Monatshefte für Chemie 129, 1035–1048 (1998)

Monatshefte für Chemie
Chemical Monthly

Synthesis of Polycylic Aromatic Heterocyclic Compounds *via* Thermal Isomerizations of 1,8-Diarylethynylnaphthalenes

Thomas Eckert and **Junes Ipaktschi***

Institute of Organic Chemistry, Justus Liebig University, D-35392 Giessen, Germany

Summary. The palladium catalyzed reaction between 1,8-diiodonaphthalene and ethynylarenes affords 1,8-*Bis*(heteroarylethynyl)naphthalenes which can cyclize thermally *via* diradical intermediates to the corresponding heterocyclic acenaphthene derivatives in high yields.

Keywords. Thermal cyclization; Diradicals; Aromatic heterocyclic compounds; Alkynes; Palladium catalyzed cross coupling reactions.

Synthese von polycyclischen heteroaromatischen Verbindungen durch thermische Isomerisierung von 1,8-Diarylethinylnaphthalinen

Zusammenfassung. Es wurden über eine palladiumkatalysierte Reaktion zwischen 1,8-Diiodnaphthalin und Ethinylarenen 1,8-*Bis*(heteroarylethinyl)naphthaline hergestellt, welche thermisch über eine Diradikalzwischenstufe in hohen Ausbeuten zu den entsprechenden Acenaphthenderivaten cyclisieren.

Introduction

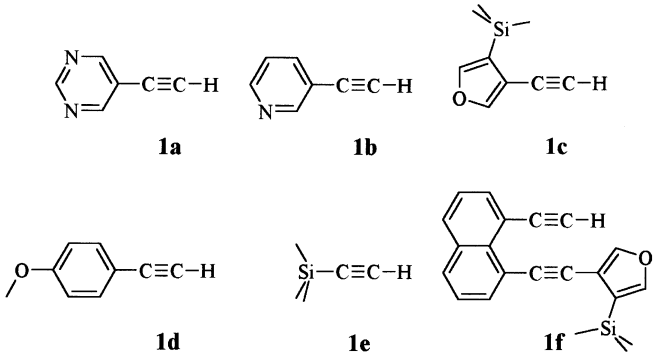
In extension of our work on thermal isomerizations of diarylethynylnaphthalenes to polycyclic aromatic compounds [1], we have investigated the thermolysis of different 1,8-*bis*(heteroarylethynyl)naphthalenes to the corresponding acenaphthochinolines, -isochinolines, -benzofuranes, and -chinazolines. In this paper we describe a convenient synthesis of these polycyclic heteroaromatic compounds.

Results and Discussion

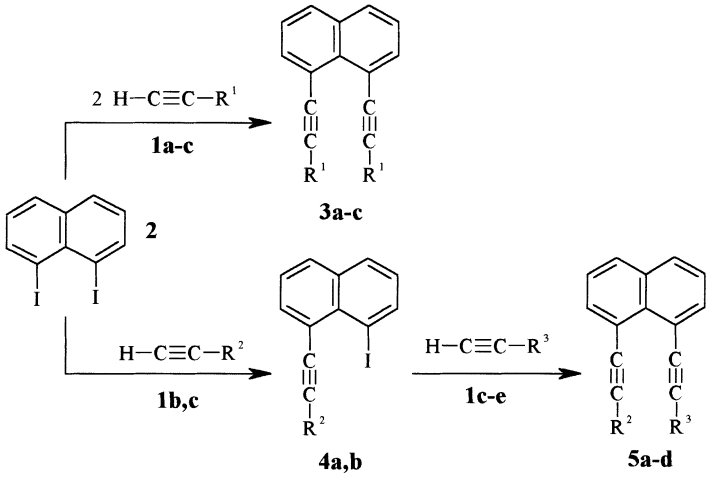
Synthesis of 1,8-bis(heteroarylethynyl)naphthalenes **3a–c**, **4a**,**b**, *and* **5a–d**

The 1,8-*bis*(heteroarylethynyl)naphthalenes **3a–c**, **4a**,**b**, and **5a–d** (Scheme 2) were prepared in high yield *via* a palladium catalyzed coupling reaction of 1,8-diiodonaphthalene (**2**) with the terminal alkynes **1a–e** under *Sonogashira* conditions [2]

* Corresponding author



Scheme 1



Alkyne	H−C≡C−R^1	H−C≡C−R^2	H−C≡C−R^3
3a	1a		
3b	1b		
3c	1c		
4a		1b	
4b		1c	
5a		1b	1d
5b		1b	1c
5c		1b	1e
5d		1c	1e

Scheme 2

(Scheme 1). In all cases, triethylamine was used as base and simultaneously as solvent in the presence of $Pd[P(Ph)_3]_2Cl_2$/CuI as catalyst.

Treatment of 1 equivalent of **2** with 2.2 equivalents of 5-ethynylpyrimidine (**1a**), 3-ethynylpyridine (**1b**), or 3-ethynyl-4-trimethylsilylfuran (**1c**), respectively, resulted in the symmetrically substituted naphthalene derivatives **3a–c** in 35–97% yield as colorless crystalline compounds. The unsymmetrically substituted naphthalenes **5a–d** were synthesized similarly *via* two consecutive coupling reactions of 1,8-diiodonaphthalene (**2**) with terminal alkynes. In the first step, **2** is

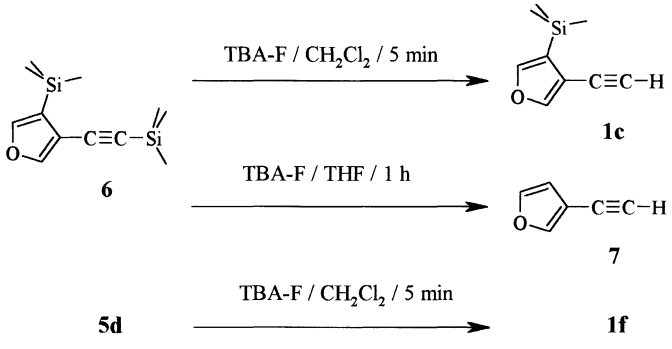
Table 1. Preparation of mono- and dialkynylated naphthalenes **3a**–**c**, **4a**,**b**, and **5a**–**d** from the iodonaphthalenes **2** and **4a**,**b** and from the corresponding terminal alkynes **1a**–**e** *via* palladium catalyzed reactions[a]

iodonaphthalene	alkyne	time (h)	product	yield (%)
2	**1a**	48	**3a**	35
2	**1b**	48	**3b**	82
2	**1c**	48	**3c**	97
2	**1b**	36	**4a**	54
2	**1c**	48	**4b**	69
4a	**1d**	48	**5a**	89
4b	**1b**	48	**5b**	86
4a	**1e**	48	**5c**	95
4b	**1e**	36	**5d**	80

[a] All reactions were carried out in triethylamine at 25°C under argon with 2 mol% $Pd[P(C_6H_5)_3]_2Cl_2$ and 4 mol% CuI (referred to alkyne) as catalyst using of 1 eq. aryliodide and 1.2 eq. of the alkyne (monoalkynylation) or 2.2 eq. of the alkyne (dialkynylation), respectively

transformed to the 1-heteroarylethynyl-8-iodonaphthalnes **4a**,**b** using the alkynes **1b** and **1c** in 69% and 54% yield, respectively. In a subsequent step, **4a** and **4b** are converted in high yields to **5a** and **5b**, respectively, by coupling with alkynes **1b** and 4-ethynylanisole (**1d**). The results are summarized in Table 1.

