Synthesis and Modification of Substituted 2-Azaanthraquinones

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Z. Naturforsch. **2010**, *65b,* 833 – 842; received March 18, 2010

The cycloaddition-ring transformation reaction sequence of pyrido[1,2-*a*]pyrazines with substituted naphthoquinones furnished a series of new highly substituted azaanthraquinones. Whereas monosubstituted naphthoquinones were normally leading to two regioisomeric products, in some cases a preference for only one regioisomer was observed. The amino derivative **3b** which was isolated as the main product proved to be suitable for further modifications at the primary amino group. The derivatives obtained possess groups capable of connecting the molecule with other substructures for applications as functional dyes. The newly synthesized azaquinones show strong and very broad absorptions between 400 and 600 nm in their UV/Vis spectra.

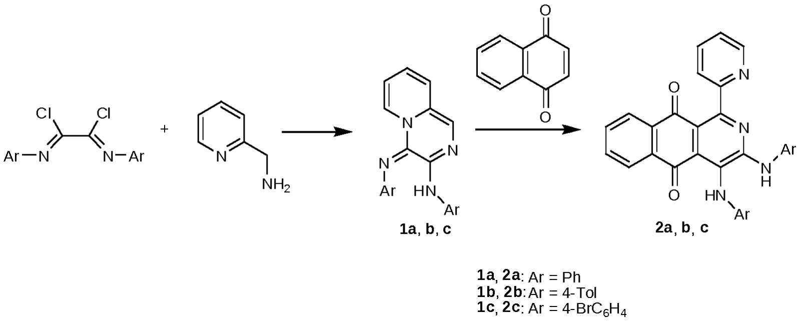
Key words: Azaanthraquinones, Ring Transformation, Cycloaddition, Functional Dyes

Introduction

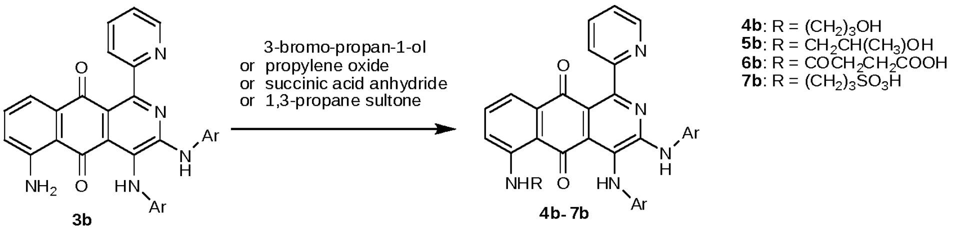
The partial replacement of carbon by nitrogen in anthraquinone results in azaanthraquinones which can be regarded as electronically distorted variants of the parent compounds. These derivatives are rarely found in nature, however, they are of special interest due to their important physiological properties [1 – 4]. In addition, many synthetic representatives show interesting biological effects [5 – 8]. 1- and 2-azaanthraquinones are generally synthetically accessible, and successful procedures are available in the chemical literature [9 – 15]. A major drawback, however, is the fact that the substitutional variety at the trinuclear core is relatively limited.

In the past, we have reported an efficient synthesis for highly substituted azaanthraquinones by a complex cycloaddition/ring transformation cascade of the easily accessible pyrido[1,2-*a*]pyrazines **1** [16] (Scheme 1). The azaanthraquinones obtained feature the coexistence of a 2,2′-bipyridine substructure and two vicinal arylamino moieties.

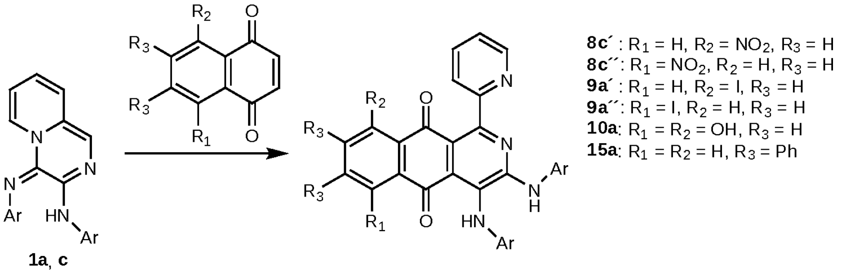
Due to the fact that quinones have manifold applications as functional dyes, *e. g.* as a dark quencher for polymerase chain reaction (“PCR”) [17], and as electron-accepting parts in systems for studying artificial energy and electron transfer processes [18], there is a need for new multifunctional derivatives. We have now expanded our research to consider the reaction of **1** with a series of substituted 1,4-naphthoquinones which results in new azaanthraquinones.



Scheme 1. Synthesis of starting materials **1** and their subsequent ring-transformation reaction into azaanthraquinones **2** (the indices **a**, **b**, **c** for the appropriate aryl moieties are used below for all other azaanthraquinones).



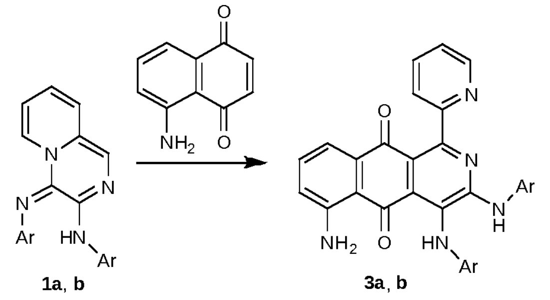
Scheme 3. Modification reactions at the primary amino group of azaanthraquinone **3**.



Scheme 4. Synthesis of substituted azaanthraquinones.

Results and Discussion

With respect to the applications of 2-azaanthraquinones, for example as dark quencher or antenna systems, the presence of groups which are capable of connecting the molecule with other substructures is necessary. Due to the fact that usually hydroxyl or carboxy groups have been employed, we tested the reactions of 2-azaanthraquinones with halogeno alcohols, propylene oxide, and succinic acid anhydride. Unfortunately, this method failed, and the desired products were formed only in traces. The low nucleophilicity of both amino functions is most likely mainly responsible for this failure. Next, we made attempts to synthesize derivatives which possess other functional groups. To this end, pyrido[1,2-*a*]pyrazine **1a** was ring-transformed with 5-aminonaphthoquinone in order to obtain derivative **3a** bearing the more reactive amino function (Scheme 2). Unexpectedly, only one regioisomer was isolated; the single crystal X-ray structure of which is depicted in Fig. 1.



Scheme 2. Synthesis of amino-azaanthraquinones **3a** and **3b**.

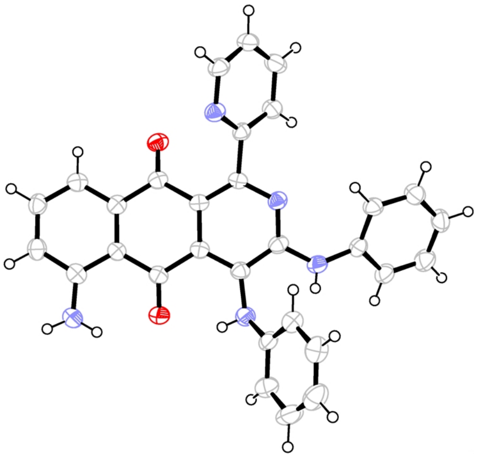


Fig. 1. Molecular structure of azaanthraquinone **3a** in the crystal.

Subsequently, the modification reactions of the amino group of **3b** with the reagents mentioned above were successful, yielding derivatives **4–6b** in moderate up to good yields. In addition, the reaction with propane sultone furnished derivative **7b**, which features water solubility (Scheme 3).

