution, yielding the protected acetylene **17** − took place in higher yields (58% overall, Scheme 3).



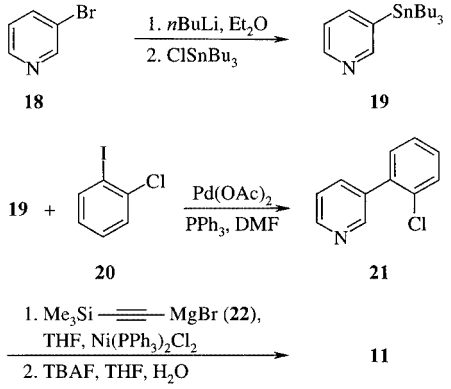
Scheme 3. The preparation of 4-(2-ethynylphenyl)pyridine (**10**)

For deprotection, **17** was stirred with tetra-*n*-butylammonium fluoride (TBAF) in moist tetrahydrofuran. Isomer **10**, obtained as a beige solid in 84% yield, was characterized by the usual spectroscopic and analytical methods (see Exp. Sect.).

b) 3-(2-Ethynylphenyl)pyridine (11)

To arrive at isomer **11**, the commercial 3-bromopyridine (**18**) was first subjected to halogen/metal exchange with *n*-butyllithium in diethyl ether, and the resulting organolithium intermediate was quenched with tri-*n*-butyltin chlor-

ide. The thus formed stannane **19** was subjected to Stille coupling [$Pd(OAc)_2$, triphenylphosphane, DMF] with 1-chloro-2-iodobenzene (**20**) to furnish **21** (yield for the **18** → **21** conversion 43%), which, after Kumada coupling [$Ni(PPh_3)_2Cl_2$, THF] with 2-(trimethylsilyl)ethynylmagnesium bromide (**22**) and subsequent TBAF deprotection, gave the desired **11** in 48% yield. At 21%, the overall yield of this sequence (Scheme 4) was acceptable; the spectroscopic data for **11** can once again be found in the Exp. Sect.



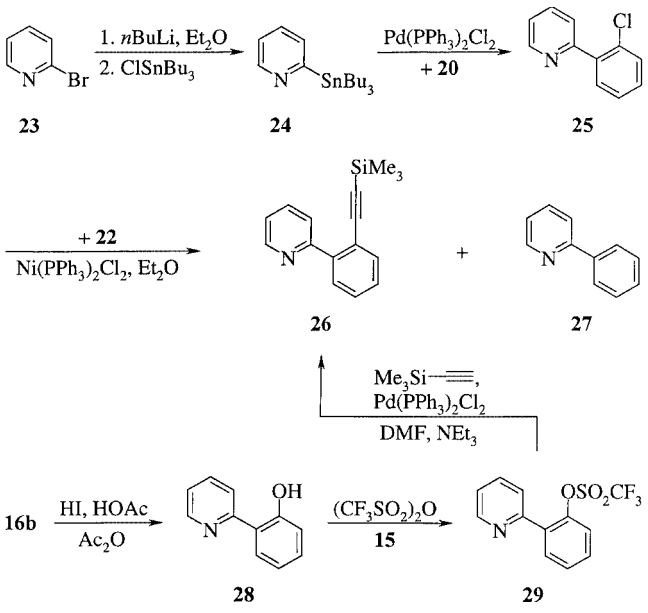
Scheme 4. The preparation of 3-(2-ethynylphenyl)pyridine (**11**)

c) 2-(2-Ethynylphenyl)pyridine (12)

After these two successful syntheses, the preparation of the last isomer, **12**, was considered to be mere routine. And, indeed, the assembly steps all the way to the (trimethylsilyl)-protected target molecule **26** could be carried out in full analogy to the **18** → **11** conversion: Stannylation of **23** to **24** was performed as above in 89% yield, and the subsequent Stille (**25**: 64%) and Kumada steps (**26**: 80%) also went well (Scheme 5), although the resulting **26** was always contaminated with 2-phenylpyridine (**27**), as could be shown by GC/MS analysis. Such reductive dehalogenations had previously been noted by Kumada during coupling reactions involving bromo- and iodobenzene.[17] Since the separation of **27** from **26** by chromatography failed, the pure (ethynylphenyl)pyridine was prepared by an alternate route also shown in Scheme 5: Ether cleavage of the *ortho* isomer of **16**, **16b** (see Scheme 3) provided the phenol **28** (63%), which was converted into the triflate **29** by treatment with triflic anhydride in pyridine (88%). Sonogashira coupling with (trimethylsilyl)ethyne under the above conditions then provided **26** (41%).

To our surprise, however, none of the expected **12** was obtained when **26** was deprotected with TBAF/THF/H_2O. Rather, a curious "dimer" of it, 6,6′-methanediylbis(pyrido[2,1-*a*]isoindole) (**37**) was isolated in the remarkable yield of 41%. The structure of this product followed from the spectroscopic data (Exp. Sect.), and in particular from an X-ray structural study of the nicely crystalline compound (needles from diethyl ether; Figure 1).

As can be seen in Figure 1, the molecule displays imposed twofold symmetry, the corresponding crystallographic axis passing through C13. Each "monomeric" half



Scheme 5. The preparation of 2-{2-[2-(trimethylsilyl)ethynyl]-phenyl}pyridine (**26**)

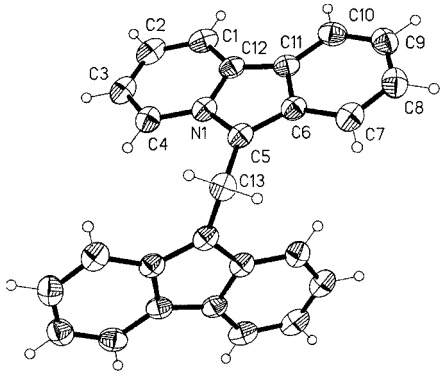
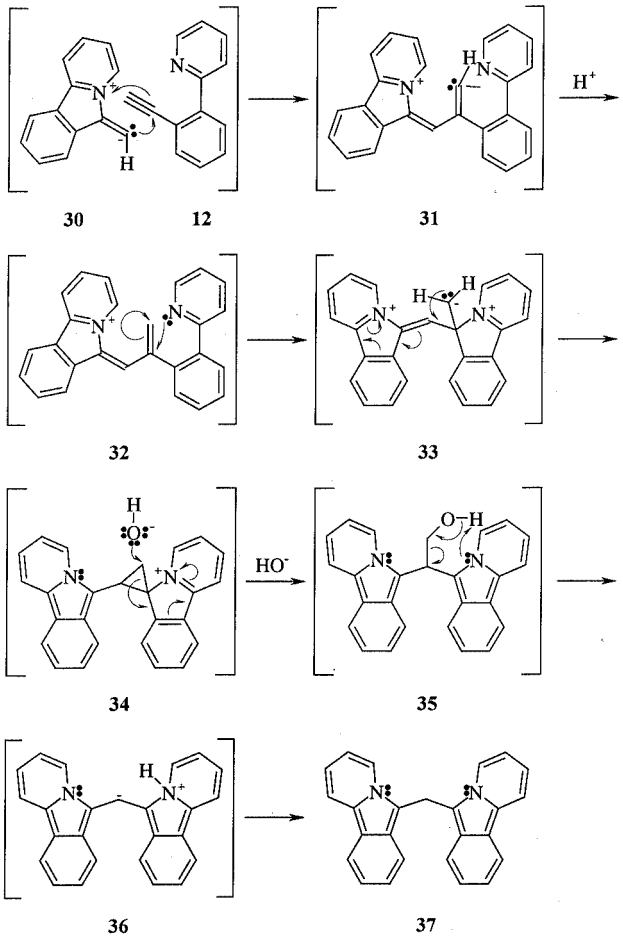


Figure 1. The structure of **37** in the crystal

of the molecule is planar (mean deviation 0.014 Å) and the torsion angle N1−C5−C5′−N1′ is 102°.

