# 2-Azaanthraquinones: Building Blocks for New Ring-Fused Imidazoles and their Transformation into Benzo[*f*]isoindole-4,9-diones

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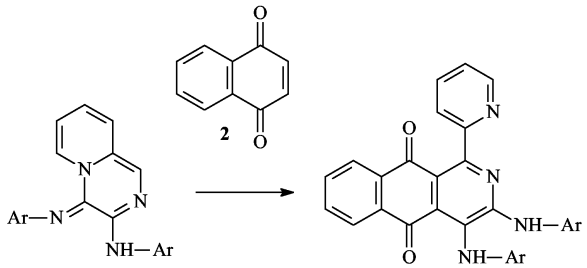
The modification of 2-azaanthraquinones with selected $C_1$ building blocks gives a series of new imidazo-fused derivatives. Employing 2,3-dichloro-5,6-dicyanopyrazine as cyclization partner a rearrangement to yield derivatives of benzo[*f*]isoindole-4,9-dione takes place. The Sonogashira cross-coupling reaction of the aminalester derivative of the azaanthraquinone resulted in well soluble silyl substituted acetylenes as well as ethinyl aniline which allows further derivatization reactions.

*Key words:* Azaanthraquinones, Ring Transformation, Cross-Coupling Reactions, Crystal Structure

## Introduction

Quinones – especially their ring-fused derivatives – are interesting in many respects. They are redoxactive compounds which are modeled after natural products and therefore, many of their derivatives and synthetic analogues exhibit biological activity. In addition, their synthetic applications are manifold. For example, carbonyl dyes based on quinones dyes rank among the most frequently used dyestuffs in the textile industry. More recent applications of quinones are as substructures in systems for studying artificial energy- and electron transfer processes [1]. Partial replacement of carbon by nitrogen results in azaanthraquinones, which can be regarded as being electronically distorted variants of the parent compounds. These derivatives are also found in nature; 1- and 2-azaanthraquinones have been identified as natural products [2 – 4]. Many synthetic representatives show interesting biological effects. Some azaanthraquinones are teratogens for insects [5] and others are being tested as anti-cancer reagents [6, 7]. 1- and 2-Azaanthraquinones are generally synthetically accessible and quite a few successful procedures are available in the chemical literature [8 – 11]. However, a major drawback is the fact that substitutional variety at the trinuclear core is highly restricted. In the past, we have reported an efficient synthesis for obtaining highly substituted 2-azaanthraquinones by ring transformation of the easily accessible pyrido[1,2-*a*]pyrazines **1** [12]. Reaction of **1** with quinones yields, *via* a complex cycloaddition/ring transformation cascade, novel azaanthraquinone derivatives featuring a 2,2'-bipyridine substructure. We have now expanded our research to consider the reaction of **1** with 1,4-naphthoquinone **2** which results in new azaanthraquinones of type **3** (Scheme 1). Furthermore, we demonstrate that **3** is a useful building block for obtaining metal-chelating substructures and redox-active dyes.




**1a**: Ar = 4-$IC_6H_4$
**1b**: Ar = 4-$BrC_6H_4$

**3a,b**

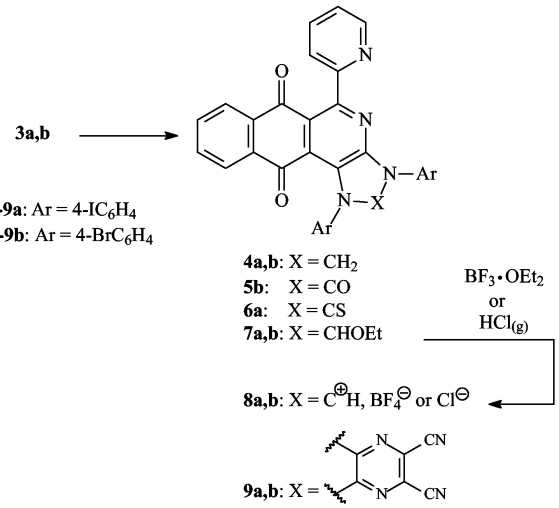
Scheme 1.

## Results and Discussion

The azaanthraquinones of type **3** have been synthesized starting from appropriate pyrido[1,2-*a*]pyrazines **2** using our proved protocol [12]. In a smooth reac-

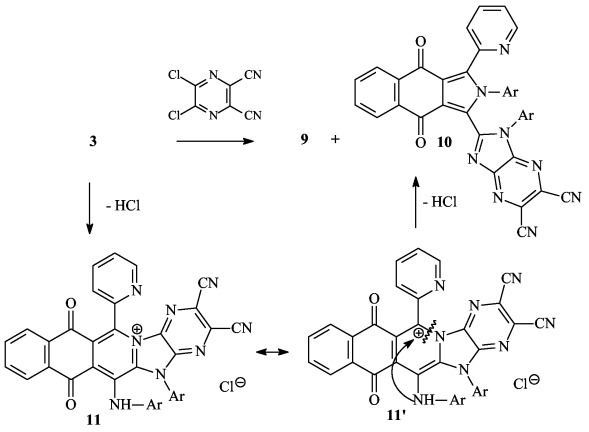
tion both derivatives **3a,b** were obtained in yields of about 85%. The presence of the two secondary arylamine substructures at 3- and 4-positions in **3** has concrete advantages and disadvantages for further synthetic transformations. A distinct disadvantage is the fact that they hinder successful metal-complexation reactions at the bipyridine substructure. Compound **3** is thus unsuitable for applications as a metal chelating ligand. We therefore attempted to simply remove the arylamine substituents *via* an acylation/reduction sequence – and failed completely. The advantage of the arylamine substituents in **3** is the fact that their presence makes further synthetic transformations (alkylation, acylation, ring closure reactions) quite feasible. In addition, cross-coupling reactions involving the arylic halogens allow the introduction of further functional groups.