For the synthesis of diethynylnaphthalene **3c**, the required 3-ethynyl-4-trimethylsilylfuran (**1c**) was prepared by desilylation of 1-((4-trimethylsilyl)-3-furanyl)-2-trimethylsilylacetylene (**6**) (Scheme 3). During the desilylation experiments we found that tetrabutylammoniumfluoride (*TBA*-F) in dichloromethane as solvent could be used as a convenient reagent for selective removal of the trimethylsilyl group from the C≡C-bond. After 5 min, alkyne **1c** was generated in 74% yield. Prolongation of the reaction for further 48 h caused no cleavage of the trimethylsilyl group on the furan ring. Contradictory to this observation, in *THF* as solvent both trimethylsilyl groups on the C≡C-bond as well as on the furan ring of **6** were replaced by hydrogen to afford 3-ethynylfuran (**7**) within 1 h.

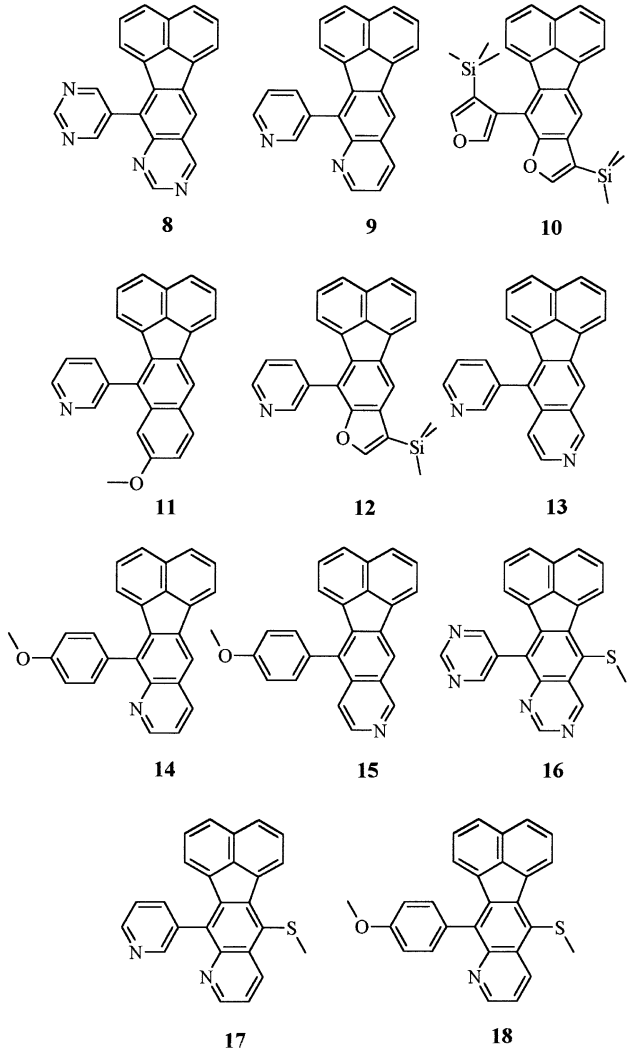


Scheme 3

Thermal cyclization reaction of naphthalene derivatives **3a–c** *and* **5a**,**b**

The 1,8-*bis*(heteroarylethynyl)naphthalenes **3a–c** and **5a**,**b** were converted to their corresponding acenaphthene derivatives by heating in organic solvents such as toluene or *DMSO* to 125°C and 150°C, respectively. The cyclization of **3a–c** and **5a**,**b** in toluene afforded the acenaphthene derivatives **8**–**12** (Scheme 4) in 67–99% yield. In addition, the thermal isomerization of substituted naphthalene derivatives **3b** and **5a** led to a mixture of the heterocyclic by-products **13**–**15** in 7–23% yield. In *DMSO* as solvent, also the thio compounds **16**–**18** were formed in 3–5% yield by isomerization of **3a**,**b** and **5a**. All acenaphthenes were characterized by their spectra (see experimental section). The results are summarized in Table 2.

To study the thermal isomerization of naphthalene derivatives with an aromatic and a non-aromatic substituent at the C≡C-bond, we synthesized compounds **5c** and **5d** *via* a palladium catalyzed reaction of **4a** and **4b** with trimethylsilylace-



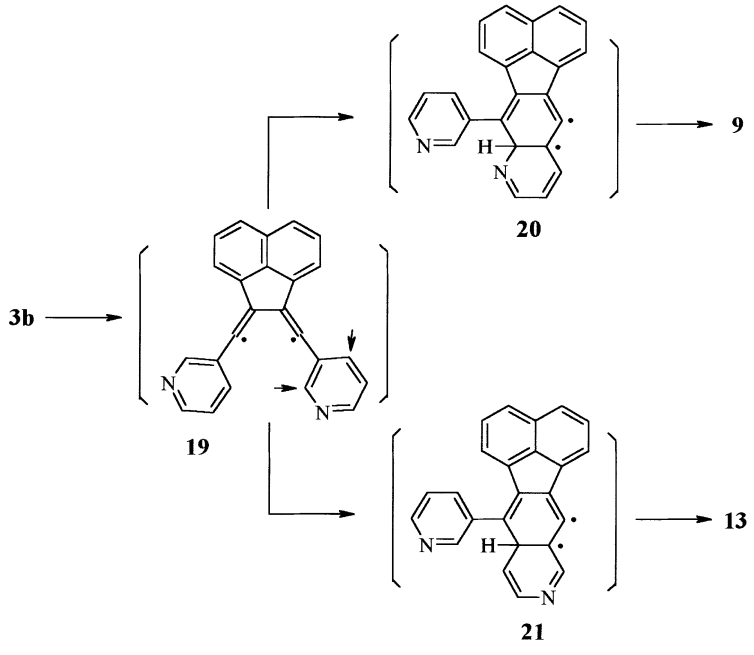
Scheme 4

Table 2. Thermal cyclization of 1,8-(arylethynyl)naphthalenes **3a–c**, **5a–d**, and **1f** to acenaphthenes **8–18** in *DMSO*

1,8-(arylethynyl)-naphthalene	*T* (°C)	time (h)	product(s) (%)
3a	150	9	**8** (92), **16** (5)
3b	150	4	**9** (68), **13** (23), **17** (5)
3c	130	2,5	**10** (99)
5a	140	7,5	**11** (67), **14** (20), **15** (7), **18** (3)
5b	125	2,5	**12** (97)
5c	185	10	no reaction
5d	185	10	no reaction
1f	90	10	decomposition

tylene (**1e**) and **1f** by removal of the acetylenic trimethylsilyl group from **5d**. Interestingly, in spite of the high temperature of 185°C no thermal cyclization of **5c** and **5d** occurred. Instead, compound **1f** decomposed at 90°C.

The results reported in this work reveal a mechanism *via* diradical intermediates for the thermal cyclization of 1,8-diarylethynylnaphthalenes. This is discussed here exemplarily for the isomerization of **3b** to **9** and **13** *via* diradicals **19–21** (Scheme 5). In the intermediate **19**, formed in the first step of the reaction, the two radical centers are sp-hybridized, and each electron is delocalized over one pyridine ring. In **20** and **21**, respectively, one of the electrons is localized in a sp^2-orbital, and the other one is delocalized in an aza pentadienyl system. In the



Scheme 5

following step, diradicals **20** and **21** are stabilized by transfer of a hydrogen atom (presumably by abstraction and readdition) to give products **9** and **13** (ratio 3:1). This ratio seems to be characteristic for radical addition to position 2 *versus* 4 of a pyridine ring [3] and was also found by cyclization of the naphthalene derivative **5a** to the acenaphthenes **14** and **15**. The resonance stabilization of the diradicals during the isomerization of the naphthalene derivatives **3a–c**, **5a**, and **5b** is responsible for the thermal cyclization at relative low temperatures. The lack of thermal isomerization of naphthalene derivatives **5c**, **5d**, or **1f** is attributed to the lower resonance stabilization energy of their corresponding intermediates.