A comparison of starting material **26** and product **37** shows that not only has desilylation taken place but that the unusual "dimerization" has been accompanied by loss of a single carbon atom! To account for this feature we propose the interpretation summarized in Scheme 6.

As the primary step it is indeed very likely that desilylation would proceed as intended, yielding the originally desired **12**. However, because of the proximity of the basic nitrogen atom of the pyridine ring and the triple bond, intramolecular attack of the former on the latter could take place, resulting in the 1,3-dipolar intermediate **30**. This could cycloadd to unchanged **12**, and the zwitterion **31** thus produced could be protonated to afford **32**. If the pyridyl substituent of this intermediate were to enter into neighboring-group participation, zwitterion **33** could be formed, and this could relieve itself of some of its charge separation by formation of the spiro intermediate **34**. Ring opening of **34**



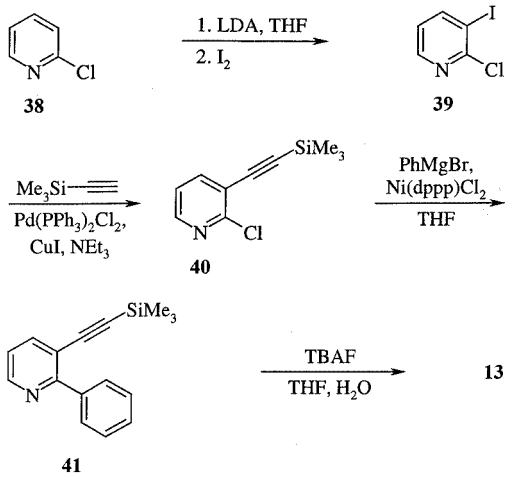
Scheme 6. The "dimerization" of 2-(2-ethynylphenyl)pyridine (**12**)

by hydroxide to give the primary alcohol **35** could take place next, with release of strain and compensation of charge providing the driving force. The carbon elimination could now occur through a six-membered transition state involving the loss of formaldehyde, and the resulting dipolar species **36** could finally stabilize itself by a 1,3-proton shift process. Fragmentations of primary alcohols with expulsion of formaldehyde are not without precedent. For example, heating of 2,2,2-triphenylethanol to its melting point (107 °C) causes decomposition to triphenylmethane and formaldehyde.[18]

d) 3-Ethynyl-2-phenylpyridine (13)

This doubly substituted pyridine derivative was prepared by initial conversion of 2-chloropyridine (**38**) into the iodide **39** (31%) by a reported procedure,[19] and coupling of the latter with (trimethylsilyl)ethyne under Sonogashira conditions to provide **40** (99%). Kumada coupling with phenylmagnesium bromide and deprotection with TBAF concluded the synthesis (24%), Scheme 7.

Note that in **13** the pyridine nitrogen atom and the triple bond are at a "safe distance" again, preventing intramolecular interaction between them.



Scheme 7. The preparation of 3-ethynyl-2-phenylpyridine (**13**)

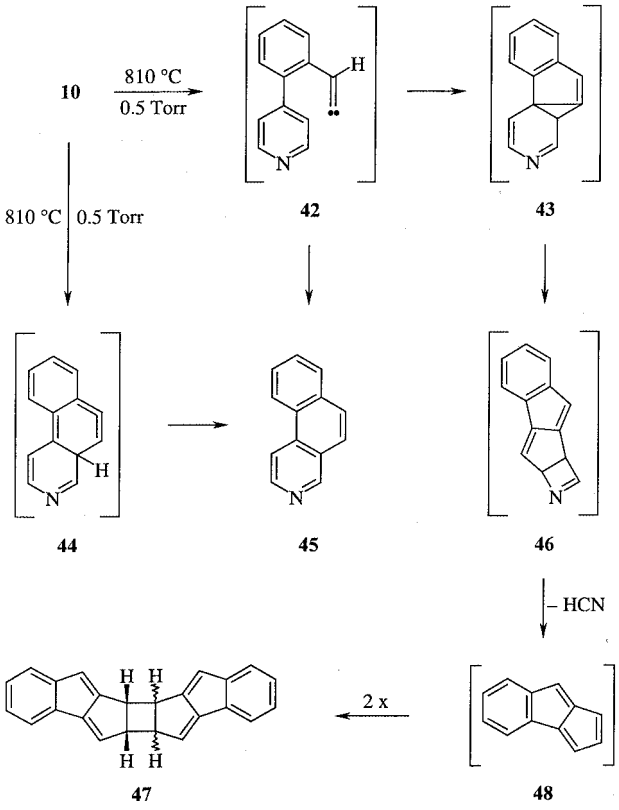
Pyrolyses

Flash vacuum pyrolyses were performed in our standard apparatus,[1] involving a tubular furnace containing an empty quartz tube (l = 60 cm, *o.d.* = 4 cm), which was connected at one end to a vaporization flask (heated externally by a kugelrohr oven) and at the other, via a cold-trap (liquid nitrogen), to a high vacuum line.

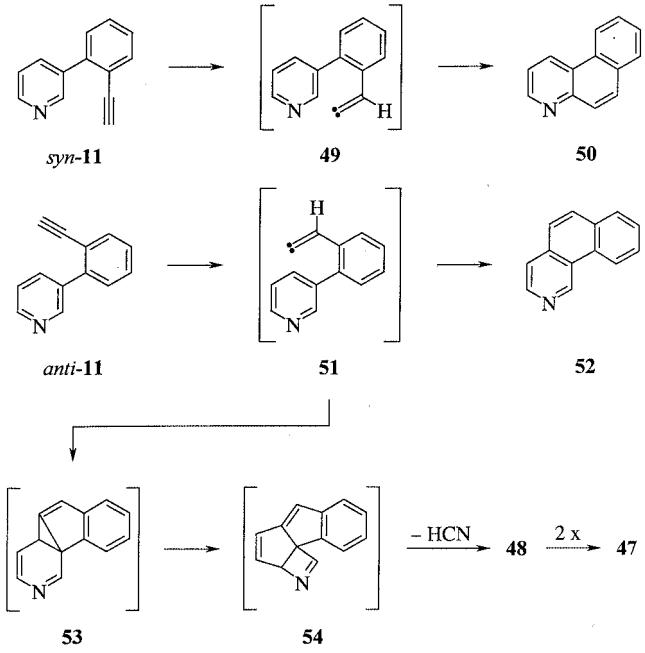
a) Pyrolysis of 4-(2-Ethynylphenyl)pyridine (10)

In the pyrolysis of **10** (810 °C, 0.5 Torr), ca. 70% of the evaporated material (120 °C) was recovered as the pyrolysate. From this a 33% yield of benzo[*f*]isoquinoline (**45**) was isolated by flash chromatography, with the remainder consisting of five side products, as shown by HPLC/UV analysis. One of these products was the dimer of benzopentalene (**48**), the $C_{24}H_{18}$ hydrocarbon **47** (Scheme 8), confirmed by spectral comparison of its UV spectrum with that of an authentic sample (see below).