In an attempt to reintroduce metal-complexing ability into **3** while retaining the synthetic advantage of the arylamine substituents, we modified **3** by tying the aniline nitrogen atoms together *via* a ring closure reaction. In the course of this study, we discovered that these amine substituents can be bridged by several different $C_1$ building blocks (Scheme 2). Methylene iodide in the presence of cesium carbonate reacts with **3** to form the desired products **4a,b**, albeit in rather low yields (*ca.* 18%). Evidence for the successful cyclization are the molar mass at $m/z = 638$ for **4b** as well as the signals obtained at 5.91 ppm (N-$CH_2$-N) in the $^1$H NMR spectra of **4b**. In contrast to the deeply violet starting material **3** the products are red colored crystals that, when dissolved in trichloromethane, display a strong orange fluorescence. Another $C_1$ building block that works is phosgene that is generated *in situ* from diphosgene. In this manner, a bridging C=O group can be introduced and the derivate **5b** was obtained in a moderate yield. The ring thus introduced can be classified as having a cyclic urea substructure. In an analogous manner, the corresponding sulfur derivative (X=S) **6a** was obtained in a 10% yield with thiophosgene. However, cycloacylation with 1,1'-thiocarbonyldiimidazole failed. A further cyclization agent which we have successfully employed in the past [13–15] is triethyl orthoformate. Heating compounds **3a,b** under reflux for several hours in neat triethyl orthoformate resulted in the desired products **7a,b** which could be isolated as orange solids in quite satisfactory yields of *ca.* 65%. Dissolved in various solvents, these derivatives fluoresce orange-yellow with quantum yields of up to 45%.




Scheme 2.

A final building block that can be successfully employed is 2,3-dichloro-5,6-dicyanopyrazine. This pyrazine derivative is well-suited for the assembly of condensed heterocycles with high fluorescence [16, 17]. Heating of **3** and 2,3-dichloro-5,6-dicyanopyrazine in the presence of cesium carbonate (as base) resulted in a mixture with the new derivatives **9** (*ca.* 40%) and **10** (*ca.* 35%) as the main products. Compound **9** is red and possesses a strong orange fluorescence in solvents such as trichloromethane and is remarkable because of its Stokes shift of 100 nm. The spectral data of **9** are in agreement with the structural assignment presented in Scheme 2 and are similar to those reported for other pyrazino-fused systems [16]. Compound **10** is yellow and its elemental analysis as well as its mass spectrum indicate the same molecular assembly as in compound **9**. The X-ray structural analysis obtained from a single crystal (Fig. 1) revealed a fused pyrrole substructure which is connected with an imidazo[4,5-*b*]pyrazine and a pyridine ring. Compound **10** does not fluoresce; a fact which may have a structural origin since the solid state structure shows that both heteroaromatic residues are twisted out of plane. The formation of this unexpected heterocyclic quinone **10** is undoubtedly the result of a rearrangement reaction. As a mechanism (Scheme 3) for the formation of **10**, we postulate the attack of 2,3-dichloro-5,6-dicyanopyrazine at one pyridine nitrogen and the neighbouring NH-aryl group. The resulting mesomeric iminium system **11**/**11'** is then attacked by the remaining NH group to finally provide the novel benzo[*f*]isoindole-4,9-dione **10**. Although, these types



Scheme 3.

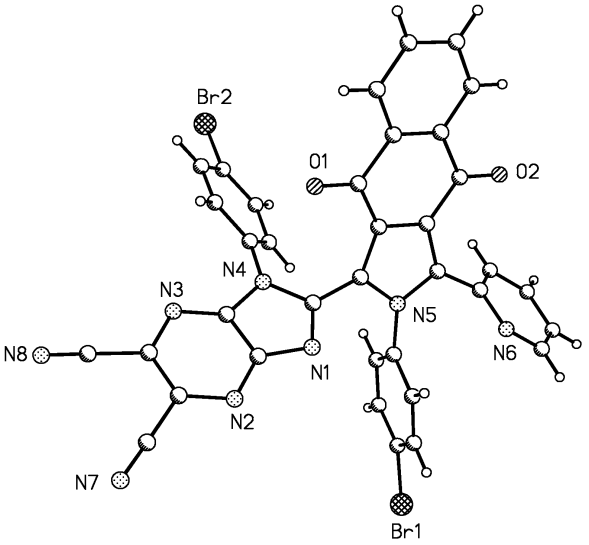
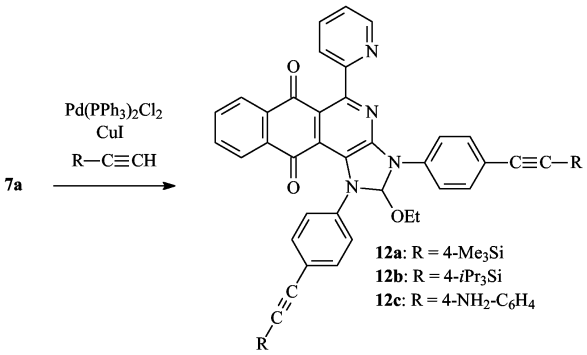



Fig. 1. Molecular structure of isoindoloquinone **10b**. Selected bond lengths [Å] and angles [°]: N5-C17 1.392(7), N5-C6 1.386(8), C1-C6 1.447(9), N1-C1 1.321(7), N4-C1 1.391(8), C6-N5-C17 109.7(5), N1-C1-N4 113.4(5).

of heterocyclic quinones are well documented [18], derivatives which possess in 1,3-position additional heterocyclic substructures are unknown to date. Very recently, ring-fused isoindoloquinones have been identified as novel antibiotics from a terrestrial streptomycete [19] and in addition, are already patented for the use in the treatment of cancer [20].

These successful modifications have resulted in a series of compounds **4**–**9** in which the arylamine substituents are now bound in a heterocyclic ring (Scheme 3). The flexibility of the arylamine substituents has thus been considerably reduced and the resulting planarization of the nitrogen atoms has de-



Scheme 4.

localized the lone pair. This extension of the heterocyclic system should contribute to new properties; applications as chromophores/fluorophores and/or interesting biological activities. We are now investigating whether or not these modified compounds **4**–**9** can be employed as ligands in metalla-complexes.

The syntheses of pyrido[1,2-*a*]pyrazines **1** are restricted to simple aryl residues due to the substituents already present in the starting material, namely the *bis*-imidoylchlorides of oxalic acid. Nonetheless, we recently succeeded in obtaining an entry to amino and acetylene substituted derivatives *via* palladium-catalyzed cross-coupling methods [14, 15]. In order to achieve an increased solubility of azaanthraquinones, the Sonogashira reaction was our method of choice (Scheme 4). Even with the standard catalytic system $PdCl_2(PPh_3)_2$/CuI both iodine atomes in **7a** could be replaced by trimethylsilylacetylene as well as by triisopropylacetylene. This exchange resulted in the well soluble derivatives **12a** and **12b**, respectively, which could be purified by chromatography. Furthermore, 4-ethinylaniline could be introduced in good yield to give derivative **12c** that due to its *para*-amino groups provides an access to other compounds.