Because of the electrophilicity of the radical intermediates, the thermolysis of the unsymmetrically naphthalene derivative **5a** leads to benzo[*k*]fluoranthene **11** as a major product and the pyrolysis of **5b** exclusively to acenaphthobenzofuran **12**.

The formation of **16–18** from the thermolysis of **3a**,**b** and **5a** could be explained by the trapping of a thiomethoxy group from *DMSO* by the corresponding diradical intermediates.

Experimental

General

All reactions were carried out under argon with dried solvents. Elemental analyses: Carlo Erba Modell 1104; IR: Bruker IFS 25; UV: Hewlett-Packard 8452A diode array spectrophotometer; ^{1}H and ^{13}C NMR: Bruker AM 400 resp. AC 200; MS: Varian MAT 311A resp. Varian MAT 111; melting points: Büchi SMP-20. Trimethylsilylacetylene [4], 3-ethynylpyridin [5], 4-ethynylanisol [6], *bis*(triphenylphosphanyl)palladium(II) chloride [7], 1,8-diiodonaphthalene [8], and 1-((4-trimethylsilyl)-3-furanyl)-2-trimethylsilylacetylene [9] were prepared by known procedures. 5-Bromopyrimidine was purchased from Aldrich.

1-(5-Pyrimidyl)-2-trimethylsilylacetylene

To a solution of 1.59 g (10 mmol) 5-bromopyrimidine and 1.18 g (12 mmol) trimethylsilylacetylene in triethylamine (30 ml), $Pd[P(C_6H_5)_3]_2Cl_2$ (168 mg, 0.24 mmol = 2 mol%) and CuI (92 mg, 0.48 mmol = 4 mol%) were added. The reaction was carried out in an autoclave at 80°C. After removal of the solvent, the residue was extracted with diethyl ether. Subsequently, the filtered solution was evaporated, and the crude product was purified by distillation at 65°C and 5 torr to yield 1.73 g (98%) of colorless crystals.

M.p.: 33°C; IR (film): $\tilde{\nu}$ = 3042, 2960, 2900, 2166, 1571, 1543, 1250, 864, 845 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 240 (4.16), 250 (4.26), 258 (4.11) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.25 (s, 9H), 8.75 (s, 2H), 9.10 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.40 (3×CH_3), 97.60 (C), 102.75 (C), 119.51 (C), 156.73 (CH), 158.99 (2×CH) ppm; MS (70 eV): *m*/*z* (%) = 176 (28) [M^+], 161 (100); HRMS: calcd.: 176.0770 found 176.0775 (HRMS); $C_9H_{12}N_2Si$ (176.30); calcd.: C 61.32, H 6.86, N 15.89; found: C 61.28, H 6.64, N 15.87.

General procedure for the preparation of 5- ethynylpyrimidine (**1a**), *3-ethynyl-4-trimethylsilylfuran* (**1c**), *and 1-ethynyl-8-((4-trimethylsilyl)-3-furanylethynyl)naphthalene* (**1f**) *from their 1-aryl-2-trimethylsilylacetylenes*

To a solution of the 1-aryl-2-trimethylsilylacetylene (1-(5-pyrimidyl)-2-trimethylsilylacetylene, 1-((4-trimethylsilyl)-3-furanyl)-2-trimethylsilylacetylene, and **5d**) (10 mmol) in dichloromethane

(20 ml) *TBA-F* · $3H_2O$ (tetrabutylammoniumfluoride, 3.465 g, 11 mmol) at 0°C in dichloromethane (20 ml). Then the mixture was stirred at 25°C for 5 min. Subsequently, the mixture was washed with water. After drying over $MgSO_4$, **1a** and **1c** were distilled. The naphthalene derivative **1f** was purified by silica gel column chromatography.

5-Ethynylpyrimidine (**1a**)

Yield: 0.916 g (88%); colorless crystals after distillation at 100°C and 100 torr; m.p.: 79.5°C; IR (KBr): $\tilde{\nu} = 3323$, 3169, 2104, 1616, 1577, 1546, 1224, 1178, 718 cm^{-1}; UV (ethanol): λ_{max} ($lg\varepsilon$) = 238 (3.98) nm; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.45$ (s, 1H), 8.84 (s, 2H), 9.20 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 76.87$ (C), 84.39 (CH), 118.71 (C), 157.21 (CH), 159.27 (2×CH) ppm; MS (70 eV): *m/z* (%) = 104 (49) [M^+], 77 (11), 49 (100); HRMS: calcd.: 104.0374, found: 104.0354; $C_6H_4N_2$ (104.11); calcd.: C 69.22, H 3.87, N 26.91; found: C 69.19, H 3.63, N 27.08.

3-Ethynyl-4-trimethylsilylfuran (**1c**)

Yield: 1.624 g (74%); colorless oil after distillation at 90°C and 15 torr; – IR (film): $\tilde{\nu} = 3320$, 3150, 2960, 2900, 2110, 1510, 1250, 1130, 850, 810 cm^{-1}; UV (ethanol): λ_{max} ($lg\varepsilon$) = 206 (3.72), 226 (3.62) nm; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.29$ (s, 9H), 3.07 (s, 1H), 7.22 (d, $J = 1.4$ Hz, 1H), 7.69 (d, $J = 1.4$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -1.23$ (3×CH_3), 76.33 (CH), 79.95 (C), 110.08 (C), 121.19 (C), 147.29 (CH), 147.52 (CH) ppm; MS (70 eV): *m/z* (%) = 164 (27) [M^+], 149 (100); HRMS: calcd.: 164–0657, found: 164.0658; $C_9H_{12}OSi$ (164.28); calcd.: C 65.80, H 7.36; found C 65.52, H 7.55.

1-Ethynyl-8-((4-trimethylsilyl)-3-furanylethynyl)naphthalene (**1f**)

Yield: 2.862 g (91%); light yellow oil after silica gel column chromatography (pentane); IR (film): $\tilde{\nu} = 3296$, 3090, 2955, 2897, 2166, 1572, 1511, 1501, 1249, 842, 826, 766 cm^{-1}; UV (ethanol): λ_{max} ($lg\varepsilon$) = 208 (4.17), 236 (4.28), 286 (3.42), 324 (3.75), 336 (3.79), 346 (3.67) nm; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.35$ (s, 9H), 3.45 (s, 1H), 7.31 (d, $J = 1.4$ Hz, 1H), 7.40–7.48 (m, 2H), 7.74–7.86 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -0.93$ (3×CH_3), 83.71 (C), 83.90 (CH), 89.30 (C), 91.81 (C), 112.10 (C), 119.73 (C), 120.86 (C), 121.08 (C), 125.44 (CH), 125.65 (CH), 129.48 (CH), 130.14 (CH), 131.70 (C), 133.85 (CH), 134.05 (C), 135.87 (CH), 145.60 (CH), 147.46 (CH) ppm; MS (70 eV): *m/z* (%): 314 (53) [M^+], 299 (100), 239 (91), 73 (87); HRMS: calcd.: 314.1127, found 314.1102; $C_{21}H_{18}OSi$ (314.46); calcd.: C 80.21, H 5.77; found: C 80.43, H 5.87.

General procedure for the preparation of the symmetric 1,8-dialkynylated naphthalenes **3a–c** *from* **2** *and the corresponding ethynylarenes* **1a–c**

To a solution of 1,8-diiodonaphthalene (**2**) (10 mmol) and of the alkyne **1a–c** (21 mmol) in triethylamine (20 ml) a catalyst mixture of $Pd[P(C_6H_5)_3]_2Cl_2$ (280 mg, 2 mol%) and CuI (152 mg, 4 mol%) was added at 25°C. The obtained mixture was stirred for 48 h (see Table 1). Subsequently, the triethylamine was evaporated, and the residue was extracted with diethyl ether. The crude products were purified by silica gel column chromatography.