To account for these findings we propose two possibilities. Firstly, the ethynyl function of **10** could undergo the already mentioned 1,2-hydrogen shift (see Introduction) and the resulting vinylidenecarbene intermediate **42** could subsequently insert into the C-3−H bond of **10** to furnish the main product **45**. Alternatively, **10** could cyclize by an electrocyclic process to the isobenzene intermediate **44**, which could then rearrange to **45** by a hydrogen shift. The former explanation also explains the production of **47** without invoking too many intermediates. Thus, the intermediate **43** could be generated by carbene addition to a carbon−carbon double bond of the pyridine ring. Clearly, this would have many options for further transformation. On the assumption that it would prefer a vinylcyclopropane rearrangement, it could isomerize to the tetracyclic intermediate **46**, which could fragment into hydrogen cyanide and benzopentalene (**48**) by a retro-[2+2] process.[20] The [2+2] dimerization of this reactive hydrocarbon has been described,[21,22] and we assume that the dimer **47** is actually produced as a mixture of isomers (see below).



Scheme 8. The pyrolysis of 4-(2-ethynylphenyl)pyridine (**10**)



Scheme 9. The pyrolysis of 3-(2-ethynylphenyl)pyridine (**11**)

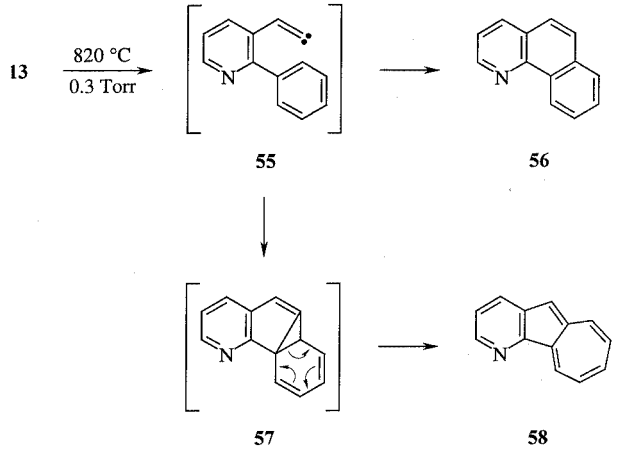
b) Pyrolysis of 3-(2-Ethynylphenyl)pyridine (11)

Because of its substitution pattern, isomer **10** could only give rise to one condensed aromatic product, **45**. This is different for **11**. Depending on whether it assumed a "*syn* conformation", in which its ethynyl group and its pyridine nitrogen atom pointed in the same direction (*syn*-**11**, Scheme 9), or one in which they were opposing each other (*anti*-**11**), two conformers of the vinylidene carbene intermediate − **49** and **51**, respectively − could be generated. These would react further to afford benzo[*f*]quinoline (**50**) and benzo[*h*]isoquinoline (**52**). Indeed, when **11** was pyrolyzed at 820 °C/0.1 Torr, these two isomers were produced in 12 and 10% yields, respectively.

Material loss was smaller in this case (recovery ca. 80%) and, again, the benzopentalene dimer **47** was also isolated. This time, however, it was obtained in a yield of 34%, allowing its purification and determination of its complete spectroscopic data. These (see Exp. Sect.) and comparison with literature data[21,22] proved the structure assignment to be correct and showed, furthermore, that the dimer produced was a mixture of isomers. Since the UV spectrum of the dimer obtained in the pyrolysis of **10** (see above) was superimposable on that formed during cyclization/dimerization of **11**, we were able to confirm our previous structure assignment. To understand the formation of **48**/**47** in this isomerization, we postulate the intermediate generation of **53** and **54**.

c) Pyrolysis of 3-Ethynyl-2-phenylpyridine (13)

The separation of the phenyl group and the ethynyl substituent in **13** resulted in the cleanest pyrolysis reaction and the best yield: When **13** was heated to 820 °C/0.3 Torr, benzo[*h*]quinoline (**56**) was formed in 58% yield, accompanied by azuleno[1,2-*b*]pyridine (**58**) in 9% yield (Scheme 10). At 86%, the material recovery was excellent, and azuleno derivatives such as **58** have apparently not been described in the literature.



Scheme 10. The pyrolysis of 3-ethynyl-2-phenylpyridine (**13**)

In analogy with Brown's original proposal for the isomerization of **1**, we interpret these findings by postulating the initial generation of the carbene **55**, which can subsequently either undergo C−H insertion to give **56** or C−C addition to provide the norcaradiene derivative **57**, which ring-opens to afford **58**.

Experimental Section

General Remarks: Melting points: Mel-Temp II apparatus, uncorrected values. Analytical TLC: Macherey−Nagel Polygram Sil G/UV$_{254}$ and Polygram Alox N/UV$_{254}$. Column chromatography: Merck 60 Kieselgel (70−230 mesh). Analytical GC: Dani 86.10, OV-1 capillary column. NMR: Bruker AC 200 F (^{1}H NMR: 200.1 MHz; ^{13}C NMR: 50.3 MHz) and Bruker AM 400 (^{1}H NMR: 400.1 MHz;^{13}C NMR: 100.6 MHz). MS: Finnigan MAT 8430 (EI, 70 eV). HRMS: by peak matching, resolution 10000. GC/MS: Carlo Erba HRGC 5160 coupled to a Finnigan MAT 4515 (EI, 40 eV). IR: Nicolet 320 FT-IR spectrometer. UV/Vis: Hewlett Packard 8452 diode array. Elemental analyses: Institute of Pharmaceutical Chemistry of the Technical University of Braunschweig.