Our goal was finally to construct electron-rich tetraaminoethenes which are connected with electron-accepting structures of azaquinones *via* dimerization of *in situ* generated carbenes. Unfortunately, all attempts to synthesize these dimers from **7a,b** (Scheme 2) by thermal induced $\alpha$-elimination were fruitless. Treatment at temperatures higher than 270 °C under argon atmosphere led only to tarry pyrolysis products. Encouraged by the quantum leap in the chemistry of nucleophilic carbenes in the last years, the synthesis and isolation of carbenes by deprotonation of imidazolium salts seemed feasible to us. Therefore, the transformation of aminal esters **7** into imidazolium salts has been

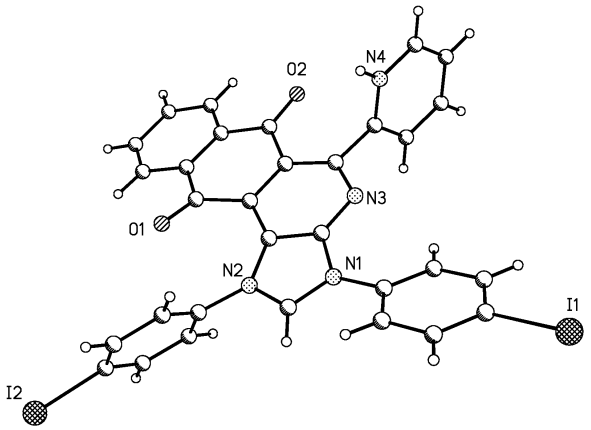



Fig. 2. Molecular structure of imidazolium salt **8a**. Selected bond lengths [Å] and angles [°]: N1-C1 1.335(5), N2-C1 1.327(6), N1-C2 1.399(5), N2-C1-N1 112.2 (4).

chosen as another promising way. Derivatives **7a,b** were reacted with boron trifluoride to give in a smooth reaction salts of type **8**. Alternatively, these compounds could be prepared from **7** with gaseous hydrogen chloride. Elemental analyses and the sharp singulets at over 10 ppm in their $^1$H NMR spectra suggest the structure of an imidazolium salt. A single crystal X-ray analysis of **8a** allowed an unambiguous structural assignment of these compounds, as shown in Fig. 2.

Upon treatment of salts **8a,b** with different bases however, neither carbenes nor their dimers could be isolated. With pyridine as solvent and sulfur as quenching reagent the thione **6a** (Scheme 2) was obtained in good yields. This method is superior to the acylation with thiophosgene described above, and is the method of choice for the preparation of **6a**. Finally, **6a** was also formed by reaction of aminalesters **7** with sulfur in a microwave reactor.

## Experimental Section

*Materials and methods*

All reagents were of commercial quality (Aldrich, Fluka, Merck). Solvents were dried and purified using standard techniques. Reactions were monitored by thin layer chromatography (tlc), Polygram SIL G/UV254 from Macherey-Nagel or Polygram Alox N/UV254 from Macherey-Nagel. Flash chromatography was carried out on silica gel (Merck, Silica gel 60, particle size 0.040 – 0.063 mm, 230 – 400 mesh ASTM) or neutral aluminia (Merck, aluminium oxide 90 active neutral, activity V, particle size 0.063 – 0.2 mm, 70 – 230 mesh ASTM). Melting points were measured with a Galen III (Boëtius system) from Cambridge Instruments and are not corrected: The UV-vis spectra were obtained using a Perkin Elmer Lambda 19 spectrophotometer. The $^1$H and $^{13}$C NMR spectra were obtained on Bruker DRX 400 and Bruker AC 250 spectrometers. Mass spectra were obtained with a Finnigan MAT SAQ 710 spectrometer. Elemental analyses were carried out using an automatic analyzer LECO CHNS 932. Microwave reactions were carried out with a CEM "Discovery". Synthesis of pyrido[1,2-*a*]pyrazine **1a**: see literature [12].

*Crystallographic data*

The intensity data for the compounds were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo-K$_\alpha$ radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects [21, 22]. The structures were solved by direct methods (SHELXS [23]) and refined by full-matrix least squares techniques against $F_o{}^2$ (SHELXL-97 [24]). For the imidazolium C and the pyridine N in **8a** the hydrogen atoms werer located by difference Fourier synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [24]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

*Crystal data for* **8a** [25]: $C_{31}H_{18}B_2F_8I_2N_4O_2 \times 2\ C_4H_8O$, $M = 1050.12$ g mol$^{-1}$, orange-red prism, size $0.03 \times 0.03 \times 0.02$ mm$^3$, monoclinic, space group $P2_1/n$, $a = 11.8822(3)$, $b = 14.1197(2)$, $c = 24.3073(5)$ Å, $\beta = 95.941(1)^\circ$, $V = 4056.2(1)$ Å$^3$, $T = -90$ °C, $Z = 4$, $\rho_{\text{calcd.}} = 1.720$ g cm$^{-3}$, $\mu$ (Mo-K$_\alpha$) $= 16.33$ cm$^{-1}$, $F(000) = 2064$, 28532 reflections in $h(-15/12)$, $k(-18/17)$, $l(-31/30)$, measured in the range $1.84^\circ \leq \Theta \leq 27.47^\circ$, completeness $\Theta_{\max} = 99.8\%$, 9276 independent reflections, $R_{\text{int}} = 0.036$, 6922 reflections with $F_o > 4\sigma(F_o)$, 535 parameters, 0 restraints, $R1_{\text{obs}} = 0.055$, $wR^2_{\text{obs}} = 0.146$, $R1_{\text{all}} = 0.079$, $wR^2_{\text{all}} = 0.1624$, GOOF = 1.009, largest difference peak and hole: 1.844/–1.810 e Å$^{-3}$.

*Crystal data for* **10b** [25]: $C_{36}H_{16}Br_2N_8O_2 \times 1/2\ C_7H_8$, $M = 798.46$ g mol$^{-1}$, colorless prism, size $0.04 \times 0.04 \times 0.03$ mm$^3$, triclinic, space group $P\bar{1}$, $a = 11.2316(7)$, $b = 11.3079(7)$, $c = 15.1176(9)$ Å, $\alpha = 96.198(3)$, $\beta = 91.194(4)$, $\gamma = 104.125(3)^\circ$, $V = 1848.9(2)$ Å$^3$, $T = 20$ °C, $Z = 2$, $\rho_{\text{calcd.}} = 1.434$ g cm$^{-3}$, $\mu$ (Mo-K$_\alpha$) $= 22.38$ cm$^{-1}$, $F(000) = 798$, 10039 reflections in $h(-14/14)$, $k(-14/14)$, $l(-18/19)$, measured in the range $2.73^\circ \leq \Theta \leq 27.50^\circ$, completeness $\Theta_{\max} = 88\%$, 7488 independent reflections, $R_{\text{int}} = 0.038$, 4142 reflections with $F_o > 4\sigma(F_o)$, 449 parameters, 1 restraint, $R1_{\text{obs}} = 0.091$, $wR^2_{\text{obs}} = 0.253$, $R1_{\text{all}} = 0.157$, $wR^2_{\text{all}} = 0.310$, GOOF = 1.017, largest difference peak and hole: $1.195/-0.692$ e Å$^{-3}$.