1,8-Bis-(5-pyrimidylethynyl)naphthalene (**3a**)

Yield: 1.992 g (60%); light yellow crystals after silica gel column chromatography (diethyl ether); m.p.: 195°C; IR (KBr): $\tilde{\nu} = 3027$, 2208, 1542, 1416, 829, 764, 723, 635 cm^{-1}; UV (ethanol): λ_{max} ($lg\varepsilon$) = 238 (4.67), 263 (4.28), 340 (4.29) nm; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.53$ (dd, $J = 7.2$ Hz,

8.3 Hz, 2H), 7.92 (dd, $J = 1.0$ Hz, 7.2 Hz, 2H), 7.97 (dd, $J = 1.0$ Hz, 8.3 Hz, 2H), 8.66 (s, 4H), 9.03 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 89.31$ (2×C), 96.51 (2×C), 119.02 (2×C), 119.93 (2×C), 125.89 (2×CH), 130.98 (2×CH), 131.11 (C), 134.01 (C), 135.55 (2×CH), 156.73 (2×CH), 158.08 (4×CH) ppm; MS (70 eV): *m/z* (%) = 332 (14) [M^+], 304 (7), 277 (41), 206 (59), 152 (57), 98 (100); HRMS: calcd.: 332.1062, found: 332.0990; $C_{22}H_{12}N_4$ (332.34); calcd.: C 79.50, H 3.64, N 16.86; found: C 79.90, H 3.24, N 16.86.

1,8-Bis-(3-pyridylethynyl)naphthalene (**3b**)

Yield: 2.706 g (82%); light yellow crystals after silica gel column chromatography (diethyl ether); m.p.: 123.5°C; IR (KBr): $\tilde{\nu} = 3060$, 2220, 1590, 1565, 1485, 840, 810, 780, 710 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 240 (4.45), 262 (4.15), 340 (4.24) nm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.02$ (ddd, $J = 0.8$ Hz, 4.2 Hz, 7.9 Hz, 2H), 7.45–7.50 (m, 2H), 7.51–7.56 (m, 2H), 7.84–7.89 (m, 4H), 8.40 (dd, $J = 1.6$ Hz, 4.9 Hz, 2H), 8.59–8.62 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 92.80$ (2×C), 92.94 (2×C), 119.83 (2×C), 120.63 (2×C), 122.63 (2×CH), 125.65 (2×CH), 130.22 (2×CH), 131.34 (C), 133.98 (C), 135.03 (2×CH), 137.94 (2×CH), 148.28 (2×CH), 151.82 (2×CH) ppm; MS (70 eV): *m/z* (%) = 330 (81) [M^+], 329 (94), 45 (100); HRMS: calcd.: 330.1153, found: 330.1106; $C_{24}H_{14}N_2$ (330.39); calcd.: C 87.25, H 4.27, N 8.48; found: C 87.19, H 4.11, N 8.51.

1,8-Bis-((4-trimethylsilyl)-3-furanylethynyl)naphthalene (**3c**)

Yield: 4.384 g (97%); colorless crystals after silica gel column chromatography (pentane/dichloromethane = 10:1); m.p.: 68°C; IR (KBr): $\tilde{\nu} = 3060$, 2970, 2900, 2220, 1575, 1510, 1260, 950, 800, 760 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 240 (4.23), 284 (3.59), 336 (3.78), 352 (3.75) nm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.32$ (s, 18H), 7.24–7.29 (m, 4H), 7.42–7.49 (m, 2H), 7.75–7.85 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -0.11$ (6×CH_3), 89.10 (2×C), 91.90 (2×C), 111.92 (2×C), 121.09 (2×C), 121.18 (2×C), 125.61 (2×CH), 129.38 (2×CH), 131.13 (C), 134.15 (C), 134.23 (2×CH), 146.56 (2×CH), 147.28 (2×CH) ppm; MS (70 eV): *m/z* (%) = 452 (21) [M^+], 437 (7), 73 (100); HRMS: calcd.: 452.1628, found: 452.1641; $C_{28}H_{28}O_2Si_2$ (452.70); calcd.: C 74.29, H 6.23; found: C 74.33, H 6.04.

General procedure for the preparation of 1-(arylethynyl)-8-iodonaphthalenes **4a**,**b** *from* **2** *and the corresponding ethynylarene*

To a solution of **2** (3.80 g, 10 mmol) and of alkyne **1b**,**c** (12 mmol) in triethylamine (20 ml), a catalyst mixture of $Pd(P(C_6H_5)_3)_2Cl_2$ (140 mg, 2 mol%) and CuI (76 mg, 4 mol%) was added. The obtained mixture was stirred between 36 h and 48 h, respectively (see Table 1). Subsequently, the triethylamine was evaporated and the residue extracted with diethyl ether. The crude products wee purified by silica gel column chromatography.

1-Iodo-8-(3-pyridylethynyl)naphthalene (**4a**)

Yield: 1.919 g (54%); colorless crystals after silica gel column chromatography (pentane/dichloromethane = 1:1); m.p.: 60°C; IR (KBr): $\tilde{\nu} = 3070$, 2000, 1585, 1550, 1480, 1030, 830, 770, 710 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 240 (4.35), 278 (3.74), 336 (4.07), 352 (4.01) nm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.08$–7.14 (m, 1H), 7.31 (ddd, $J = 0.6$ Hz, 4.9 Hz, 7.9 Hz, 1H), 7.46 (dd, $J = 7.3$ Hz, 8.0 Hz, 1H), 7.82–7.85 (m, 2H), 7.91–7.94 (m, 2H), 8.30 (dd, $J = 1.0$ Hz, 7.3 Hz, 1H), 8.58 (dd, $J = 1.6$ Hz, 4.9 Hz, 1H) 8.89 (d, $J = 1.6$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 92.45$ (C), 92.74 (C), 97.37 (C), 121.10 (C), 122.06 (C), 123.11 (CH), 125.43 (CH), 127.23 (CH), 130.21 (CH), 130.97 (CH), 131.92 (C), 134.91 (C), 136.23 (CH), 137.59 (CH), 142.82 (CH), 148.66 (CH), 151.55

(CH) ppm; MS (70 eV): *m/z* (%) = 355 (100) [M^+], 228 (46), 227 (62), 201 (39), 200 (46); HRMS: calcd.: 354.9869, found: 354.9871; $C_{17}H_{10}IN$ (355.17); calcd.: C 57.49, H 2.84, N 3.94; found: C 57.31, H 2.62, N 4.04.

1-Iodo-8-((4-trimethylsilyl)-3-furanylethynyl)naphthalene (**4b**)

Yield: 2.873 g (69%); colorless crystals after silica gel column chromatography (pentane/dichloromethane = 50:1); m.p.: 64°C; IR (KBr): $\tilde{\nu}$ = 3070, 2960, 2900, 2220, 1600, 1565, 1520, 1135, 860, 820, 770 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 238 (4.51), 334 (4.12), 344 (4.03) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.36 (s, 9H), 7.00–7.06 (m, 1H), 7.31 (d, J = 1.4 Hz, 1H), 7.35–7.39 (m, 1H), 7.70–7.78 (m, 2H), 7.82 (dd, J = 1.2 Hz, 7.1 Hz, 1H), 7.87 (d, J = 1.4 Hz, 1H), 8.25 (dd, J = 1.2 Hz, 7.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.84 (3×CH_3), 91.06 (C), 92.89 (C), 94.34 (C), 112.05 (C), 120.85 (C), 122.97 (C), 125.40 (CH), 127.00 (CH), 130.04 (CH), 130.13 (CH), 131.62 (C), 134.80 (C), 135.13 (CH), 142.57 (CH), 145.73 (CH), 147.44 (CH) ppm; MS (70 eV) *m/z* (%) = 416 (100) [M^+], 401 (7), 274 (45), 259 (62), 73 (74); HRMS calcd: 416.0093, found: 416.0076; $C_{19}H_{17}IOSi$ (416.33); calcd.: C 54.81, H 4.11; found: C 54.51, H 3.91.