4-(2-Ethynylphenyl)pyridine (10)

a) 4-(2-Methoxyphenyl)pyridine (16a) and 2-(2-Methoxyphenyl)pyridine (16b): A solution of sodium nitrite (7.8 g, 0.113 mol) in water (50 mL) was added dropwise at 0 °C to a solution of *o*-anisidine (**14**, 12.64 g, 0.103 mol) in hydrochloric acid (6 N, 100 mL). After stirring for 1 h at 0 °C, this solution was added at 80 °C to pyridine (**15**, 250 mL). After stirring for 1 h, the reaction mixture was allowed to cool to room temp., the solvents were removed in vacuo, and the residue was treated with concd. aqueous ammonia solution (100 mL). The liquid phase was again removed under vacuum, and the residue was distilled under high vacuum. Flash chromatography (silica gel; petroleum ether/diethyl ether, 1:1) provided the pure isomers, both of which have been described in the literature.[23] **16a** (1.26 g, 7%): ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.83 (s, OCH_3, 3 H), 6.98−7.09 (m, 9-H, 11-H, 2 H), 7.31−7.49 (m, 4 H), 8.62 (d, $J_{2\text{-H/3-H}}$ = 5.8 Hz, 2-H, 6-H, 2 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 55.5 (q, OCH_3), 111.4 (d, C-9), 121.0 (d), 124.3 (d), 127.6 (s, C-7), 130.1 (d), 130.4 (d), 146.4 (s, C-4), 149.3 (d, C-2, C-6), 156.5 (s, C-8) ppm. MS (70 eV): *m*/*z* (%) = 185 (100) [M$^+$], 184 (62), 170 (100), 157 (30). **16b** (5.27 g, 28%): ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.84 (s, OCH_3, 3 H), 6.97−7.11 (m, 2 H), 7.16−7.22 (m, 1 H), 7.32−7.41 (m, 1 H), 7.64−7.83 (m, 3 H), 8.70 (d, $J_{6\text{-H/5-H}}$ = 4.8 Hz, 6-H, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 55.6 (q, OCH_3), 111.4 (d, C-9), 121.0 (d), 121.6 (d), 125.1 (d), 129.0 (s, C-7), 129.9 (d), 131.1 (d), 135.6 (d, C-4), 149.3 (d, C-6), 156.1 (s, C-2 or C-8), 156.9 (s, C-2 or C-8) ppm. MS (70 eV): *m*/*z* (%) = 185 (100) [M$^+$], 184 (82), 154 (82).

b) 4-{2-[2-(Triisopropylsilyl)ethynyl]phenyl}pyridine (17): A mixture of **16a** (0.43 g, 2.3 mmol) and HI (57%, 20 mL) was heated under reflux for 3 h. The HI was removed by distillation, the residue was diluted with water, and the product mixture was treated successively with sodium carbonate solution, sodium bicarbonate solution, and acetic acid. The phenol intermediate was extracted with diethyl ether, and the organic phase was separated and dried with sodium sulfate. The residue obtained after solvent removal in vacuo was dissolved in anhydrous pyridine (10 mL), and the solution was treated at 0 °C with triflic anhydride (0.6 mL, slow addition). After 1 h, the reaction mixture was allowed to warm to room temp. and stirred overnight. The mixture was poured into ice-cold water, and the triflate intermediate was isolated by ether extraction. The organic phase was dried (sodium sulfate), and the solvent was removed. The residue was dissolved in anhydrous DMF (10 mL) and triethylamine (2 mL), and $Pd(PPh_3)_2Cl_2$ (0.058 g) and (triisopropylsilyl)ethyne (0.7 mL) were added. The mixture was heated to 120 °C and subsequently stirred at 80 °C for 4 d. After it had cooled to room temp., dichloromethane and water were added, the organic phase was separated and dried (sodium sulfate), and the solvent was removed in vacuo. Flash chromatography (silica gel; diethyl ether) provided 0.45 g (58%) of **17** as a yellow oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.016 and 1.022 (2 s, 15-H, 16-H, 21 H), 7.35−7.44 (m, 3 H), 7.58−7.59 (m, 2 H), 7.63−7.66 (m, 1 H), 8.63−8.65 (m, 2-H, 6-H, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 11.2 (d, C-15), 18.5 (q, C-16), 95.6 (s, C-14), 105.2 (s, C-13), 121.9 (s), 124.4 (d), 128.4 (d), 128.8 (d), 128.9 (d), 134.1 (d), 140.8 (s), 148.6 (d, C-2, C-6), 149.0 (s) ppm. IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (w), 3027 (w), 2958 (s), 2943 (s), 2891 (s), 2865 (s), 2155 (m), 1600 (m), 1593 (m), 1473 (s), 1464 (s), 1442 (m), 1410 (m), 993 (m), 883 (s), 842 (m), 822 (s), 760 (s), 736 (m), 678 (s), 663 (s), 639 (s), 626 (m), 618 (s). UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.45), 266 (4.19), 296 (3.37) ppm. MS (70 eV): *m*/*z* (%) = 335 (14) [M$^+$], 292 (100). HRMS: $C_{22}H_{29}NSi$, calcd: 335.2069; found 335.2061 ± 2 ppm.

c) 4-(2-Ethynylphenyl)pyridine (10): A solution of TBAF in THF (1.1 M, 2 mL) was added to a solution of **17** (0.4 g, 1.2 mmol) in THF (20 mL), followed by water (2 mL). The mixture was stirred for 1 d, the solvents were removed in vacuo, and dichloromethane and water were added. The organic phase was separated and dried with sodium sulfate, and the solvent was removed under vacuum. Flash chromatography (silica gel; diethyl ether) provided 0.18 g (84%) of **10**, beige solid, m.p. 78 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.10 (s, 14-H, 1 H), 7.33−7.67 (m, 6 H), 8.67 (d, $J_{2\text{-H/3-H}}$ = 6.0 Hz, 2-H, 6-H, 2 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 81.2 (d, C-14), 82.1 (ps-s, C-13), 120.4 (s, C-8), 124.0 (d), 128.3 (d), 129.1 (d), 129.2 (d), 134.1 (d), 141.4 (s), 147.8 (s), 149.4 (d, C-2, C-6) ppm. IR (KBr): $\tilde{\nu}$ = 3211 cm^{-1} (s), 3052 (w), 3022 (w), 2096 (w), 1601 (m), 1594 (m), 1542 (m), 1475 (m), 1411 (m), 991 (m), 826 (s), 765 (m), 751 (s), 740 (s), 732 (s), 712 (s), 677 (s). UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.12), 254 (4.1), 290 (3.15), 294 (2.95) ppm. MS (70 eV): *m*/*z* (%) = 179 (100) [M$^+$], 178 (50), 152 (37), 151 (36). $C_{13}H_9N$ (179.22): calcd. C 87.12, H 5.06, N 7.82; found C 87.22, H 5.03, N 7.74.

3-(2-Ethynylphenyl)pyridine (11)

a) 3-(2-Chlorophenyl)pyridine (21): This intermediate has been described without experimental details in a short communication.[24] A solution of *n*-butyllithium in hexane (1.8 M, 35.2 mL) was added at − 90 °C to a solution of 3-bromopyridine (**18**, 4.99 g, 31.6 mmol) in anhydrous diethyl ether (50 mL). The mixture was stirred for 30 min, and tri-*n*-butyltin chloride (technical grade, ca. 90%, 9.5 mL) was added. After stirring at −70 °C for 4 h, the mixture was allowed to come to room temp. overnight. For workup, water (50 mL) was added, the organic phase was separated and dried (sodium sulfate), and the solvent was removed in vacuo. The remaining 3-(tri-*n*-butylstannyl)pyridine (**19**) was vacuum-distilled and although it (10.4 g) was not completely pure, it could be used without further purification. A mixture containing **19** (2.02 g, 5.6 mmol), 1-chloro-2-iodobenzene (**20**, 1.56 g, 6.5 mmol), palladium(II) acetate (0.128 g, 0.6 mmol), and triphenylphosphane (0.61 g, 2.3 mol) in DMF was heated at 120 °C under nitrogen for 6 d. After the solvent had been removed in vacuo, the residue was dissolved in diethyl ether, and the solution was filtered and washed three times with hydrochloric acid. The aqueous acidic phase was carefully washed with ether, and the ether fractions were combined and dried with sodium sulfate. After solvent removal, the remaining oil was purified by flash chromatography (silica gel, diethyl ether) to afford **21** (0.5 g, 43% with respect to **18**) as a yellow oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.29−7.37 (m, 4 H), 7.47−7.50 (m, 1 H), 7.77−7.80 (m, 1 H), 8.62 (dd, $J_{6\text{-H/4-H}}$ = 1.5, $J_{6\text{-H/5-H}}$ = 4.8 Hz, 6-H, 1 H), 8.69 (d, $J_{2\text{-H/4-H}}$ = 2.3 Hz, 2-H, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 122.8 (d), 127.1 (d), 129.4 (d),