*3-(4-Bromophenylamino)-4-(4-bromophenylimino)-4H-pyrido[1,2-a]pyrazine (***1b***)*

The synthesis from 1.1 g (10 mmol) of 2-(aminomethyl)pyridine and 4.35 g (10 mmol) of oxalic acid bis(4-

bromophenylimidoyl) chloride according to literature [12] yielded 3.19 g (68%); m.p. 179 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 324 (4.1), 428 (4.1). – $^1$H NMR (250 MHz, $CD_2Cl_2$): $\delta$ = 6.29 (t, $^3J$ = 6.3 Hz, 1 H), 6.56 – 6.66 (m, 3 H), 7.09 (d, $^3J$ = 9.1 Hz, 1 H), 7.28 – 7.34 (m, 5 H), 7.48 – 7.56 (m, 3 H), 8.20 (s, 1 H). – $^{13}$C NMR (62.5 MHz, $CD_2Cl_2$): $\delta$ = 114.3, 118.8, 121.0, 122.4, 123.4, 125.6, 127.1, 127.9, 131.7, 137.9, 137.9, 140.1, 142.6, 148.4. – MS (DCI, $H_2O$): *m/z* (%) = 473 (47) [$M^+$+5], 471 (100) [$M^+$+3], 469 (53) [$M^+$+1]. – $C_{20}H_{14}Br_2N_4$ (470.2): calcd. C 51.09, H 3.00, Br 33.99, N 11.92; found C 50.46, H 3.12, Br 34.06, N 12.10.

*Azaanthraquinone* **3a**

A solution of 564 mg (1 mmol) of pyrido[1,2-*a*]pyrazine **1a** and 158 mg (1.1 mmol) of 1,4-naphthoquinone **2** in 30 ml of methylene chloride was heated at reflux, and the progress of the reaction was controlled by TLC. The reaction time was 3 – 4 h. The solvent was removed *in vacuo* and the residue was separated by column chromatography on alumina ($CHCl_3$/*n*-heptane: 1/1) to yield 627 mg (87%) dark violet solid; m.p. 256 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 360 (3.9), 509 (4.0). – $^1$H NMR (250 MHz, [$D_6$]-DMSO): $\delta$ = 6.72 (d, $^3J$ = 8.7 Hz, 2 H), 7.39 – 7.61 (m, 9 H), 7.83 – 7.94 (m, 4 H), 7.94 – 8.12 (m, 1 H), 8.53 (d, $^3J$ = 4.1 Hz, 1 H), 9.39 (s, 1 H) – MS (DCI, $H_2O$): *m/z* (%) = 721 (17) [$M^+$+1], 594 (9), 321 (86), 161 (100). – $C_{30}H_{18}I_2N_4O_2$ (720.3): calcd. C 50.02, H 2.52, I 35.24, N 7.78; found C 49.91, H 2.65, I 35.10, N 7.89.

*Azaanthraquinone* **3b**

Prepared in a manner analogous to that for compound **3a**, Yield: 520 mg (83%); dark violet solid, m.p. 250 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 360 (4.0), 504 (4.0). – $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 6.87 (d, $^3J$ = 8.7 Hz, 2 H), 7.05 (s, 1 H), 7.35 – 7.46 (m, 5 H), 7.55 – 7.65 (m, 3 H), 7.76 – 7.85 (m, 2 H), 7.92 (t, $^3J$ = 5.0 Hz, 1 H), 8.09 (m, 1 H), 8.22 (d, $^3J$ = 8.0 Hz, 1 H), 8.65 (d, $^3J$ = 8.0 Hz, 1 H), 10.04 (s, 1 H). – MS (DCI, $H_2O$): *m/z* (%) = 629 (43) [$M^+$+5], 627 (100) [$M^+$+3], 625 (57) [$M^+$+1], 546 (17). – $C_{30}H_{18}Br_2N_4O_2$ (626.3): calcd. C 57.53, H 2.90, Br 25.52, N 8.95; found C 57.61, H 3.04, Br 25.40, N 9.12.

*Cyclization of azaanthraquinones* **3a**, **b** *with methylene iodide to compounds* **4a**, **b**

300 mg (0.35 mmol) of the appropriate azaanthraquinone **3** were dissolved in 20 ml of DMF. After addition of 226 mg (0.7 mmol) of $Cs_2CO_3$ the mixture was stirred for 10 min. and then 0.03 ml (0.37 mmol) of $CH_2I_2$ was dropped into the mixture. After heating for 8 h and then cooling to r.t., the crude product was precipitated by addition of water. The orange crude product was filtered off and purified by column chromatography on alumina ($CHCl_3$/toluene: 3/1).

*1,3-Bis(4-iodophenyl)-5-pyridin-2-yl-2,3-dihydro-1H-1,3,4-triazacyclopenta[a]anthracene-6,11-dione (***4a***)*

Yield: 44 mg (17%); red crystals, decomposition at 305 – 310 °C. – UV/vis ($CHCl_3$): $\lambda_{max}$ ($\lg\varepsilon$) = 395 (3.9), 509 (4.1). – $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.02 (s, 2 H), 6.83 (d, $^3J$ = 8.7 Hz, 1 H), 7.14 – 8.04 (m, 14 H), 8.60 (d, $^3J$ = 4.5 Hz, 1 H). – $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ = 73.5, 119.5, 120.8, 122.1, 122.9, 126.4, 126.7, 126.9, 128.0, 128.9, 133.2, 133.7, 133.8, 134.6, 136.4, 137.5, 137.7, 137.8, 138.1, 138.2, 138.4, 141.0, 142.8, 146.7, 148.5, 153.1, 154.0, 154.5, 158.8, 181.3, 181.8. – MS (FAB in dmba): *m/z* (%) = 733 (7) [$M^+$], 505 (11), 439 (23), 336 (100). – Fluorescence ($CHCl_3$): $\lambda_{max,em}$ = 594 nm, $\Phi$ = 0.24. – $C_{31}H_{18}I_2N_4O_2$ (732.3): calcd. C 50.84, H 2.48, I 34.66, N 7.65; found C 50.75, H 2.57, I 34.40, N 7.39.