In order to study the regioselectivity of the initial Diels-Alder reaction, further 1,4-naphthoquinones substituted in the 5-position were reacted with **1**. However, neither the nitro- nor the iodo-substituted naphthoquinone showed any selectivity, giving only mixtures of **8′**/**8″** and **9′**/**9″**, respectively (Scheme 4).

We succeeded in obtaining single crystals of each regioisomeric compound, which allowed structure de-

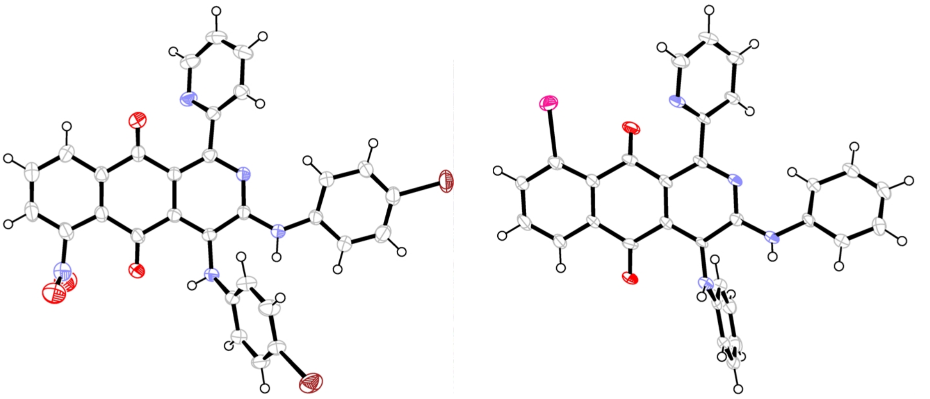
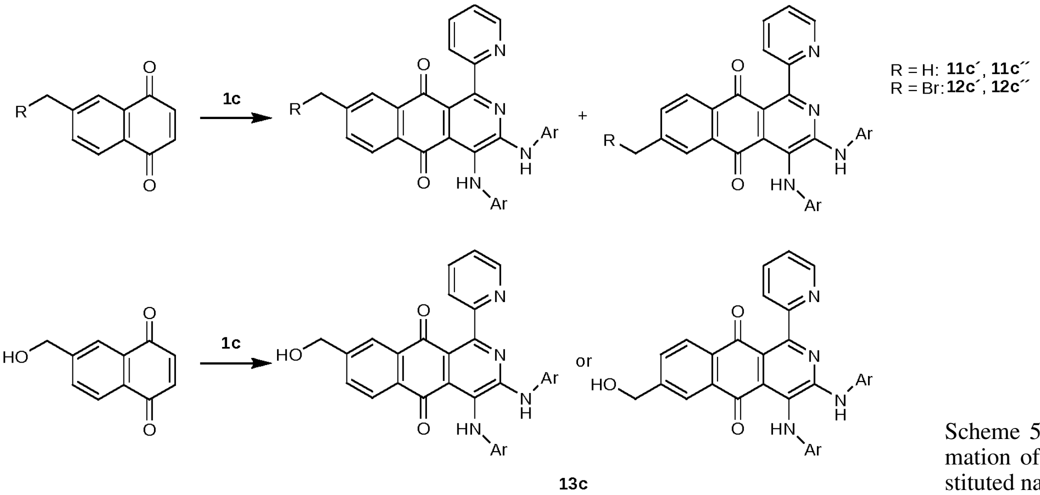


Fig. 2. Molecular structures of the nitro derivative **8c″** (left) and the iodo derivative **9a′** (right).



Scheme 5. Ring transformation of **1c** with 6-substituted naphthoquinones.

terminations by X-ray diffraction analysis and, thus, a reliable assignment (Fig. 2).

In further experiments, 5,8-dihydroxy-1,4-naphthoquinone (“naphthazarine”) was reacted with **1**. As the main product, 5,8-dihydroxy-2-aza-anthraquinone **10** was isolated in fair yield (Fig. 3). However, all attempts to introduce further substructures at the OH groups by reaction with ω-halogeno alcohols/ω-halogeno fatty acids failed. A possible reason for this failure seems to be the nature of the OH groups. As depicted in the X-ray structure, the quinone carbonyl bonds are elongated, and in parallel, both phenolic C–O bonds are shortened. This fact is in agreement with data existing for chinizarine [19], indicating the existence of an equilibrium between the 9,10- and 5,8-anthraquinone structures in solution.

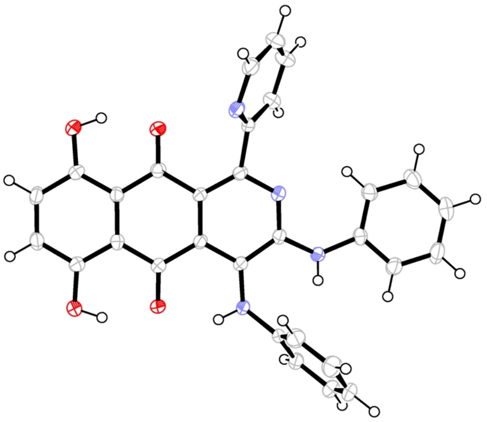
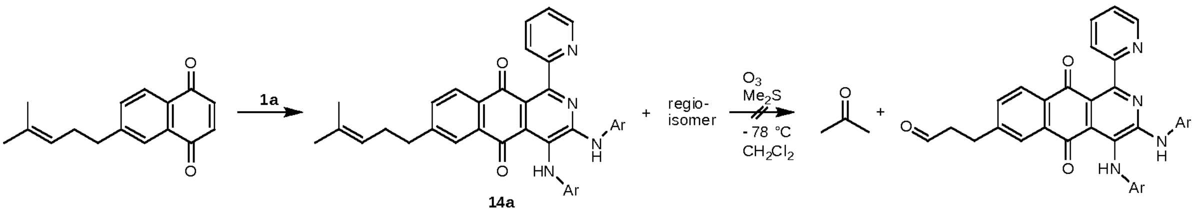


Fig. 3. Molecular structure of 5,8-dihydroxyazaanthraquinone **10a**.

With respect to their reactivity towards **1**, besides naphthoquinones substituted in the 5-position, functionalized derivatives in the 6-position were also tested (Scheme 5). Interestingly, in the cases where R = CH_3/CH_2Br, two regioisomeric compounds were again formed in a statistical distribution, whereas when



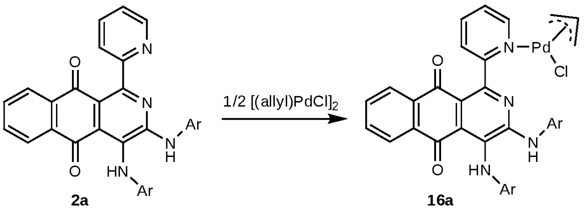
Scheme 6. Synthesis of azaanthraquinone **14** and its attempted ozonolysis reaction.

R = CH_2OH, one regioisomer was clearly favored ($> 10:1$). No structure determination was possible due to the lack of single crystals. The hydroxymethyl function proved to be an excellent coupling group for its use as a functional dye.