General procedure for the preparation of the asymmetric 1,8 dialkynlated naphthalenes **5a–d** *from 1-iodo-8-heteroarylethynylnaphthalenes* **4a**,**b** *and the corresponding ethynylarenes*

To a solution of 1-iodo-8-(heteroarylethynyl)naphthalene **4a**,**b** (10 mmol) and alkyne **1c–e** (12 mmol), a catalyst mixture of $Pd[P(C_6H_5)_3]_2Cl_2$ (140 mg, 2 mol%) and CuI (76 mg, 4 mol%) was added at 25°C in triethylamine (20 ml). The obtained mixture was stirred between 36 h and 48 h, respectively (see Table 1). Subsequently, the triethylamine was evaporated, and the residue was extracted with diethyl ether. The crude products were purified by silica gel column chromatography.

1-(4-Anisylethynyl)-8-(3-pyridylethynyl)naphthalene (**5a**)

Yield: 3.154 g (89%); colorless crystals after silica gel column chromatography (diethyl ether); m.p.: 93°C; IR (KBr): $\tilde{\nu}$ = 3100, 3010, 2970, 2950, 2920, 2850, 2210, 1610, 1575, 1520, 1250, 830, 815, 775, 710 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 238 (4.48), 266 (3.61), 326 (4.00), 342 (4.00) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 3H), 6.64–6.69 (m, 2H), 6.99 (ddd, J = 0.9 Hz, 4.9 Hz, 7.9 Hz, 1H), 7.26–7.31 (m, 2H), 7.44–7.53 (m, 3H), 7.80–7.88 (m, 4H), 8.39 (dd, J = 1.6 Hz, 4.9 Hz, 1H), 8.63–8.65 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.24 (CH_3) 88.25 (C), 92.96 (C), 93.12 (C), 96.73 (C), 113.74 (2×CH), 115.73 (C), 120.12 (C), 121.00 (C), 121.03 (C), 122.53 (CH), 125.49 (CH), 125.72 (CH), 129.37 (CH), 130.15 (CH), 131.50 (C), 132.86 (2×CH), 134.11 (C), 134.56 (CH), 135.03 (CH), 138.24 (CH), 147.98 (CH), 151.97 (CH), 159.47 (C) ppm; MS (70 eV) : *m/z* (%) = 359 (100) [M^+], 344 (22), 315 (36), 158 (38), HRMS: calcd.: 359.1310, found: 359.1310; $C_{26}H_{17}NO$ (359.42); calcd.: C 86.89, H 4.77, N 3.90; found: C 86.96, H 4.64, N 4.06.

1-(3-Pyridylethynyl)-8-((4-trimethylsilyl)-3-furanylethynyl)naphthalene (**5b**)

Yield: 3.363 g (86%); colorless crystals after silica gel column chromatography (pentane/diethyl ether = 1:1); m.p.: 110°C; IR (KBr): $\tilde{\nu}$ = 3049, 2953, 2190, 1560, 1507, 1249, 1116, 843, 827, 788, 769 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 240 (4.67), 338 (4.28), 353 (4.18) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 9H), 6.92 (dd, J = 4.9 Hz, 7.9 Hz, 1H), 7.07 (d, J = 1.4 Hz, 1H), 7.11 (d, J = 1.4 Hz, 1H), 7.32–7.38 (m, 2H), 7.43–7.47 (m, 1H), 7.62–7.71 (m, 4H), 8.28 (dd, J = 1.4 Hz, 4.9 Hz, 1H), 8.48 (d, J = 1.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = −1.03 (3×CH_3), 89.18 (C), 91.83 (C), 93.12 (C), 93.20 (C), 111.88 (C), 120.75 (C), 121.01 (C), 121.05 (2×C), 122.49 (CH), 125.53 (CH), 125.73 (CH), 129.55 (CH), 130.11 (CH), 131.43 (C), 134.20 (C), 134.50 (CH),

135.05 (CH), 139.25 (CH), 146.25 (CH), 147.42 (CH), 148.22 (CH), 150.15 (CH) ppm; MS (70 eV): *m/z* (%) = 391 (41) [M^+], 376 (37), 316 (11), 73 (37), 38 (100); HRMS: calcd: 391.1392, found 391.1416; $C_{26}H_{21}NOSi$ (391.55); calcd.: C 79.75, H 5.40, N 3.58; found: C 79.55, H 5.37, N 3.46.

1-(3-Pyridylethynyl)-8-trimethylsilylethynylnaphthalene (**5c**)

Yield: 2.600 g (80%); colorless crystals after silica gel column chromatography (pentane/diethyl ether = 5:1); m.p.: 54.5°C; IR (film): $\tilde{\nu}$ = 3070, 2970, 2910, 2220, 1590, 1575, 1490, 1260, 870, 770, 710 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 240 (4.70), 328 (4.24), 340 (4.26) nm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.01$ (s, 9H), 7.28 (dd, J = 4.9 Hz, 7.9 Hz, 1H), 7.38–7.45 (m, 2H), 7.77–7.89 (m, 5H), 8.55 (dd, J = 1.6 Hz, 4.9 Hz, 1H), 8.83 (d, J = 1.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -0.23$ (3×CH_3), 92.87 (C), 93.30 (C), 102.52 (C), 104.99 (C), 119.93 (C), 120.65 (C), 121.32 (C), 123.01 (CH), 125.48 (CH), 125.60 (CH), 129.83 (CH), 130.12 (CH), 130.12 (CH), 131.23 (C), 133.93 (C), 134.74 (CH), 136.75 (CH), 138.31 (CH), 148.51 (CH), 152.22 (CH), ppm; MS (70 eV): *m/z* (%) = 325 (100) [M^+], 310 (66), 295 (8), 280 (15), 73 (21); HRMS: calcd.: 325.1288, found: 325.1295; $C_{22}H_{19}NSi$ (325.49); calcd.: C 81.18, H 5.88, N 4.30; found: C 80.58, H 5.67, N 4.77.

1-Trimethylsilylethynyl-8-((4-trimethylsilyl)-3-furanylethynyl)naphthalene (**5d**)

Yield: 3.667 g (95%); colorless crystals after silica gel column chromatography (pentane/diethyl ether = 5:1); m.p.: 90.5°C; IR (KBr): $\tilde{\nu}$ = 3140, 3070, 2970, 2910, 2220, 2140, 1630, 1570, 1520, 1255, 850, 770 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 238 (4.42), 269 (3.51), 326 (3.89), 342 (3.89) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 9H), 0.33 (s, 9H), 7.29 (d, J = 1.5 Hz, 1H), 7.37–7.44 (m, 2H), 7.73–7.82 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -0.96$ (3×CH_3), −0.02 (3×CH_3), 89.44 (C), 91.73 (C), 102.37 (C), 104.83 (C), 112.23 (C), 120.86 (C), 120.93 (C), 121.36 (C), 125.44 (CH), 125.53 (CH), 129.45 (CH), 129.67 (CH), 131.37 (C), 134.01 (C), 134.35 (CH), 136.50 (CH), 145.91 (CH), 147.37 (CH) ppm; MS (70 eV): *m/z* (%) = 386 (31) [M^+], 371 (45), 355 (26), 314 (76), 298 (55), 283 (29), 239 (46), 142 (64), 73 (100); HRMS: calcd.: 386.1522, found: 386.1523; $C_{24}H_{26}OSi_2$ (386.64); calcd.: C 74.56, H 6.78; found: C 74.55, H 6.81.