*1,3-Bis-(4-bromophenyl)-5-pyridin-2-yl-2,3-dihydro-1H-1,3,4-triazacyclopenta[a]anthracene-6,11-dione (***4b***)*

Yield: 40 mg (18%); red crystals, decomposition at 289 – 294 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 395 (4.0), 510 nm (4.1). – $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 5.91 (s, 2 H), 6.90 (d, $^3J$ = 8.7 Hz, 1 H), 7.19 – 7.94 (m, 14 H), 8.51 (d, $^3J$ = 4.3 Hz, 1 H). – $^{13}$C NMR (100.6 MHz, $CD_2Cl_2$): $\delta$ = 74.1, 119.6, 121.0, 122.0, 122.3, 126.8, 127.3, 127.3, 128.2, 128.3, 129.4, 131.7, 131.9, 132.2, 132.6, 132.8, 132.9, 133.7, 143.1, 134.3, 134.4, 135.1, 136.8, 138.1, 142.7, 149.2, 153.6, 154.5, 159.2, 181.8, 182.2. – MS (DCI, $H_2O$): *m/z* (%) = 638 (3) [M], 557 (3), 427 (12), 391 (23), 279 (100), 159 (100). – $C_{31}H_{18}Br_2N_4O_2$ (638.3): calcd. C 58.33, H 2.84, Br 25.04, N 8.78; found C 58.23, H 3.01, Br 25.19, N 8.57.

*1,3-Bis(4-bromophenyl)-5-pyridin-2-yl-1,3-dihydro-1,3,4-triaza-cyclopenta[a]anthracene-2,6,11-trione (***5b***)*

200 mg (0.32 mmol) of azaanthraquinone **3b** and 61 mg (0.64 mmol) of sodium *tert*-butoxide were stirred at r.t. in 50 ml of THF. After 5 min 32 mg (0.16 mmol) of diphosgene were added and then the mixture was heated at reflux for 6 h. After cooling to r.t. the solvent was removed *in vacuo*. Purification of the yellow product by column chromatography on alumina (toluene/ethyl acetate: 20/1) gave 49 mg (23%) of **5b**; decomposition at 274 – 307 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 247 (4.5), 409 nm (3.9). – $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 7.17 – 7.20 (m, 2 H), 7.30 – 7.36 (m, 1 H), 7.46 (d, $^3J$ = 6.8 Hz, 1 H), 7.57 – 7.68 (m, 8 H), 7.77 – 7.86 (m, 2 H), 7.99 – 8.02 (m, 1 H), 8.57 (d, $^3J$ = 4.2 Hz, 1 H). – $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 119.9, 121.0, 121.1, 121.9, 122.2, 125.6, 126.3, 126.5, 126.6, 130.1, 131.0, 131.4, 132.2, 132.9, 133.0, 133.7, 134.6, 135.7, 145.5, 148.0, 152.2, 153.3, 157.5, 180.4, 180.9. – MS (DCI, $H_2O$): *m/z* = 653 (72) [$M^+$], 93 (100). –

$C_{31}H_{16}Br_2N_4O_3$ (652.3): calcd. C 57.08, H 2.47, Br 24.50, N 8.59; found C 56.91, H 2.58, Br 24.72, N 8.41.

*1,3-Bis(4-bromophenyl)-5-pyridin-2-yl-2-thioxo-2,3-dihydro-1H-1,3,4-triazacyclopenta[a]-anthracene-6,11-dione (***6a***)*

200 mg (0.32 mmol) of azaanthraquinone **3a** and 61 mg (0.64 mmol) sodium *tert*-butoxide were stirred at r.t. in 50 ml of THF. After about 5 min 0.02 ml (0.32 mmol) of thiophosgene were added and the mixture was heated at reflux for 7 h. After cooling to r.t. and the solvent was removed *in vacuo*. Chromatographic purification on alumina (toluene/ethyl acetate: 20/1) gives 21 mg (10%) of a red product. This product was obtained in a better yield (71%) starting from 100 mg (0.11 mmol) of the imidazolium salt **8a** which was heated in 10 ml of pyridine in the presence of elemental sulphur (8 mg, 0.22 mmol). Decompostion at 312 – 317 °C. – UV/vis (acetonitrile): $\lambda_{max}(\lg\varepsilon) = 324$ (3.8), 450 (4.1) – $^1$H NMR (400 MHz, [D$_8$]-THF): $\delta = 7.28 - 7.32$ (m, 1 H), 7.41 (d, $^3J = 8.0$ Hz, 2 H), 7.51 (d, $^3J = 8.0$ Hz, 1 H), 7.61 (d, $^3J = 8.0$ Hz, 2 H), 7.66 – 7.81 (m, 7 H), 7.87 (d, $^3J = 8.0$ Hz, 1 H), 7.99 (d, $^3J = 8.0$ Hz, 1 H), 8.50 (d, $^3J = 4.0$ Hz, 1 H). – $^{13}$C NMR (100.6 MHz, [D$_8$]-THF): $\delta = 122.7$, 122.8, 123.4, 123.6, 124.4, 126.7, 127.1, 127.4, 128.8, 129.5, 130.5, 130.9, 131.4, 132.3, 132.6, 133.0, 134.3, 134.6, 134.8, 135.1, 135.4, 136.7, 138.3, 140.0, 149.5, 150.1, 156.7, 159.9, 177.6, 181.9, 182.5. – MS(CI): *m/z* (%) = 670 (12) [M$^+$+2], 668 (24) [M], 666 (12) [M-2], 635 (5). – $C_{31}H_{16}Br_2N_4O_2S$ (668.4): calcd. C 55.71, H 2.41, Br 23.91, N 8.38, S 4.80; found C 55.62, H 2.28, Br 23.76, N 8.56, S 4.63.

*Cyclization of azaanthraquinones* **3a**, **b** *with triethyl orthoformate to aminal esters* **7a**, **b**

A mixture of 0.35 mmol of the appropriate azaanthraquinone **3** und 15 ml of triethyl orthoformate was heated at reflux for about 14 h. The solvent was removed *in vacuo* and the crude product was purified by column chromatography on alumina ($CHCl_3$/*n*-heptane: 1/1).