130.1 (d), 131.2 (d), 132.7 (s), 135.0 (s), 136.81 (s), 136.85 (d, C-4), 148.7 (d) 149.9 (d) ppm.

b) 3-(2-Ethynylphenyl)pyridine (11): A solution of ethylmagnesium bromide in anhydrous THF (50 mL) was prepared from ethyl bromide (2.8 mL, 4.03 g, 37.0 mmol) and magnesium turnings (0.9 g, 37.0 mmol). With cooling (ice bath), trimethylsilylethyne (7 mL, 4.9 g, 49.5 mmol) was added, and the mixture was stirred for 45 min at room temp. $Ni(PPh_3)_2Cl_2$ (0.39 g, 0.6 mmol) and **21** (2.15 g, 11.3 mmol) in anhydrous THF (38 mL) were added, and the reaction mixture was heated under reflux for 13 d. For workup, a saturated aqueous ammonium chloride solution was added, followed by diethyl ether. The organic phase was dried (sodium sulfate), and the solvents were removed in vacuo. Flash chromatography (silica gel; petroleum ether/diethyl ether, 1:1) yielded 3-{2-[2-(trimethylsilyl)ethynyl]phenyl}pyridine (1.47 g), which was dissolved in THF (30 mL). Under nitrogen, a solution of TBAF in THF (1.1 M, 5 mL) and water (5 mL) was added. After the mixture had been stirred for 3 d, diethyl ether and water were added, and the organic phase was separated and dried with sodium sulfate. The oil obtained after solvent removal was purified by flash chromatography (silica gel; diethyl ether) to afford **11** (0.98 g, 48%) as a reddish oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.07 (s, 14-H, 1 H), 7.33−7.38 (m, 3 H), 7.42−7.46 (m, 1 H), 7.64 (dd, J_1 = 1.2, J_2 = 7.9 Hz, 1 H), 7.90−7.93 (m, 4-H, 1 H), 8.61 (dd, $J_{6\text{-H}/4\text{-H}}$ = 1.6, $J_{6\text{-H}/5\text{-H}}$ = 4.7 Hz, 6-H, 1 H), 8.81−8.82 (m, 2-H, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 80.8 (d, C-14), 82.4 (ps-s, C-13), 120.7 (s), 122.8 (d), 127.8 (d), 129.2 (d), 129.4 (d), 133.9 (d), 135.8 (s), 136.5 (d), 140.7 (s), 148.6 (d), 149.8 (d) ppm. IR (film): $\tilde{\nu}$ = 3288 cm^{-1} (m), 3205 (w), 3197 (w), 2101 (w), 1468 (m), 1408 (m), 760 (s), 713 (s). UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 236 nm (3.7), 242 (4.07), 252 (4.06), 272 (3.84), 302 (2.61), 310 (2.13) ppm. MS (70 eV): *m/z* (%) = 179 (100) [M^+], 178 (44), 152 (24), 151 (22). $C_{13}H_9N$ (179.22): calcd. C 87.12, H 5.06, N 7.82; found C 87.17, H 5.07, N 7.69.

2-{2-[2-(Trimethylsilyl)ethynyl]phenyl}pyridine (26) from 2-Bromopyridine (23)

a) 2-(2-Chlorophenyl)pyridine (25): 2-Tris(*n*-butylstannyl)pyridine (**24**) was prepared from **23** by a published procedure.[25] A mixture of **24** (10.29 g, 28.0 mmol), 1-chloro-2-iodobenzene (**20**, 8.2 mL, 16.0 g, 67.1 mmol), and $Pd(PPh_3)_2Cl_2$ (0.41 g, 0.6 mmol) was heated at 100 °C under nitrogen for 5 d. After the mixture had cooled to room temp., dichloromethane was added, and the mixture was treated with 3 N hydrochloric acid. The aqueous phase was washed carefully with dichloromethane, sodium carbonate solution, and again with dichloromethane, and the organic phases were combined and dried with sodium sulfate. After solvent removal in vacuo, the residue was purified by flash chromatography (silica gel; petroleum ether/diethyl ether, 1:1) to provide the known[26] **25** (3.42 g, 64%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.26−7.82 (m, 7 H), 8.72−8.74 (m, 6-H, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 122.4 (d), 124.9 (d), 127.0 (d), 129.6 (d), 130.1 (d), 131.5 (d), 132.0 (s), 135.9 (d), 139.1 (s), 149.4 (d, C-6), 156.8 (s, C-2) ppm. MS (70 eV): *m/z* (%) = 191/189 (15/45) [M^+], 154 (100), 127 (25).

b) 2-{2-[2-(Trimethylsilyl)ethynyl]phenyl}pyridine (26): A solution of ethylmagnesium bromide in diethyl ether (70 mL) was prepared from magnesium turnings (0.92 g, 38.0 mmol) and ethyl bromide (4.1 g, 37.6 mmol). (Trimethylsilyl)ethyne (6 mL, 4.2 g, 42.5 mmol) was added to this Grignard reagent at 0 °C, and the mixture was allowed to warm slowly to room temp. The formed **22** was treated with **25** (3.41 g, 18.0 mmol) in diethyl ether (60 mL) and with $Ni(PPh_3)_2Cl_2$ (0.28 g, 0.4 mmol). After the mixture had been heated for 6 d under reflux, water was added for hydrolysis, and the separated organic phase was dried with sodium sulfate. The solvent was removed in vacuo, and the residue was subjected to flash chromatography (silica gel; dichloromethane). The resulting product (3.43 g, largely **26**) always contained 2-phenylpyridine (**27**) as an impurity, as shown by GC analysis (comparison with authentic **27**). Pure **26** was prepared by the procedure described below.