General procedure for the preparation of acenaphthene derivatives **8**–**18** *from the corresponding 1,8-dialkynylated naphthalenes* **3a**–**c** and **5a**,**b**

A solution of the 1,8-dialkynylated naphthalenes **3a**–**c** and **5a**,**b**, respectively, (5 mmol in 20 ml *DMSO*) was heated between 2.5 h and 9 h and between 125°C and 150°C (see Table 2). Subsequently, the solution was diethyl ether (200 ml), and most of the *DMSO* was extracted with water (4×200 ml) from the etheral phase which was dried over $MgSO_4$. The crude products were purified by silica gel column chromatography and by HPLC, respectively.

7-(5-Pyrimidyl)acenaphtho[1,2-g]chinazoline (**8**)

Yield: 1.527 g (92%); light yellow crystals after HPLC (LiChrosorb-NH_2-phase (7 µm), *tert*.butylmethyl ether/hexane = 7:3); m.p.: 232°C; IR (KBr): $\tilde{\nu}$ = 3044, 1580, 1569, 1552, 1437, 1414, 1395, 813, 767, 726 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 244 (4.61), 312 (4.61), 344 (3.82), 377 (3.79), 386 (3.76) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, J = 7.2 Hz, 1H), 7.52 (dd, J = 7.2 Hz, 8.0 Hz, 1H), 7.79 (dd, J = 6.9 Hz, 8.1 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 6.9 Hz, 1H), 8.48 (s, 1H), 9.05 (s, 2H), 9.28 (s, 1H), 9.52 (s, 1H), 9.54 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.01 (CH), 120.51 (CH), 123.91 (CH), 124.50 (C), 127.74 (CH), 127.86 (C), 128.35 (CH), 128.40 (CH), 128.61 (CH), 130.26 (C), 130.44 (C), 134.31 (C), 134.56 (C), 135.51 (C), 139.35 (C), 143.23 (C), 149.04 (C), 155.24 (CH), 158.34 (2×CH), 158.42 (CH), 159.95

(CH) ppm; MS (70 eV): *m/z* (%) = 332 (92) [M^+], 331 (100), 304 (38); HRMS: calcd.: 331.0984, found: 331.0989; $C_{22}H_{12}N_4$ (332.37); calcd.: C 79.50, H 3.64, N 16.86; found: C 79.37, H 3.49, N 17.05.

7-(3-Pyridyl)acenaphtho[1,2-g]chinoline (**9**)

Yield: 1.115 g (68%); light yellow crystal after HPLC (SiO_2-100, *tert*.butylmethyl ether/acetonitrile = 19:1); m.p.: 211°C; IR (KBr): $\tilde{\nu}$ = 3025, 1594, 1571, 1495, 882, 827, 814, 775, 713 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 214 (4.37), 242 (4.48), 298 (4.35), 312 (4.55), 340 (3.77), 352 (3.65), 372 (3.73), 392 (3.64) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85 (d, *J* = 7.1 Hz, 1H), 7.34–7.40 (m, 2H), 7.55 (dd, *J* = 5.2 Hz, 7.5 Hz, 1H), 7.65 (dd, *J* = 7.1 Hz, 8.1 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.87–7.93 (m, 1H), 8.03 (d, *J* = 7.0 Hz, 1H), 8.22 (dd, *J* = 1.7 Hz, 8.2 Hz, 1H), 8.29 (s, 1H), 8.82–8.86 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.53 (CH), 119.64 (CH), 120.89 (CH), 122.91 (CH), 123.53 (CH), 126.82 (CH), 126.93 (CH), 128.06 (CH), 128.07 (2×C), 128.18 (CH), 130.34 (C), 132.69 (C), 133.86 (C), 135.42 (C), 136.00 (C), 136.27 (CH), 137.97 (C), 138.11 (CH), 139.18 (C), 147.36 (C), 148.99 (CH), 149.90 (CH), 150.94 (CH) ppm; MS (70 eV): *m/z* (%) = 330 (50) [M^+], 329 (100), 302 (12); HRMS: calcd.: 330.1157, found; 330.1142; $C_{24}H_{14}N_2$ (330.39); calcd.: C 87.25, H 4.27, N 8.48; found: C 87.20, H 4.03, N 8.41.

7-((4-Trimethylsilyl)-3-furanyl)-10-trimethylsilylacenaphtho[1,2-f]benzofuran (**10**)

Yield: 2.237 g (99%); colorless crystals after silica gel column chromatography (pentane/diethyl ether = 1:5); m.p.: 62°C; IR (KBr): $\tilde{\nu}$ = 3070, 2960, 2900, 1620, 1510, 1255, 840, 760 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 234 (4.56), 260 (3.95), 292 (4.48), 302 (4.64), 328 (3.75), 358 (3.77), 374 (3.79) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.17 (s, 9H), 0.44 (s, 9H), 7.31 (d, *J* = 7.0 Hz, 1H), 7.58 (dd, *J* = 7.0 Hz, 8.2 Hz, 1H), 7.65 (s, 1H), 7.79 (dd, *J* = 6.9 Hz, 8.2 Hz, 1H), 7.84 (s, 2H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 8.15 (d, *J* = 6.9 Hz, 1H), 8.24 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.97 (3×CH_3), −0.51 (3×CH_3), 113.98 (CH), 114.82 (C), 115.93 (C), 118.89 (CH), 120.24 (C), 122.27 (CH), 122.34 (C), 125.87 (CH), 126.04 (CH), 127.75 (CH), 127.93 (CH), 129.93 (C), 130.49 (C), 133.65 (C), 135.29 (C), 136.18 (C), 136.73 (C), 137.06 (C), 141.05 (CH), 148.96 (CH), 150.36 (CH), 155.43 (C) ppm; MS (70 eV): *m/z* (%) = 452 (49) [M^+], 437 (5), 349 (9), 73 (100); HRMS: calcd.: 452.1629, found: 452.1659; $C_{28}H_{28}O_2Si_2$ (452.70); calcd.: C 74.29, H 6.23; found: C 74.37, H 6.34.

7-(3-Pyridyl)-9-methoxybenzo[k]fluoranthene (**11**)

Yield: 1.202 g (67%); light yellow crystals after HPLC (SiO_2-100, *tert*.butylmethyl ether/hexane = 3:7); m.p.: 105°C; IR (KBr): $\tilde{\nu}$ = 3040, 2932, 2828, 1615, 1562, 1506, 1430, 1406, 1228, 1220, 1227, 825, 773 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 220 (4.63), 240 (4.73), 274 (4.35), 288 (4.29), 315 (4.75), 390 (3.88), 410 (3.87) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.75 (s, 3H), 6.58 (d, *J* = 7.1 Hz, 1H), 6.80 (d, *J* = 2.5 Hz, 1H), 7.19 (dd, *J* = 2.5 Hz, 8.9 Hz, 1H), 7.30–7.38 (m, 1H), 7.60 (dd, *J* = 4.9 Hz, 7.9 Hz, 1H), 7.65 (dd, *J* = 7.1 Hz, 8.1 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.82–7.89 (m, 1H), 7.90 (d, *J* = 8.9 Hz, 1H), 8.01 (d, *J* = 6.9 Hz, 1H), 8.32 (s, 1H), 8.79 (d, *J* = 1.7 Hz, 1H), 8.89 (dd, *J* = 1.7 Hz, 4.9 Hz, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.23 (CH_3), 105.60 (CH), 117.92 (CH), 118.79 (CH), 120.38 (CH), 121.97 (CH), 124.05 (CH), 126.00 (CH), 126.36 (CH), 127.97 (CH), 128.11 (CH), 128.56 (C), 130.05 (C), 130.32 (CH), 130.38 (C), 134.11 (C), 134.75 (C), 135.12 (C), 135.43 (C), 136.43 (C), 136.57 (C), 136.65 (C), 137.89 (CH), 149.40 (CH), 150.96 (CH), 158.19 (C), ppm; MS (70 eV): *m/z* (%) = 359 (100) [M^+] 344 (23), 157 (21), 84 (52); HRMS: calcd.: 359.1310, found: 359.1170; $C_{26}H_{17}ON$ (359.42); calcd.: C 86.88, H 4.76, N 3.90; found: C 87.06, H 4.44, N 3.73.