*2-Ethoxy-1,3-bis(4-iodophenyl)-5-pyridin-2-yl-2,3-dihydro-1H-1,3,4-triazacyclopenta[a]-anthracene-6,11-dione (***7a***)*

Yield: 185 mg (68%); orange powder, decomposition at 256 – 263 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 370 (3.9), 479 nm (4.1). – $^1$H NMR (250 MHz, $CDCl_3$): $\delta = 1.13$ (t, $^3J = 7.0$ Hz, 3 H), 3.26 (m, 1 H), 3.51 (m, 1 H), 6.84 (s, 1 H), 6.92 (s, br, 2 H), (d, $^3J = 7.6$ Hz, 1 H), 7.48 (d, $^3J = 7.8$ Hz, 1 H), 7.64 – 7.59 (m, 6 H), 7.82 – 7.75 (m, 3 H), 7.97 – 7.93 (m, 1 H), 8.05 – 8.02 (m, 1 H), 8.61 (d, $^3J = 4.90$ Hz, 1 H). – $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta = 14.6$, 56.0, 101.8, 117.9, 118.3, 118.8, 119.1, 121.5, 122.4, 122.8, 126.6, 126.8, 127.3, 128.2, 129.0, 133.5, 133.7, 134.1, 134.5, 136.6, 136.8 141.9, 149.1, 152.3, 152.8, 159.7, 181.1, 181.7. – MS (DCI, $H_2O$): *m/z* (%) = 777 (13) [M+], 731 (14), 204 (100), 181 (56), 139 (40). – Fluorescence ($CHCl_3$): $\lambda_{max,em} = 579$ nm, $\Phi = 0.35$. – $C_{33}H_{22}I_2N_4O_3$ (776.4): calcd. C 51.05, H 2.86, I 32.69, N 7.22; found C 51.21, H 2.71, I 32.47, N 7.35.

*2-Ethoxy-1,3-bis(4-bromophenyl)-5-pyridin-2-yl-2,3-dihydro-1H-1,3,4-triazacyclopenta[a]-anthracene-6,11-dione (***7b***)*

Yield: 150 mg (63%); orange powder, decomposition at 261 – 265 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 370 (4.1), 478 nm (4.2). – $^1$H NMR (250 MHz, $CDCl_3$): $\delta = 1.14$ (t, $^3J = 7.5$ Hz, 3 H), 3.22 – 3.34 (m, 1 H), 3.47 – 3.59 (m, 1 H), 6.84 (s, 1 H), 7.05 (s, br, 2 H), 7.31 – 7.37 (m, 1 H), 7.41 – 7.50 (m, 5 H), 7.60 – 7.64 (m, 2 H), 7.79 – 7.97 (m, 4 H), 8.03 – 8.06 (m, 1 H), 8.62 (d, $^3J = 4.2$ Hz, 1 H). – $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta = 14.6$, 56.0, 101.9, 117.9, 118.3, 118.8, 119.1, 121.3, 122.2, 122.8, 126.6, 126.9, 127.3, 131.8, 132.2, 133.5, 133.7, 134.1, 134.5, 136.1, 136.6, 141.2 149.1, 152.3, 152.8, 159.7, 181.1, 181.7. – MS (DCI, $H_2O$): *m/z* (%) = 683 (100) [M$^+$], 637 (59), 604 (4). – Fluorescence ($CHCl_3$): $\lambda_{max,em} = 579$ nm, $\Phi = 0.45$. – $C_{33}H_{22}Br_2N_4O_3$ (682.4): calcd. C 58.09, H 3.25, Br 23.42, N 8.21; found C 58.18, H 3.38, Br 23.67, N 8.10.

*Transformation of aminal esters* **7a**, **b** *into imidazolium salts* **8a**, **b** *employing $BF_3$-etherate or gaseous hydrogen chloride*

To a solution of 0.35 mmol of the correspoding azaanthraquinone **7** in dry toluene an equimolar amount of $BF_3$-etherate was dropped slowly. Alternatively, gaseous hydrogen chloride was passed into the solution of **7**. Immediately, yellow precipitates were obtained which were filtered off, washed with *n*-heptane and dried.

*Imidazolium salt* **8a** *(tetrafluoroborate)*

Yield: 263 mg (83%); yellow product, decomposition at 312 – 317 °C. – UV/vis (THF): $\lambda_{max}$ ($\lg\varepsilon$) = 371 (4.0), 483 nm (4.0). – $^1$H NMR (400 MHz, [D$_8$]-THF): $\delta =$ 7.33 (d, $^3J = 8.0$ Hz, 2 H), 7.56 (d, $^3J = 8.0$ Hz, 2 H), 7.68 – 8.04 (m, 9 H), 8.23 (d, $^3J = 8.0$ Hz, 1 H), 8.51 – 8.59 (m, 1 H); 8.86 (d, $^3J = 8$ Hz, 1 H), 10.42 (s, 1 H). – MS (micro-ESI, THF): *m/z* (%) = 731 (100) [M$^+$], 685 (13). – $C_{31}H_{18}B_2F_8I_2N_4O_2$ (905.9): calcd. C 41.10, H 2.00, N 6.18; found C 40.86, H 2.27, N 5.87.

*Imidazolium salt* **8b** *(tetrafluoroborate)*

Yield: 225 mg (79%); yellow product, decomposition at 305 – 308 °C. – UV/vis (THF): $\lambda_{max}$ ($\lg\varepsilon$) = 370 (3.9), 483 nm (4.0). – $^1$H NMR (250 MHz, [D$_8$]-THF): $\delta = 7.32 - 7.47$ (m, 2 H), 7.61 – 7.72 (m, 4 H), 7.80 – 8.05 (m, 8 H), 8.16 (d, $^3J = 8.0$ Hz, 1 H), 8.47 – 8.53 (m, 2 H); 8.80 (d, $J = 8$ Hz, 1 H), 10.45 (s, 1 H). – MS (micro-ESI, THF): *m/z* (%) = 639 (100) [M$^+$+1].

– $C_{31}H_{18}B_2F_8Br_2N_4O_2$ (811.9): calcd. C 45.86, H 2.66, N 6.90; found C 45.72, H 2.83, N 6.74.

*Cyclization of azaanthraquinones* **3a**, **b** *with 2,3-dichloro-5,6-dicyanopyrazine to compounds* **9a**, **b** *and* **10a**, **b**

0,35 mmol of the corresponding azaanthraquinone **3** was mixed with 226 mg (0,7 mmol) of $Cs_2CO_3$ in 30 ml of toluene. After stirring for about 5 min, 70 mg (0,35 mmol) of 2,3-dichloro-5,6-dicyanopyrazine were added. The mixture was heated at reflux for about 12 h. The solvent was removed *in vacuo* and the products were separated by column chromatography on alumina (toluene/ethyl acetate: 10/1).