Another promising way to obtain coupling-active functions should exist in the oxidation of hydroxymethyl derivatives to furnish the appropriate carboxylic acids. Since attempts to carry out this oxidation failed completely, the derivative **14a** containing a double bond in its side chain was synthesized. It was hoped that in a subsequent reaction this double bond could be transformed *via* ozonolysis into acetone and aldehyde (Scheme 6). Derivative **14a** (two regioisomers) was obtained by a [4+2] cycloaddition reaction between myrcene and 1,4-benzoquinone [20] followed by ring transformation with pyridopyrazine **1a**. However, when employing typical conditions for ozonolysis (−78 °C, CH_2Cl_2, 10 min), all attempts to isolate the desired product were in vain.

Finally, starting from acetone, benzil and 1,4-benzoquinone, 6,7-diphenyl-1,4-naphthoquinone [21] was synthesized and then ring transformed into derivative **15** (Scheme 4). Since this procedure might allow the introduction of numerous functional groups, we are also studying the chemistry of appropriate benzils.

Due to their polyfunctionality, the azaanthraquinones synthesized here are not only powerful chromophores, but also possess the prerequisites (bipyridine, redox activity) to act as multifunctional ligands.



Scheme 7. Synthesis of the palladium complex **16a**.

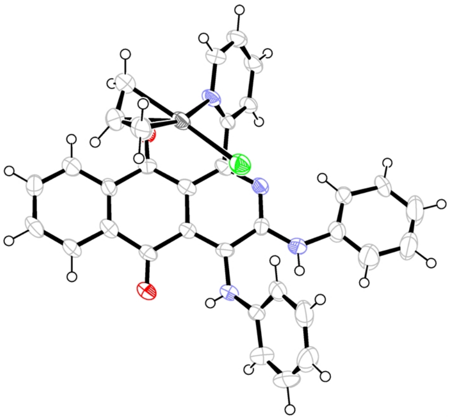


Fig. 4. Molecular structure of the palladium complex **16a**.

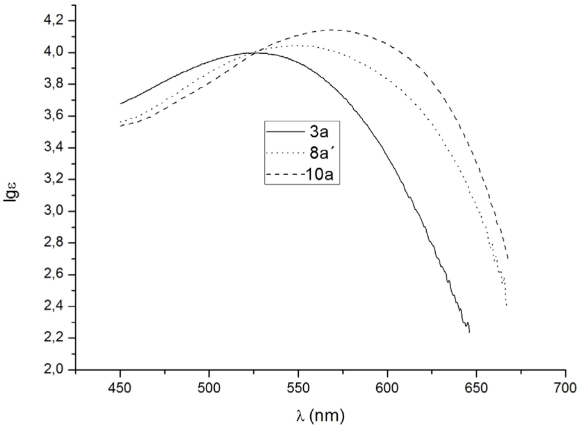


Fig. 5. UV/Vis spectra of the derivatives **3a**, **8a′** and **10a** measured in $CHCl_3$.

As a model reaction, **2a** was treated with the allyl palladium(II) chloride dimer in THF. A quantitative reaction forming a deep-red compound **16a** took place even at r. t. (Scheme 7). Interestingly, the absence/presence of TEA as a base showed no influence on the formation of the product. Compound **16a** proved to be stable towards air and was further purified by column chromatography. The X-ray structure analysis obtained from a single crystal clearly demonstrated that the metal is coordinated only at the unsubstituted pyridine substructure (Fig. 4). Obviously, the oxygen atom

Table 1. Crystal data and data collection and refinement details for the X-ray structure determinations of **3a**, **8c″**, **9a′**, **10a** and **16a**.

Compound	**3a**	**8c″**	**9a″**	**10a**	**16a**
Formula	$C_{30}H_{21}N_5O_2$, $CHCl_3$	$C_{30}H_{17}Br_2N_5O_4$, $CHCl_3$	$C_{30}H_{19}IN_4O_2$	$C_{30}H_{20}N_4O_4$, $C_6H_6O_2$, $CHCl_3$	$C_{33}H_{25}ClN_4O_2Pd$
Mw, g mol^{-1}	602.89	790.67	594.39	729.98	651.42
T, °C	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	9.664(3)	8.8003(6)	8.5103(5)	10.1828(5)	9.944(2)
b, Å	9.981(3)	11.4569(6)	10.5368(8)	22.4527(8)	23.364(5)
c, Å	15.973(5)	15.8348(11)	14.5961(9)	14.6117(8)	12.349(3)
α, deg	105.965(16)	106.125(3)	100.603(3)	90	90
β, deg	97.011(17)	90.978(4)	104.944(4)	100.774(2)	95.65(3)
γ, deg	105.70(2)	90.398(4)	106.245(5)	90	90
V, Å^3	1393.5(7)	1533.38(17)	1166.89(13)	3281.8(3)	2855(1)
Z	2	2	2	4	4
ρ, g mol^{-1}	1.44	1.71	1.69	1.48	1.52
μ, cm^{-1}	3.7	29.5	14.1	3.4	7.8
Measured data	4495	10594	8168	18624	11870
Data with $I \geq 2\sigma(I)$	2452	5113	3544	4778	3407
Unique data / R_{int}	3408 / 0.0372	6859 / 0.0282	5220 / 0.0599	7425 / 0.0592	5918 / 0.0855
$R1$ $[I \geq 2\sigma(I)]^{a}$	0.0624	0.0581	0.0672	0.0527	0.0829
$wR2$ (all data)^{a}	0.1719	0.1800	0.1652	0.1292	0.1830
S^{b}	1.040	1.023	1.022	1.008	1.101
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	0.38 / −0.33	1.10 / −0.89	1.82 / −1.16	0.32 / −0.29	0.80 / −0.86
CCDC no.	767539	767540	767541	767542	767543

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2)+(aP)^2+bP]^{-1}$, where $P = (\text{Max}(F_o^2, 0)+2F_c^2)/3$ and a and b are constants adjusted by the program; [b] $S = \text{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

of the quinone subunit sterically prevents the formation of a bipyridine complex.

All newly synthesized azaquinones are dark-blue crystalline compounds. They show very broad absorptions between 400 and 600 nm with high extinctions in their UV/Vis spectra. The UV/Vis spectra of **3a**, **8a′** and **10a**, are depicted in Fig. 5. Their chemical stability, the presence of coupling-active groups, and their spectral features mentioned above make them interesting candidates for applications in antenna systems and as dark quenchers for PCR.

Experimental Section

The reagents employed in the following section were purchased from commercial sources and used directly unless otherwise stated. All solvents were of reagent grade and were dried according to common practice and distilled prior to use. Reactions were monitored by TLC using aluminum plates coated with Al_2O_3 or SiO_2 from Fluka. The ^{1}H and ^{13}C NMR spectra were obtained on Bruker AC 250 (250 MHz) or DRC-400 (400 MHz) spectrometers; shifts are given relative to the signals of the solvent. Mass spectra were measured on a spectrometer SAQ 710 from Finnigan MAT, while the high-resolution mass spectra were recorded on a Finnigan MAT 95 XL-Trap. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer. The IR spectra were obtained on a Biorad FTS-25 instrument.

Crystal structure determinations

The intensity data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromatized MoK_α radiation. Data were corrected for Lorentz and polarization, but not for absorption [22, 23]. The structures were solved by Direct Methods (SHELXS [24]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97 [25]). For the amino groups of **3a**, **8c″**, **9a′** and **16a** the hydrogen atoms were located by difference Fourier syntheses and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [25]. XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. Details of the structure determinations are given in Table 1.