7-(3-Pyridyl)-10-trimethylsilylacenaphtho[1,2-f]benzofuran (**12**)

Yield: 1.896 g (97%); light yellow crystals after silica gel column chromatography (diethyl ether); m.p.: 92°C; IR (KBr): $\tilde{\nu} = 3043$, 2953, 2895, 1610, 1566, 1516, 1254, 840, 822, 773 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 207 (4.57), 236 (4.67), 302 (4.58), 328 (3.87), 373 (3.87) nm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.45$ (s, 9H), 7.12 (d, $J = 7.1$ Hz, 1H), 7.35 (dd, $J = 7.1$ Hz, 8.1 Hz, 1H), 7.48 (s, 1H), 7.15–7.95 (m, 1H), 7.64 (dd, $J = 7.0$ Hz, 8.1 Hz, 1H), 7.74 (d, $J = 8.1$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.99–8.06 (m, 2H), 8.10 (s, 1H), 8.78–8.84 (m, 1H), 8.93–9.01 (m, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -0.68$ (3×CH_3), 114.26 (CH), 115.97 (C), 119.11 (CH), 119.17 (C), 119.70 (C), 121.79 (CH), 123.78 (CH), 126.11 (CH), 126.43 (CH), 127.85 (CH), 127.91 (CH), 130.04 (C), 130.98 (C), 133.65 (C), 134.36 (C), 136.00 (C), 136.40 (C), 136.45 (C), 137.49 (CH), 149.45 (CH), 150.70 (CH), 150.76 (CH), 154.38 (C) ppm; MS (70 eV): *m/z* (%) = 391 (100) [M^+], 376 (60), 73 (14); HRMS: calcd.: 391.1392, found: 391.1401; $C_{26}H_{21}ONSi$ (391.54); calcd.: C 79.75, H 5.40, N 3.58; found: C 79.42, H 5.09, N 3.49.

12-(3-Pyridyl)acenaphtho[1,2-g]isochinoline (**13**)

Yield: 0.380 g (23%); light yellow crystals after HPLC (SiO_2-100, *tert*.butylmethyl ether/acetonitrile = 19:1); m.p.: 93°C; IR (KBr): $\tilde{\nu} = 3027$, 1592, 825, 775, 715 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 246 (4.75), 296 (4.52), 308 (4.63), 342 (3.88), 360 (3.85), 380 (4.07), 402 (4.08) nm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.78$ (d, $J = 7.2$ Hz, 1H), 7.33 (d, $J = 5.9$ Hz, 1H), 7.41 (dd, $J = 7.2$ Hz, 8.1 Hz, 1H), 7.63 (ddd, $J = 0.8$ Hz, 4.9 Hz, 7.8 Hz, 1H), 7.73 (dd, $J = 7.0$ Hz, 8.2 Hz, 1H), 7.83–7.88 (m, 2H), 7.91 (d, $J = 8.1$ Hz, 1H), 8.14 (d, $J = 7.0$ Hz, 1H), 8.48 (d, $J = 5.9$ Hz, 1H), 8.53 (s, 1H), 8.79 (d, $J = 1.6$ Hz, 1H), 8.93 (dd, $J = 1.6$ Hz, 4.9 Hz, 1H), 9.39 (s, 1H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 118.23$ (CH), 119.28 (CH), 119.57 (CH), 122.82 (CH), 123.70 (CH), 126.74 (CH), 127.13 (CH), 127.80 (C), 127.83 (CH), 127.97 (CH), 129.49 (C), 130.05 (C), 132.77 (C), 134.96 (C), 135.11 (C), 135.18 (C), 135.30 (C), 137.39 (CH), 138.30 (C), 139.30 (C), 143.53 (CH), 149.53 (CH), 150.42 (CH), 152.46 (CH), ppm; MS (70 eV): *m/z* (%) = 330 (100) [M^+], 329 (28), 301 (7); HRMS: calcd.: 330.1157, found 330.1180; $C_{24}H_{14}N_2$ (330.39); calcd.: C 87.25, H 4.27, N 8.48; found: C 87.44, H 4.02, N 8.69.

7-(4-Anisyl)acenaphtho[1,2-g]chinoline (**14**)

Yield: 0.359 g (20%); light yellow crystals after HPLC (SiO_2-100, *tert*.butylmethyl ether/hexane = 3:7); m.p.: 185°C; IR (KBr): $\tilde{\nu} = 3041$, 2996, 2952, 2832, 1609, 1514, 1491, 1437, 1243, 826, 811, 775 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 216 (4.83), 243 (4.72), 270 (4.11), 312 (4.74), 340 (3.99), 352 (3.90), 372 (3.89), 392 (3.91) nm; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.98$ (s, 3H), 6.93 (d, $J = 7.1$ Hz, 1H), 7.16–7.22 (m, 2H), 7.35–7.45 (m, 2H), 7.46–7.52 (m, 2H), 7.69 (dd, $J = 6.9$ Hz, 8.1 Hz, 1H), 7.80 (d, $J = 8.2$ Hz, 1H), 7.88 (d, $J = 8.1$ Hz, 1H), 8.07 (d, $J = 6.9$ Hz, 1H), 8.25 (dd, $J = 1.7$ Hz, 8.2 Hz, 1H), 8.30 (s, 1H), 8.91 (dd, $J = 1.7$ Hz, 4.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.28$ (CH_3), 114.37 (2×CH), 118.93 (CH), 119.30 (CH), 120.59 (CH), 123.14 (CH), 126.44 (CH), 126.62 (CH), 127.91 (CH), 128.21 (C), 128.25 (CH), 130.17 (C), 130.30 (C), 131.11 (2×CH), 135.48 (C), 135.80 (C), 136.26 (CH), 136.46 (C), 136.69 (C), 137.91 (C), 139.07 (C), 147.91 (C), 149.89 (CH), 159.24 (C) ppm; MS (70 eV): *m/z* (%) = 359 (99) [M^+], 358 (100), 344 (12), 315 (27), 158 (36); HRMS: calcd.: 359.1310, found 359.1148; $C_{26}H_{17}ON$ (359.42); calcd.: C 86.88, H 4.76, N 3.90; found: C 86.92, H 4.43, N 3.84.

12-(4-Anisyl)acenaphtho[1,2-g]isochinoline (**15**)

Yield: 0.126 g (7%); light yellow crystals after HPLC (SiO_2-100, *tert*.butylmethyl ether/hexane = 3:7); m.p.: 187°C; IR (KBr): $\tilde{\nu} = 3060$, 3033, 2992, 2958, 2916, 2830, 1612, 1594, 1514, 1437, 1250,

823, 775 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 213 (4.49), 247 (4.64), 283 (4.20), 297 (4.39), 308 (4.49), 342 (3.77), 360 (3.76), 380 (3.98), 401 (4.00) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3H), 6.89 (d, J = 7.1 Hz, 1H), 7.14–7.22 (m, 2H), 7.35–7.48 (m, 4H), 7.70 (dd, J = 7.1 Hz, 8.1 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 8.10 (d, J = 6.9 Hz, 1H), 8.40–8.50 (m, 2H), 9.34 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.43 (CH_3), 114.73 (2×CH), 118.80 (C), 119.34 (CH), 119.62 (CH), 123.33 (CH), 126.83 (CH), 126.93 (CH), 128.12 (CH), 128.21 (CH), 128.34 (CH), 129.17 (C), 130.35 (C), 130.99 (2×CH), 133.82 (C), 135.51 (C), 135.69 (C), 136.17 (C), 136.23 (C), 138.64 (C), 139.21 (C), 143.44 (CH), 152.60 (CH), 159.72 (C) ppm; MS (70 eV): *m/z* (%) = 359 (99) [M^+], 358 (66), 344 (4), 315 (16), 57 (100); HRMS: calcd.: 359.1310, found 359.1286; $C_{26}H_{17}ON$ (359.42); calcd.: C 86.88, H 4.76, N 3.90; found: C 86.37, H 4.18, N 4.05.