*5,14-Bis(4-iodophenyl)-8,13-dioxo-7-pyridin-2-yl-5,8,13,14-tetrahydro-1,4,5,6,14-pentaaza-pentaphene-2,3-dicarbonitrile* (**9a**)

Yield: 118 mg (40%); red product, decomposition at 305 – 307 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 347 (4.0), 491 nm (3.9). – $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 6.91 (d, $^3J$ = 8.7 Hz, 3 H), 7.09 – 7.30 (m, 4 H), 7.54 – 7.80 (m, 7 H), 7.85 (m, 1 H), 8.45 (d, $^3J$ = 4.5 Hz, 1 H). – $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 92.3, 94.2, 112.0, 112.1, 121.9, 122.7, 123.6, 124.3, 124.8, 125.8, 126.3, 127.2, 128.0, 129.4, 129.6, 132.2, 132.5, 133.0, 133.4, 136.9, 137.4, 138.3, 139.0, 143.7, 145.1, 147.3, 147.5, 153.4, 155.5, 179.9, 180.7. – MS (DCI, $H_2O$): *m/z* (%) = 847 (17) [$M^+$], 237 (42), 219 (100). – Fluorescence ($CHCl_3$): $\lambda_{max,em}$ = 594 nm, $\Phi$ = 0.07. – $C_{36}H_{16}I_2N_8O_2$ (846.4): calcd. C 51.09, H 1.91, I 29.99, N 13.24; found C 50.87, H 2.08, I 29.74, N 13.01.

*5,14-Bis(4-bromophenyl)-8,13-dioxo-7-pyridin-2-yl-5,8,13,14-tetrahydro-1,4,5,6,14-pentaaza-pentaphene-2,3-dicarbonitrile (***9b***)*

Yield: 100 mg (38%); red product, decomposition at 300 – 307 °C.- UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 345 (4.1), 491 nm (4.1). – $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 7.02 – 7.33 (m, 7 H), 7.44 – 7.62 (m, 6 H), 7.70 (d, $^3J$ = 7.7 Hz, 1 H), 7.85 (d, $^3J$ = 7.5 Hz, 1 H), 8.45 (d, $^3J$ = 4,5 Hz, 1 H). – $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 112.0, 112.1, 120.8, 121.9, 122.5, 122.7, 123.6, 123.7, 124.3, 124.8, 125.8, 126.3, 127.2, 128.0, 129.2, 129.6, 131.4, 132.3, 132.5, 132.9, 135.9, 136.3, 143.8, 145.1, 147.3, 147.6, 153.5, 155.5, 179.9, 180.7. – MS (DCI, $H_2O$): *m/z* (%) = 753 [$M^+$], 399, 93. – Fluorescence ($CHCl_3$): $\lambda_{max,em}$ = 596 nm, $\Phi$ = 0.10. – $C_{36}H_{16}Br_2N_8O_2$ (752.4): calcd. C 57.47, H 2.14, Br 21.24, N 14.89; found C 57.19, H 2.38, Br 21.01, N 14.73.

*1-(4-Iodophenyl)-2-[2-(4-iodophenyl)-4,9-dioxo-3-pyridin-2-yl-4,9-dihydro-2H-benzo[f]-isoindol-1-yl]-1H-imidazolo[4,5-b]pyrazine-5,6-dicarbonitrile (***10a***)*

Yield: 104 mg (35%); yellow crystals, decomposition at 259 – 267 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 334 (4.2). – $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 6.85 (d, $^3J$ = 8.7 Hz, 3 H), 7.17 – 7.23 (m, 2 H), 7.46 (d, $^3J$ = 8.3 Hz, 2 H), 7.64 – 7.73 (m, 6 H), 7.97 – 8.01 (m, 1 H), 8.10 – 8.14 (m, 1 H), 8.39 (d, $^3J$ = 4.7 Hz, 1 H). – MS (DCI, $H_2O$): *m/z* (%) = 847 (31) [$M^+$+1]. – $C_{36}H_{16}I_2N_8O_2$ (846.4): calcd. C 51.09, H 1.91, I 29.99, N 13.24; found C 50.85, H 2.27, I 29.78, N 13.08.

*1-(4-Bromophenyl)-2-[2-(4-bromophenyl)-4,9-dioxo-3-pyridin-2-yl-4,9-dihydro-2H-benzo-[f]isoindol-1-yl]-1H-imidazolo[4,5-b]pyrazine-5,6-dicarbonitrile (***10b***)*

Yield: 98 mg (33%); yellow crystals, decomposition at 264 – 268 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 335 nm (4.3). – $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 7.00 (d, $^3J$ = 8.7 Hz, 3 H), 7.02 – 7.29 (m, 4 H), 7.52 (d, $^3J$ = 8.7 Hz, 2 H), 7.62 – 7.72 (m, 4 H), 7.98 – 8.02 (m, 1 H), 8.11 – 8.15 (m, 1 H), 8.39 (d, $^3J$ = 4.8 Hz, 1 H). – $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 113.4, 119.8, 122.3, 124.0, 124.1, 124.8, 124.9, 125.3, 126.9, 127.3, 127.4, 127.8, 127.9, 128.2, 129.0, 129.4, 130.7, 132.3, 133.1, 133.8, 134.2, 134.3, 134.4, 135.4, 136.2, 137.9, 139.7, 141.0, 147.1, 148.4, 149.4, 154.7, 179.1, 179.5. – MS (DCI, $H_2O$): *m/z* (%) = 753 (25) [$M^+$+1], 335 (21), 181 (58), 93 (100). – $C_{36}H_{16}Br_2N_8O_2$ (752.4): calcd. C 57.47, H 2.14, Br 21.24, N 14.89; found C 57.19, H 2.30, Br 21.13, N 15.09.