2-{2-[2-(Trimethylsilyl)ethynyl]phenyl}pyridine (26) from 2-(2-methoxyphenyl)pyridine (16b)

a) 2-(2-Hydroxyphenyl)pyridine (28): This compound was prepared from **16b** by ether cleavage by a known method,[23] in 63% yield. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 6.86−6.94 (m, 11-H, 1 H), 7.03 (d, $J_{9\text{-H}/10\text{-H}}$ = 8.2 Hz, 9-H, 1 H), 7.19−7.35 (m, 2 H), 7.76−7.92 (m, 3 H), 8.49 (d, $J_{6\text{-H}/5\text{-H}}$ = 5.0 Hz, 6-H, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 118.6 (d), 118.8 (d), 119.1 (d), 121.5 (d), 126.1 (d), 131.5 (d), 137.8 (d), 145.7 (d, C-6), 157.8 (s), 159.9 (s) ppm; one quaternary carbon atom was not visible in the spectrum. MS (70 eV): *m/z* (%) = 171 (100) [M^+], 170 (70), 143 (16).

b) 2-[2-(Trifluoromethylsulfonyl)phenyl]pyridine (29): Triflic anhydride (1.8 mL, 3.0 g, 10.7 mmol) was slowly added at 0 °C to a solution of **28** (1.4 g, 8.2 mmol) in pyridine (20 mL). The mixture was stirred for 1 h at 0 °C and for 24 h at room temp., and then poured into ice-cold water. After extraction with dichloromethane and drying (sodium sulfate), the solvent was removed in vacuo. Flash chromatography (silica gel; petroleum ether/diethyl ether, 1:1) yielded **29** (2.19 g, 88%) as a yellow oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.30−7.33 (m, 1 H), 7.38−7.42 (m, 1 H), 7.46−7.52 (m, 2 H), 7.60−7.62 (m, 1 H), 7.75−7.81 (m, 2 H), 8.75−8.76 (m, 6-H, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 118.4 (q, $^1J_{C\text{-F}}$ = 320.5 Hz, CF_3), 122.2 (d), 122.9 (d), 124.3 (d), 128.6 (d), 130.2 (d), 131.9 (d), 133.9 (s), 136.6 (d), 146.9 (s, C-8), 149.7 (d, C-6), 153.7 (s, C-2) ppm. IR (film): $\tilde{\nu}$ = 3086 cm^{-1} (w), 3064 (w), 1612 (m), 1588 (m), 1567 (m), 1493 (m), 1471 (m), 1450 (m), 1424 (s), 1248 (s), 1210 (s), 1140 (s), 1114 (m), 1107 (m), 1094 (m), 1057 (m), 1045 (m), 1026 (m), 890 (s), 787 (s), 768 (s), 757 (m), 720 (m). UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.02), 270 (3.89), 300 (2.53). MS (70 eV): *m/z* (%) = 303 (56) [M^+], 170 (100). $C_{12}H_8F_3NO_3S$ (303.26): calcd. C 47.53, H 2.66, N 4.62, S 10.57; found C 47.31, H 2.43, N 4.39, S 10.70.

c) 2-{2-[2-(Trimethylsilyl)ethynyl]phenyl}pyridine (26): Triethylamine (4 mL), (trimethylsilyl)ethyne (2.2 mL, 3.17 g, 32.2 mmol), and $Pd(PPh_3)_2Cl_2$ (0.29 g, 0.4 mmol) were added to a solution of **29** (2.81 g, 9.3 mmol) in DMF (20 mL), and the mixture was heated at 80 °C for 4 h. The solvents were removed in vacuo, and the residue was taken up in diethyl ether. After filtration through a short silica gel column, analytically pure material was obtained by flash chromatography (silica gel; dichloromethane), affording **26** (0.96 g, 41%) as a reddish oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.15 (s, 9 H, $SiMe_3$), 7.22−7.26 (m, 1 H), 7.30−7.34 (m, 1 H), 7.39−7.44 (m, 1 H), 7.56−7.59 (m, 1 H), 7.67−7.72 (m, 1 H), 7.74−7.76 (m, 1 H), 7.97−7.99 (m, 1 H), 8.69−8.71 (m, 6-H, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 0.0 (q, $SiMe_3$), 98.4 (s, C-14), 104.8 (s, C-13), 121.4 (s), 122.5 (d), 124.9 (d), 128.4 (d), 129.2 (d), 129.9 (d), 133.7 (d), 135.7 (d), 142.7 (s), 149.6 (d), 157.7 (s, C-2) ppm. IR (film): $\tilde{\nu}$ = 3064 cm^{-1} (w), 3008 (w), 2960 (m), 2899 (w), 2156 (m), 1585 (m), 1570 (m), 1460 (s), 1424 (m), 1250 (s), 865 (s), 843 (s), 796 (m), 758 (s), 747 (m), 736 (m). UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.27), 246 (4.14), 262 (4.15), 272 (4.08), 274 (4.07), 276 (4.06), 280 (4.04), 308 (3.08), 312 (2.80). MS (70 eV): *m/z* (%) = 251 (40) [M^+], 250 (100), 236 (16). $C_{16}H_{17}NSi$

(251.40): calcd. C 76.46, H 6.82, N 5.58; found C 76.46, H 6.76, N 5.49.

6,6′-Methanediylbis(pyrido[2,1-*a*]isoindole) (37): A solution of **26** (2.63 g, 10.5 mmol) in THF (100 mL) was treated under nitrogen with a solution of TBAF·3H_2O (1.18 g, 3.7 mmol) in water (10 mL). After the mixture had been stirred for 1 d at room temp., the solvents were removed in vacuo and the remaining oil was dissolved in dichloromethane. The solution was washed carefully with water, the organic phase was dried with sodium sulfate, and the solvent was distilled off. The remaining solid (0.57 g) was extracted with refluxing chloroform/petroleum ether, and the insoluble yellow solid was removed by filtration. An additional 0.17 g of the yellow product crystallized from the mother liquor (total yield of **37**: 0.74 g, 41%). Analytically pure material was obtained by recrystallization from diethyl ether, yellow needles, m.p. 200 °C (decomp.). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 5.04 (s, 11-H, 2 H), 6.70−6.74 (m, 4 H), 7.15 (ddd, J_1 = 0.8, J_2 = 6.6, J_3 = 8.2 Hz, 2 H), 7.32 (ddd, J_1 = 0.9, J_2 = 6.6, J_3 = 8.5 Hz, 2 H), 7.51 (ps-d, J = 8.6 Hz, 2 H), 7.80−7.83 (m, 2 H), 8.03−8.06 (m, 2 H), 8.15 (ps-dt, J_1 = 0.9, J_2 = 8.3 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.2 (t, C-11), 106.9 (s), 112.6 (d), 115.5 (d), 116.0 (d), 116.4 (s), 118.2 (d), 118.6 (d), 119.8 (d), 120.3 (d), 124.7 (d), 125.7 (s), 126.2 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3047 cm^{-1} (w), 1602 (s), 1446 (m), 1350 (m), 1308 (s), 1256 (m), 1211 (m), 1127 (m), 996 (m), 740 (s), 726 (s), 715 (s), 700 (s). UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 252 nm (4.84), 274 (4.44), 362 (4.32), 374 (4.36), 416 (3.60), 442 (3.52), 472 (3.35), 602 (3.45), 644 (4.04). MS (70 eV): *m*/*z* (%) = 346 (100) [M^+], 345 (58), 180 (78). $C_{25}H_{18}N_2$ (346.43): calcd. C 86.68, H 5.24, N 8.09; found C 86.70, H 5.24, N 7.97.