CCDC-767539 (**3a**), 767540 (**8c″**), 767541 (**9a′**), 767542 (**10a**), and 767543 (**16a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

*General procedure for ring transformation of pyrido[1,2-a]pyrazines **1** with substituted naphthoquinones*

A solution of the pyrido[1,2-*a*]pyrazine **1** (1 mmol) and the appropriate quinone (1 mmol) was heated under reflux in 50 mL of anhydrous methylene chloride, and the progress of the reaction was monitored by TLC. Usually, reaction times were between 12 and 30 h. The solvent was removed *in vacuo*, and the residue was purified by chromatography on silica gel.

*6-Amino-3,4-bis(phenylamino)-1-pyridin-2-yl-benzo[g]isoquinoline-5,10-dione (**3a**)*

Dark-red crystals, yield: 60 %. – ^{1}H NMR (CDCl$_3$): δ = 6.88 (d, J = 6 Hz, 2H), 6.94 (s, 1H), 6.97 (d, J = 8 Hz, 2H), 7.10 – 7.44 (m, 11H), 7.51 (d, J = 8 Hz, 1H), 7.67 (d, J = 8 Hz, 1H), 7.90 (t, J = 8 Hz, 1H), 8.66 (d, J = 5 Hz, 1H), 10.37 (s, 1H). – ^{13}C NMR ([D$_6$]DMSO): δ = 113.6, 115.6, 118.8, 119.3, 120.8, 121.0, 122.4, 122.8, 123.3, 123.3, 123.8, 125.9, 127.8, 128.8, 129.4, 134.3, 135.1, 136.5, 139.7, 142.6, 148.7, 151.1, 151.6, 160.5, 183.8, 186.6. – MS (EI): *m/z* (%) = 483 (100) [M]$^+$, 405 (40), 242 (30). – UV/Vis (CHCl$_3$): $\lambda_{\max}$ (lg ε) = 367 (3.6), 535 (4.0) nm. – IR (ATR): ν = 3421, 2923, 1600, 1251 cm^{-1}. – HRMS: *m/z* = 484.17769 (calcd. 484.17735 for $C_{30}H_{22}N_5O_2$, [M+H]$^+$).

*6-Amino-1-pyridin-2-yl-3,4-bis(p-tolylamino)-benzo[g]isoquinoline-5,10-dione (**3b**)*

Brown crystals, yield: 71 %. – ^{1}H NMR (CDCl$_3$): δ = 2.25 (s, 3H), 2.32 (s, 3H), 6.83 (d, J = 6 Hz, 2H), 6.88 (s, 1H), 6.92 (d, J = 8 Hz, 2H), 6.99 (d, J = 8 Hz, 2H), 7.10 (d, J = 8 Hz, 2H), 7.25 (d, J = 8 Hz, 2H), 7.28 (8. J = 6 Hz, 1H), 7.33 (d, J = 8 Hz, 1H), 7.36 (t, J = 8 Hz, 1H), 7.47 (d, J = 8 Hz, 1H), 7.64 (d, J = 8 Hz, 1H), 7.87 (t, J = 8 Hz, 1H), 8.63 (d, J = 5 Hz, 1H), 10.51 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 20.7, 20.8, 114.7, 116.4, 118.5, 120.0, 120.3, 122.4, 123.1, 123.3, 124.6, 127.5, 129.2, 130.0, 132.8, 133.6, 133.7, 135.1, 136.2, 136.9, 138.0, 148.0, 149.1, 150.3, 160.0, 184.2, 187.3. – MS (EI): *m/z* (%) = 511 (100) [M]$^+$, 433 (50), 91 (40). – UV/Vis (CHCl$_3$): $\lambda_{\max}$ (lg ε) = 375 (3.8), 547 (4.1) nm. – IR (ATR): ν = 3404, 2964, 1598, 1246 cm^{-1}. – HRMS: *m/z* = 512.20870 (calcd. 512.20958 for $C_{32}H_{26}N_5O_2$, [M+H]$^+$).

*6-(3-Hydroxytextitpropyl)amino-1-pyridin-2-yl-3,4-bis(p-tolylamino)-benzo[g]isoquinoline-5,10-dione (**4b**)*

A mixture of 0.01 mmol **3b** and 0.07 g K$_2$CO$_3$ in 2 mL of 3-bromopropan-1-ol was heated with stirring at 80 °C for 80 h. After removing the liquid phase *in vacuo* the residue was purified by chromatography on silica gel. Red crystals, yield: 39 %. – ^{1}H NMR (CDCl$_3$): δ = 1.88 (m, 2H), 2.26 (s, 3H), 2.29 (s, 3H), 2.78 (m, 2H), 3.59 (m, 2H), 6.79 (s, 1H), 6.95 (d, J = 8 Hz, 2H), 7.00 (d, J = 8 Hz, 2H), 7.11 (d, J = 8 Hz, 2H), 7.24 (d, J = 8 Hz, 2H), 7.38 (t, J = 8 Hz, 1H), 7.46 (d, J = 8 Hz, 1H), 7.55 (d, J = 8 Hz, 1H), 7.70 – 7.75 (m, 2H), 7.92 (t, J = 8 Hz, 1H), 8.66 (d, J = 5 Hz, 1H), 9.21 (t, J = 8 Hz, 1H), 10.51 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 20.8, 20.8, 34.4, 44.7, 60.3, 114.7, 117.6, 120.1, 120.4, 122.3, 124.5, 125.8, 126.7, 128.8, 129.2, 129.7, 130.0, 130.2, 130.9, 132.9, 133.2, 133.6, 134.3, 136.2, 138.0, 148.4, 148.9, 150.9, 156.6, 185.6, 188.2. – MS (FAB): *m/z* (%) = 569 (10) [M]$^+$, 57 (100). – UV/Vis (CHCl$_3$): $\lambda_{\max}$ (lg ε) = 569 (3.9) nm. – IR (ATR): ν = 2923, 1739, 1460, 1149 cm^{-1}. – HRMS: *m/z* = 570.25306 (calcd. 570.25051 for $C_{35}H_{32}N_5O_3$, [M+H]$^+$).

*6-(2-Hydroxypropyl)amino-1-pyridin-2-yl-3,4-bis(p-tolylamino)-benzo[g]isoquinoline-5,10-dione (**5b**)*

1 mmol of **3b** was dissolved under argon together with a catalytic amount of lithium bromide in 4 mL of propylene oxide, and the mixture was stirred at r. t. for 7 d. The solution was evaporated to dryness, and the residue was purified by chromatography on silica gel. Brown crystals, yield: 19 %. – ^{1}H NMR (CDCl$_3$): δ = 1.35 (m, 3H), 2.31 (s, 3H), 2.34 (s, 3H), 2.78 (m, 1H), 3.59 (m, 2H), 6.87 (s, 1H), 6.92 (d, J = 8 Hz, 2H), 7.01 (d, J = 8 Hz, 2H), 7.27 (d, J = 8 Hz, 2H), 7.40 – 7.55 (m, 7H), 7.79 (d, J = 8 Hz, 1H), 8.01 (t, J = 8 Hz, 1H), 8.52 (d, J = 8 Hz, 1H), 9.37 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 18.3, 20.8, 20.9, 49.8, 68.3, 114.7, 117.7, 120.0, 120.4, 122.3, 124.6, 125.8, 126.8, 128.8, 129.3, 129.7, 130.1, 130.2, 130.9, 132.9, 133.3, 133.6, 134.3, 136.2, 137.9, 148.4, 149.0, 151.1, 156.6, 185.2, 188.0 ppm. – MS (Micro-ESI): *m/z* (%) = 570 (100) [M+1]$^+$. – UV/Vis (CHCl$_3$): $\lambda_{\max}$ (lg ε) = 545 (3.9) nm. – IR (ATR): ν = 3401, 2924, 1567, 1421, 1111 cm^{-1}. – HRMS: *m/z* = 570.25347 (calcd. 570.25051 for $C_{35}H_{32}N_5O_3$, [M+H]$^+$).