*2-Ethoxy-5-pyridin-2-yl-1,3-bis(4-trimethylsilanylethynyl-phenyl)-2,3-dihydro-1H-1,3,4-triaza-cyclopenta[a]anthracene-6,11-dione (***12a***)*

A solution of 200 mg (0.26 mmol) of azaanthraquinone **7a** in 10 ml of triethylamine and 10 ml of THF was degassed and then 76 mg (0.77 mmol) of trimethylsilylacetylene, 18 mg (5 mol%) of dichlorobis(triphenylphosphane)-palladium(II) und 10 mg (10 mol%) of copper(I) iodide were added. After heating for 5 h at 60 °C the reaction was completed. Purification by column chromatography on alumina (toluene/ethyl acetate: 20/1) gave 149 mg (80%) of a red product, decomposition at 296 – 301 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 358 (4.1), 468 nm (4.0). – $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 0.08 (m, 18 H), 1.11 (t, $^3J$ = 7.5 Hz, 3 H), 3.34 (m, 1 H), 3.52 (m, 1 H), 6.71 (s, 1 H), 6.99 – 7.51 (m, 9 H), 7.66 – 7.90 (m, 6 H), 8.5 (d, $^3J$ = 4.8 Hz, 1 H). – $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta$ = 0.1, 14.6, 56.1, 86.0, 88.0, 94.5, 94.6, 101.7, 104.7, 116.5, 119.0, 119.4, 120.3, 122.9, 123.4, 125.5, 126.5, 127.0, 127.3, 127.7, 128.4, 128.6, 132.0, 132.1, 132.4, 132.9, 133.5, 133.8, 134.0, 134.4, 136.7, 136.9, 141.9, 144.9, 149.3, 152.3, 159.4, 180.8, 181.6 ppm. – MS (DEI): *m/z* (%) = 716 (15) [$M^+$], 671 (100), 432 (21). – Fluorescence ($CHCl_3$): $\lambda_{max,em}$ = 579 nm, $\Phi$ = 0.25. – $C_{43}H_{40}N_4O_3Si_2$ (717.0): calcd. C 72.03, H 5.62, N 7.81; found C 71.85, H 5.82, N 8.03.

*2-Ethoxy-5-pyridin-2-yl-1,3-bis-(4-triisopropyl silanylethynyl-phenyl)-2,3-dihydro-1H-1,3,4-triaza-cyclopenta[a]anthracene-6,11-dione (***12b***)*

A suspension of 300 mg (0.39 mmol) of **7a** in 40 ml of THF and 5 ml of triethylamine was degassed for 10 min and then 211 mg (1.16 mmol) of triisopropylacetylene, 27 mg (5 mol%) of dichlorobis(triphenylphosphane)-palladium(II) and 15 mg (10 mol%) of CuI were added. The orange mixture was heated at reflux for about 4 h until it became clear and was red colored. The solution was cooled to r.t. and the solvent was removed *in vacuo*. Purification by column chromatography on silica (toluene/ethyl acetate: 5/1) gave 293 mg (85%) of a red product, decomposition at 298 – 314 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 373 (4.1), 482 nm (4.1). – $^1$H NMR (250 MHz, $CD_2Cl_2$): $\delta = 0.01$ (m, 36 H), 1.11 (t, $^3J = 7.5$ Hz, 3 H), 1.47 (m, 6 H), 3.28 (m, 1 H), 3.51 (m, 1 H), 6.90 (s, 1 H), 7.11 – 7.47 (m, 8 H), 7.61 – 7.65 (m, 2 H), 7.78 (m, 1 H), 7.91 – 7.97 (m, 4 H), 8.54 (d, $^3J = 4.3$ Hz, 1 H). – $^{13}$C NMR (62.5 MHz, $CD_2Cl_2$): $\delta = 0.1$, 10.6, 17.6, 55.4, 81.0, 89.2, 101.1, 105.8, 105.8, 117.7, 118.6, 118.8, 119.0, 119.6, 119.7, 121.8, 122.2, 125.7, 126.1, 131.5, 132.0, 132.7, 133.1, 133.2, 133.8, 135.5, 136.3, 141.3, 148.2, 151.6, 151.8, 159.1, 180.2, 180.9. – MS (FAB, dmba): *m/z* (%) = 886 (41) [$M^+$+1], 870 (13), 842 (21), 336 (84), 210 (100). – $C_{55}H_{64}N_4O_3Si_2$ (858.3): calcd. C 74.62, H 7.29, N 6.33; found C 74.51,H 7.26, N 6.58.

*1,3-Bis[4-(4-aminophenylethynyl)phenyl]-2-ethoxy-5-pyridin-2-yl-2,3-dihydro-1H-1,3,4-triaza-cyclopenta[a]anthracene-6,11-dione (***12c***)*

To a degassed suspension of 300 mg (0,39 mmol) of **7a** in 10 ml of triethylamine and 10 ml of toluene, 91 mg (0.78 mmol) of 4-ethynylaniline, 27 mg (5 mol%) of $PdCl_2(PPh_3)_2$ and 15 mg (10 mol%) of CuI were added. Immediately, a deep red product precipitated from the deeply orange solution. After 3 h of heating to 60 °C, the reaction was completed. The solvent was removed *in vacuo* and the crude product was purified by column chromatography on alumina (toluene/ethyl acetate: 8/1) to yield 235 mg (80%) of a red product, decomposition at 305 – 308 °C. – UV/vis (acetonitrile): $\lambda_{max}$ ($\lg\varepsilon$) = 325 (4.8), 369 (4.1). – $^1$H NMR (250 MHz, $CDCl_3$): $\delta = 1.11$ (t, $^3J = 7.0$ Hz, 3 H), 3.31 (m, 1 H), 3.54 (m, 1 H), 3.78 (s, 4 H), 6.54 – 6.58 (m, 4 H), 6.92 (s, 1 H), 7.09 – 7.36 (m, 7 H), 7.43 (d, $^3J = 8.9$ Hz, 4 H), 7.52 (d, $^3J = 7.8$ Hz, 1 H), 7.59 – 7.63 (m, 2 H), 7.83 (m, 1 H), 7.92 – 8.06 (m, 4 H), 8.63 (d, $^3J = 4.3$ Hz, 1 H). – $^{13}$C NMR (62.5 MHz, $CDCl_3$): $\delta = 8.7$, 46.2, 87.0, 90.5, 112.5, 114.7, 118.2, 119.0, 119.4, 120.3, 121.2, 125.3, 127.0, 128.2, 129.0, 132.1, 132.9, 133.4, 133.8, 134.6, 136.3, 136.6, 137.8, 141.2, 146.7, 149.0, 152.3, 152.6, 159.7, 181.0, 181.8. – MS (FAB, dmba): *m/z* (%) = 755 (32) [$M^+$], 336 (72), 210 (100). – $C_{49}H_{34}N_6O_3$ (754.8): calcd. C 77.97, H 4.54, N 11.13; found C 78.31, H 4.59, N 11.21.

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[25] CCDC 263637 (**8a**) and 263638 (**10b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).