3-Ethynyl-2-phenylpyridine (13)

a) 2-Chloro-3-[2-(trimethylsilyl)ethynyl]pyridine (40): $Pd(PPh_3)_2Cl_2$ (0.065 g, 0.09 mmol), trimethylsilylethyne (0.5 mL), and a small amount of CuI were added to a solution of 2-chloro-3-iodopyridine [**39**, 0.44 g, 1.8 mmol, prepared from 2-chloropyridine (**38**) according to ref.[27]] in triethylamine (20 mL), and the mixture was stirred for 5 h at room temp. Petroleum ether was added, the solid material was removed by filtration, and the solvent was removed in vacuo. Flash chromatography (silica gel; pentane/diethyl ether, 10:1) provided the known[28] acetylene **40** (0.38 g, 99%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.09 (s, $SiMe_3$, 9 H), 7.00 (dd, $J_{5\text{-H/6-H}}$ = 4.8, $J_{5\text{-H/4-H}}$ = 7.7 Hz, 5-H, 1 H), 7.60 (dd, $J_{4\text{-H/6-H}}$ = 1.9, $J_{4\text{-H/5-H}}$ = 7.7 Hz, 4-H, 1 H), 8.13 (dd, $J_{6\text{-H/4-H}}$ = 1.9, $J_{6\text{-H/5-H}}$ = 4.8 Hz, 6-H, 1 H) ppm.

b) 3-Ethynyl-2-phenylpyridine (13): A solution of phenylmagnesium bromide in THF (22 mL) was prepared from bromobenzene (3.6 g, 22.9 mmol) and magnesium turnings (0.55 g, 22.6 mmol). Compound **40** (2.37 g, 11.3 mmol) and Ni(dppp)Cl_2 (0.233 g, 0.43 mmol) were added to this solution. The mixture was heated under reflux for 5 h and stirred for 3 d at room temp. For workup, saturated ammonium chloride solution was added, followed by extraction with diethyl ether. The organic phase was dried (sodium sulfate) and the solvent was removed in vacuo. The obtained **41** was purified by flash chromatography (silica gel; dichloromethane). It was dissolved in THF (17 mL), and a solution of TBAF in THF (1.1 M, 3 mL) and water (2 mL) were added. The mixture was stirred at room temp. overnight and extracted carefully with dichloromethane. After drying (sodium sulfate) and solvent evaporation, flash chromatography (silica gel; dichloromethane) yielded **13** (0.49 g, 24%) as a colorless solid, m.p. 72 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.15 (s, 14-H, 1 H), 7.13 (dd, $J_{5\text{-H/6-H}}$ = 4.8, $J_{5\text{-H/4-H}}$ = 7.8 Hz, 5-H, 1 H), 7.34−7.40 (m, phenyl, 3 H), 7.82 (dd, $J_{4\text{-H/5-H}}$ = 7.8, $J_{4\text{-H/6-H}}$ = 1.8 Hz, 4-H, 1 H), 7.85−7.87 (m, phenyl, 2 H), 8.57 (dd, $J_{6\text{-H/5-H}}$ = 4.8, $J_{6\text{-H/4-H}}$ = 1.8 Hz, 6-H, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 81.3 (ps-s, C-13), 82.9 (d, C-14), 116.8 (s, C-3), 121.3 (d), 127.9 (d), 128.9 (d), 129.2 (d), 138.9 (s), 141.9 (d), 148.9 (d), 160.2 (s, C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3195 cm^{-1} (s), 3041 (w), 2100 (w), 1556 (w), 1426 (s), 802 (m), 744 (s), 696 (s). UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 236 nm (3.67), 242 (3.99), 262 (4.04), 282 (3.89), 310 (2.94), 314 (2.58), 320 (2.09). MS (70 eV): *m*/*z* (%) = 179 (100) [M^+], 178 (52). $C_{13}H_9N$ (179.22): calcd. C: 87.12, H 5.06, N 7.82; found C 86.79, H 5.15, N 7.63.

Pyrolysis of 4-(2-Ethynylphenyl)pyridine (10): A sample of **10** (0.072 g, 0.4 mmol) was pyrolyzed at 810 °C and 0.5 mbar (evaporation temperature 120 °C). HPLC/UV analysis of the pyrolysate (0.050 g, mass recovery 69%) showed that benzo[*f*]isoquinoline (**45**) was formed as the main product, together with five side products, of which one was identified by spectral comparison as the benzopentalene dimer **47** (see spectroscopic data below). By flash chromatography (silica gel; diethyl ether) compound **45** (0.024 g, 33%), a known compound,[29] was isolated. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.71−7.75 (m, 2 H), 7.84 (AB-q, J = 8.9 Hz, 8-H, 9-H, 2 H), 7.94−7.96 (m, 1 H), 8.44 (d, J = 5.8 Hz, 1 H), 8.66−8.69 (m, 1 H), 8.76 (d, J = 6.0 Hz, 1 H), 9.26 (s, 10-H, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 116.2 (d), 123.2 (d), 124.6 (d), 127.2 (d), 128.3 (s), 128.6 (d), 128.8 (d), 128.9 (d), 133.6 (s), 135.1 (s), 144.4 (d, C-2), 151.2 (d, C-10) ppm; the signal of one quaternary carbon atom was not visible in the spectrum. IR (KBr): $\tilde{\nu}$ = 3389 cm^{-1} (w), 3289 (w), 3050 (w), 1620 (m), 1583 (m), 1519 (m), 1427 (m), 1394 (m), 1286 (m), 1251 (m), 1192 (m), 1106 (m), 1036 (m), 873 (m), 834 (s), 814 (s), 749 (s), 730 (s), 717 (s). UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 234 nm (3.95), 238 (4.16), 248 (4.66), 252 (4.70), 272 (4.10), 280 (3.99), 294 (4.00), 320 (3.00), 334 (3.28), 350 (3.37). MS (70 eV): *m*/*z* (%) = 179 (100) [M^+], 178 (24), 152 (14), 151 (16).