*4-(5,10-Dioxo-1-(pyridin-2-yl)-3,4-bis(p-tolylamino)-5,10-dihydrobenzo[g]isoquinolin-6-ylamino)-4-oxobutanoic acid (**6b**)*

1 mmol of **3b** was dissolved with 3 mmol of succinic acid anhydride in 20 mL of anhydrous toluene, and the mixture was heated under reflux. The reaction was monitored by TLC. After 30 h the solvent was removed *in vacuo*, and the residue was purified by chromatography on silica gel. Dark-red crystals, yield: 45 %. – ^{1}H NMR (CDCl$_3$): δ = 2.10 (m, 2H), 2.27 (s, 3H), 2.32 (s, 3H), 2.52 (m, 2H), 6.87 (d, J = 8 Hz, 2H), 7.02 (s, 1H), 7.04 (d, J = 8 Hz, 2H), 7.22 (d, J = 8 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 7.43 – 7.74 (m, 5H), 7.83 (m, 1H), 8.60 (d, J = 5 Hz, 1H), 8.84 (m, 1H), 10.47 (s, 1H), 11.83 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 20.8, 20.9, 29.2, 32.5, 114.7, 116.4, 118.5, 120.0, 120.3, 122.4, 123.1, 123.3, 124.6, 127.5, 129.2, 130.0, 132.8, 133.6, 133.7, 135.1, 136.2, 136.9, 138.0, 143.2, 148.0, 149.1, 150.3, 160.0, 171.2, 177.2, 184.2, 187.3. – MS (EI): *m/z* (%) = 611 (10) [M]$^+$, 511 (20), 107 (100). – UV/Vis (CHCl$_3$): $\lambda_{\max}$ (lg ε) = 398

(3.4), 552 (3.9) nm. – IR (ATR): ν = 3410, 2924, 1704, 1514, 1251 cm^{-1}. – HRMS: *m/z* = 612.22246 (calcd. 612.22469 for $C_{36}H_{30}N_5O_5$, [M+H]$^+$).

*3-(5,10-Dioxo-1-(pyridin-2-yl)-3,4-bis(p-tolylamino)-5,10-dihydrobenzo[g]isoquinolin-6-ylamino)propane-1-sulfonic acid (**7b**)*

1 mmol of **3b** was dissolved in 20 mL of anhydrous toluene with 1 mmol of 1,3-propane sultone. The mixture was heated under reflux for 20 h. The solvent was removed, and the residue was purified by chromatography on silica gel. Brown crystals, yield: 20 %. – ^{1}H NMR ([D$_6$]DMSO): δ = 1.82 (m, 2H), 2.20 (s, 3H), 2.47 (m, 2H), 2.22 (s, 3H), 3.43 (m, 2H), 6.85 (d, *J* = 6 Hz, 2H), 7.00 (d, *J* = 8 Hz, 2H), 7.03 (d, *J* = 8 Hz, 2H), 7.20 (d, *J* = 8 Hz, 1H), 7.31 (d, *J* = 8 Hz, 1H), 7.37 (m, 1H), 7.39 (d, *J* = 8 Hz, 2H), 7.55 – 7.58 (m, 2H), 7.89 (t, *J* = 8 Hz, 1H), 8.30 (s, 1H), 8.54 (d, *J* = 8 Hz, 1H), 9.02 (m, 1H), 9.84 (s, 1H). – ^{13}C NMR ([D$_6$]DMSO): δ = 20.8, 20.9, 25.6, 41.7, 49.1, 113.8, 114.6, 118.6, 118.9, 121.0, 122.9, 123.2, 126.1, 126.2, 129.3, 129.8, 131.3, 132.3, 135.0, 135.5, 136.7, 137.2, 139.7, 148.8, 150.6, 150.8, 152.7, 160.3, 167.2, 184.2, 186.3. – MS (FAB): *m/z* (%) = 634 (30) [M]$^+$, 205 (100). – UV/Vis (CHCl$_3$): λ_{max} (lg ε) = 383 (3.5), 571 (3.9) nm. – IR (ATR): ν = 3414, 2924, 1591, 1510, 1179 cm^{-1}. – HRMS: *m/z* = 634.21397 (calcd. 634.21242 for $C_{35}H_{32}SN_5O_5$, [M+H]$^+$).

*6/9-Nitro-3,4-bis(phenylamino)-1-pyridin-2-yl-benzo[g]-isoquinoline-5,10-dione (**8a′**)*

Red crystals, yield: 45 %. – ^{1}H NMR (CDCl$_3$): δ = 6.95 (s, 1H), 7.06 (d, *J* = 8 Hz, 2H), 7.13 (d, *J* = 8 Hz, 2H), 7.17 – 7.45 (m, 8H), 7.57 (t, *J* = 8 Hz, 1H), 7.73 (t, *J* = 8 Hz, 1H), 8.08 (t, *J* = 8 Hz, 1H), 8.41 (d, *J* = 8 Hz, 1H), 8.76 (d, *J* = 5 Hz, 1H), 10.38 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 118.4, 120.7, 120.8, 123.3, 123.4, 123.6, 124.3, 125.0, 125.6, 127.0, 128.4, 128.9, 129.0, 129.2, 129.6, 134.8, 135.0, 137.8, 138.0, 139.4, 148.1, 148.8, 149.5, 158.3, 179.6, 183.4. – MS (EI): *m/z* (%) = 513 (10) [M]$^+$, 209 (30), 57 (100). – UV/Vis (CHCl$_3$): λ_{max} (lg ε) = 403 (3.6), 550 (4.0) nm. – IR (ATR): ν = 3326, 2923, 1662, 1441, 1254 cm^{-1}. – HRMS: *m/z* = 514.15284 (calcd. 514.15153 for $C_{30}H_{20}N_5O_4$, [M+H]$^+$).

*6/9-Nitro-3,4-bis(phenylamino)-1-pyridin-2-yl-benzo[g]-isoquinoline-5,10-dione (**8a″**)*

Red crystals, yield: 31 %. – ^{1}H NMR (CDCl$_3$): δ = 6.97 (s, 1H), 7.00 (d, *J* = 8 Hz, 2H), 7.07 (d, *J* = 8 Hz, 2H), 7.17 – 7.45 (m, 8H), 7.70 (t, *J* = 8 Hz, 1H), 7.81 (t, *J* = 8 Hz, 1H), 7.96 (t, *J* = 8 Hz, 1H), 8.30 (d, *J* = 8 Hz, 1H), 8.76 (d, *J* = 5 Hz, 1H), 10.38 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 116.1, 120.4, 121.1, 123.4, 123.5, 123.7, 124.1, 124.9, 125.6, 127.0, 128.3, 128.9, 129.6, 129.7, 130.0, 134.6, 135.8, 137.6, 138.0, 139.4, 148.1, 148.8, 149.6, 158.2, 179.3, 183.2. – MS (EI): *m/z* (%) = 513 (20) [M]$^+$, 399 (15), 84 (100). – UV/Vis (CHCl$_3$): λ_{max} (lg ε) = 394 (3.6), 559 (4.0) nm. – IR (ATR): ν = 3365, 2924, 1657, 1440, 1248 cm^{-1}. – HRMS: *m/z* = 514.15274 (calcd. 514.15153 for $C_{30}H_{20}N_5O_4$, [M+H]$^+$).