12-Methylthio-7-(5-pyrimidyl)acenaphtho[1,2-g]chinazoline (**16**)

Yield 0.095 g (5%); light yellow crystals after HPLC (LiChrosorb-NH_2-phase 1558, (7 µm), *tert*.butylmethyl ether/hexane = 7:3); m.p.: 310°C; Ir (KBr): $\tilde{\nu}$ = 3046, 2919, 2849, 1573, 1430, 1411, 1366, 828, 778, 727 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 241 (4.04), 317 (3.93) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 7.11 (d, J = 7.2 Hz, 1H), 7.53 (dd, J = 7.2 Hz, 8.1 Hz, 1H), 7.89 (dd, J = 7.2 Hz, 8.0 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 9.03 (s, 2H), 9.22 (d, J = 7.2 Hz, 1H), 9.34 (s, 1H), 9.54 (s, 1H), 10.35 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.53 (CH_3), 123.97 (CH), 126.18 (CH), 127.00 (C), 128.06 (CH), 128.24 (CH), 128.35 (C), 128.87 (CH), 128.89 (CH), 130.35 (2×C), 134.06 (C), 134.69 (C), 135.22 (C), 135.99 (C), 142.16 (C), 143.77 (C), 149.85 (C), 155.23 (CH), 158.30 (2×CH), 158.51 (CH), 158.88 (CH) ppm; MS (70 eV): *m/z* (%) = 378 (8) [M^+]; HRMS: calcd.: 378.0939, found: 378.0922; $C_{23}H_{14}N_4S$ (378.46); calcd.: C 72.99, H 3.73, N 14.80; found: C 73.20, H 3.64, N 14.66.

12-Methylthio-7-(3-pyridyl)acenaphtho[1,2-g]chinoline (**17**)

Yield: 0.083 g (5%); light yellow crystals after HPLC (SiO_2-100, *tert*.butylmethyl ether/acetonitrile = 19:1); m.p.: 233°C; IR (KBr): $\tilde{\nu}$ = 3030, 2916, 1599, 1560, 1428, 825, 811, 775, 720 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 246 (4.49), 306 (4.37), 318 (4.58), 344 (3.81), 376 (3.64), 398 (3.61) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 3H), 6.77 (d, J = 7.2 Hz, 1H), 7.39 (dd, J = 7.2 Hz, 8.1 Hz, 1H), 7.53 (dd, J = 4.1 Hz, 8.5 Hz, 1H), 7.59 (dd, J = 2.5 Hz, 4.9 Hz, 1H), 7.78 (dd, J = 7.3 Hz, 8.2 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.88–7.95 (m, 2H), 8.78–8.90 (m, 3H), 9.14 (d, J = 7.3 Hz, 1H), 9.20 (dd, J = 1.6 Hz, 8.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.06 (CH_3), 121.39 (CH), 123.03 (CH), 123.62 (CH), 125.41 (CH), 127.20 (CH), 127.42 (CH), 127.89 (CH), 128.46 (CH), 129.48 (C), 130.11 (C), 130.11 (C), 133.70 (C), 133.93 (C), 134.53 (CH), 135.42 (C), 135.74 (C), 135.76 (C), 137.96 (CH), 139.52 (C), 141.14 (C), 147.69 (C), 149.18 (CH), 149.88 (CH), 150.88 (CH) ppm; MS (70 eV): *m/z* (%) = 376 (72) [M^+], 375 (100), 360 (33); HRMS: calcd.: 376.1034, found: 376.0960; $C_{25}H_{16}N_2S$ (376.48); calcd.: C 79.76, H 4.29, N 7.44; found: C 79.49, H 4.69, N 7.24.

7-(4-Anisyl)-12-methylthioacenaphtho[1,2-g]chinoline (**18**)

Yield: 0.061 g (3%); light yellow crystals after HPLC (SiO_2-100, *tert*.butylmethyl ether/hexane = 3:7); m.p.: 192°C; IR (KBr): $\tilde{\nu}$ = 3062, 2923, 2855, 2836, 1612, 1515, 1486, 1245, 1174, 1041, 909 cm^{-1}; UV (ethanol): λ_{max} (lgε) = 219 (4.26), 245 (4.30), 307 (4.14), 317 (4.32), 344 (3.58), 360 (3.54), 375 (3.44), 397 (3.36) nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (s, 3H), 3.96 (s, 3H), 6.80 (d, J = 7.1 Hz, 1H), 7.14–7.20 (m, 2H), 7.35–7.42 (m, 1H), 7.39–7.46 (m, 2H), 7.51 (dd, J = 4.1 Hz, 8.5 Hz, 1H), 7.72–7.79 (m, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 8.92 (dd, J = 1.5 Hz, 4.1 Hz, 1H), 9.11 (d, J = 7.2 Hz, 1H), 9.19 (dd, J = 1.5 Hz, 8.5 Hz, 1H) ppm; ^{13}C NMR

(100 MHz, $CDCl_3$): $\delta = 19.02$ (CH_3), 55.32 (CH_3)), 114.49 (2×CH), 121.07 (CH), 123.29 (CH), 125.20 (CH), 126.75 (CH), 127.25 (CH), 127.94 (CH), 128.28 (CH), 128.46 (C), 130.15 (C), 130.16 (C), 131.00 (2×CH), 134.59 (2×C), 135.78 (C), 136.01 (CH), 136.01 (C), 137.34 (C), 139.49 (C), 141.15 (C), 148.07 (C), 149.80 (CH), 159.35 (C) ppm; MS (70 eV); *m/z* (%) = 405 (100) [M^+], 404 (77), 374 (19); HRMS: calcd.: 404.1109, found 404.1140; $C_{27}H_{19}ONS$ (405.52); calcd.: C 79.97, H 4.72, N 3.45; found: C 79.54, H 4.60, N 3.66.

Acknowledgements

We thank the *Fonds der Chemischen Industrie* for financial support.

References

[1] Staab HA, Ipaktschi J (1971) Chem Ber **104**: 1170
[2] Sonogashira K (1991) In: Trost BM, Fleming I (eds) Comprehensive Organic Synthesis, vol 3. Pergamon, Oxford, p 521
[3] Hey DH, Stirling CJM, William GH (1955) J Chem Soc 3963
[4] Holmes AB, Sporikou CN (1987) Org Synth **65**: 61
[5] Sakamoto T, Shiraiwa M, Kondo Y, Yamanaka H (1983) Synthesis 312
[6] Crisp GT, Flynn BL (1993) J Org Chem **58**: 6614
[7] Heck RF (1985) In: Palladium Reagents in Organic Syntheses. Academic Press, London, p 18
[8] House HO, Koepsell DG, Campbell WJ (1972) J Org Chem **37**: 1003
[9] Liotta D, Saindane M, Ott W (1983) Tetrahedron Lett **24**: 2473

Received February 26, 1998. Accepted (revised) May 4, 1998