Pyrolysis of 3-(2-Ethynylphenyl)pyridine (11): A sample of **11** (0.484 g, 2.70 mmol) was pyrolyzed at 820 °C and 0.1 mbar (evaporation temperature 120 °C). The pyrolysate (0.380 g, mass recovery 79%) was separated by flash chromatography (silica gel, diethyl ether) to afford benzo[*h*]isoquinoline (**52**, 0.050 g, 10%)[30] and benzo[*f*]quinoline (**50**, 0.060 g, 12%),[31] together with a yellow solid (0.140 g), shown by ^{1}H NMR analysis to be a mixture of isomers. Although this last product could be purified by recrystallization (petroleum ether, dichloromethane) and high-vacuum sublimation, NMR analysis showed that it still consisted of two isomers. Its spectroscopic data[21,22] showed it to be benzopentalene dimer (**47**). Spectroscopic data: **52:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.63−7.75 (m, 4 H), 7.90−7.93 (m, 2 H), 8.70 (d, $J_{2\text{-H/3-H}}$ = 5.2 Hz, 2-H, 1 H), 8.77 (d, $J_{9\text{-H/8-H}}$ = 8.3 Hz, 9-H, 1 H), 10.03 (s, 10-H, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 121.2 (d), 121.9 (d), 124.8 (d), 125.3 (d), 127.4 (d), 128.9 (d), 129.3 (s), 131.7 (d), 132.1 (s), 135.9 (s), 144.9 (d), 146.6 (d) ppm; the signal of one quaternary carbon atom was not visible in the spectrum. IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (m), 3037 (m), 2957 (w), 2934 (w), 1610 (s), 1596 (m), 1565 (w), 1501 (w), 1449 (m), 1440 (m), 1422 (m), 1406 (m), 1240 (s), 996 (m), 869 (m), 844 (s), 809 (w), 748 (s), 714 (m). MS (70 eV): *m*/*z* (%) = 179 (100) [M^+], 178 (18), 152 (10), 151 (12). **50:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.51 (dd, $J_{3\text{-H/2-H}}$ = 4.4, $J_{3\text{-H/2-H}}$ = 8.4 Hz, 3-H, 1 H), 7.60−7.68 (m, 2 H), 7.89−7.91 (m, 1 H), 7.95 (d, ^3J = 9.2 Hz, 9-H or 10-H, 1 H), 7.99 (d, ^3J = 9.3 Hz, 9-H or 10-H, 1 H), 8.56 (ps-d, ^3J = 8.0 Hz, 5-H, 1 H), 8.89 (dd, $J_{4\text{-H/2-H}}$ = 1.7, $J_{4\text{-H/3-H}}$ = 8.4 Hz, 4-H, 1 H), 8.94 (dd, $J_{2\text{-H/4-H}}$ = 1.6, $J_{2\text{-H/3-H}}$ = 4.4 Hz, 2-H, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 121.2 (d), 122.5 (d), 125.4 (s), 127.1 (d), 127.3 (d), 128.1 (d), 128.7 (d), 129.6 (s), 130.7 (d), 130.9 (d), 131.6 (s), 148.1 (s, C-10a),

149.6 (d, C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (w), 3049 (w), 1635 (w), 1629 (w), 1591 (w), 1585 (w), 1572 (m), 1494 (m), 1452 (m), 1386 (m), 1299 (m), 838 (s), 816 (s), 748 (s). MS (70 eV): *m/z* (%) = 179 (100) [M^+], 178 (22), 152 (8), 151 (12). **47:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.22 (d, *J* = 4.1 Hz), 3.32−3.35 (m), 3.64−3.68 (m), 3.78−3.80 (m), 6.43 (s), 6.49 (s), 6.89 (t, *J* = 2.0 Hz), 7.14 (dt, J_1 = 1.5, J_2 = 7.2 Hz), 7.27−7.32 (m), 7.65−7.68 (m) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 40.9 (d), 41.1 (d), 57.6 (d), 58.0 (d), 116.5 (d), 116.7 (d), 120.8 (d), 122.5 (d), 123.7 (d), 128.4 (d), 129.9 (s), 134.1 (d), 134.9 (d), 151.0 (s), 151.9 (s), 155.7 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1} (w), 3038 (w), 2853 (w), 1708 (w), 1702 (w), 1653 (w), 1637 (w), 1600 (s), 1588 (w), 1435 (w), 1187 (w), 1169 (w), 935 (w), 879 (w), 869 (w), 838 (m), 762 (s), 750 (s), 705 (s). MS (70 eV): *m/z* (%) = 304 (6) [M^+], 152 (100). MS (CI, NH_3, pos.): *m/z* (%) = 305 (100).

Pyrolysis of 3-Ethynyl-2-phenylpyridine (13): A sample of **13** (0.467 g, 2.60 mmol) was pyrolyzed at 820 °C and 0.3 mbar (evaporation temperature 120 °C). The pyrolysate (0.400 g, mass recovery 86%) was separated by flash chromatography (silica gel; dichloromethane) to afford benzo[*h*]quinoline (**56**, 0.400 g, 58%), as shown by spectral and analytical comparison with an authentic sample, and azuleno[1,2-*b*]pyridine (**58**, 0.043 g, 9%) as a deep blue solid, m.p. 80 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 6.82 (dd, J_1 = 8.4, J_2 = 10.8 Hz, 7-H, 1 H), 7.05 (dd, J_1 = 8.3, J_2 = 11.1 Hz, 9-H, 1 H), 7.11 (s, 5-H, 1 H), 7.17−7.24 (m, 8-H, 1 H), 7.44 (dd, $J_{3\text{-H/2-H}}$ = 4.7, $J_{3\text{-H/4-H}}$ = 8.0 Hz, 3-H, 1 H), 7.87 (d, $J_{6\text{-H/7-H}}$ = 11.4 Hz, 6-H, 1 H), 8.06 (dd, $J_{4\text{-H/2-H}}$ = 1.5, $J_{4\text{-H/3-H}}$ = 7.9 Hz, 4-H, 1 H), 8.70 (dd, $J_{2\text{-H/4-H}}$ = 1.4, $J_{2\text{-H/3-H}}$ = 4.5 Hz, 2-H, 1 H), 8.78−8.81 (m, 10-H, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 112.1 (d), 122.6 (d), 124.9 (d), 126.3 (d), 127.7 (d), 131.1 (d), 135.7 (s), 137.0 (d), 137.2 (d), 138.8 (s), 138.9 (s), 143.8 (d, C-2), 147.9 (s, C-10b) ppm. IR (KBr): $\tilde{\nu}$ = 3038 cm^{-1} (w), 3013 (w), 2990 (w), 1623 (w), 1593 (s), 1481 (m), 1446 (m), 1389 (s), 1365 (m), 1285 (m), 1262 (m), 1238 (m), 1209 (m), 1102 (m), 1045 (m), 1033 (m), 1021 (m), 811 (s), 780 (m), 770 (m). UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 238 nm (3.95), 242 (4.10), 308 (4.63), 340 (3.64), 346 (3.57), 360 (3.63), 380 (3.70), 386 (3.50), 390 (3.37), 400 (3.55). MS (70 eV): *m/z* (%) = 179 (100) [M^+], 178 (28), 152 (18), 151 (16), CN-H]. HRMS: $C_{13}H_9N$: calcd. 179.0735; found 179.0732.

X-ray Structure Determination of Compound 37: Crystal data: Orthorhombic, space group *Fdd*2, *a* = 21.825(3), *b* = 34.559(3), *c* = 4.5823(10) Å, *V* = 3456.2 $Å^3$, *Z* = 8, μ(Mo-K_α) = 0.08 mm^{-1}, *T* = −130 °C. Data collection: A crystal (ca. 0.75 × 0.45 × 0.4 mm) was used to record 1193 intensities with a Stoe STADI-4 diffractometer (Mo-K_α radiation, $2\theta_{max}$ = 50°). Friedel opposite reflections were merged to give 867 independent reflections. Structure refinement: The structure was refined anisotropically on F^2 (G. M. Sheldrick, SHELXL-97, Univ. of Göttingen) to *wR*2 = 0.122, *R*1 = 0.046 for 123 parameters and 136 restraints (to displacement parameters); *S* = 1.05, max. Δρ= 0.2 e $Å^{-3}$. The hydrogen atoms were included by use of a riding model. CCDC-175519 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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