*3,4-Bis(4-bromophenylamino)-9-nitro-1-pyridin-2-yl-benzo-[g]isoquinoline-5,10-dione (**8c′**)*

Brown crystals, yield: 44 %. – ^{1}H NMR (CDCl$_3$): δ = 6.88 (d, *J* = 8 Hz, 2H), 6.90 (s, 1H), 7.20 – 7.31 (m, 5H), 7.34 (d, *J* = 8 Hz, 2H), 7.43 (t, *J* = 5 Hz, 1H), 7.63 (d, *J* = 8 Hz, 1H), 7.74 (d, *J* = 8 Hz, 1H), 7.86 (t, *J* = 8 Hz, 1H), 8.34 (d, *J* = 8 Hz, 1H), 8.64 (d, *J* = 5 Hz, 1H), 9.95 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 113.4, 115.7, 117.2, 119.0, 120.6, 121.7, 122.0, 122.2, 125.1, 125.7, 127.5, 128.8, 129.9, 131.9, 132.0, 132.5, 132.7, 135.2, 135.5, 137.0, 145.3, 152.5, 154.4, 157.2, 183.1, 185.2. – MS (EI): *m/z* (%) = 671 (15) [M]$^+$, 641 (20), 530 (50), 57 (100). – UV/Vis (CHCl$_3$): λ_{max} (lg ε) = 380 (3.6), 545 (3.9) nm. – IR (ATR): ν = 3375, 2923, 1662, 1485, 1242 cm^{-1}. – HRMS: *m/z* = 669.97180 (calcd. 669.97257 for $C_{30}H_{18}Br_2N_5O_4$, [M+H]$^+$).

*3,4-Bis(4-bromophenylamino)-6-nitro-1-pyridin-2-yl-benzo-[g]isoquinoline-5,10-dione (**8c″**)*

Brown crystals, yield: 28 %. – ^{1}H NMR (CDCl$_3$): δ = 6.89 (d, *J* = 8 Hz, 2H), 6.92 (s, 1H), 7.21 – 7.32 (m, 5H), 7.35 (d, *J* = 8 Hz, 2H), 7.41 (t, *J* = 5 Hz, 1H), 7.60 (d, *J* = 8 Hz, 1H), 7.73 (d, *J* = 8 Hz, 1H), 7.85 (t, *J* = 8 Hz, 1H), 8.35 (d, *J* = 8 Hz, 1H), 8.66 (d, *J* = 5 Hz, 1H), 9.98 (s, 1H) ppm. – ^{13}C NMR (CDCl$_3$): δ = 113.6, 115.9, 117.1, 119.2, 120.8, 121.7, 122.0, 122.3, 125.0, 125.7, 127.5, 128.9, 130.1, 131.9, 132.0, 132.6, 132.7, 135.3, 135.6, 137.2, 145.1, 152.6, 154.3, 157.5, 183.4, 185.1. – MS (EI): *m/z* (%) = 671 (10) [M]$^+$, 641 (20), 530 (40), 57 (100). – UV/Vis (CHCl$_3$): λ_{max} (lg ε) = 382 (3.6), 548 (3.9) nm. – IR (ATR): ν = 3402, 2921, 1660, 1484, 1242 cm^{-1}. – HRMS: *m/z* = 669.97240 (calcd. 669.97257 for $C_{30}H_{18}Br_2N_5O_4$, [M+H]$^+$).

*9-Iodo-3,4-bis(phenylamino)-1-pyridin-2-yl-benzo[g]-isoquinoline-5,10-dione (**9a′**)*

Red crystals, yield: 49 %. – ^{1}H NMR (CDCl$_3$): δ = 6.83 (s, 1H), 7.00 – 7.34 (m, 11H), 7.35 (t, *J* = 6 Hz, 1H), 7.90 (d, *J* = 8 Hz, 1H), 7.93 (t, *J* = 8 Hz, 1H), 8.15 (d, *J* = 8 Hz, 1H), 8.29 (d, *J* = 8 Hz, 1H), 8.66 (d, *J* = 5 Hz, 1H), 10.09 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 92.1, 119.9, 120.2, 120.6, 123.2, 123.3, 123.6, 123.9, 125.6, 126.0, 127.3, 128.8, 129.6, 132.6, 135.9, 136.8, 137.0, 138.6, 140.3, 147.6, 148.6, 149.2, 152.1, 157.4, 184.1, 185.6. – MS (EI): *m/z* (%) = 594 (30) [M]$^+$, 516 (10), 149 (100). – UV/Vis (CHCl$_3$): λ_{max} (lg ε) = 380 (3.7), 531 (3.9) nm. – IR (ATR): ν = 3382, 2921, 1670, 1506, 1250 cm^{-1}. – HRMS: *m/z* = 595.06422 (calcd. 595.06310 for $C_{30}H_{20}IN_4O_2$, [M+H]$^+$).

*6-Iodo-3,4-bis(phenylamino)-1-pyridin-2-yl-benzo[g]isoquinoline-5,10-dione (**9a″**)*

Red crystals, yield: 25 %. – ^{1}H NMR (CDCl$_3$): δ = 6.97 (s, 1H), 7.00 – 7.38 (m, 11H), 7.39 (t, J = 6 Hz, 1H), 7.69 (d, J = 8 Hz, 1H), 7.90 (t, J = 8 Hz, 1H), 8.15 (d, J = 8 Hz, 1H), 8.29 (d, J = 8 Hz, 1H), 8.63 (d, J = 5 Hz, 1H), 10.15 (s, 1H). – ^{13}C NMR (63 MHz, CDCl$_3$): δ = 92.5, 120.0, 120.2, 120.6, 123.0, 123.2, 123.7, 123.8, 126.5, 126.7, 127.8, 128.8, 129.6, 133.4, 134.0, 136.8, 137.1, 138.4, 140.6, 147.6, 148.7, 150.3, 153.0, 158.9, 180.4, 185.2. – MS (EI): *m/z* (%) = 594 (100) [M]$^+$, 516 (40), 209 (100). – UV/Vis (CHCl$_3$): $\lambda_{\max}$ (lg ε) = 373 (3.8), 531 (4.0) nm. – IR (ATR): ν = 3382, 2922, 1656, 1472, 1225 cm^{-1}. – HRMS: *m/z* = 595.06377 (calcd. 595.06310 for $C_{30}H_{20}IN_4O_2$, [M+H]$^+$).

*6,9-Dihydroxy-3,4-bis(phenylamino)-1-pyridin-2-yl-benzo[g]isoquinoline-5,10-dione (**10a**)*

Red crystals, yield: 65 %. – ^{1}H NMR (CDCl$_3$): δ = 7.01 – 7.35 (m, 13H), 7.48 (t, J = 6 Hz, 1H), 7.66 (d, J = 8 Hz, 1H), 7.99 (t, J = 8 Hz, 1H), 8.67 (d, J = 5 Hz, 1H), 10.44 (s, 1H), 12.54 (s, 1H), 12.81 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 116.1, 118.4, 119.5, 120.4, 120.5, 120.7, 121.2, 123.2, 123.7, 124.0, 124.5, 125.9, 127.8, 128.2, 128.8, 129.2, 129.7, 137.3, 138.0, 140.0, 149.6, 149.8, 157.0, 157.5, 185.1, 189.7. – MS (EI): *m/z* (%) = 500 (40) [M]$^+$, 422 (20), 91 (100). – UV/Vis (CHCl$_3$): $\lambda_{\max}$ (lg ε) = 389 (3.7), 570 (4.1) nm. – IR (ATR): ν = 3350, 2929, 2852, 1594, 1442, 1155 cm^{-1}. – HRMS: *m/z* = 501.15514 (calcd. 501.15628 for $C_{30}H_{21}N_4O_4$, [M+H]$^+$).

*3,4-Bis(4-bromophenylamino)-7/8-methyl-1-pyridin-2-yl-benzo[g]isoquinoline-5,10-dione (**11c′**)*

Brown crystals, yield: 38 %. – ^{1}H NMR (CDCl$_3$): δ = 2.46 (s, 3H), 6.83 (s, 1H), 6.88 (d, J = 8 Hz, 2H), 7.14 – 7.55 (m, 8H), 7.77 (d, J = 8 Hz, 1H), 7.90 (s, 1H), 8.06 (d, J = 8 Hz, 1H), 8.14 (m, 1H), 8.73 (d, J = 5 Hz, 1H), 10.38 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 22.0, 116.6, 119.2, 121.4, 122.1, 127.2, 127.5, 128.2, 128.8, 131.3, 131.9, 132.1, 132.4, 132.6, 132.9, 134.3, 135.9, 139.4, 140.5, 141.6, 143.6, 146.3, 149.9, 153.2, 157.7, 181.8, 184.6. – MS (EI): *m/z* (%) = 639 (30) [M]$^+$, 398 (50), 91 (100). – UV/Vis (CHCl$_3$): $\lambda_{\max}$ (lg ε) = 514 (4.0) nm. – IR (ATR): ν = 3260, 2923, 1652, 1484, 1260 cm^{-1}. – HRMS: *m/z* = 639.00496 (calcd. 639.00315 for $C_{31}H_{21}Br_2N_4O_2$, [M+H]$^+$).

*3,4-Bis(4-bromophenylamino)-7/8-methyl-1-pyridin-2-yl-benzo[g]isoquinoline-5,10-dione (**11c″**)*

Brown crystals, yield: 40 %. – ^{1}H NMR (CDCl$_3$): δ = 2.48 (s, 3H), 6.81 (s, 1H), 6.90 (d, J = 8 Hz, 2H), 7.10 – 7.50 (m, 8H), 7.72 (d, J = 8 Hz, 1H), 7.92 (s, 1H), 8.04 (d, J = 8 Hz, 1H), 8.15 (m, 1H), 8.75 (d, J = 5 Hz, 1H), 10.45 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 22.0, 116.7, 119.2, 121.5, 122.1, 127.2, 127.6, 128.2, 129.0, 131.3, 131.8, 132.1, 132.4, 132.6, 132.9, 134.4, 136.0, 139.4, 140.6, 141.6, 143.6, 146.3, 150.0, 153.1, 157.8, 182.0, 184.4. – MS (EI): *m/z* (%) = 639 (30) [M]$^+$, 398 (40), 91 (100). – UV/Vis (CHCl$_3$): $\lambda_{\max}$ (lg ε) = 514 (4.0) nm. – IR (ATR): ν = 3253, 2922, 1653, 1484, 1261 cm^{-1}. – HRMS: *m/z* = 639.00527 (calcd. 639.00315 for $C_{31}H_{21}Br_2N_4O_2$, [M+H]$^+$).

*7/8-Bromomethyl-3,4-bis(4-bromophenylamino)-1-pyridin-2-yl-benzo[g]isoquinoline-5,10-dione (**12c′**)*

Brown crystals, yield: 32 %. – ^{1}H NMR (CDCl$_3$): δ = 4.51 (s, 2H), 6.85 (d, J = 8 Hz, 2H), 6.99 (s, 1H), 7.16 – 7.33 (m, 4H), 7.41 (t, J = 6 Hz, 1H), 7.44 (d, J = 8 Hz, 2H), 7.61 (d, J = 8 Hz, 1H), 7.73 (d, J = 8 Hz, 1H), 7.91 (t, J = 8 Hz, 1H), 8.12 (s, 1H), 8.15 (d, J = 8 Hz, 1H), 8.67 (d, J = 5 Hz, 1H), 10.16 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 29.7, 116.2, 120.8, 121.6, 122.9, 125.3, 126.4, 127.6, 129.0, 131.8, 132.5, 133.8, 134.9, 136.7, 137.3, 139.8, 141.0, 143.0, 144.8, 148.9, 158.6, 183.1, 188.4. – MS (EI): *m/z* (%) = 718 (10) [M]$^+$, 149 (60), 57 (100). – UV/Vis (CHCl$_3$): $\lambda_{\max}$ (lg ε) = 369 (3.7), 526 (4.0) nm. – IR (ATR): ν = 3245, 2923, 1653, 1484, 1263 cm^{-1}. – HRMS: *m/z* = 716.91418 (calcd. 716.91367 for $C_{31}H_{20}Br_3N_4O_2$, [M+H]$^+$).

*7/8-Bromomethyl-3,4-bis(4-bromophenylamino)-1-pyridin-2-yl-benzo[g]isoquinoline-5,10-dione (**12c″**)*

Brown crystals, yield: 35 %. – ^{1}H NMR (CDCl$_3$): δ = 4.55 (s, 2H), 6.86 (d, J = 8 Hz, 2H), 7.00 (s, 1H), 7.25 – 7.39 (m, 6H), 7.62 (t, J = 6 Hz, 1H), 7.75 (d, J = 8 Hz, 1H), 7.91 (t, J = 8 Hz, 1H), 8.09 (d, J = 8 Hz, 1H), 8.18 (s, 1H), 8.32 (d, J = 8 Hz, 1H), 8.65 (d, J = 5 Hz, 1H), 10.16 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 30.1, 116.3, 120.8, 121.5, 122.9, 124.9, 126.5, 127.6, 129.0, 131.8, 132.4, 133.8, 134.8, 137.0, 136.9, 138.4, 141.1, 142.9, 144.4, 148.8, 158.1, 183.3, 187.9. – MS (EI): *m/z* (%) = 718 (15) [M]$^+$, 654 (20), 57 (100). – UV/Vis (CHCl$_3$): $\lambda_{\max}$ (lg ε) = 378 (3.6), 535 (4.0) nm. – IR (ATR): ν = 3245, 2922, 1651, 1485, 1263 cm^{-1}. – HRMS: *m/z* = 716.91420 (calcd. 716.91367 for $C_{31}H_{20}Br_3N_4O_2$, [M+H]$^+$).

*3,4-Bis(4-bromophenylamino)-7/8-hydroxymethyl-1-pyridin-2-yl-benzo[g]isoquinoline-5,10-dione (**13c**)*

Brown crystals, yield: 65 %. – ^{1}H NMR (CDCl$_3$): δ = 4.77 (s, 2H), 5.30 (s, 1H), 6.84 (d, J = 8 Hz, 2H), 6.97 (s, 1H), 7.23 – 7.64 (m, 9H), 7.95 – 7.99 (m, 2H), 8.05 (d, J = 8Hz, 1H), 8.67 (d, J = 5 Hz, 1H), 10.12 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 63.6, 116.7, 120.1, 121.0, 121.6, 122.0, 123.1, 123.9, 126.1, 126.7, 127.1, 131.8, 132.2, 132.5, 132.8, 133.3, 137.2, 137.4, 139.8, 148.0, 148.3, 149.8, 149.9, 152.7, 159.1, 180.8, 186.5. – MS (EI): *m/z* (%) = 656 (5)

$[M]^+$, 397 (40), 171 (100). – UV/Vis (CHCl$_3$): λ_{max} (lg ε) = 512 (3.9) nm. – IR (ATR): ν = 3409, 2927, 1645, 1485, 1258, 1070 cm^{-1}. – HRMS: *m/z* = 654.99783 (calcd. 654.99800 for $C_{31}H_{21}Br_2N_4O_3$, $[M+H]^+$).

*7/8-(4-Methyl-pent-3-enyl)-3,4-bis(phenylamino)-1-pyridin-2-yl-benzo[g]isoquinoline-5,10-dione (**14a′**)*

Red crystals, yield: 31 %. – ^{1}H NMR (CDCl$_3$): δ = 1.53 (s, 3H), 1.68 (s, 3H), 2.35 (q, J = 7 Hz, 2H), 2.72 (t, J = 8 Hz, 2H), 5.12 (t, J = 8 Hz, 1H), 7.00 – 7.38 (m, 11H), 7.40 (t, J = 6 Hz, 1H), 7.47 (d, J = 8 Hz, 1H), 7.64 (d, J = 8 Hz, 1H), 7.90 (t, J = 8 Hz, 1H), 7.95 (s, 1H), 8.07 (d, J = 8 Hz, 1H), 8.66 (d, J = 5 Hz, 1H), 10.46 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 17.7, 25.7, 29.3, 36.4, 120.0, 120.1, 122.8, 122.7, 122.8, 123.6, 123.7, 126.7, 126.8, 126.9, 127.2, 127.4, 128.8, 129.0, 129.2, 129.6, 131.8, 133.0, 133.7, 134.6, 136.9, 138.6, 140.8, 148.6, 150.2, 159.6, 181.7, 186.8. – MS (EI): *m/z* (%) = 550 (30) $[M]^+$, 472 (10), 93 (100). – UV/Vis (CHCl$_3$): λ_{max} (lg ε) = 523 (4.0) nm. – IR (ATR): ν = 3412, 2923, 1660, 1494, 1255 cm^{-1}. – HRMS: *m/z* = 551.24257 (calcd. 551.24470 for $C_{36}H_{31}N_4O_2$, $[M+H]^+$).

*7/8-(4-Methyl-pent-3-enyl)-3,4-bis(phenylamino)-1-pyridin-2-yl-benzo[g]isoquinoline-5,10-dion (**14a″**)*

Red crystals, yield: 35 %. – ^{1}H NMR (CDCl$_3$): δ = 1.56 (s, 3H), 1.70 (s, 3H), 2.35 (q, J = 7 Hz, 2H), 2.77 (t, J = 8 Hz, 2H), 5.15 (t, J = 8 Hz, 1H), 7.00 – 7.40 (m, 11H), 7.42 (t, J = 6 Hz, 1H), 7.51 (d, J = 8 Hz, 1H), 7.66 (d, J = 8 Hz, 1H), 7.90 (t, J = 8 Hz, 1H), 7.99 (s, 1H), 8.05 (d, J = 8 Hz, 1H), 8.66 (d, J = 5 Hz, 1H), 10.44 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 17.3, 25.2, 28.8, 35.7, 120.0, 120.1, 122.7, 122.9, 123.2, 123.6, 123.8, 126.4, 127.1, 127.5, 128.2, 128.7, 128.8, 129.0, 129.2, 129.6, 132.6, 133.1, 133.8, 134.9, 138.6, 140.7, 148.4, 148.7, 150.1, 159.6, 181.4, 187.2. – MS (EI): *m/z* (%) = 550 (30) $[M]^+$, 472 (10), 93 (100). – UV/Vis (CHCl$_3$): λ_{max} (lg ε) = 364 (3.7), 521 (4.0) nm. – IR (ATR): ν = 3412, 2922, 1658, 1494, 1261 cm^{-1}. – HRMS: *m/z* = 551.24284 (calcd. 551.24470 for $C_{36}H_{31}N_4O_2$, $[M+H]^+$).

*7,8-Diphenyl-3,4-bis(phenylamino)-1-pyridin-2-yl-benzo-[g]isoquinoline-5,10-dione (**15a**)*

Red crystals, yield: 65 %. – ^{1}H NMR (CDCl$_3$): δ = 7.00 – 7.37 (m, 21H), 7.40 (t, J = 6Hz, 1H), 7.70 (d, J = 8 Hz, 1H), 7.91 (t, J = 8 Hz, 1H), 8.17 (s, 1H), 8.23 (s, 1H), 8.66 (d, J = 5 Hz, 1H), 10.50 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 117.5, 120.0, 120.1, 121.3, 122.3, 123.2, 123.6, 123.8, 125.5, 127.5, 127.6, 128.1, 128.2, 128.6, 128.8, 129.1, 129.4, 129.6, 129.7, 132.5, 133.3, 137.0, 138.5, 139.6, 139.7, 140.5, 145.6, 146.8, 148.4, 150.0, 152.8, 159.3, 181.2, 186.6. – MS (EI): *m/z* (%) = 620 (60) $[M]^+$, 542 (50), 310 (50), 77 (100). – UV/Vis (CHCl$_3$): λ_{max} (lg ε) = 354 (4.6), 529 (4.0) nm. – IR (ATR): ν = 3406, 2923, 1656, 1441, 1237 cm^{-1}. – HRMS: *m/z* = 621.22640 (calcd. 621.22905 for $C_{42}H_{29}N_4O_2$, $[M+H]^+$).

*Allyl palladium(II) chloride complex of an azaanthraquinone (**16a**)*

To a solution of 0.1 mmol of **2a** in 20 mL of anhydrous THF a solution of 0.05 mmol of allyl palladium(II) chloride in THF was added dropwise. The mixture was stirred at r. t. for 3 h. The solvent was removed, and the residue was purified by chromatography on silica gel. Red crystals, yield: 90 %. – ^{1}H NMR (CDCl$_3$): δ = 2.44 (m, 2H), 3.64 (m, 2H), 4.93 (m, 1H), 7.00 (s, 1H), 7.02 – 7.25 (m, 8H), 7.37 (t, J = 7 Hz, 1H), 7.44 (d, J = 7 Hz, 2H), 7.65 (d, J = 8 Hz, 1H), 7.77 (m, 2H), 7.93 (t, J = 8 Hz, 1H), 8.16 (d, J = 8 Hz, 1H), 8.25 (d, J = 8 Hz, 1H), 8.91 (m, 1H), 10.72 (s, 1H). – ^{13}C NMR (CDCl$_3$): δ = 29.2, 29.7, 60.4, 111.8, 117.7, 120.3, 120.4, 122.4, 123.3, 123.5, 123.9, 124.3, 125.8, 126.8, 127.2, 129.0, 129.7, 133.5, 133.8, 134.6, 134.7, 137.5, 138.1, 140.2, 149.7, 151.7, 160.2, 181.1, 186.7. – MS (FAB): *m/z* (%) = 616 (70) $[M_{cat}]^+$, 574 (60), 469 (100). – UV/Vis (CHCl$_3$): λ_{max} (lg ε) = 374 (3.8), 526 (4.0) nm. – IR (ATR): ν = 3409, 2919, 1654, 1562, 1290 cm^{-1}. – HRMS: *m/z* = 611.10335 (calcd. 611.10269 for $C_{33}H_{25}N_4O_2{}^{102}Pd$, $[M]^+$).

Acknowledgement

We thank Roche Diagnostics GmbH, Penzberg, for generous support.

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